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ADSORPTION OF LEAD AND ZINC IONS ON SEDIMENTS



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ABSTRACT

Adsorption is one of the most important processes in water quality control, it may determine the fate and transport of pollutants in the aquatic environment. The adsorption of lead and zinc ions on the bed sediments of river Kali in western Uttar Pradesh, India has been studied. The role of the coarser sediment fraction (210-250 μm) has been elucidated and compared to those of the clay and silt fractions. The parameters controlling the uptake, viz., initial metal ion concentration, solution pH, sediment dose, contact time, and particle size have been evaluated. The adsorption of metal ions increases with increasing initial metal ion concentration. The optimum contact time in which equilibrium is attained was found to be 45 min for both the metal ions. The extent of adsorption increases with an increase of pH. The adsorption of metal ions on the sediments follows two phases, a linear phase of adsorption followed by a flat plateau section. Further, the adsorption of metal ions increases with increasing adsorbent doses and decreases with adsorbent particle size. The two geochemical phases, namely iron and manganese oxide, act as the active support material for the adsorption of two metal ions.

1.0 INTRODUCTION

1.1 General

Adsorption of trace metals on sediments and suspended matter represents an important control on their speciation and hence on their bioavailability and mobility in the aquatic environment (Gardiner, 1974; Laxen, 1983; Laxen and Harrison, 1981). The suspended and bed sediments play an important role in the transport and control of metal pollution in aquatic systems. The important components of the suspended load for geochemical transport are silts, clays, hydrous iron and manganese oxides and organic matter (Horowitz and Elrick, 1987; Horowitz, 1985; Gibbs, 1973).

Soong (1974) has studied the competitive sorption of heavy metals onto clay mineral and reported that lead has a special affinity for the clay minerals. Jenne (1976) found that the most significant role of clay-size mineral in trace element sorption by soils and sediments is that of a mechanical substrate for the precipitation and flocculation of organics and secondary minerals. Among the latter group of substances hydrous iron and manganese oxides have shown particularly strong affinities for trace elements. These affinities involve mechanisms of adsorption and coprecipitation.

The adsorption interactions between trace metals and phenolic compounds on suspended clay minerals have been studied by Gagnon et al. (1992). The large surface area of clay particles and the crystal structure of the aluminosilicates clays make them uniquely suitable as sites for soil-chemical reactions with large sorption capacities. Exchange of pollutants occur between the liquid phase and the clay component of the solid phase. These processes play an important part in the fate (transport and immobilization) of organic compounds and trace metals which enter the environment. It was reported that chlorite was a better adsorbent with 71% of Cd and 79% of Ni adsorbed at concentrations of suspended particulate matter of 400 mg/L. The data suggests that adsorption is not a simple process, adsorption/desorption

equilibria occur in the estuary and further studies are needed to better understand processes affecting the sorption of metals and organic compounds.

Palheiros et al. (1989) have studied the effect of pH, ionic strength and chloride concentration on the adsorption of cadmium onto a riverbed sediment collected from a small river located near Aveiro (Portugal) and reported that pH is the most important parameter in the control of cadmium adsorption. Both ionic strength and chloride concentration are related to salinity and the authors aimed to decide the relative importance of each. In the pH interval 4 to 7.7, the adsorption capacity of the soils increased to 2 to 3 times for a pH increase of one unit (Christensen, 1984). It has also been reported that for cadmium the predominant process taking place at a pH of 6 is adsorption. Bajracharya et al. (1996) studied the effect of zinc and ammonium ions on the adsorption of cadmium on soils at a pH of 6 and reported that both zinc and ammonium ions suppressed the ability of cadmium to adsorb onto soil.

Numerous laboratory studies addresses the effect of environmental conditions such as pH, ionic strength, complexing agents, competing surfaces, redox potential and sorbent concentration (Honeyman and Santchi, 1988; and references therein). However, low pH values, the use of buffers, high adsorbate concentration ranges, storage and preparation procedures that radically change the nature of the sample or the use of isolated artificial model phases in such studies frequently limit the applicability of the results because they deviate significantly from natural conditions (Oakly et al., 1981; Jenne and Zachara, 1987).

Koelmans and Luklema (1992) have studied the sorption of tetrachlorobenzene and cadmium on sediments and suspended solids in lake Volkerak/Zoom and reported that the sorption coefficients for tetrachlorobenzene are proportional to the organic carbon content, which is highly influenced by algal blooms. Due to a decrease in relative clay content during algal blooms, a proportional decrease in the cadmium distribution was

found. A similar analysis shows that cadmium is bound almost completely to the geochemical iron, manganese and organic phases, the first being exclusively associated with the clay fraction.

The adsorption of heavy metal ions on oxides, another potential adsorber in sediments, have been studied extensively. Many laboratory studies concerning adsorption of heavy metals onto well characterized model particulates (predominately metal oxides) have been performed in the past two decades (Huang and Stumm, 1973; Hohl and Stumm, 1976; Davis and Leckie, 1978; Balistriero and Murray, 1982; Fu et al., 1991). Moreover, mathematical models have been developed to explain the adsorption of metal ions onto hydrous oxide surfaces (Davis et al., 1978; Morel et al., 1981; Schindler and Stumm, 1987). These models of well characterized particles are useful for our understanding of the basic physical-chemical nature of metal-particle interaction. However, it has not been shown whether such models can be directly applied to the natural particulate-water interface.

Benjamin and Leckie (1980) reported the adsorption of Cd, Cu and Pb on a number of hydrous oxides and indicated source surface sites for adsorption. Dempsey and Singer (1980) reported adsorption of zinc on hydrous ferric and manganese oxides which may in turn be associated with clays and effect of calcium ions on the adsorption. Loganathan and Bureau (1973) reported the adsorption of heavy metal ions by hydrous manganous oxide. These oxides constitute significant sinks of heavy metals in the aquatic systems. Förstner and different co-authors (1973, 1977, 1983) compiled the associations of heavy metals in particulate form in sediments, where he described the active constituents with the nature of association.

The affinity of heavy metals for organic substances and for their decomposition products is of great importance for the behavior of trace substances in aquatic systems. Singer (1977) summarized the influence of dissolved organics on the distribution of metals. Dissolved organic substances are capable of (i) complexing metals and increasing metal solubility; (ii) altering the distribution between oxidized and reduced forms of

metals; (iii) alleviating metal toxicity and altering metal availability to aquatic life; (iv) influencing the extent to which metals are adsorbed on suspended matter, and (v) affecting the stability of metal-containing colloids.

Saxby (1973) has suggested the three major processes leading to the incorporation of particular metal-organic species onto a sediment: (i) reaction between a metal ion and an organic ligand in solution leading to a species which can either precipitate directly or be adsorbed on sedimentary material; (ii) incorporation in a sedimentary pile of all or part of an organism containing biologic coordination compounds, and (iii) adsorption on a sediment of molecules resulting from the solubilization of minerals by natural waters containing organic ligands. Curtis (1966) has proposed a simplified scheme to explain why certain metals (Cr, Cu, Mn, Mo, Ni, U, V) shows a positive association with organic carbon in a sediment, while other elements exhibit no significant correlation, or may even be negatively correlated with organic carbon.

In most of the publications described above, the clay and silt fractions of the sediments and organic matter has been considered as the main adsorbing agent, while the contribution of sediment fraction of higher particle size is somewhat ignored. Although clay and silt component adsorb metal ions much better than sediment fraction (sand) of higher size, one should take into account that river sediments contain 90-95% sand and only 0-10% clay and silt. Therefore, in river sediments with high sand percentage and low clay and silt content, the overall contribution of sand content to adsorption of metal ions may be comparable to or even higher than that of clay and silt fraction.

In the present report an attempt has been made to study the adsorption of lead and zinc ions on different fractions of the sediment of a highly polluted river in western Uttar Pradesh, India. The objective was to demonstrate the relative contribution of coarser fraction of the sediments for the control of metal pollution. Both the metal ions are toxic and relatively widespread in the environment (Förstner and Wittmann, 1979). The

role of important geochemical phases have also been investigated.

1.2 Scope of the Study

Heavy metals added to a river system by natural or manmade sources during their transport are distributed between the aqueous phase and the suspended sediments. The fraction in the sediment, is expected not to present direct danger, if the metal ions are tightly bound to it and subsequently settled to bottom in course of time. This state of affairs is maintained until there is remobilization from the sediment due to changing conditions in the system.

Thus, in the natural conditions of river water, suspended load and sediments have the important function of buffering higher metal concentrations of water particularly by adsorption or precipitation. Therefore, the study of the sorptive properties of the sediments can provide valuable information relating to the tolerance of the system to the added heavy metal load.

The Kali river, which flows in western Uttar Pradesh, India, is a small perennial river having a basin area of about 750 km² (Fig. 1). The climate in this region is moderate subtropic monsoonal. The average annual rainfall in the area is about 1000 mm, major part of which is received during monsoon period. The major land use is agriculture and there is no effective forest cover. The soils of the area are loam to silty loam and are normally free from carbonates.

The river basin contains towns and villages surrounded by agricultural areas. The quantity and quality of the river water is affected by the discharge from municipal and industrial areas as well as runoff from agricultural areas.

The river Kali is a typical water course for municipal and industrial effluents; all those who have access to the river use it for bathing, laundry and even for defecating and are very difficult to regulate. The main sources which create pollution in river Kali include, municipal waste of Muzaffarnagar city, waste from a variety of industries (such as steel, rubber, ceramic, chemical, plastic, dairy, pulp and paper, and laundries), Mansurpur sugar mill and distillery waste. The composite waste from a variety of industries is transferred through Muzaffarnagar main drain into the river. The chemical characteristics of this river have been reported earlier with special reference to the disposal of municipal and industrial wastes (Jain, 1992). In an other publication a mass balance approach has been utilised to discriminate between point and non-point sources of pollution to the river (Jain, 1996).

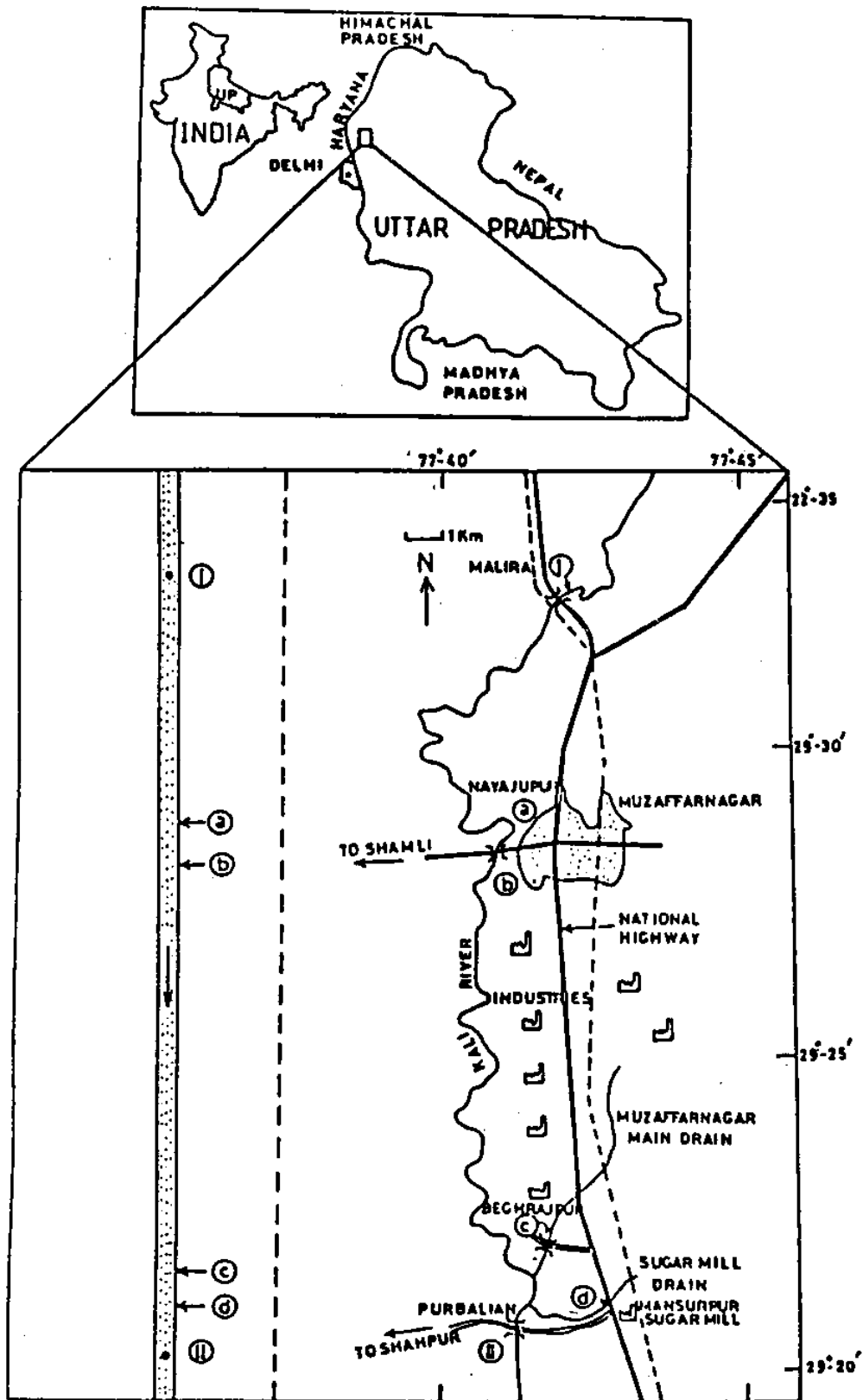


Fig. 1. The river system

3.0 EXPERIMENTAL METHODOLOGY

3.1 Sampling and Storage

For the adsorption studies of heavy metal ions freshly deposited sediments from shallow water near the river bank were collected from the upstream section of the river in polyethylene bags and brought to the laboratory. Samples were taken from the upper 5 cm of the sediments at places where flow rates were low and sedimentation was assumed to occur. Sakai et al. (1986) and Subramanian et al. (1987) have adopted the same method in their work.

The size distribution of the sediment samples was done by dry sieving method using ASTM standard sieves to obtain various fractions, viz., 0-75, 75-150, 150-210, 210-250, 250-325, and 325-425 μm . Sieved sediments were oven dried overnight at 105° C and, after cooling in desiccator, stored in air-tight containers for adsorption studies.

3.2 Materials and Reagents

All chemicals used in the study were of analytical grade. Aqueous solutions of lead and zinc were prepared from lead nitrate and zinc sulphate respectively. Deionized water was used throughout the study. All glasswares and other containers were thoroughly cleaned by soaking in detergent followed by soaking in 10 % nitric acid for 48 h and finally rinsed with deionized water several times prior to use.

3.3 Adsorption Experiments

Adsorption experiments were conducted in Erlenmeyer flasks with ground-glass stoppers. 50 mL of the chosen desired concentration of the metal ion solution were transferred in 100 mL flasks together with the desired adsorbent doses (W_s in g l^{-1}), and the contents of the flask shaken on a water bath shaker maintained at 25°C for the desired durations of the contact time of the tests. The bottles were also shaken for sufficiently long

time to attain an equilibrium which was ascertained and ensured through the last two consecutive readings. Adsorption tests were terminated after the attainment of equilibrium conditions. After attainment of equilibrium, the bottle contents were filtered through 0.45 μm membrane filters and analysed for residual concentration of respective metal ions.

3.4 Metal Ion Analysis

Metal ion concentrations were determined by flame atomic absorption spectrometry using Perkin-Elmer Atomic Absorption Spectrometer (Model 3110) using air-acetylene flame. The detection limits for the two metal ions studied are 0.03 and 0.002 mg/L for lead and zinc respectively. Operational conditions were adjusted in accordance with the manufacturer's guidelines to yield optimal determinations. Quantification of the metals was based upon calibration curves of standard solutions of respective metals. These calibration curves were determined several times during the period of analysis.

The sediment under study has a rather coarse texture, composed of more than 99% sand and less than 1% silt and clay. The organic content was of the order of 0-1%. The important geochemical constituents in different particle size fractions alongwith weight percentage of different fractions are given in Table 1. It is evident from the data that the manganese and iron contents in the various fractions of the sediment decreases with increasing particle size of the sediment. This indicates the possibility of the two geochemical phases to act as the active support material for the adsorption of lead and zinc ions. However, relative contribution of individual components cannot be obtained from the present studies because in natural systems, type and composition of sediment's mineral and organic fractions vary simultaneously and the effect of individual constituents cannot be isolated. It is further evident from Table 1 that the sediment fraction of 210-250 μm particle size constitute 35.6% of the total sediment load. Therefore, it was felt worth to study the adsorption of metal ions on this fraction and to compare with the clay and silt fraction (<75 μm particle size) to demonstrate the importance of the coarser fraction in the control of metal pollution.

4.1 Initial Metal Ion Concentration (C_0)

To evaluate the effect of initial metal ion concentration (C_0) on adsorption behavior of lead and zinc on bed sediments of river Kali, studies were conducted with initial metal ion concentrations ranging from 2 to 25 mg/L with a fixed adsorbent dose of 5 g/L at a pH value of 5.0 ± 0.1 . Based on the adsorption data (Table 2) the plots were prepared between the metal ion adsorbed (C_t) versus equilibrium metal ion concentration at a particle size of 0-75 and 210-250 μm (Fig. 2). It is inferred that for the same equilibration time, the metal ion adsorbed is higher for greater values of initial metal ion concentration or the percentage adsorption is more for lower concentration of metal ions and decreases with increasing initial metal ion concentration. This is obvious because more efficient

Table 1. Characteristics of sediments

Particle Fraction (μm)	Weight (%)	Total Mn (mg/g)	Total Fe (mg/g)
< 75	0.6	1.32	32.41
75-150	3.9	1.03	21.48
150-210	19.1	0.39	10.75
210-250	35.6	0.23	7.88
250-300	15.0	0.15	7.87
300-425	24.3	0.12	7.05
425-600	1.5	-	-

Table 2(A). Adsorption data for lead and zinc on bed sediments of river Kali on 0-75 μm sediment fraction; pH = 5.0; Adsorbent dose = 5 g/L; Temperature = 25°C.

Metal Ion	Initial concn. C_0 (mg/L)	Concn. remaining at equilibrium C_e (mg/L)	Metal ion adsorbed		
			mg/L	$\mu\text{g/g}$	Percent
Pb	2.00	0.13	1.87	374	93.5
	4.00	0.29	3.71	742	92.7
	6.00	0.47	5.53	1106	92.2
	8.00	0.70	7.30	1460	91.3
	10.00	1.00	9.00	1830	90.0
	15.00	1.86	13.14	2628	87.6
	20.00	2.89	17.11	3434	85.6
Zn	2.00	0.45	1.55	310	77.5
	4.00	1.63	2.37	474	59.3
	6.00	2.55	3.45	690	57.5
	8.00	7.18	4.15	830	51.9
	10.00	9.00	5.50	1100	50.5
	15.00	13.84	6.05	1210	40.3
	20.00	18.68	6.55	1310	32.8

Table 2(B). Adsorption data for lead and zinc on bed sediments of river Kali on 210-250 μm sediment fraction; pH = 5.0; Adsorbent dose = 5 g/L; Temperature = 25°C.

Metal Ion	Initial concn. C_0 (mg/L)	Concn. remaining at equilibrium C_e (mg/L)	Metal ion adsorbed		
			mg/L	$\mu\text{g/g}$	Percent
Pb	2.00	0.88	1.12	225	56.3
	4.00	2.23	1.77	354	44.3
	6.00	3.90	2.10	420	35.0
	8.00	5.70	2.30	460	28.8
	10.00	7.52	2.48	496	24.8
	15.00	12.22	2.78	556	18.5
	20.00	17.00	3.00	600	15.0
	25.00	21.80	3.20	640	12.8
Zn	2.00	1.69	0.31	62	15.5
	4.00	3.45	0.55	110	13.8
	6.00	5.24	0.76	152	12.7
	8.00	7.18	0.82	164	10.3
	10.00	9.00	1.00	200	10.0
	15.00	13.84	1.16	233	7.7
	20.00	18.68	1.32	264	6.6
	25.00	23.63	1.37	275	6.9

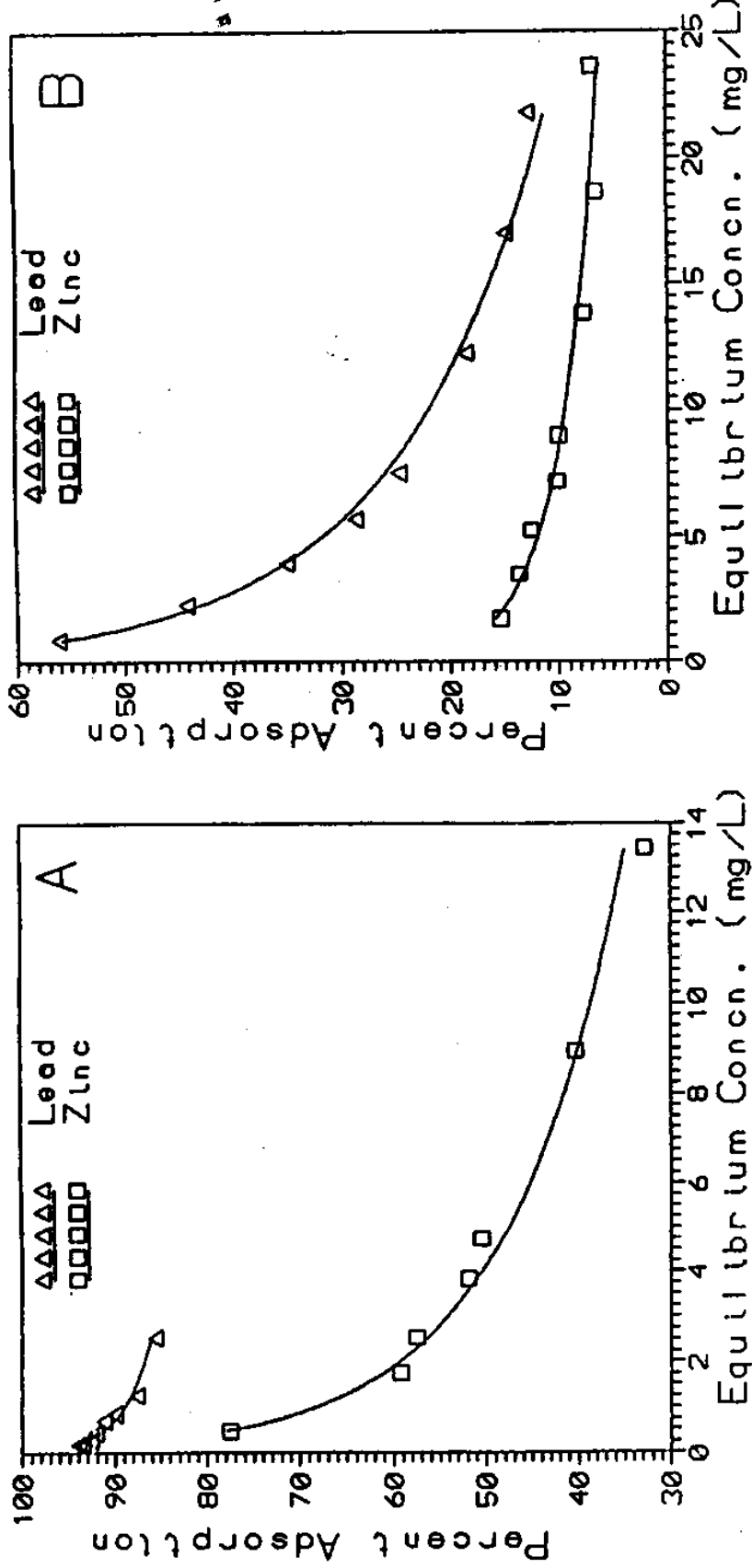


Fig. 2. Percent adsorption of lead and zinc ions on bed sediments. (A) 0-75 μm fraction; (B) 210-250 μm fraction

utilization of the adsorptive capacities of the adsorbent is expected due to a greater driving force (by a higher concentration gradient pressure). Comparing the two plots it is clearly evident that the affinity of the two metal ions is more for <75 μm fraction, i.e., clay and silt. It is also evident from Table 1 that <75 μm fraction contain more iron and manganese content than that of 210-250 μm fraction. This is responsible for the higher adsorption of the two metal ions on the clay and silt fraction. However, the clay and silt constitute only 0.6% of the total sediment load and therefore, comparing the two weight percentage of the two fractions and their corresponding adsorption capacities for the metal ions, it is clear that the contribution of sediment fraction of size 210-250 μm is more in controlling the metal pollution as compared to clay and silt content. Among the two ions, lead and zinc, the affinity is more pronounced in the case of lead as compared to zinc ions. Special affinity of lead ions was also reported by Soong (1974) on clay mineral structures.

4.2 Effect of pH

The adsorption of two metal ions on the bed sediments of river Kali was studied over the pH range 2-6 for a fixed adsorbent dose of 5 g/L at a particle size of 0-75 and 210-250 μm (Table 3, Fig. 3). The pH was adjusted using dilute nitric acid and sodium hydroxide solutions. The pH was measured before and after the attainment of equilibrium, the difference between the two values being generally less than 0.1 unit in the case of sediment of size 210-250 μm and 0.2 pH unit in the case of sediment of size < 75 μm (i.e. clay and silt fraction). A general increase in adsorption with increasing pH of solution has been observed, for both the metal ions upto the pH value of 6.0, beyond this pH the determination could not be performed due to low solubility of the metal ions. A similar behavior has been reported by many authors (Farrah and Pickering, 1976a,b, 1979; Netzer and Wilkinson, 1976; Benjamin and Leckie, 1980) for the uptake of metal ions on various adsorbents. From the results it is evident that the pH for maximum uptake of lead ion (530 $\mu\text{g/g}$) is 6.0. At this pH the concentration of lead ion in solution is

Table 3 (A). Adsorption of lead and zinc on bed sediments of river Kali at different pH values on 0-75 μm sediment fraction; Adsorbent dose = 5 g/L; Temperature = 25°C.

Metal Ion	Initial concn. C_0 (mg/L)	pH	Concn. after pH adjustment (mg/L)	Metal ion adsorbed	
				$\mu\text{g/g}$	Percent
Pb	10.0	2.0	9.99	90	4.5
		3.0	9.96	480	24.0
		4.0	9.78	1810	90.5
		5.0	8.64	1840	92.0
		6.0	6.31	1860	93.0
Zn	10.0	2.0	10.00	110	5.5
		3.0	9.19	330	16.5
		4.0	7.82	1440	72.0
		5.0	7.32	1550	77.5
		6.0	6.84	1590	79.5

Table 3 (B). Adsorption of lead and zinc on bed sediments of river Kali at different pH values on 210-250 μm sediment fraction; Adsorbent dose = 5 g/L; Temperature = 25°C.

Metal Ion	Initial concn. C_0 (mg/L)	pH	Concn. after pH adjustment (mg/L)	Metal ion adsorbed	
				$\mu\text{g/g}$	Percent
Pb	10.0	2.0	9.99	2	0.1
		3.0	9.96	17	0.9
		4.0	9.78	314	13.8
		5.0	8.64	510	29.5
		6.0	6.31	530	42.0
Zn	10.0	2.0	10.00	Nil	Nil
		3.0	9.19	40	2.2
		4.0	7.82	158	10.1
		5.0	7.32	198	13.5
		6.0	6.84	206	15.1

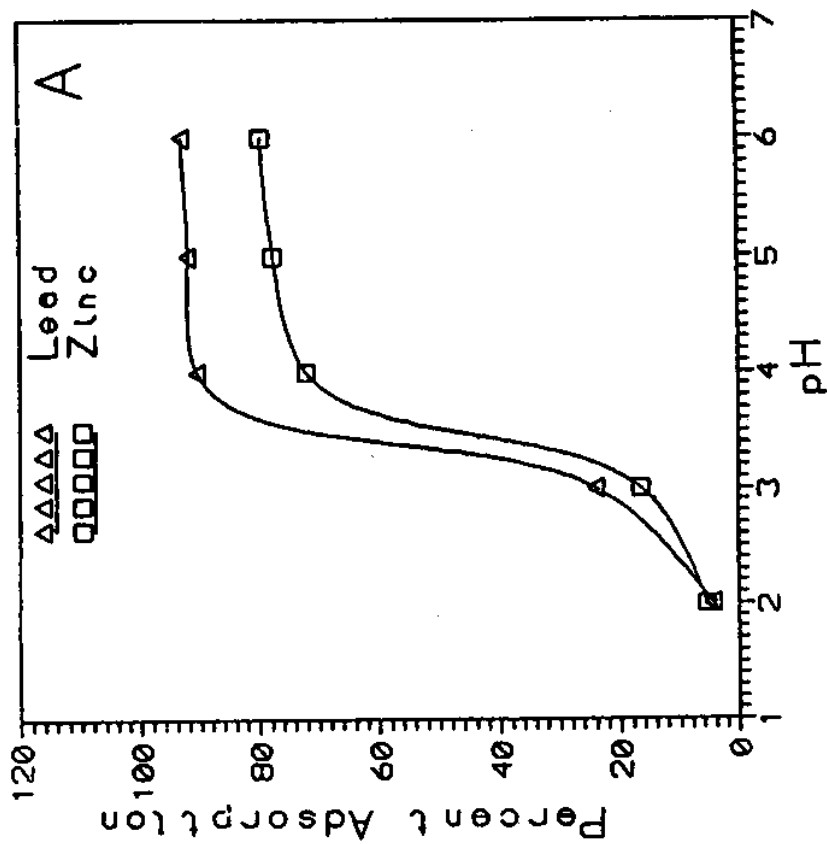
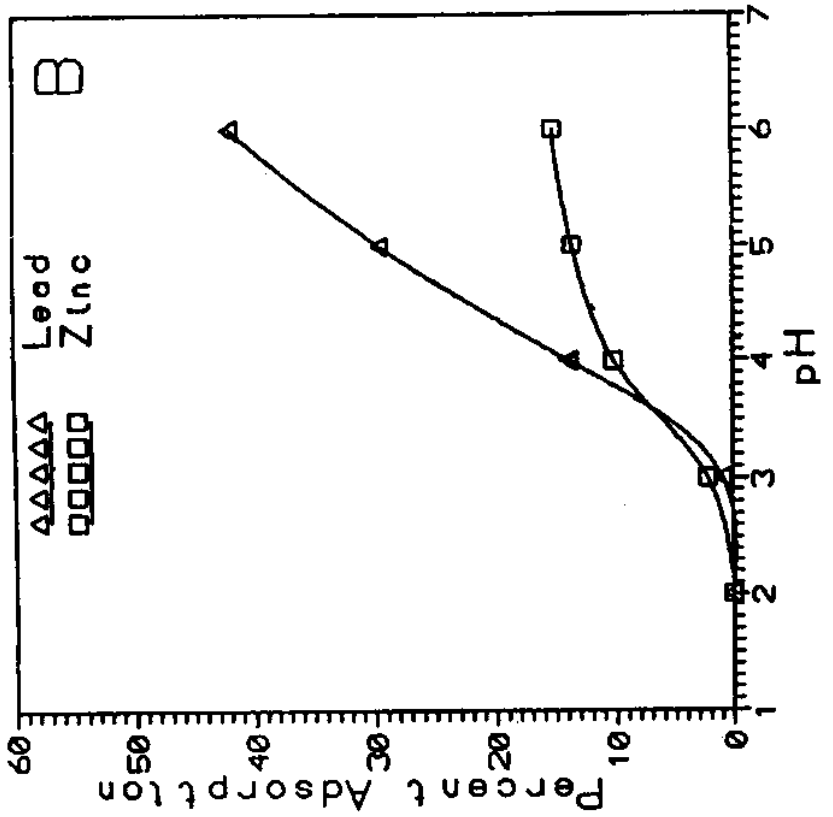


Fig. 3. Effect of pH on percent adsorption of lead and zinc ions on bed sediments. (A) 0-75 μm fraction; (B) 210-250 μm fraction

quite low (reduced to 6.31 mg/L from 10.0 mg/L due to pH adjustment). Further, it is apparent from Fig. 2 that the adsorption of lead rises from 13.8% at pH 4.0 to 42% at pH 6.0 which reveals the sediment's capacity for adsorbing lead ions even in acidic media.

The maximum removal of zinc is also observed to take place at pH 6.0 with corresponding adsorption value being 206 $\mu\text{g/g}$. At this pH the concentration of zinc ion in solution decreased from 10.0 mg/L to 6.84 mg/L due to pH adjustments. In this case adsorption of zinc rises from about 2% at pH 3.0 to 15% at pH 6.0. In this case also the percentage adsorption is more for <75 μm fraction as compared to 210-250 fraction.

4.3 Contact Time (t)

The adsorption data for the uptake of metal ions versus contact time for a fixed adsorbent dose of 5 g/L and with an initial metal ion concentration of 10 mg/L are given in Table 4 and graphically represented in Fig. 4 for the two particle size of adsorbent (0-75 and 210-250 μm) at pH 5.0. These plots indicate that the remaining concentration of metal ions becomes asymptotic to the time axis such that there is no appreciable change in the remaining metal ion concentration after 45 min in the case of 210-250 μm fraction and 30 min in the case of 0-75 μm fraction. This time presumed to represent the equilibrium time at which an equilibrium metal ion concentration (C_e) is presumed to have been attained.

An empirically found functional relationship, common to the most adsorption processes, is that the uptake varies almost proportionality with $t^{1/2}$ rather than with the contact time, t (Weber and Morris, 1963). Therefore, in Fig. 5, plots of metal ions adsorbed, C_t vs $t^{1/2}$ are presented for both the metal ions under consideration for the two particle size fraction. It is evident that adsorption of two metal ions on the bed sediments follows two phases, a linear phase of adsorption and then a almost flat plateau section. This may be attributed to the instantaneous utilization of the most readily available adsorbing

Table 4(A). Adsorption of lead and zinc on bed sediments of river Kali at different durations of contact time on 0-75 μm sediment fraction; Adsorbent dose = 5 g/L; pH = 5.0; Temperature = 25°C.

Metal Ion	Initial concn., C_0 (mg/L)	Contact time, t (min)	Concn. at time t (mg/L)	Metal ion adsorbed		
				mg/L	$\mu\text{g/g}$	Percent
Pb	10.0	5	2.05	7.95	1590	79.5
		10	1.45	8.55	1710	85.5
		15	1.05	8.95	1790	89.5
		30	0.85	9.15	1830	91.5
		45	0.85	9.15	1830	91.5
		60	0.80	9.20	1840	92.0
		90	0.85	9.15	1830	91.5
		120	0.90	9.10	1820	91.0
		150	0.95	9.05	1810	90.5
		180	0.90	9.10	1820	91.0
Zn	10.0	5	3.95	6.05	1212	60.5
		10	3.35	6.65	1330	66.5
		15	2.05	7.95	1590	79.5
		30	1.60	8.40	1680	84.0
		45	1.50	8.50	1700	85.0
		60	1.40	8.60	1720	86.0
		90	1.45	8.55	1710	85.5
		120	1.40	8.60	1720	86.0
		150	1.50	8.50	1700	85.0
		180	1.40	8.60	1720	86.0

Table 4(B). Adsorption of lead and zinc on bed sediments of river Kali at different durations of contact time on 210-250 μm fraction; Adsorbent dose = 5 g/L; pH = 5.0; Temperature = 25°C.

Metal Ion	Initial concn., C_0 (mg/L)	Contact time, t (min)	Concn. at time t (mg/L)	Metal ion adsorbed		
				mg/L	$\mu\text{g/g}$	Percent
Pb	10.0	5	9.21	0.79	158	7.9
		10	8.44	1.56	312	15.6
		15	8.15	1.85	370	18.5
		30	7.56	2.44	488	24.4
		45	7.48	2.52	504	25.2
		60	7.50	2.50	500	25.0
		90	7.52	2.48	496	24.8
		120	7.47	2.53	506	25.3
		150	7.46	2.54	508	25.4
		180	7.50	2.50	500	25.0
		Zn	10.0	5	9.62	0.38
10	9.35			0.65	130	6.5
15	9.10			0.90	180	9.0
30	9.00			1.00	200	10.0
45	8.95			1.05	210	10.5
60	8.96			1.04	208	10.4
90	8.93			1.07	214	10.7
120	8.95			1.05	210	10.5
150	8.95			1.05	210	10.5
180	8.93			1.07	214	10.7

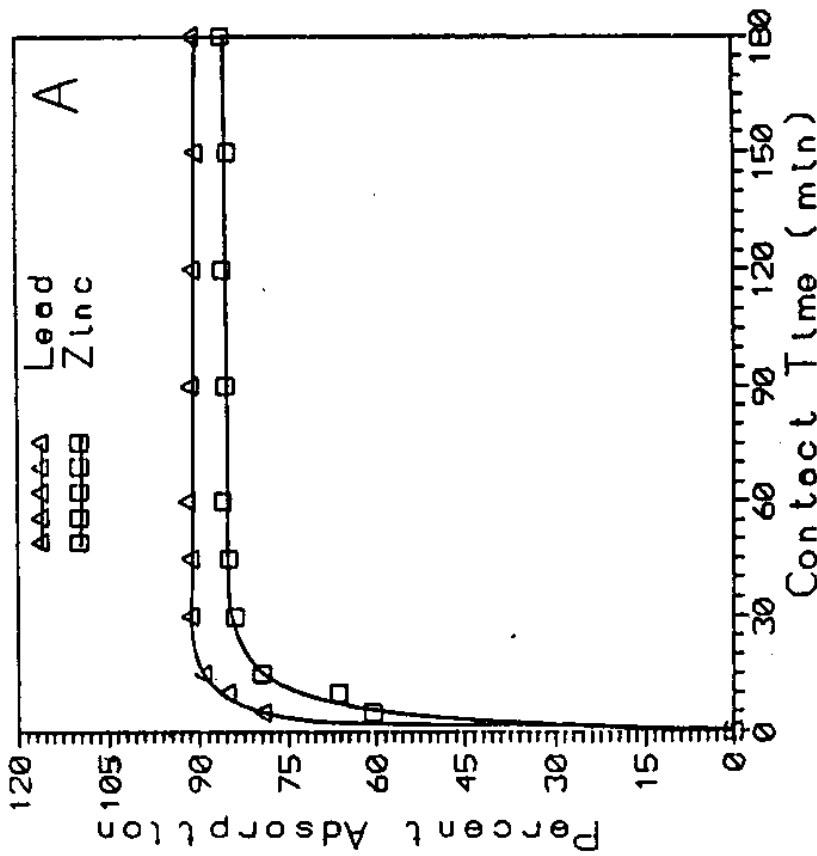
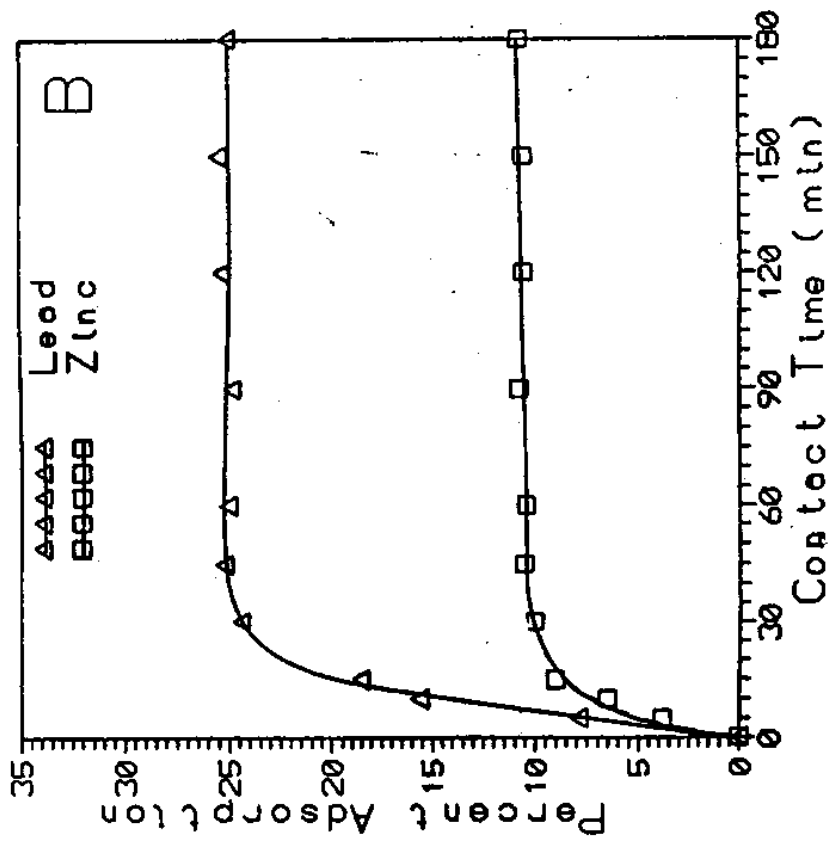


Fig. 4. Effect of contact time on percent adsorption of lead and zinc ions on bed sediments. (A) 0-75 μm fraction; (B) 210-250 μm fraction

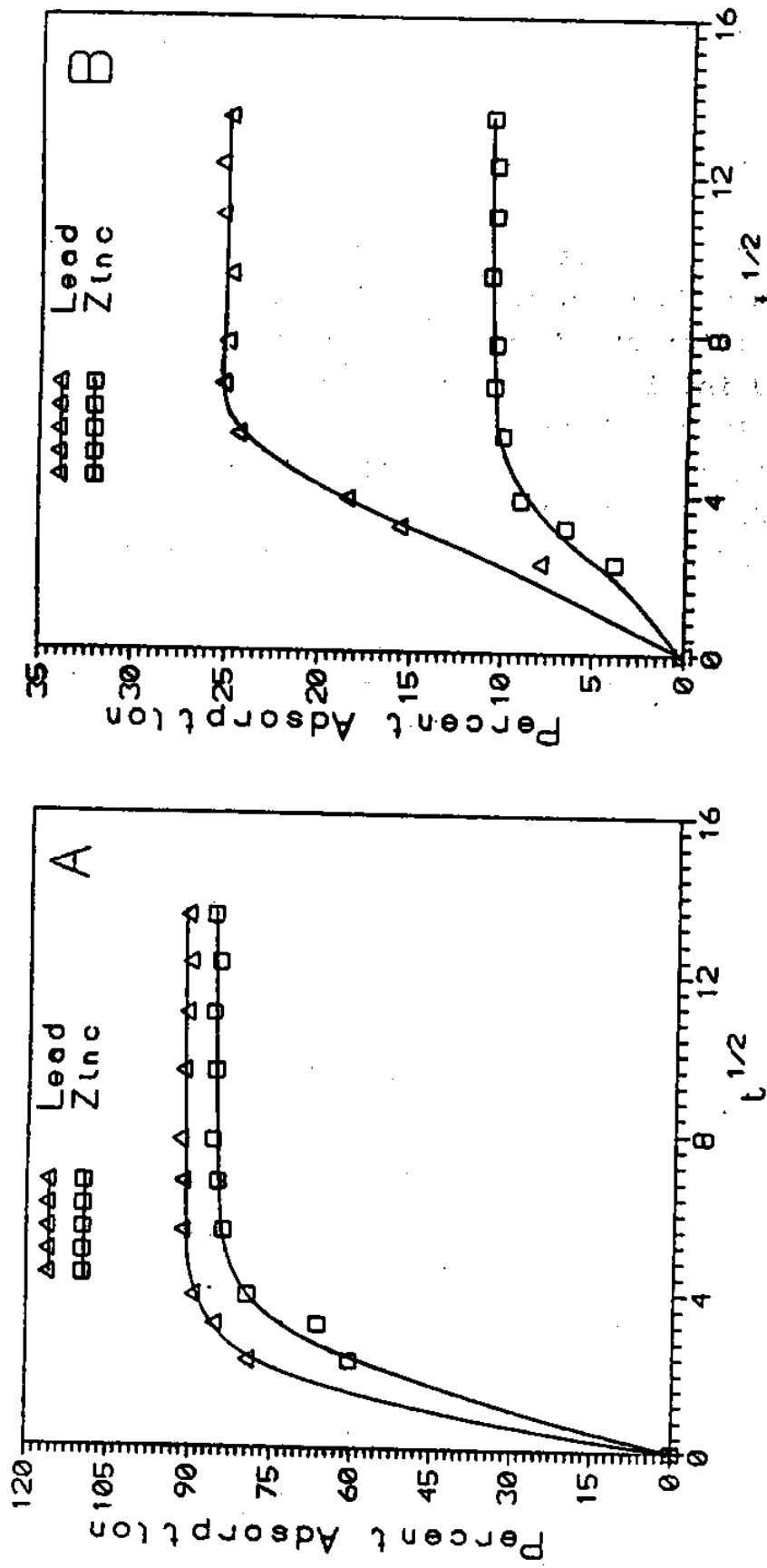


Fig. 5. Effect of $t^{1/2}$ on percent adsorption of lead and zinc ions on bed sediments (A) 0-75 μm fraction; (B) 210-250 μm fraction

sites on the adsorbent surface. The visual observation clearly indicate the minor importance of any precipitation from ion exchange.

4.4 Adsorbent Dose (W_s)

The effect of adsorbent dose on the adsorption properties of bed sediments of river Kali has been studied at pH 5.0 with different adsorbent doses varying from 2 to 10 g/L and at a fixed initial metal ion concentration of 10 mg/L (Table 5, Fig. 6). It is observed that for a fixed initial metal ion concentration ($C_0 = 10$ mg/L), the adsorption of metal ions per unit weight of adsorbent decreases with increasing adsorbent dose. The adsorption increases from 15 to 31 percent in the case of lead and from 6 to 15 percent in the case of zinc for the 210-250 μm fraction (Fig. 6) with increasing adsorbent dose for both the metal ions under study. However, the percent adsorption (or removal) of metal ions is about 3 to 5 times more for the 0-75 μm fraction as compared to 210-250 μm fraction. This is because of the higher content of iron and manganese in the 0-75 μm fraction, which act as the active support material for the adsorption of metal ions.

4.5 Particle Size (d_p)

The adsorption data for the two metal ions with a fixed adsorbent dose of 5 g/L and at a pH value of 5.0 are given in Table 6 and graphically represented in Fig. 7 for different sizes of adsorbent. The plots between percent adsorption of metal ions at equilibrium vs adsorbent sizes reveals that for a fixed adsorbent dose ($W_s = 5$ g/L), the metal ion adsorbed is higher for smaller adsorbent size. Further, it is observed that the percent metal ion adsorbed decreases from 90 to 20 percent in the case of lead and 50 to 8 percent in the case of zinc with the increasing geometric mean of adsorbent size. This is because, adsorption being a surface phenomenon, the smaller adsorption sizes offered comparatively larger surface area and hence higher adsorption occurs at equilibrium. In addition to the particle size of adsorbent, the geochemical phases, namely iron and

Table 5(A). Adsorption of lead and zinc on bed sediments of river Kali at different adsorbent doses on 0-75 μm sediment fraction; pH = 5.0; Temperature = 25°C.

Metal Ion	Initial concn., C_0 (mg/L)	Adsorbent dose, W_s (g/L)	Metal ion adsorbed	
			$\mu\text{g/g}$	Percent
Pb	10.0	2.0	1640	82.0
		4.0	1696	84.8
		6.0	1776	88.8
		8.0	1852	92.6
		10.0	1864	93.2
Zn	10.0	2.0	1280	64.0
		4.0	1504	75.2
		6.0	1680	84.0
		8.0	1680	84.0
		10.0	1840	92.0

Table 5(B). Adsorption of lead and zinc on bed sediments of river Kali at different adsorbent doses on 210-250 μm sediment fraction; pH = 5.0; Temperature = 25°C.

Metal Ion	Initial concn., C_0 (mg/L)	Adsorbent dose, W_s (g/L)	Metal ion adsorbed	
			$\mu\text{g/g}$	Percent
Pb	10.0	2.0	760	15.2
		4.0	550	22.0
		6.0	440	26.4
		8.0	370	29.6
		10.0	310	30.8
Zn	10.0	2.0	290	5.8
		4.0	225	9.0
		6.0	185	11.1
		8.0	163	13.0
		10.0	155	14.5

Table 6. Adsorption of lead and zinc on bed sediments of river Kali at different adsorbent sizes; Adsorbent dose = 5 g/L; pH = 5.0; Temperature = 25°C.

Metal Ion	Initial concn., C ₀ (mg/L)	Particle size, d _p (μm)	Metal ion adsorbed	
			μg/g	Percent
Pb	10.0	8.7	1800	90.0
		106.1	590	29.5
		177.5	520	26.0
		229.1	485	24.3
		273.8	430	21.5
		357.1	410	20.5
Zn	10.0	8.7	1010	50.5
		106.1	220	11.0
		177.5	205	10.3
		229.1	195	9.8
		273.8	188	9.4
		357.1	168	8.4

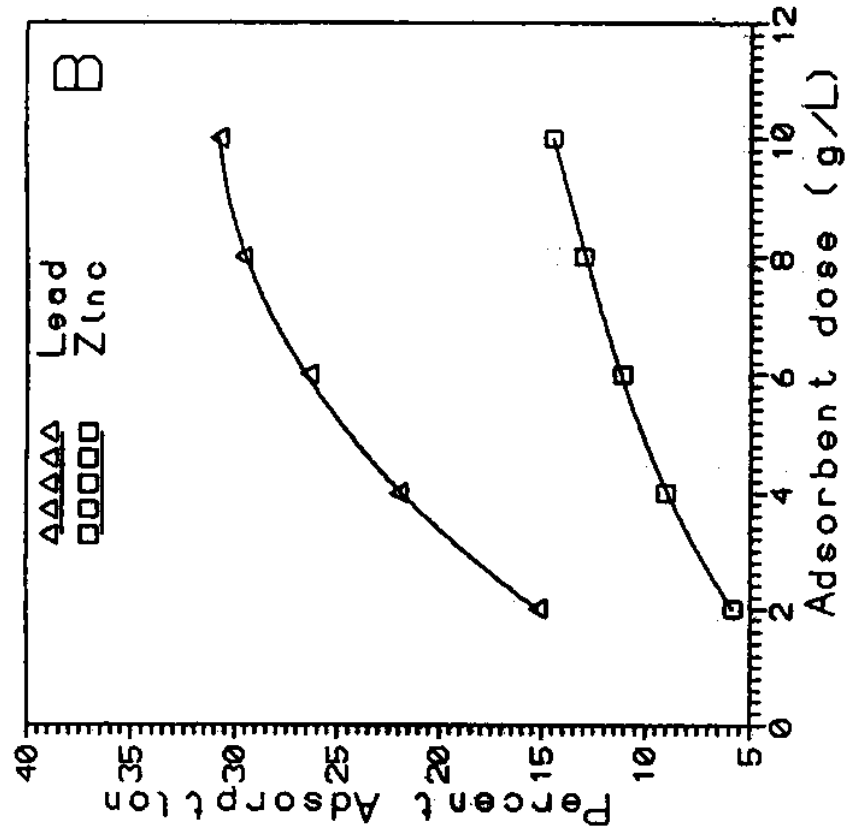
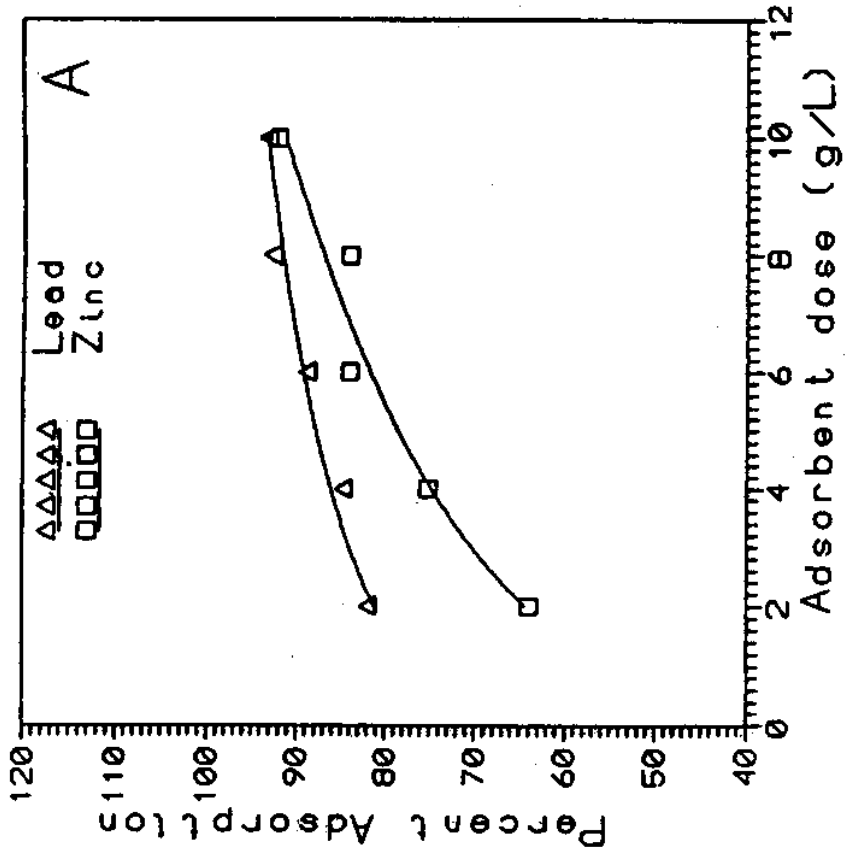


Fig. 6. Effect of adsorbent dose on percent adsorption of lead and zinc ions on bed sediments. (A) 0-75 μm fraction; (B) 210-250 μm fraction

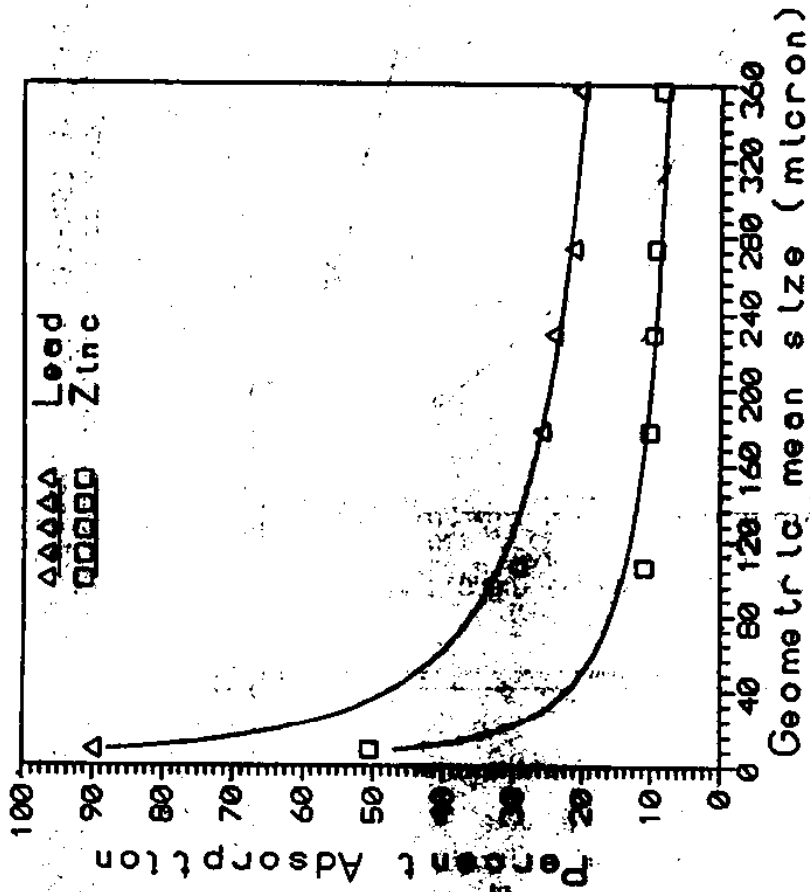


Fig. 7. Effect of adsorbent size on percent adsorption of lead and zinc ions on bed sediments.

The present study has shown the potentiality of freshly deposited sediments to adsorb heavy metals which may enter the river system through the disposal of municipal and industrial effluents or by biological and chemical degradation. The study indicates, though the two metal ions have more affinity for the clay and silt fraction of the sediment, but the overall contribution of coarser fraction (210-250 μm) to adsorption is more as compared to clay and silt fraction. The adsorption data further suggests that the pH of the solution is the most important parameter in the control of metal ions adsorption onto the bed sediments. The percent metal ion removal at equilibrium increases with increasing adsorbent doses, and as such removal increases with decreasing size of the adsorbent material. Among the two ions studied, the bed sediments of river Kali have greater affinity for lead as compared to zinc ions. The two important geochemical phases, namely iron and manganese oxide, may act as the active support material for the adsorption of the two metal ions in addition to the particle size of the sediments. However, in natural river systems, salinity and pH highly affect the speciation of the metal ions and greatly interfere with their fixation on clay minerals. Adsorption/desorption equilibria and complexation with fulvic and humic acids also play an important role on speciation and further studies are needed to better understand processes affecting the sorption of metal ions in natural systems.

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