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Adsorption of Cadmium on Bed Sediments



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**NATIONAL INSTITUTE OF HYDROLOGY
JAL VIGYAN BHAWAN
ROORKEE - 247 667 (U.P.) INDIA**

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ABSTRACT

The report presents original study range of cadmium adsorption according to the experimental data. The effect of operating variables, viz., solution pH, sediment dose, contact time, and particle size, have been studied on the adsorption of cadmium ions on bed sediments of the highly polluted river in western Uttar Pradesh, India. The role of the coarser sediment fraction has been compared to those of the clay and silt fractions. The optimum contact time needed to reach equilibrium is of the order of 30 and 60 minutes for 0-60 and 210-250 μm size of the sediment respectively. The extent of adsorption increases with an increase of pH. Furthermore the adsorption of cadmium increases with increasing adsorbent doses and decreases with adsorbent particle size. The important geochemical phases, iron and manganese oxide, act as the active support material for the adsorption of cadmium. The competitive experiments conducted in the presence of lead and zinc ions indicate that both the ions suppresses the ability of cadmium to adsorb onto sediments.

1.0 INTRODUCTION

The tremendous increase in the use of heavy metals over the past few decades has resulted in an increased concentration of metals in the aquatic systems. Because of their toxicity and non-biodegradable nature, metals are of special significance. One of the most important and toxic metals, cadmium finds its way to the aquatic systems through waste waters from metal plating industries and industries of cadmium nickel batteries, phosphate fertilizers, mining, pigments, stabilizers and alloys (Low and Lee, 1991). The permissible limits of cadmium for the discharge of waste water and drinking water are 0.1 and 0.05 mg L⁻¹, respectively.

A number of technologies have been developed to remove toxic cadmium from water. The most important of these include chemical precipitation, ion exchange, reverse osmosis and adsorption. The suspended and riverbed sediments play an important role in the transport of metals in aquatic systems. The important components of the suspended load for geochemical transport are silt, clay, hydrous iron and manganese oxides and organic matter. Generally, the adsorption study for sediment less than 50 μm has been made greatly, while that for the sediment more than 75 μm are few because of little adsorption action. Adsorption properties of the sediments provide valuable information relating to the tolerance of the system to the added heavy metal load.

Despite the apparent wealth of information on cadmium adsorption (Fu and Alen, 1992; Namasivayam and Ranganathan, 1995; Bajracharya et al., 1996), little is known about quantitatively describing cadmium adsorption by coarser sediment. Palheiros et al. (1989) have studied the adsorption of cadmium on riverbed sediment of less than 63 μm size and reported that pH is the most important parameter in the control of cadmium adsorption. Chrintensen (1984) reported that adsorption capacity of soils increased 2 to 3 times for a pH increase of one unit. It was further reported that for cadmium the predominant process taking

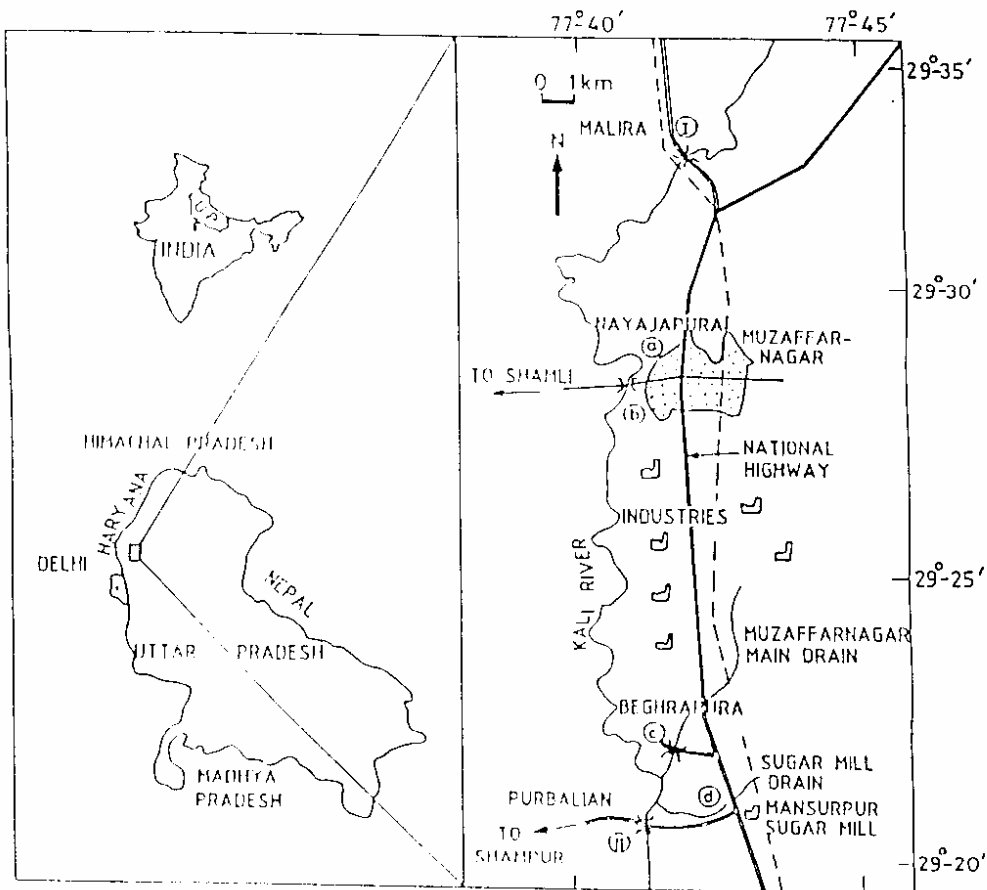
place at a pH of 6 is adsorption. Bajracharya et al. (1996) studied the effect of zinc and ammonium ions on the adsorption of cadmium on sand and soil and reported that both the ions suppress the adsorption capacity significantly.

Although clay and silt component adsorb metal ions much better than coarser fraction of sediment, one should take into account that most river sediments contain 90-95% sand and only 0-10% clay and silt. Therefore, in river systems with high sand percentage and low clay and silt content, the overall contribution of sand content to adsorption of metal ions could be comparable to or even higher than that of clay and silt fraction (Jain and Ram, 1997). In the present report, the adsorption of cadmium ions on different fractions of the sediment of a highly polluted river in western Uttar Pradesh, India, was studied with a view to demonstrate the role of coarser fraction of the sediments in controlling metal pollution. The importance of geochemical phases have also been investigated.

2.0 THE RIVER SYSTEM

The Kali river in western Uttar Pradesh, India, is a small perennial river having a basin area of about 750 km², and lies between latitude 29°33' N to 29°21'30" N and longitude 77°43' E to 77°39'15" E in the Muzaffarnagar district of Uttar Pradesh (Fig. 1). The climate in this region is moderate subtropic monsoonal. The average annual rainfall in the area is about 1000 mm, a major part of which is received during the 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 pollution sources include Muzaffarnagar city, a variety of industries (steel, rubber, ceramic, chemical, plastic, dairy, pulp and paper, and laundries), and the Mansurpur sugar mill and distillery. 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: I - upstream section;
 II - downstream section; a to d - wastewater
 outfalls**

3.0 EXPERIMENTAL METHODOLOGY

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; Subramanian et al., 1987).

The size distribution of the sediment samples was carried out using nylon sieves to obtain various fractions, viz., 0-75, 75-150, 150-210, 210-250, 250-325, and 325-425 μm . Textural features of the sediments were observed and a preliminary classification made according to grain-size and distinctive geochemical features. The important geochemical phases for the adsorption process are organic matter, manganese oxides, iron oxides and clays. The contents of manganese oxide and iron oxide were measured as total manganese and total iron, respectively, and extracted from the sediment samples using a acid digestion mixture ($\text{HF} + \text{HClO}_3 + \text{HNO}_3$) in an open system. Organic matter was determined by oxidation with hydrogen peroxide.

All chemicals used in the study were obtained from Merck, India and were of analytical grade. Aqueous solutions of cadmium were prepared from cadmium nitrate. 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.

Adsorption experiments were conducted in a series of Erlenmeyer flasks of 100 mL capacity covered with teflon sheet to prevent introduction of any foreign particles. Fifty mL of cadmium ion solution ($100\text{-}1000 \mu\text{g L}^{-1}$) were transferred in the flasks together with desired adsorbent doses (W_0 in g L^{-1}), and placed in a water bath shaker maintained at 25°C . The pH of 7.5 ± 0.1 was maintained throughout the experiment using dilute HNO_3 and NaOH solutions. Aliquots were retrieved periodically and

filtered through 0.45 μm cellulose nitrate membrane filters. The filters were soaked in dilute (1% v/v) HNO_3 for 1 h and thoroughly rinsed with deionized water prior to use.

The concentration of cadmium ions were determined by flame atomic absorption spectrometry, using a Perkin-Elmer Atomic Absorption Spectrometer (Model 3110) with air-acetylene flame. The detection limit for the cadmium ion was 0.001 mg L^{-1} . Operational conditions were adjusted to yield optimal determinations. Quantification of the metals was based upon calibration curves of standard solutions of cadmium ion. These calibration curves were determined several times during the period of analysis.

4.0 RESULTS AND DISCUSSION

The sediment under study has a rather coarse texture, composed of more than 99% sediment of size $>75 \mu\text{m}$ and $<1\%$ silt and clay. The organic content of the sediment was of the order of 0-1%. The background cadmium level in the various fractions of the sediments was negligible (below detection limits) in the unpolluted zone, compared to the amount of adsorbate added for the adsorption tests. This confirms the absence of any cadmium particulate attached to the sediment particles.

The content of two important geochemical phases (iron and manganese) in different particle size fractions along with weight percentages 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. This indicates the possibility of the two geochemical phases to act as the active support material for the adsorption of cadmium 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. The content of iron in the sediment fractions is relatively higher and indicate the possibility of presence of iron minerals other than hydroxides. However, this need to be confirmed by further investigations. 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 cadmium ions on coarser fraction and to compare with the clay and silt fraction ($<75 \mu\text{m}$ particle size) to demonstrate the importance of the coarser fraction in controlling metal pollution in this particular case study.

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	-	-

4.1 Equilibrium Time (t)

In order to determine the equilibrium time for the adsorption process, adsorption experiments were performed for the uptake of cadmium ions for different duration of contact times for a fixed adsorbent dose of 5 g L^{-1} and with an initial metal ion concentration of $600 \text{ } \mu\text{g L}^{-1}$ (Table 2, Fig. 2) for the two particle size of adsorbent (0-75 and 210-250 μm) at a pH value of 7.5. The solution pH for the experiments was chosen as close to that encountered in the river water. These plots indicate that the remaining concentration of cadmium ions becomes asymptotic to the time axis such that there is no appreciable change in the remaining concentration after 30 and 60 minutes for 0-75 and 210-250 μm particle size of the adsorbent, respectively. This time presumed to represent the equilibrium time at which an equilibrium concentration is presumed to have been attained. All the further experiments were conducted for 60 minutes.

According to Weber and Morris (1963), for most adsorption processes, the uptake varies almost proportionately with $t^{1/2}$ rather than with the contact time. Therefore, plot of cadmium adsorbed, C_t vs $t^{1/2}$, is presented for the two particle size of adsorbent in Fig. 3. It is clearly evident that adsorption of cadmium ions on the river bed sediments follows two phases on both the fractions of the adsorbent, a linear phase of adsorption followed by an almost flat plateau section due to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface. The visual observation indicate the minor importance of any precipitation from ion exchange.

4.2 Adsorption Isotherm

The adsorption isotherms for the cadmium adsorption on the bed sediments are shown in Fig. 4 with a fixed adsorbent dose of 5 g L^{-1} at a pH of 7.5 ± 0.1 . The adsorption data (Table 3) indicate linear distribution in the range 0 to $700 \text{ } \mu\text{g L}^{-1}$. It is evident that for the same equilibration time, the cadmium adsorbed is higher for greater values of initial concentration

Table 2. Adsorption of cadmium on bed sediments of river Kali at different durations of contact time on 0-75 and 210-250 μm sediment fractions; Adsorbent dose = 5 g/L; pH = 7.5; Temperature = 25°C.

Sediment fraction (μm)	Initial concn. ($\mu\text{g/L}$)	Contact time, t (min)	Concn. at time t ($\mu\text{g/L}$)	Metal ion adsorbed		
				$\mu\text{g/L}$	$\mu\text{g/g}$	Percent
0-75	600	5	120	480	96.0	80.0
		15	70	530	106.0	88.3
		30	50	550	110.0	91.7
		45	49	551	110.2	91.8
		60	49	551	110.2	91.8
		90	46	554	110.8	92.3
		120	45	555	111.0	92.5
		150	42	558	111.6	93.0
		180	42	558	111.6	93.0
210-250		5	429	171	34.2	28.5
		15	380	220	44.0	36.7
		30	301	299	59.8	49.8
		45	230	370	74.0	61.7
		60	181	419	83.8	69.8
		90	130	470	94.0	78.3
		120	115	485	97.0	80.8
		150	107	493	98.6	82.2
		180	105	495	99.0	82.5

Table 3. Adsorption data for cadmium on bed sediments of river Kali on 0-75 and 210-250 μm sediment fractions; pH = 7.5; Adsorbent dose = 5 g/L; Temperature = 25°C.

Sediment fraction (μm)	Initial concn. C_0 ($\mu\text{g/L}$)	Equilibrium concentration C_e ($\mu\text{g/L}$)	Metal ion adsorbed		
			$\mu\text{g/L}$	$\mu\text{g/g}$	Percent
0-75	100	5	95	19.0	95.0
	200	10	190	38.0	95.0
	300	10	290	58.0	96.7
	400	20	380	76.0	95.0
	500	40	460	92.0	92.0
	600	80	520	104.0	86.7
	700	145	555	111.0	79.3
	800	245	555	111.0	69.4
	900	335	565	113.0	62.8
	1000	433	567	113.4	56.7
210-250	100	4	96	19.2	96.0
	200	12	188	37.6	94.0
	300	24	276	55.2	92.0
	400	40	360	72.0	90.0
	500	70	430	86.0	86.0
	600	120	480	96.0	80.0
	700	190	510	102.0	72.9
	800	277	523	104.6	65.4
	900	366	534	106.8	59.3
	1000	465	535	107.0	53.5

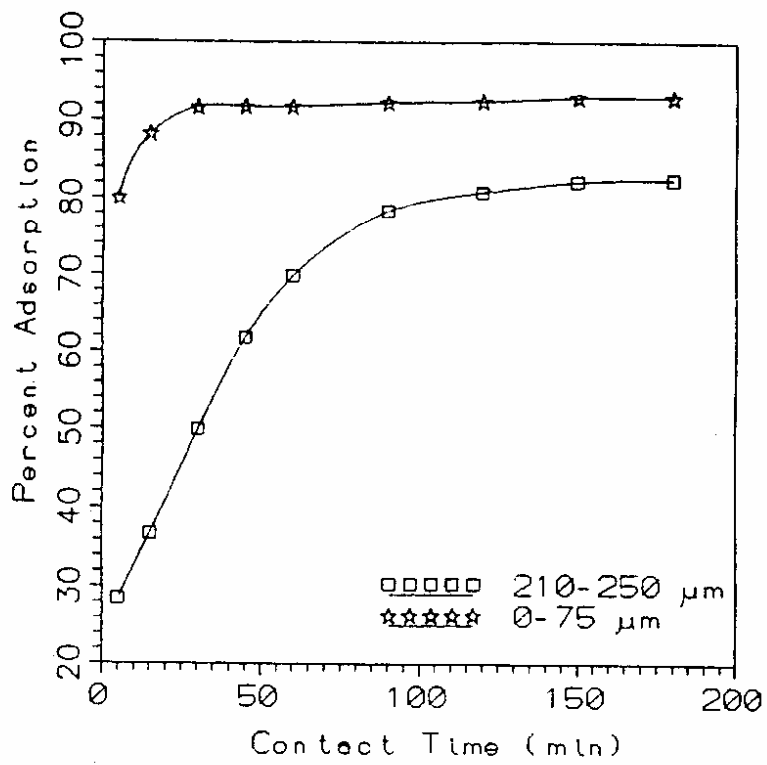


Fig. 2. Effect of contact time on percent adsorption of cadmium ions

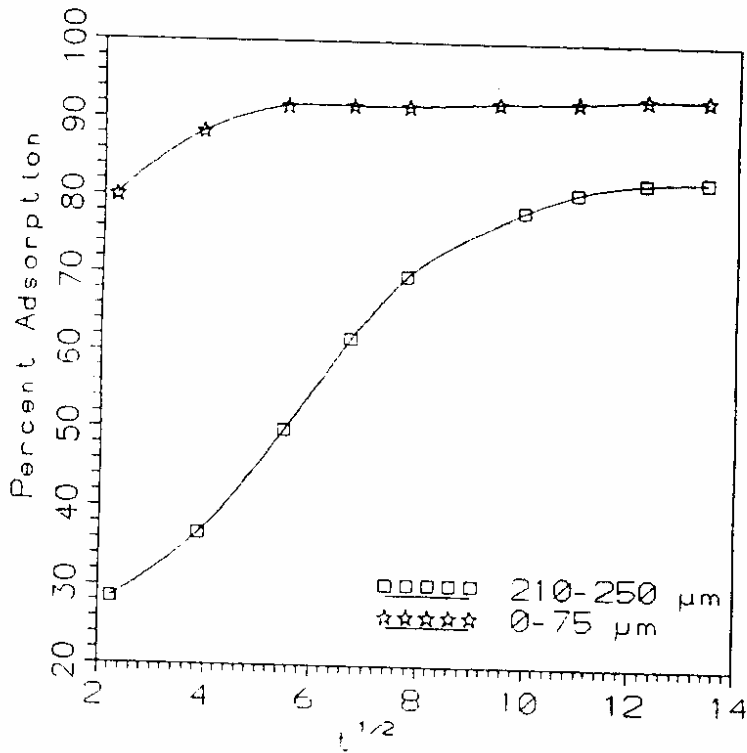


Fig. 3. Effect of $t^{1/2}$ on percent adsorption of cadmium ions

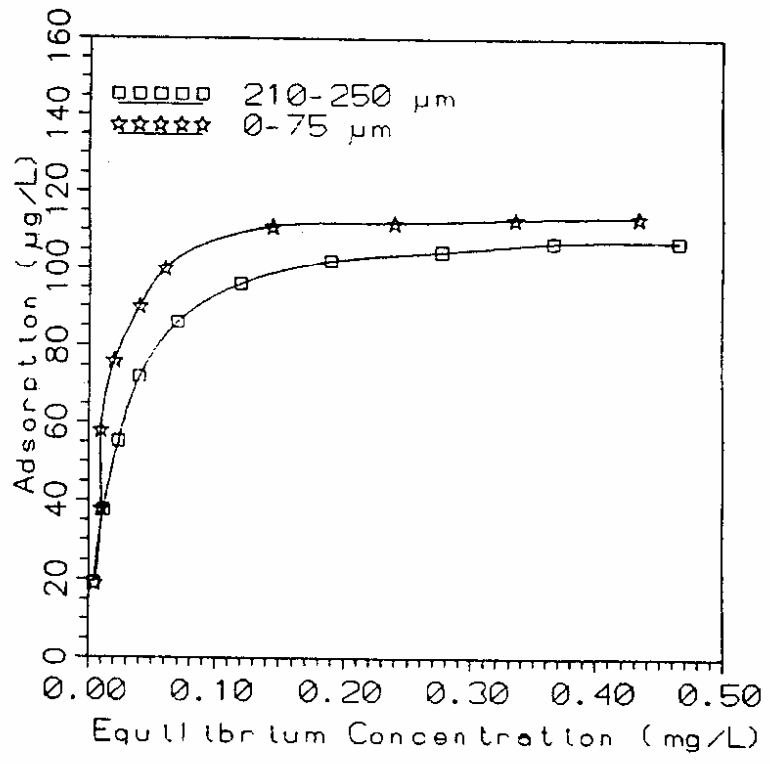


Fig. 4. Adsorption of cadmium ions on river bed sediments

of cadmium ions or the percentage adsorption is more for lower concentration of cadmium and decreases with increasing initial concentration. This is obvious because more efficient 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 cadmium is more for <75 μm fraction, i.e., clay and silt as compared to coarser fraction. It is also evident from Table 1 that <75 μm fraction contain more iron and manganese content than that of 210-250 μm fraction indicating possibility of association of these substrate with clay and silt particles. These findings illustrate the possible role of clay and silt components as substrate for cadmium adsorption. However, due to paucity of data correlation statistics could not be attempted to confirm this statement. 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 cadmium ions, it is clear that the contribution of coarser sediment is more in controlling cadmium pollution as compared to clay and silt content. Similar behaviour was also observed in the case of lead and zinc ions (Jain and Ram, 1997).

4.3 Effect of pH

The adsorption of cadmium on the riverbed sediments was studied over the pH range 2-10 for a fixed initial concentration of cadmium ($C_i = 600 \mu\text{g L}^{-1}$) and adsorbent dose of 5 g L^{-1} at a particle size of 0-75 and 210-250 μm (Table 4, Fig. 5). The pH of the solution was adjusted using dilute hydrochloric acid and sodium hydroxide solutions. The pH was measured before and after the solution had been in contact with the sediment, the difference between the two values being generally less than 0.1 pH unit. A general increase in adsorption with increasing pH of solution has been observed upto the pH value of 7.0 for both the fractions of the sediment. From the results it is evident that the pH for maximum uptake of cadmium ion is 7.0. Further, it is apparent that the adsorption of cadmium rises from 30% at pH 2.0

Table 4. Adsorption of cadmium on bed sediments of river Kali at different pH values on 0-75 and 210-250 μm sediment fractions; Adsorbent dose = 5 g/L; Temperature = 25°C.

Sediment fraction (μm)	Initial concn. C_0 ($\mu\text{g/L}$)	pH	Equilibrium concentration C_e ($\mu\text{g/L}$)	Metal ion adsorbed		
				$\mu\text{g/L}$	$\mu\text{g/g}$	Percent
0-75	600	2.0	384	216	43.2	36.0
		3.0	281	319	63.8	53.2
		4.0	175	425	85.0	70.8
		5.0	99	501	100.2	83.5
		6.0	65	535	107.0	89.2
		7.0	50	550	110.0	91.7
		8.0	49	551	110.2	91.8
		9.0	50	550	110.0	91.7
		10.0	52	548	109.6	91.3
210-250		2.0	420	180	36.0	30.0
		3.0	310	290	58.0	48.3
		4.0	215	385	77.0	64.2
		5.0	166	434	86.8	72.3
		6.0	149	451	90.2	75.2
		7.0	115	485	97.0	80.8
		8.0	113	487	97.4	81.2
		9.0	107	493	98.6	82.2
		10.0	105	495	99.0	82.5

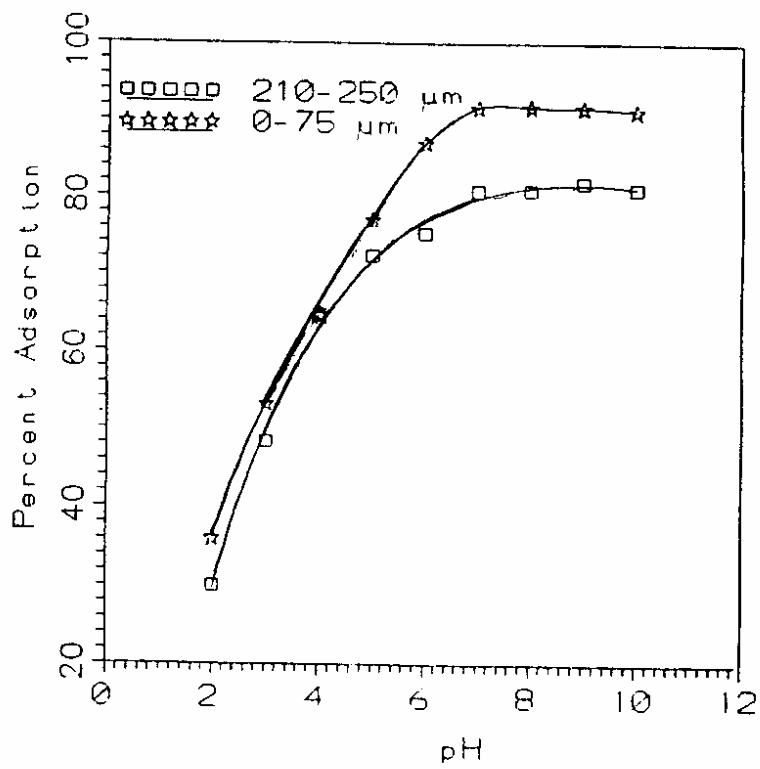


Fig. 5. Effect of pH on percent adsorption of cadmium ions

to 80% at pH 7.0 for coarser sediment fraction (210-250 μm) which reveals the sediment's capacity for adsorbing cadmium ions even in acidic media. Similar behaviour was also reported by Palheiros et al. (1989) for the adsorption of cadmium on riverbed sediment.

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 7.5 with different adsorbent doses varying from 2 to 10 g L^{-1} and at a fixed initial cadmium concentration of 600 $\mu\text{g L}^{-1}$ (Table 5, Fig. 6). The experiments were conducted in a water bath shaker to disperse the sediment particles in the aqueous media. It is observed that for a fixed initial concentration of cadmium ($C_0 = 600 \mu\text{g L}^{-1}$), the adsorption of cadmium per unit weight of adsorbent decreases with increasing adsorbent load. The adsorption increases from 59 to 82% for the 210-250 μm fraction with increasing adsorbent load from 2 to 10 g L^{-1} . However, the percent adsorption (or removal) of cadmium was 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 is the main driving force for the adsorption of cadmium ions.

4.5 Particle Size (d_p)

The effect of particle size of adsorbent on cadmium adsorption are shown in Fig. 7 for a fixed initial concentration of cadmium ($C_i = 600 \mu\text{g L}^{-1}$) and adsorbent dose of 5 g L^{-1} and at a pH value of 7.5 (Table 6). These plots reveals that for a fixed adsorbent dose, the cadmium adsorbed is higher for smaller adsorbent size. Further, it is observed that the percentage of cadmium adsorbed decreases from 92% on 0-75 μm fraction to 65% on 425-600 μm fraction, 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. The higher content of iron and manganese in the 0-75

Table 5. Adsorption of cadmium on bed sediments of river Kali at different adsorbent doses on 0-75 and 210-250 μm sediment fractions; pH = 7.5; Temperature = 25°C.

Sediment fraction (μm)	Initial concn. ($\mu\text{g/L}$)	Adsorbent dose, W_e (g/L)	Equilibrium Concn., C_e ($\mu\text{g/L}$)	Metal ion adsorbed		
				$\mu\text{g/L}$	$\mu\text{g/g}$	Percent
0-75	600	1.0	220	380	380.0	63.3
		2.0	180	420	210.0	70.0
		3.0	120	480	160.0	80.0
		4.0	88	512	128.0	85.3
		5.0	48	552	110.4	92.0
		6.0	40	560	93.3	93.3
		7.0	38	562	80.3	93.7
		8.0	34	566	70.8	94.3
		9.0	29	571	63.4	95.2
		10.0	22	578	57.8	96.3
210-250		1.0	301	299	299.0	49.8
		2.0	250	350	175.0	58.3
		3.0	198	402	134.0	67.0
		4.0	170	430	107.5	71.7
		5.0	135	465	93.0	77.5
		6.0	116	484	80.7	80.7
		7.0	110	490	70.0	81.7
		8.0	108	492	61.5	82.0
		9.0	104	496	55.1	82.7
		10.0	100	500	50.0	83.3

Table 6. Adsorption of cadmium on bed sediments of river Kali at different adsorbent sizes; Adsorbent dose = 5 g/L; pH = 7.5; Temperature = 25°C.

Particle size*, d _p (μm)	Initial concn., C ₀ (μg/L)	Equilibrium concn., C _e (μg/L)	Metal ion adsorbed		
			μg/L	μg/g	Percent
8.7	600	51	549	109.8	91.5
106.1		80	520	104.0	86.7
177.5		101	499	99.8	83.2
229.1		119	481	96.2	80.2
273.9		150	450	90.0	75.0
357.1		180	420	84.0	70.0
505.0		212	388	77.6	64.7

* Geometric mean

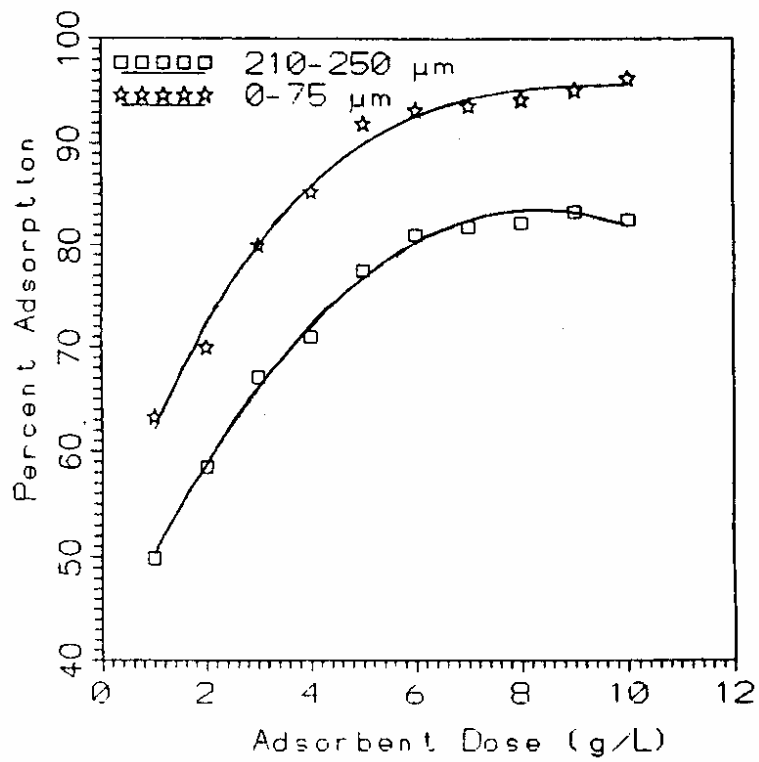


Fig. 6. Effect of adsorbent dose on percent adsorption of cadmium ions

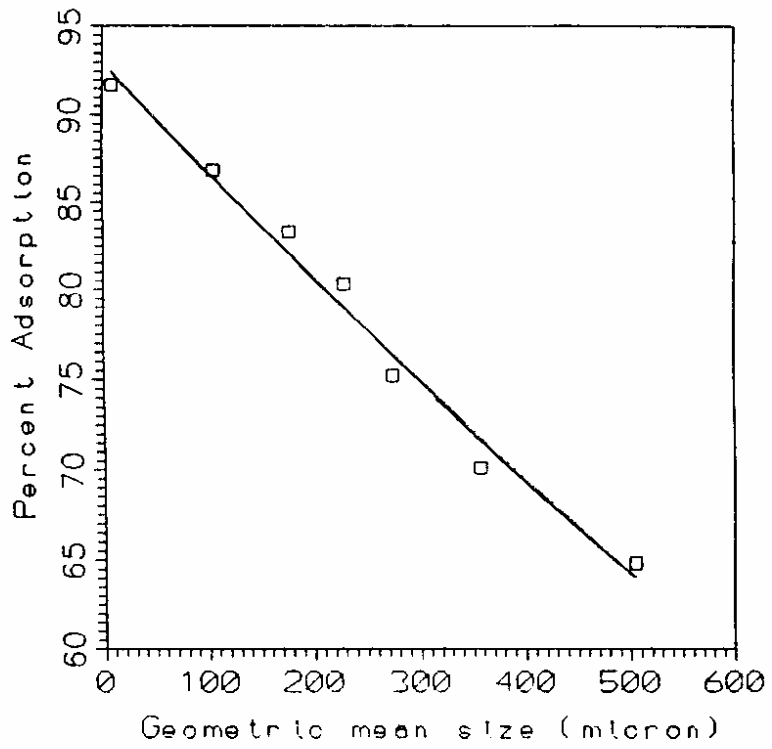


Fig. 7. Effect of adsorbent size on percent adsorption of cadmium ions

μm sediment fraction also accounts for higher adsorption of cadmium in this fraction as compared to higher fractions of the sediment.

4.6 Effect of Competing Ions

In order to examine the effect of competing ions, lead and zinc, competitive adsorption experiments were conducted by varying the concentration of lead and zinc ions ($100\text{-}1000 \mu\text{g L}^{-1}$) while keeping the cadmium concentration constant ($600 \mu\text{g L}^{-1}$). The adsorption data for the two competing ions are given in Tables 7 and 8. It is clearly evident (Fig. 8 and 9) that both the ions suppressed the ability of cadmium to adsorb onto the sediments. The extent of suppression is significant on both the fractions. This may be attributed due to the different sediment water interactions and/or adsorption capacities of the metal ions on the sediment. Bajracharya et al. (1996) also reported that adsorption ability of cadmium on soil suppressed 20 to 30% in the presence of zinc ions. Christensen (1984) found that increasing the calcium content from 40 to 400 mg L^{-1} reduces the adsorption capacity of the sandy loam by one third.

4.7 Adsorption Models

The adsorption data of the cadmium by sediments of the River Kali has been analysed with the help of Langmuir and Freundlich models to evaluate the mechanistic parameters associated with the adsorption process.

4.7.1 Langmuir isotherm

Langmuir's isotherm model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The linear form of Langmuir isotherm equation is represented by the following equation:

Table 7. Effect of lead on the adsorption of cadmium on bed sediments of river Kali at 0-75 and 210-250 μm sediment fractions; Adsorbent dose = 5 g/L; pH = 7.5; Temperature = 25°C; Initial concentration of Cd = 600 $\mu\text{g/L}$.

Sediment fraction (μm)	Concn. of lead ($\mu\text{g/L}$)	Equilibrium concentration C_e ($\mu\text{g/L}$)	Metal ion adsorbed		
			$\mu\text{g/L}$	$\mu\text{g/g}$	Percent
0-75	100	99	501	100.2	83.5
	200	100	500	100.0	83.3
	300	109	491	98.2	81.8
	400	119	481	96.2	80.2
	500	124	476	95.2	79.3
	600	130	470	94.0	78.3
	700	144	456	91.2	76.0
	800	152	448	89.6	74.7
	900	160	440	88.0	73.3
	1000	154	436	87.2	72.7
210-250	100	200	400	80.0	66.7
	200	240	360	72.0	60.0
	300	290	310	62.0	51.7
	400	305	295	59.0	49.2
	500	345	255	51.0	42.5
	600	365	235	47.0	39.2
	700	385	215	43.0	35.8
	800	401	199	39.8	33.2
	900	430	170	34.0	28.3
	1000	451	149	29.8	24.8

Table 8. Effect of zinc on the adsorption of cadmium on bed sediments of river Kali at 0-75 and 210-250 μm sediment fractions; Adsorbent dose = 5 g/L; pH = 7.5; Temperature = 25°C; Initial concentration of Cd = 600 $\mu\text{g/L}$.

Sediment fraction (μm)	Concn. of zinc ($\mu\text{g/L}$)	Equilibrium concentration C_e ($\mu\text{g/L}$)	Metal ion adsorbed		
			$\mu\text{g/L}$	$\mu\text{g/g}$	Percent
0-75	100	110	490	98.0	81.7
	200	110	490	98.0	81.7
	300	119	481	96.2	80.2
	400	123	477	95.4	79.5
	500	130	470	94.0	78.3
	600	135	465	93.0	77.5
	700	155	445	89.0	74.2
	800	168	432	86.4	72.0
	900	182	418	83.6	69.7
	1000	190	410	82.0	68.3
210-250	100	226	374	74.8	62.3
	200	241	359	71.8	59.8
	300	262	338	67.6	56.3
	400	301	299	59.8	49.8
	500	329	271	54.2	45.2
	600	371	229	45.8	38.2
	700	401	199	39.8	33.2
	800	436	164	32.8	27.3
	900	481	119	23.8	19.8
	1000	484	116	23.2	19.3

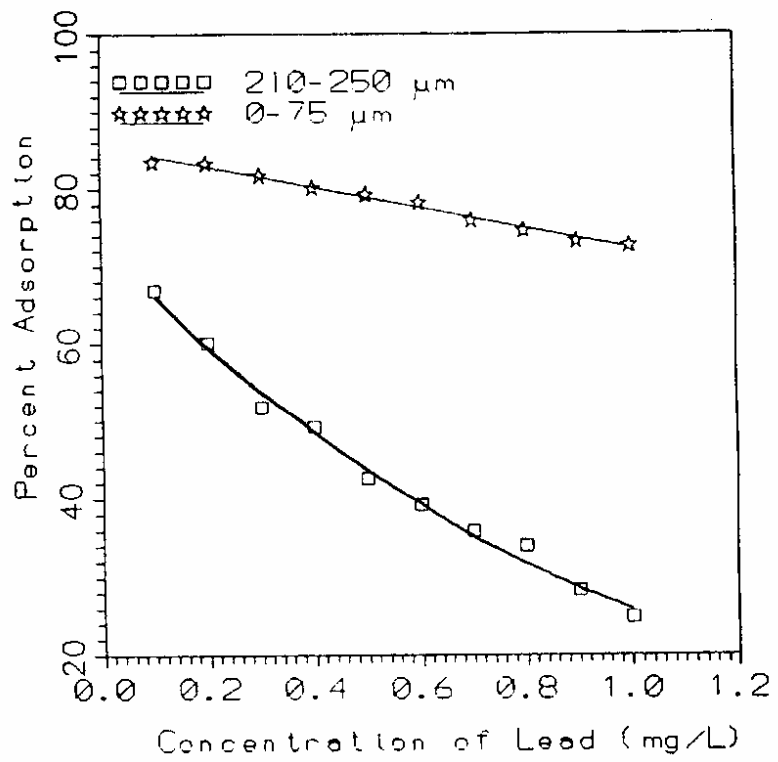


Fig. 8. Effect of lead ions on percent cadmium adsorption

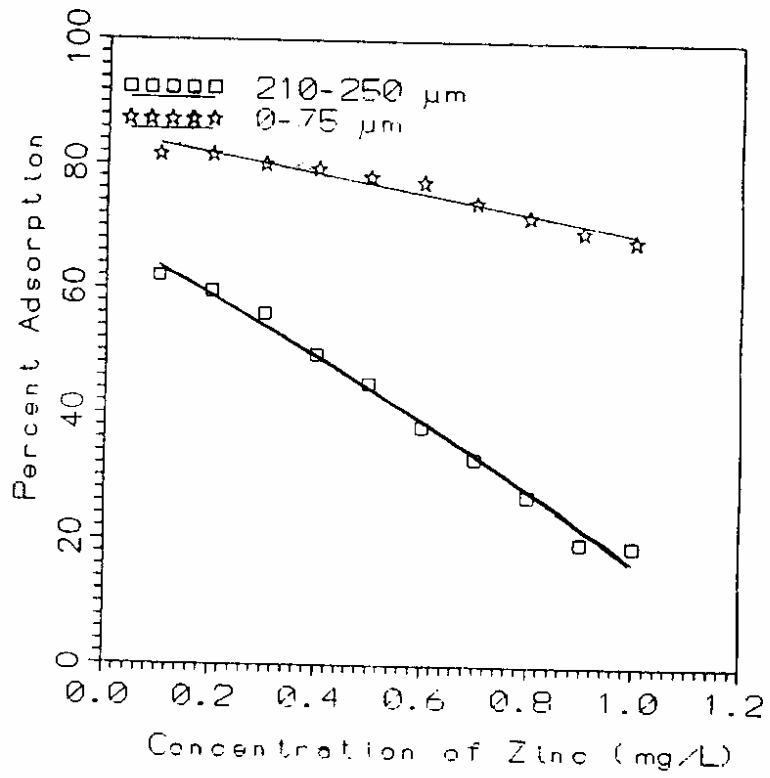


Fig. 9. Effect of zinc ions on percent cadmium adsorption

$$\frac{1}{q_e} = \frac{1}{Q^0} + \frac{1}{bQ^0 C_e}$$

Where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate ions (mg/L), and Q^0 and b are Langmuir constants related to maximum adsorption capacity (monolayer capacity) and energy of adsorption, respectively. When $1/q_e$ is plotted against $1/C_e$, a straight line with slope $1/bQ^0$ and intercept $1/Q^0$ is obtained (Fig. 10), which shows that the adsorption of metal ions follow Langmuir isotherm model. The Langmuir parameters, Q^0 and b , are calculated from the slope and intercept of the graphs and are given in Table 9. These values may be used for comparison and correlation of the sorptive properties of the sediments.

4.7.2 Freundlich isotherm

The adsorption for cadmium has also been analysed using logarithmic form of Freundlich isotherm as shown below:

$$\log q_e = \log K_f + 1/n \log C_e$$

Where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate ions (mg/L), and K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. When $\log q_e$ is plotted against $\log C_e$, a straight line with slope $1/n$ and intercept $\log K_f$ is obtained (Fig. 11). This reflects the satisfaction of Freundlich isotherm model for the adsorption of cadmium ions. The intercept of line, $\log K_f$, is roughly an indicator of the adsorption capacity and the slope, $1/n$, is an indication of adsorption intensity (Weber, 1972). The Freundlich parameters for the adsorption of two metal ions are given in Table 10.

Table 9. Langmuir parameters for the adsorption of cadmium

Particle Fraction (μm)	Adsorption Maxima 'Q ⁰ ' (mg/g)	Bonding Energy Constant 'b' (mg/L) ⁻¹
0-75	0.125	32.0
210-250	0.143	55.9

Table 10. Freundlich parameters for the adsorption of cadmium

Particle Fraction (μm)	Adsorption Capacity 'K _F ' (mg/g)	Adsorption Intensity '1/n'
0-75	0.05	0.20
210-250	0.04	0.20

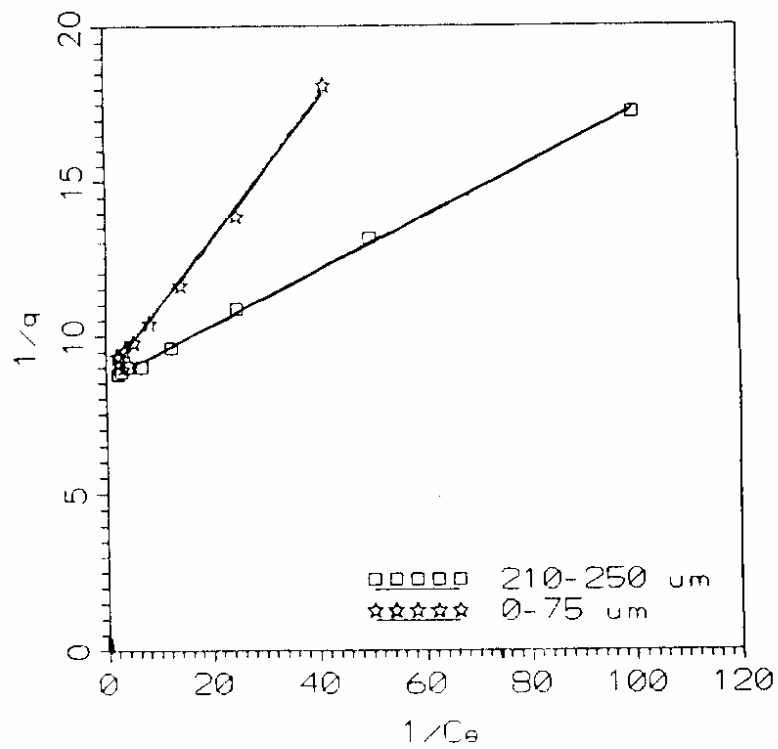


Fig. 10. Graphical representation of Langmuir isotherm for cadmium

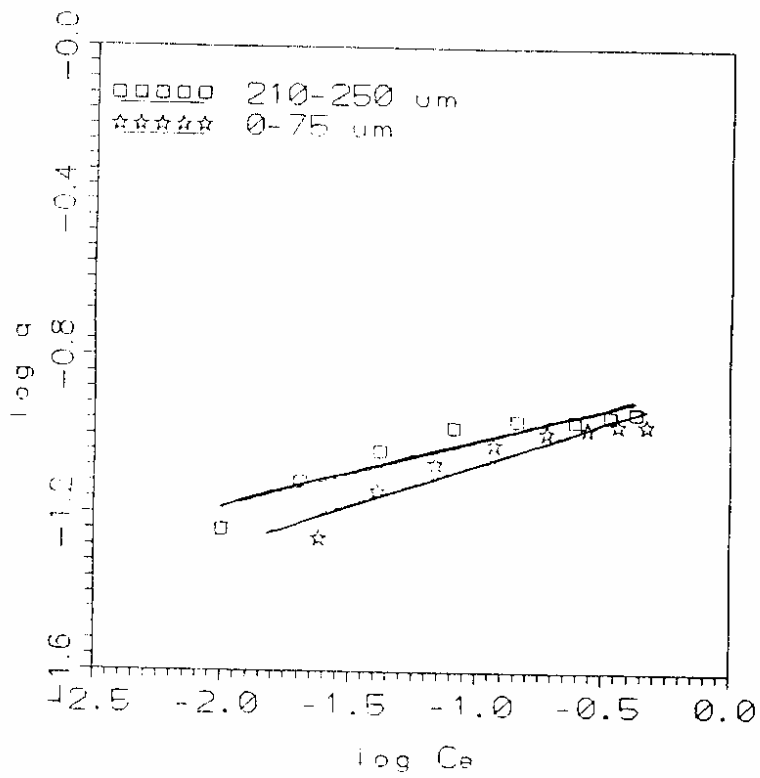


Fig. 11. Graphical representation of Freundlich isotherm for cadmium

5.0 CONCLUSION

The present study has shown the potentiality of freshly deposited sediments to adsorb cadmium ions 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 cadmium ions have more affinity for the clay and silt fraction of the sediment, but the overall contribution of coarser fraction 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 cadmium ions adsorption onto the bed sediments. The percentage adsorption increases with increasing adsorbent doses, and as such removal increases with decreasing size of the adsorbent material. The two important geochemical phases, iron and manganese oxide, also play an important role in the adsorption process and act as the active support material for the adsorption of cadmium. The results of the experimental study obtained from this study are highly useful and may be extended for other rivers of the world, especially for the rivers with coarser sediment.

The important components of the suspended load for geochemical transport are silt, clay, hydrous iron and manganese oxides and organic matter. It is evident from the present study that the manganese and iron contents in the various fractions of the sediment decreases with increasing particle size, i.e., the clay and silt fraction contain more iron and manganese content than that of 210-250 μm fraction indicating possibility of association of these substrate with clay and silt particles. These findings illustrate the possible role of clay and silt components as substrate for cadmium adsorption. However, due to paucity of data correlation statistics could not be attempted to confirm this statement. Further, the relative contribution of individual components could not 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. The

content of iron in the sediment fractions was found to be relatively higher indicating the possibility of presence of iron minerals other than hydroxides. This also need to be confirmed by further investigations.

It may also be stressed that 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 cadmium in natural systems.

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DIRECTOR

S M SETH

DIVISIONAL HEAD

K K S BHATIA

STUDY GROUP

C K JAIN, Sc. 'C'

IMRAN ALI, Sc. 'B'