

Pb(II), Cd(II) and Zn(II) adsorption on low grade manganese ore

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Abstract

Low grade manganese ore (LMO) of Orissa containing 58.37% SiO₂, 25.05% MnO₂, 8.8% Al₂O₃, and 5.03% Fe₂O₃ as the main constituents was taken to study its adsorption behaviour for Pb(II), Cd(II) and Zn(II) from aqueous solutions. The XRD studies showed the crystalline phases to be quartz, β -MnO₂, δ -MnO₂ and Fe₂O₃. Batch adsorption studies were carried out by varying the experimental parameters which included contact time, pH, adsorbate and adsorbent concentrations and temperature. The time data fitted well to pseudo second order kinetics for Pb(II), Cd(II) and Zn(II) adsorption. With the increase in adsorbent dose, loading capacities decreased. With the increase in pH from 2.0 to 5.5, Pb(II) adsorption increased while Cd(II) and Zn(II) adsorption increased till an initial pH of 3.0. Positive ΔH° values confirmed the adsorption process to be endothermic and positive ΔS° values suggest the increased randomness at the solid-solution interface during the adsorption of cations on the sample. The adsorption data showed good fit to both Langmuir and Freundlich isotherm models for the three cations. The Langmuir monolayer capacities for Pb(II), Cd(II) and Zn(II) were estimated to be ~142.85, 59.17 and 98.0 mg per gram of LMO sample respectively. From the XRD studies of loaded samples, it was observed that Pb(II) adsorption affects silica phase whereas Cd(II) adsorption affects both silica and β -MnO₂ phases. With Zn(II) adsorption both the intensity and peak position of silica phase were disturbed. From the electron probe micro analysis (EPMA) it was observed that Pb(II), Cd(II) and Zn(II) adsorption are more prone to silica, iron oxide and β -MnO₂ phase respectively though their distribution in other phases was also marked but to a lesser extent. Due to high loading capacities obtained for Pb(II) and Zn(II), low grade manganese ore can be regarded as a potential adsorbent for these metals.

Keywords: Low grade manganese ore, adsorption, Pb(II), Cd(II), Zn(II), EPMA

1. Introduction

Toxic metal compounds are frequently used in industrial processes and are widely distributed in the environment. Due to their extended persistence in biological systems and tendency to bio-accumulate as they move up the food chain, they represent important environmental and occupational hazards. The removal of toxic contaminants from industrial wastewaters is one of the most important environmental issues. Intensive research and development efforts are being made all over the world to develop low cost adsorbents and to utilize the wastes for remediation of toxic metal ions from aqueous solutions. Low cost adsorbents include agriculture wastes (Sud *et al.*, 2008), natural clay and soils (Huang and Fuerstenau, 2000; Babel and Kurniawan, 2003; Dong *et al.*, 2007; Samir 2008; Serrano *et al.*, 2009) and industrial wastes like red mud (Wang *et al.*, 2008) slag (Xue *et al.*, 2009), aluminum plant sand (Mohapatra *et al.*, 2009a) Mn nodule leach residue (Agrawal and Sahu, 2006). Low grade ores form another important category of low cost adsorbents (Mohapatra and Anand 2007; Mohapatra *et al.*, 2009b; Rout *et al.*, 2009).

Manganese oxides are typically thought to be the most important scavengers of aqueous trace metals in soils, sediments, and rocks through their seemingly dominant sorptive behavior despite the fact that they are much less abundant than iron oxides (Jenne, 1968; Burns, 1976; Chao and Theobald, 1976; Schwertmann and Taylor, 1989). In both cases of Mn and Fe oxides/hydroxides, their reactivity and generally high surface areas make them proficient sorbents of many inorganic cations such as Cu, Pb, Zn, Co and Ni among others (Jenne, 1968; McKenzie, 1980; Benjamin and Leckie, 1981; Schwertmann and Taylor, 1989; McBride, 1994; Tripathy *et al.*, 2006). Synthetic manganese dioxide and manganese dioxide coated on different materials

have been widely studied for heavy metal ion adsorption (Han *et al.*, 2006 a; Han *et al.*, 2006b ; Feng *et al.*, 2007; Eren *et al.*, 2009).

Since the manganese oxides and silica exhibit high potential for heavy metal remediation, unutilized low grade manganese ores (containing MnO₂ and quartz as main constituents) available at various locations in the world can be good adsorbents. The present studies were carried out on low grade manganese ore of Orissa to evaluate its capability for removal of Pb(II), Cd(II), and Zn(II) from aqueous solutions. The scope of the present study is to generate the technical data on batch adsorption of Pb(II), Cd(II) and Zn(II) by varying experimental parameters and to characterize the ion loaded adsorbent to investigate the adsorption sites. Section 1 has given a brief introduction for the present work. Section 2 of this paper describes experimental procedures followed to carry out the present studies. Details of raw materials and chemicals used are included. Section 3 presents results and discussion. Results pertaining to effect of various parameters such as time, pH, temperature, adsorbent and adsorbate concentrations have been discussed. The characterization studies of the ore as well as metal ion loaded ore samples are also presented. Section 4 gives brief conclusions drawn from the present studies.

2. Experimental

A typical sample of low grade manganese ore (LMO) of Orissa, India was ground and sieved to obtain 150 Mesh B.S.S passed particles (100% < 100µm). A weighed amount of the dried sample was subjected to tri-acid digestion for wet chemical analysis. Iron was analyzed volumetrically, silica was estimated gravimetrically and alumina was estimated volumetrically by EDTA method following standard procedures (Vogel, 2000). The other metal ions were analysed after proper dilutions by Atomic Absorption Spectrophotometer (Perkin- Elmer Model 2380). Nitrate salt of Pb, Cd and Zn (E-MERCK) were used to prepare stock solutions of 1000 mg/L concentrations. In all experiments distilled water was used. Other reagents used were of BDH analytical grade. The X-ray diffraction (XRD) measurements were done over a range of 10 to 70° using Phillips Powder Diffractometer Model PW3710 with CoK_α radiation at a scan speed of 1.2° /min. Surface area was estimated by BET method with Quantasorb 1750 instrument. The elemental mapping of the LMO and metal ion adsorbed LMO samples were carried out by electron probe micro analyzer (EPMA) (JEOL, JXA-8100). For this study, samples were prepared and coated with carbon by a vacuum coater. The working voltage was kept 20 kV with beam current as 40-100 nA. Area scanning mode was used for qualitative analysis and X-ray scanning to find out elemental distribution.

The adsorption experiments were carried out in an horizontal shaker having provisions for temperature and agitation control. For each experiment 50 mL of metal ion solution of desired concentration and pH was taken in 100 mL stoppered conical flask and a weighed amount of adsorbent was added to it. The contents were stirred at 160 RPM (revolutions per minute) for desired period of time at constant temperature. The contents were then filtered using a using a 0.45µ membrane filter paper and the filtrate was analyzed for residual metal ions by atomic absorption spectrophotometer. The pH mentioned in all experiments refers to initial pH of solution taken for adsorption studies. For fitting adsorption isotherm the data was generated at different initial concentrations, C₀, of metal ions (50-500 mg/L) while keeping the adsorbent dose, W, fixed as 2g/L. In order to test the reproducibility, some of the experiments were carried in duplicate and the reproducibility was found to be within ± 2%. The pH_{pzc} of prepared sample was determined following Balistrieri and Murray method (Balistrieri and Murray, 1981).

3. Results and discussion

3.1 Chemical and instrumental analysis

The chemical analysis of the major constituents present in the sample is: 58.37% SiO₂, 25.05% MnO₂, 8.8% Al₂O₃, and 5.03% Fe. The minor elements were Cu 0.008%, Ni 0.018%, Co 0.005% and Zn 0.013%. The pH_{pzc} (point of zero charge) of the sample was determined to be 7.88. The pH_{pzc} of β-MnO₂, silica, Al₂O₃ have been reported to be 7.3, 2.0, 8.0 respectively and pH_{pzc} of iron oxide may vary between 3.0-8.0. The specific surface area of the sample was 91.32 m²/g. The XRD pattern of the sample given in Figure 1 shows the crystalline phases to be SiO₂ (quartz) (JCPDS, 75-1555), β-MnO₂ (JCPDS, 24- 0735), δ-MnO₂ (JCPDS 23-1045) and Fe₂O₃ (JCPDS 23-1045).

3.2 Effect of contact time on Pb(II), Cd(II) and Zn(II) adsorption

The time data at 300 K given in Figures 2(a), 2(b) and 2(c) for Pb(II), Cd(II) and Zn(II) adsorption show that in the beginning % adsorption of Pb(II), Cd(II) and Zn(II) under the chosen conditions, increase quickly. Then the process gradually slows down until it reaches a stage (after about 60 min for initial metal ion concentration of 50 mg/L and after about 90 min for initial metal ion concentration of 100 mg/L) indicating the establishment of the equilibrium of adsorption. However, for comparison purpose in all subsequent experiments (except for isothermic equilibrium data), the contact time was maintained at 60 minutes. The time data was tested for fitting to pseudo second order kinetics (Ho and Mackay, 1998) as given by Eqn. (1).

$$t/q_t = 1/(k_1 q_e^2) + (1/q_e)t \quad (1)$$

where q_e and q_t are the amounts of metal ion adsorbed per unit weight of adsorbent (mg/g) at equilibrium and at any time t , respectively and k_1 is the rate constant of pseudo-second-order adsorption (g/mg/min).

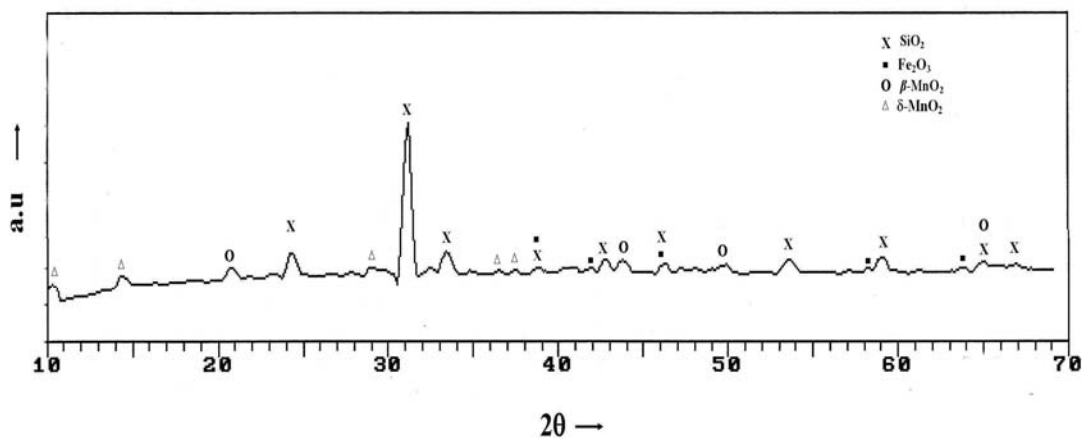


Figure 1 XRD pattern of LMO sample

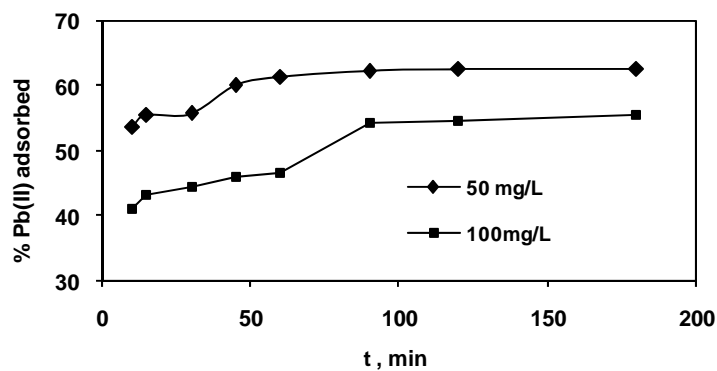


Figure 2a Effect of contact time on adsorption of Pb(II) on LMO Sample. Conditions: $W = 2$ g/L, $T = 300$ K and $pH = 5.25$.

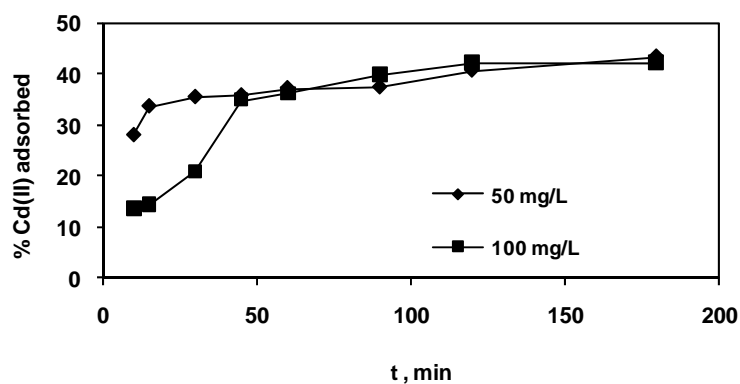


Figure 2b Effect of contact time on adsorption of Cd(II) on LMO sample. Conditions: $W = 2$ g/L, $T = 300$ K and $pH = 5.25$.

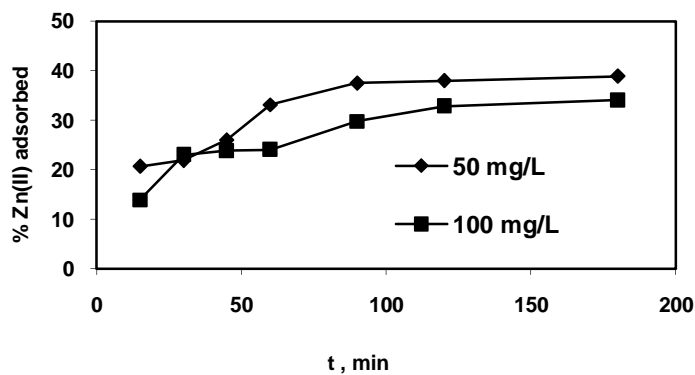


Figure 2c Effect of contact time on adsorption of Zn(II) on LMO sample. Conditions: $W = 2$ g/L, $T = 300$ K and $pH = 5.25$.

The plots of t/q_t vs t for adsorption of Pb(II), Cd(II) and Zn(II) are shown in Figures 3a, 3b and 3c respectively.

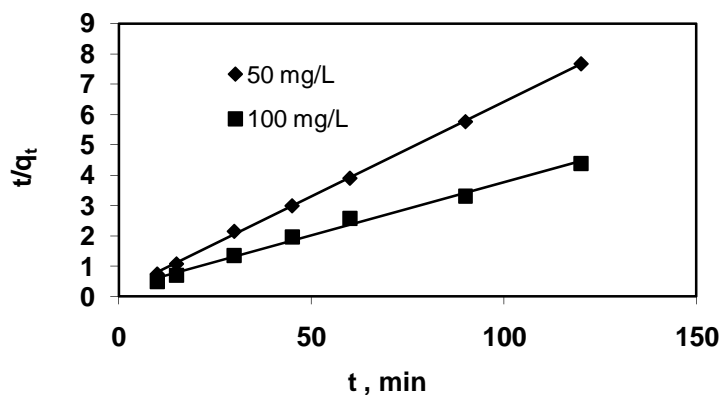


Figure 3a Pseudo second order kinetic plots for Pb(II) adsorption on LMO sample (data corresponding to Figure 2a).

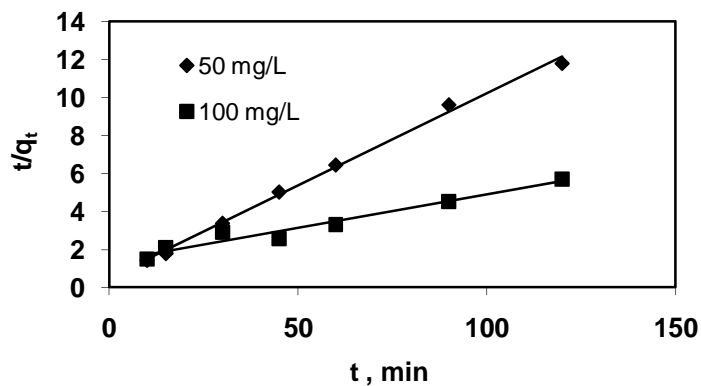


Figure 3b Pseudo second order kinetic plots for Cd(II) adsorption on LMO sample (data corresponding to Figure 2b).

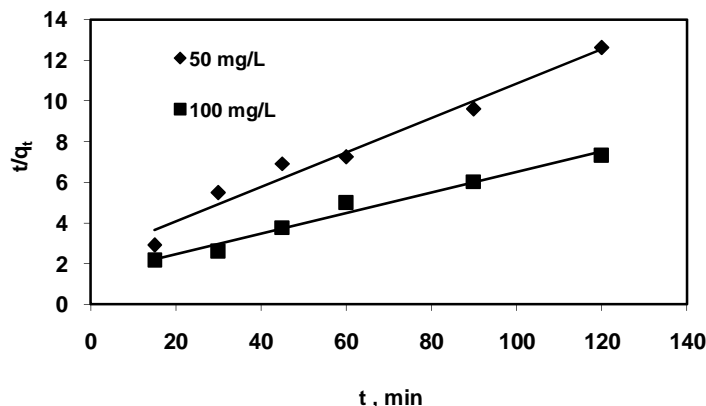


Figure 3c Pseudo second order kinetic plots for Zn(II) adsorption on LMO sample (data corresponding to Figure 2c).

The rate parameters calculated according to Eqn.(1) are given in Table 1.

Table 1 Rate coefficients for adsorption of Pb(II), Cd(II) and Zn(II) on LMO sample

	Pb(II)	Cd(II)	Zn(II)
Initial metal ion concentration 50 mg/L			
q_{exp}	10.17	10.85	9.72
$k_1 \cdot 10^{-3}$ (g /mg/ min)	22.9	18.57	2.99
q_e	15.65	10.30	11.82
r^2	0.99	0.99	0.97
Initial metal ion concentration 100 mg/L			
q_{exp}	27.76	21.15	17.0
$k_1 \cdot 10^{-3}$ (g /mg/ min)	7.09	0.90	1.84
q_e	28.98	28.49	19.41
r^2	0.99	0.96	0.97

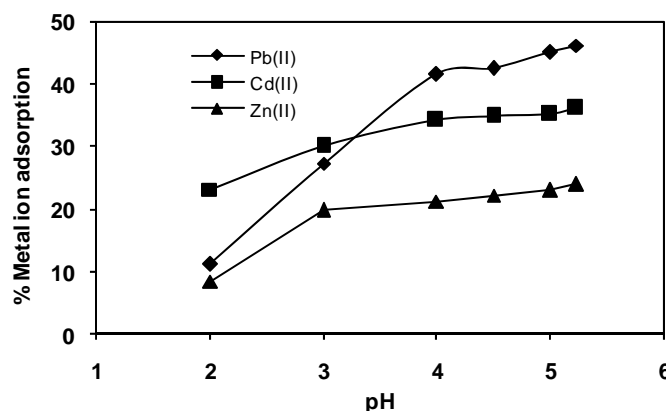
From the data given in Figures 3a, 3b,3c and Table 1, it is observed (i) reaction plots show straight lines with r^2 (regression coefficient) values varying in the range of 0.97 to 0.99 for Pb(II), Cd(II) and Zn(II) (ii) the calculated q_e values obtained from pseudo second order kinetics are close to the experimentally obtained q_e values for the three metal ions for initial metal ion concentrations of 50 and 100 mg/L (except in case of Pb(II) adsorption with initial 50 mg/L concentration and Cd(II) adsorption with initial 100 mg/L concentration). It is observed that with the increase of initial concentration, k_1 values for all the cations decrease. The loading capacities increase with the increase in initial metal ion concentration. The variation in pH was measured during progress of adsorption. As an example, the variation in final pH values for Cd(II) at 50 and 100 mg/L concentrations is given in Table 2. It is observed that there was increase in pH with the progress of reaction but maximum pH variation was 0.35 and 0.50 for 50 and 100 mg/L Cd(II) containing solutions. Similar effect was observed during Pb(II) and Zn(II) kinetic studies.

3.3 Effect of pH on Pb(II), Cd(II) and Zn(II) adsorption

To study whether the adsorption on LMO sample depended on solution pH, metal uptake was studied at pH ranging from 2.0 to 5.25 at a temperature of 300 K. Metal ion uptake was strongly affected by pH of the metal ions solutions till a pH value of 4.5 (Figure 4). The percentage of adsorption increased with the increase in pH from 2 to 4 but with further increase in pH only marginal increase was observed. At a pH of 2.0, the % adsorption on LMO is low for cations, as large quantities of protons compete with cations for the adsorption sites.

Table 2 Final pH of solution at different contact time for Cd(II) adsorption studies under the conditions: W = 2 g/L, T = 300K and pH = 5.25.

Time, min	Final pH (50 mg/L)	Final pH (100 mg/L)
10	5.21	5.61
15	5.29	5.63
30	5.27	5.65
45	5.42	5.69
60	5.59	5.72
90	5.61	5.75
120	5.62	5.75
180	5.62	5.75

**Figure 4** Effect of pH on adsorption of Pb(II), Cd(II) and Zn(II) on LMO sample. Conditions: $C_0 = 100$ mg/L, $W = 2$ g/L, $T = 300$ K and $t = 60$ min.

To know the dissolution of any major or minor metal ions from LMO at different pH values, blank experiments were carried out taking only LMO in double distilled water with pH adjusted to different initial values. The results are given in Table 3 and it is observed that no dissolution of Cu, Co, Ni and Fe takes place. Very small amounts of Mn and Zn (0.2 to 0.8 mg/L) dissolve.

Table 3 Dissolution of metal ions in mg/L from LMO at different pH values.

pH	Cu	Co	Ni	Fe	Mn	Zn
2.0	nil	nil	nil	0.006	0.803	0.2
3.0	nil	nil	nil	nil	0.716	0.145
4.0	nil	nil	nil	nil	0.521	0.121
5.0	nil	nil	nil	nil	0.276	0.096
6.0	nil	nil	nil	nil	0.239	0.032

3.4 Effect of amount of adsorbent on Pb(II), Cd(II) and Zn(II) adsorption

Another variable chosen for studying Pb(II), Cd(II) and Zn(II) adsorption was the amount of adsorbent which was varied from 1 to 6 g/L while keeping the metal ions concentrations, C_0 , as 100 mg/L, $t = 60$ min, $pH = 5.25$ and $T = 300$ K. Figures 5 and 6 show the % metal ion adsorbed and loading capacities respectively at various concentrations of adsorbent. As expected the % adsorption increases with the increase in amount of adsorbent and loading capacities, q , decrease. q is estimated as follows:

$$q, \text{ mg/g} = (C_0 - C_e)/W, \text{ where } C_0 \text{ and } C_e \text{ are in mg/L and } W \text{ in g/L.}$$

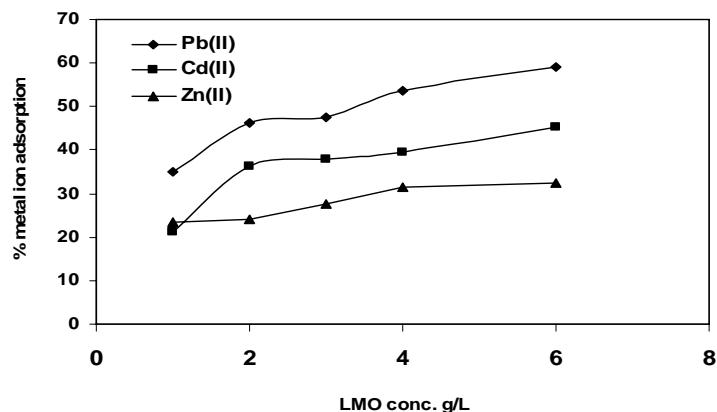


Figure 5 Effect of amount of adsorbent on adsorption of Pb(II), Cd(II) and Zn(II) on LMO sample.

Conditions: $C_0=100$ mg/L, pH =5.25, T = 300 K and t = 60 min.

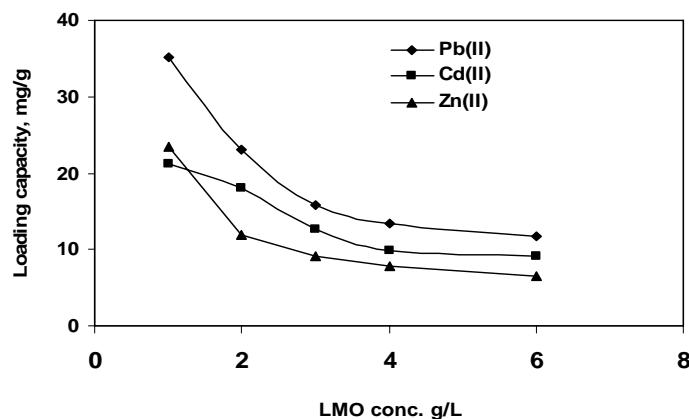


Figure 6 Effect of amount of adsorbent on loading capacities of Pb(II), Cd(II) and Zn(II) on LMO sample.

Conditions: Same as Figure 5.

The distribution coefficient (K_{DC}) generally used to define the partitioning of an element in a system (Balistreiri and Chao, 1987) is expressed by the following equation:

$$K_{DC} = [(cation_{ads}/cation_{diss})] (1/C_p) \quad (2)$$

Where C_p is the adsorbent concentration in kg/L and K_{DC} is the distribution coefficient in L/ kg. Figure 7 shows the plots for Log K_{DC} vs. adsorbent dose. The distribution coefficient K_{DC} of Pb(II), Cd(II) and Zn(II) for LMO at constant pH increased with increase of sorbent dose (Figure 7). A distribution coefficient reflects the binding ability of the surface for an element. If the surface is homogeneous, the K_{DC} values at a given pH should not change with particle concentration but in the present study for all the three metal ions K_{DC} increases thereby indicating the heterogeneous nature of the surface.

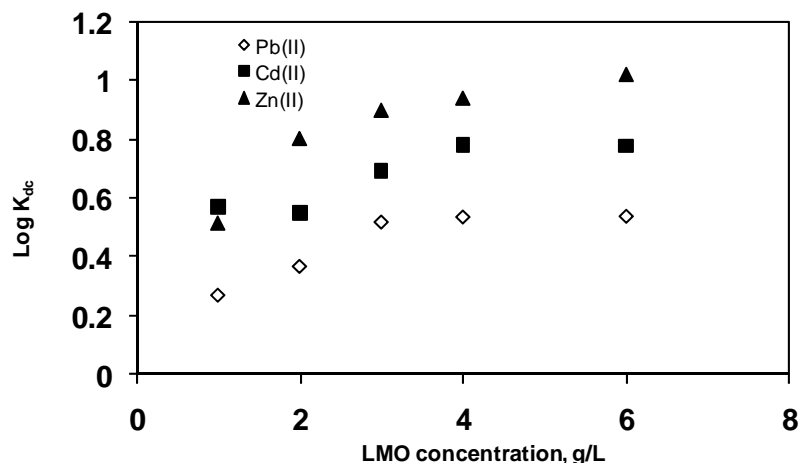


Figure 7 Plots for $\text{Log } K_{DC}$ vs. LMO concentration in g/L for Pb(II), Cd(II) and Zn(II)
Conditions: same as given in Figure 5.

3.5 Effect of initial metal ion concentration on Pb(II), Cd(II) and Zn(II) adsorption

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 5.25, at 300K for a period of 60 min. The % adsorption decreased with the increase of initial metal ion concentrations (plot not shown). To quantitatively estimate amount of metal ion adsorbed, the loading capacities were calculated at all initial metal ion concentrations and are given in Figure 8. From this figure it is observed that under the experimental conditions used, the amount of Pb(II), Cd(II) and Zn(II) adsorbed were ~67, 30 and 72 mg respectively per gram of LMO sample. The initial concentrations to obtain these capacities were: 500, 200 and 300 mg/L for Pb(II), Cd(II) and Zn(II) respectively. To evaluate the isothermic parameters the variation of metal ion concentration was studied at four hours time which is discussed in later section.

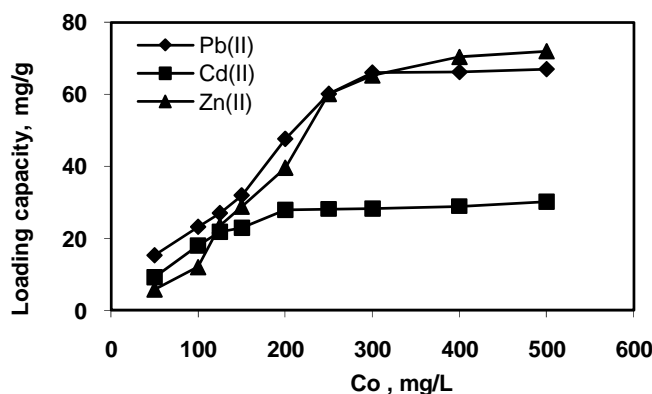


Figure 8 Effect of initial metal ion concentration on loading capacities of Pb(II), Cd(II) and Zn(II) on LMO sample at 60 minutes contact time. Conditions: $W = 2$ g/L, $\text{pH} = 5.25$, $T = 300\text{K}$.

3.6 Effect of temperature on Pb(II), Cd(II) and Zn(II) adsorption

Effect of temperature on % adsorption of Pb(II), Cd(II) and Zn(II) is shown in Figure 9. This series of experiments were conducted at pH values of 5.25 at different temperatures (300, 308, 318, 328 and 338K) while keeping rest of parameters as: adsorbent concentration 2g/L, adsorbate concentration 100 mg/L and time 60 min. Increase of temperature from 300 to 338K increased the adsorption of Zn(II) from 24 to 33% only (Figure 9). In case of adsorption of Pb(II) and Cd(II) ~4% increase was observed. The increase in percentage adsorption points towards chemisorption and endothermic nature of adsorption. Though this data does not refer to actual equilibrium due to shorter contact time, still the thermodynamic parameters were evaluated.

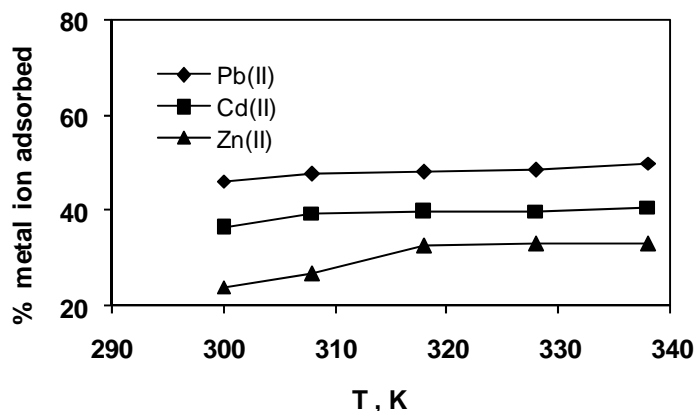


Figure 9 Effect of temperature on adsorption of Pb(II), Cd(II) and Zn(II) on LMO sample. Conditions: W = 2 g /L, pH = 5.25, and t = 60 min.

The values of ΔH° and ΔS° were determined from the Van't Hoff equation as given below.

$$\text{Log } K_c = \Delta S^\circ / 2.303R - \Delta H^\circ / 2.303RT \quad (3)$$

Where $K_c = C_A / C_e$

C_e the equilibrium concentration in solution (mg/L) and C_A is the adsorbed amount of adsorbate at equilibrium (mg/L) (Aroguz, 2006). The Vant Hoff plots are given in Figure 10. The positive values of ΔH° (2.88, 3.48 and 10.44 kJ/mol for Pb(II), Cd(II) and Zn(II) respectively) confirm the process to be endothermic in nature. The positive ΔS° values (8.45, 7.3 and 25.73 J/mol/deg for Pb(II), Cd(II) and Zn(II) respectively) suggest the increased randomness at the solid-solution interface during the adsorption of cations on the sample and thereby gaining more translational entropy than is lost by the adsorbate ions (Singh *et al.*, 1998).

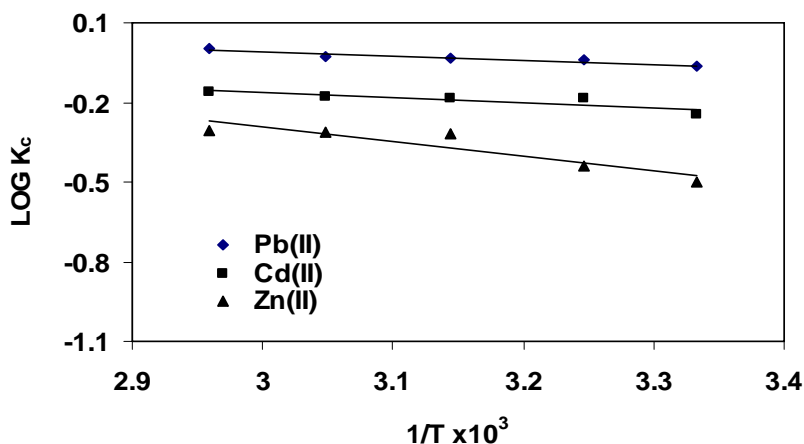


Figure 10 Vant Hoff plots showing Log Kc vs 1/T.

3.7 Isotherm models

The isothermic model are fitted for the equilibrium data, hence the adsorption studies were carried out for 240 minutes at different initial concentrations of metal ions. The isotherms are given in Figure 11.

The order of metal ion adsorption at equilibrium was Pb(II) > Zn(II) > Cd(II). The order of metal ion adsorption on synthetic and natural occurring pyrolusite has been reported (Gadde and Laitinen; 1974 and Ajmal *et al.*; 1994) as Pb(II) > Zn(II) > Cd(II).

The isothermic data was treated using Langmuir (Langmuir, 1918), and Freundlich Isotherm (Freundlich, 1926) Models. The linearised forms of Langmuir and Freundlich isotherms are expressed by Eqn. (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. Figures 12 and 13 show the Langmuir and Freundlich isotherms. The isothermic parameters are given in Table 4. Both the models showed good fit for the three cations as represented by the r^2 values.

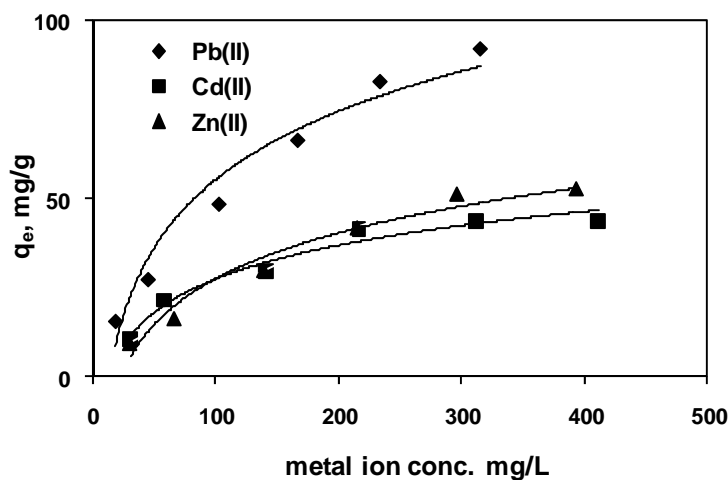


Figure 11 Adsorption isotherms of LMO for different initial metal ion concentrations. Conditions: $W = 2$ g/L, $pH = 5.25$, $T = 300K$, $t = 240$ min.

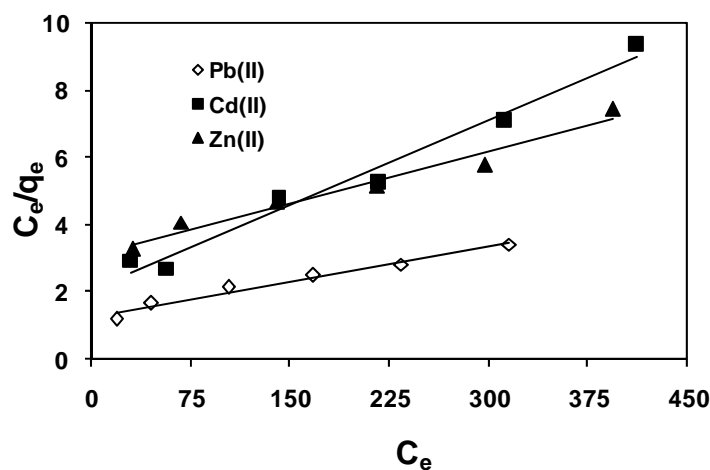


Figure 12 Langmuir adsorption isotherms for Pb(II), Cd(II) and Zn(II) (data corresponding to Figure 11)

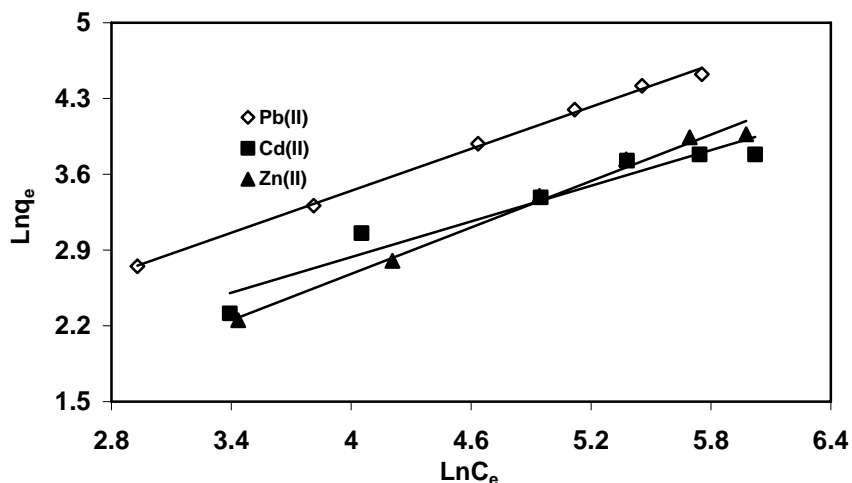


Figure 13 Freundlich isotherm for Pb(II), Cd(II) and Zn(II) (data corresponding to Figure 11)

Table 4 Isotherm parameters for Langmuir and Freundlich models.

Cation	Langmuir isotherm			Freundlich isotherm		
	R ²	Q ^o (mg/g)	b	R ²	K _F	n
Pb(II)	0.976	142.85	0.005	0.997	2.37	1.54
Cd(II)	0.975	59.17	0.008	0.93	1.9	1.82
Zn(II)	0.9633	98.03	0.003	0.988	0.835	1.4

The loading capacities of some naturally occurring waste materials are compared in Table 5. It is seen that the low grade manganese ore exhibit very high loading capacities for the three cations.

Table 5 Comparative table for loading capacities of some naturally occurring and waste materials

Adsorbent	loading capacity mg/g			Ref.
	Pb(II)	Zn(II)	Cd(II)	
Sericitic Pyrophyllite(SP)	32.5	-	-	(Prasad <i>et al.</i> , 2000)
Red mud	-	14.5	13.03	(Gupta and Sharma, 2002)
Rice husk	11.0	-	-	(Chuah, 2005)
Chromite mine overburden	27.54	-	22.47	(Mamata <i>et al.</i> , 2007; 2009c)
Nickel laterite (low iron)	28.4	-	11.0	(Mamata <i>et al.</i> , 2007)
Nickel laterite (high iron)	44.4	-	13.2	(Mamata <i>et al.</i> , 2007)
Red bauxite	64.35	65.86	38.77	(Rout <i>et al.</i> , 2009)
Iron ore slime	63.57	54.87	34.75	(Mamata <i>et al.</i> , 2009b)
Nalco Plant Sand	21.78	51.28	58.13	(Mamata <i>et al.</i> , 2009a)
Water washed clay	-	3.04	11.68	(Samir 2008)
Chemically treated clay	48.07	15.22	12.6	(Samir 2008)
Washed and treated clay	52.63	15.17	24.45	(Samir 2008)
Low grade manganese ore	142.85	98.03	59.17	Present study

3.8 XRD studies of the LMO and metal ions adsorbed LMO samples

With a view to study the effect of metal ions adsorption on the crystalline phases of LMO sample, the Pb(II), Cd(II) and Zn(II) adsorbed LMO surfaces were obtained under the experimental conditions: initial metal ion concentration 500 mg/L, t = 60 min, T = 308 K, pH 5.25. The solids were separated, washed with distilled water till free of soluble metal ions and dried in an air oven at

373 K for 24 h. The d-values and %I/I₀ are listed in Table 6. For Pb(II) adsorbed sample, the major peaks of silica phases shifted by 0.03-0.01 Å (+ve). However, the peaks corresponding to β-MnO₂ were not disturbed. For Cd(II) adsorbed sample, all the peak for β-MnO₂ shifted by 0.02 Å (+ve). The XRD pattern of Zn(II) loaded sample showed that the major peak of silica phase diminished as well as the peak width decreased. It is indicated that Pb(II) adsorption affects silica phase whereas Cd(II) adsorption affects β-MnO₂ phase. Zn(II) adsorption affects the crystallinity of silica phase with respect to intensity and peak position.

Table 6 Comparison of XRD results for LMO and metal ion loaded LMO samples

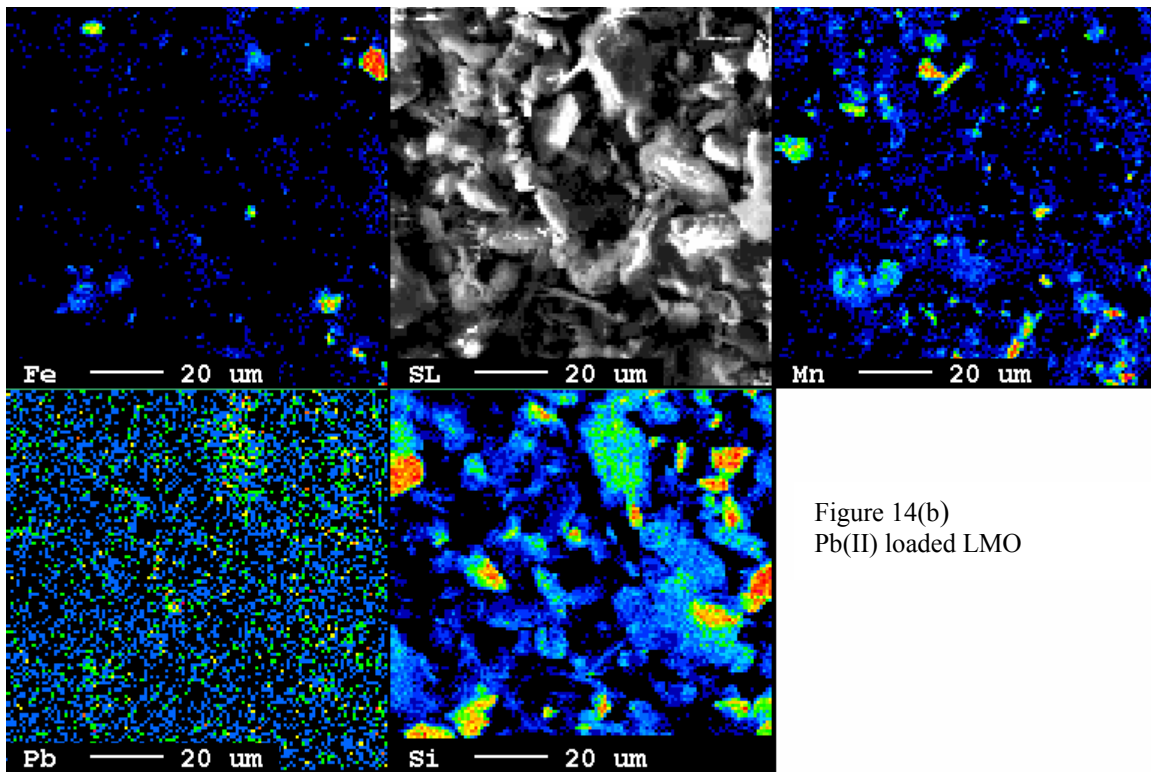
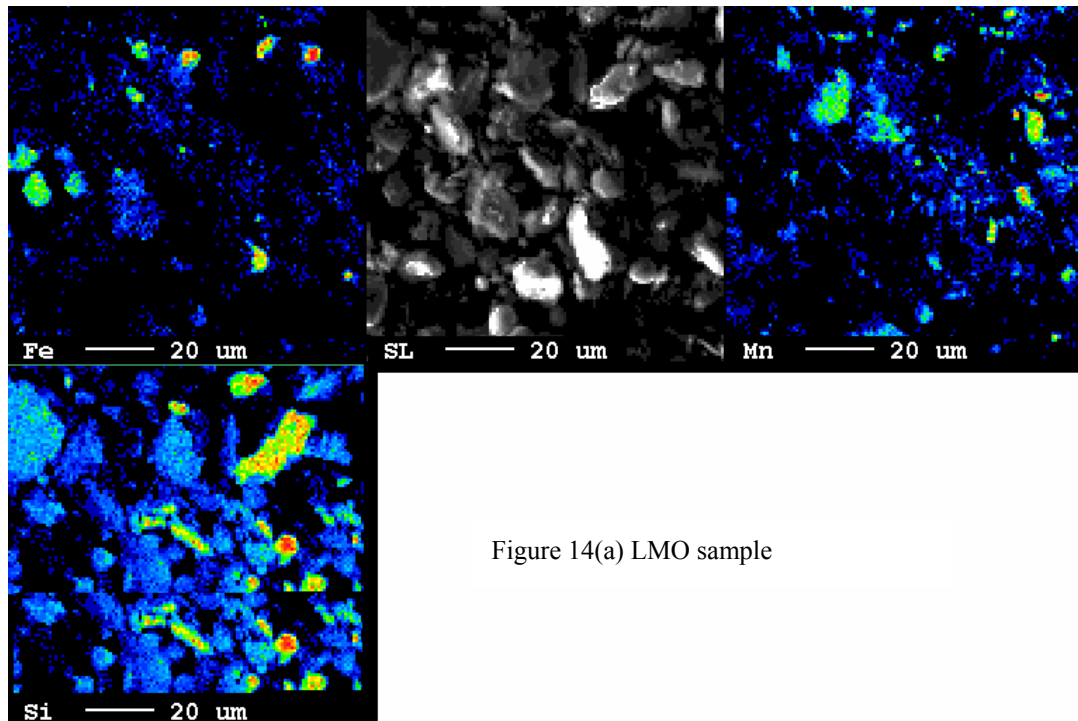
d value	LMO		Pb-LMO		Cd-LMO		Zn-LMO		Phase
	PS*	%I/I ₀	PS	%I/I ₀	PS	%I/I ₀	PS	%I/I ₀	
4.27		15.4	+ 0.03	16.7	0	18.5	0	11.9	silica
3.35		100	+ 0.02	100	0	100	0	100	silica
3.12		10.6	+ 0.01	10.0	0	6.9	0	6.0	silica
2.71		5.4	0	4.3	0	2.4	0	2.1	silica
2.46		7.1	0	9.5	0	6.2	0	4.8	silica
2.40		6.4	0	6.5	0.02	3.4	0	4.8	β-MnO ₂
2.24		5.5	A	-	A		0	4.4	silica
2.13		7.2	0	7.3	0.02	4.9	0	7.0	β-MnO ₂
1.98		6.1	0	4.1	0	2.7	0	2.7	silica
1.82		11.2	0	11.6	0	9.9	0	5.0	silica
1.66		4.0	A	A	0.02	3.3	0	3.2	silica, β-MnO ₂

PS* peak shift, I/I₀ relative intensity

3.9 EPMA studies of the metal ions adsorbed LMO samples

Electron micrographs of the samples were taken at 900X magnifications to observe the surface morphology of the iron, silica and manganese phases in LMO samples before and after Pb(II), Cd(II) and Zn(II) adsorption. The characteristic micrographs along with elemental mapping of LMO samples and Pb(II), Cd(II) and Zn(II) loaded samples are shown in Figures 14a, 14b, 14c and 14d. All figures show platelet-type silica particles with low concentrations of β-MnO₂ and iron oxide particles. In original LMO sample it is observed that silica presents itself as either liberated particles or along with β-MnO₂. Iron oxide particles are attached to the grain boundary of silica particles. No complex texture mineral association was observed. The elemental distribution mapping for the sample of LMO interacting with Pb(II) ions is illustrated in Figure 14b. It was observed that Pb is spread over the surface of pure silica particles whereas it is less concentrated on manganese and iron oxide particles. It seems to be present only on the boundary layer of both the particles. While in case of Cd(II) adsorbed LMO sample (Figure 14c), it was observed that Cd(II) was spread over the surface of manganese and iron oxide particles whereas it is less concentrated on silica particles. In case of Zn(II) loaded LMO sample (Figure 14d), Zn seems to be concentrated more in β-MnO₂ phase than iron oxide phase and present only on the boundary layer of silica particles. From this observation it was concluded that Pb(II), Cd(II) and Zn(II) adsorption are more spread over in silica, iron oxide and β-MnO₂ phases respectively though other phases also exhibited presence of adsorbed particles to certain extent.

The detailed studies carried out on manganese containing ore sample has shown that it is a potential adsorbent for cation adsorption. Various other aspects which can be looked into are: (i) toxicity characterization leaching procedure (TCLP) test on metal ion loaded samples for evaluation of safe disposal of the loaded ore (ii) regeneration of adsorbent for reutilization (iii) effect of presence of anions such as chloride and sulphate as these anions are usually associated with effluents and contaminated ground water (iv) synergistic effect of presence of two or three cations at a time due to presence of multi cations in industrial effluents (v) column adsorption experiments for final evaluation of adsorption behaviour.



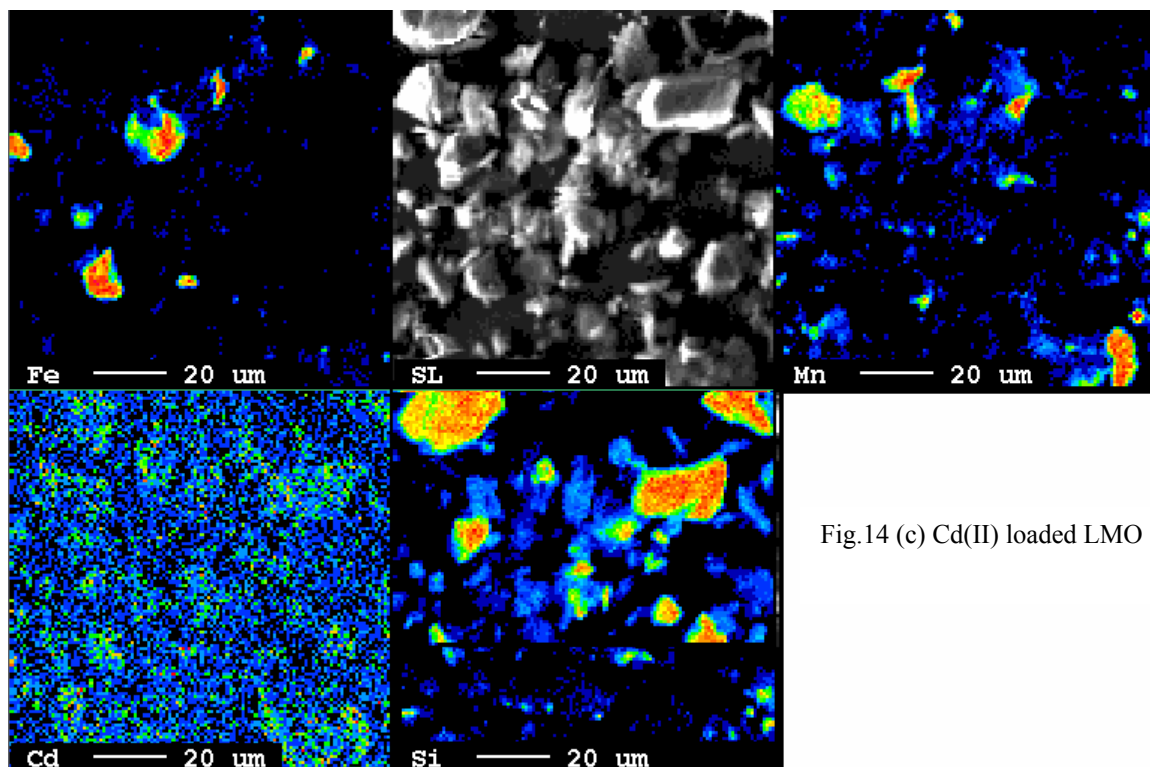


Fig.14 (c) Cd(II) loaded LMO

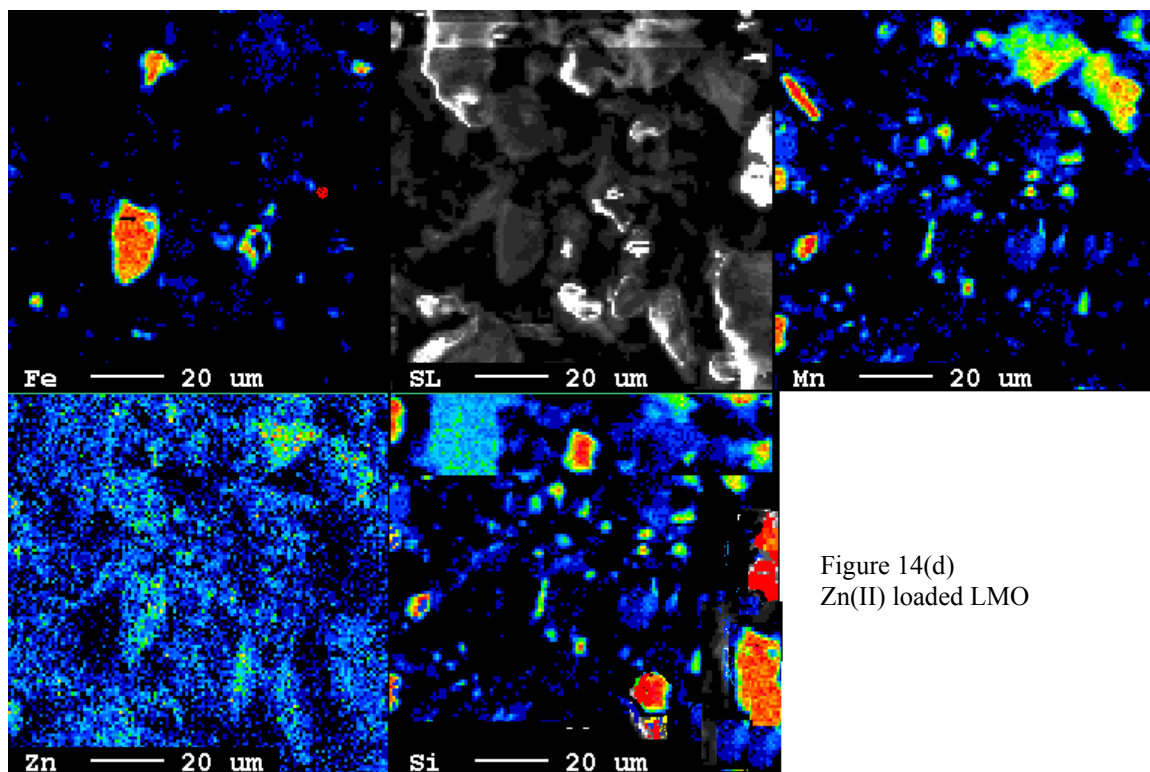
Figure 14(d)
Zn(II) loaded LMO

Figure 13 EPMA analysis of different elements for LMO and metal ion loaded sample (a) LMO (b) Pb(II) loaded sample (c) Cd(II) loaded sample and (d) Zn(II) loaded sample. The different colours in particular elemental map correspond to the different concentration of the respective element. The increasing order of the colour w.r.t concentration is red > yellow>green>blue.

4 Conclusions

Adsorption studies were carried out on low grade manganese ore of Orissa. The crystalline phases present were quartz, β - MnO_2 , δ - MnO_2 and Fe_2O_3 . The time data fitted well to pseudo second order kinetics for Pb(II), Cd(II) and Zn(II) adsorption. Pb(II) adsorption was dependent on pH till a value of 4.5 and thereafter only marginal increase in percentage adsorption was observed. The equilibrium adsorption data showed good fit to both Langmuir and Freundlich isotherm models. The Langmuir monolayer capacities were estimated to be ~142.85, 59.17 and 98.0 mg per gram of LMO for Pb(II), Cd(II) and Zn(II) respectively. The increase in % adsorption of metal ions with increase in temperature indicated the process to be chemisorption in nature. Positive values of ΔH° confirmed endothermic nature of adsorption while the positive values of ΔS° suggest the increased randomness at the solid-solution interface during the adsorption of cations on the sample. The XRD studies of loaded LMO samples showed that Pb(II) adsorption affects silica phase whereas Cd(II) adsorption affects β - MnO_2 phase. Zn(II) adsorption affects the crystallinity of silica phase as both the intensity and peak position of silica phase were disturbed after Zn(II) adsorption. From the EPMA analysis it was observed that Pb(II), Cd(II) and Zn(II) adsorption are more prone to silica, iron oxide and β - MnO_2 phase respectively. The high loading capacities for Pb(II) and Zn(II) makes the low grade manganese ore a potential adsorbent for these metal ions

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Nomenclature

b	Langmuir equilibrium coefficient, L/g
C_o	Initial concentration of adsorbate, mg/L
C_A	Adsorbed amount of adsorbate, mg/L
C_p	Adsorbent concentration, Kg/L
C_t	Concentration of adsorbate at time t, mg/L
C_e	Concentration of adsorbate at equilibrium, mg/L
K_{DC}	Distribution co-efficient, L/Kg
K_f	Freundlich constant
K_e	Equilibrium constant
k_1	Second order rate constant, g/mg/min
n	term related to adsorption intensity
q	adsorption capacity, mg/g
q_t	adsorption capacity at time t, mg/g
q_e	adsorption capacity at equilibrium, mg/g
ΔS°	Entropy, J/mol/deg
ΔH	Enthalpy, KJ/mol
R	Gas constant, J/deg/mol
r^2	Regression co-efficient
t	Time, minute
T	temperature, K
W	weight of adsorbent per liter of solution, g/L

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