ADSORPTION OF ZINC

ON

BED SEDIMENTS OF RIVER GANGA

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PREFACE

Heavy metals added to a river system by natural or manmade sources during their transport are distributed between the aqueous phase, suspended and bed 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.

Keeping this in mind, the study of adsorption of zinc ions on bed sediments of river Ganga have been taken-up in their natural state of occurrence. In the present report an attempt has been made to study the importance and adsorption characteristics of bed sediments of river Ganga for the control of metal pollution.

The report has been prepared by Dr. C. K. Jain, Scientist 'C', Environmental Hydrology Division, under the work-programme for 1998-99.

(S. M. SETH)

DIRECTOR

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ABSTRACT

The report presents original study range of zinc adsorption according to the experimental data on the bed sediments of river Ganga at Hardwar. The effect of various operating variables, viz., solution pH, sediment dose, contact time, and particle size, have been studied on the adsorption of zinc ions. The optimum contact time needed to reach equilibrium is of the order of 60 minutes and is independent of initial concentration of zinc ions. The adsorption curves are smooth and continuous leading to saturation, suggesting the possible monolayer coverage of zinc ions on the surface of the adsorbent. The extent of adsorption increases with an increase of pH. Furthermore the adsorption of zinc 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 zinc ions. The adsorption data has been analysed with the help of Langmuir and Freundlich adsorption models to determine the mechanistic parameters associated with the adsorption process. An attempt has also been made to obtain thermodynamic parameters of the prosess, viz., free energy change, enthalpy change and entropy change. The negative values of free energy change (ΔG°) indicated spontaneous nature of the adsorption of zinc on the bed sediments and positive values of enthalpy change (ΔH°) suggest the endothermic nature of the adsorption process.

1.0   INTRODUCTION

Adsorption is one of the important phenomena in water quality control, which may determine the fate and transport of pollutants in the aquatic environment. 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 and has a great significance due to their toxicity and adsorption behaviour.

The suspended and bed sediments play a major role in pollution studies due to their specific adsorption capacity. Heavy metals added to a river system by natural and manmade sources during their transport are distributed between the aqueous phase, suspended and bed sediments. The fraction in the sediment is expected not to have direct adverse effects, if the metal ions are tightly bound to it and subsequently get settled at the bottom in course of time. This state of affair is maintained until there is remobilization from the sediment due to changing conditions in the system.

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

Pollution from industrial and agricultural sources to a great extent is responsible for high concentration of zinc in river water. This may also be contributed by water distribution system due to leaching of zinc from galvanized pipes. Zinc is an essential element for both animals and man and is necessary for the functioning of various enzyme systems, deficiency of which leads to growth retardation. Low intake of zinc results in retardation of growth, immaturity and anemia, condition known as 'zinc deficiency syndrome'. Symptoms of zinc toxicity in humans include vomiting, dehydration, electrolyte imbalance, abdominal pain, nausea lethargyness, dizziness and lack of muscular coordination.

Zinc imparts undesirable, bitter astringent taste to water at levels above 5.0 mg/L (WHO, 1984). Water containing zinc at concentrations in excess of 5.0 mg/L may appear opalescent and develop a greasy film on boiling. Toxic concentrations of zinc above recommended value causes adverse effect in the morphology of fish by inducing cellular breakdown of gills. Zinc deficiency in human body may result in infantilism, impaired wound healing and several other diseases.

A number of technologies have been developed to remove toxic metals 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.

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. Gagnon et al. (1992) studied the sorption interactions between trace metals and phenolic substances on suspended clay minerals. Fu and Allen (1992) studied the adsorption of cadmium by oxic sediments using a multi-site binding model. The model has been used satisfactorily to predict the extent of adsorption over the pH range 4.5-7.0. Namasivayam and Ranganathan (1995) have used a waste product from fertilizer industry for removal of cadmium from waste water.

Despite the apparent wealth of information on adsorption processes, little is known about quantitatively describing adsorption process by coarser sediment. 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). Recently, we have studied the adsorption of cadmium on bed sediments of a highly polluted river in western Uttar Pradesh (Jain and Ali, 1998).

In the present report, the adsorption characteristics of bed sediments of river Ganga have been studied with a view to demonstrate the role of bed sediments in controlling metal pollution. The importance of geochemical phases has also been investigated. Adsorption data has also been analysed with the help of adsorption models to determine the mechanistic parameters associated with the adsorption process. Isotherms have also been used to obtain thermodynamic parameters of the process.

2.0   THE RIVER SYSTEM

Ganga is a perennial river formed by confluence of two smaller rivers at Devprayag. Bhagirathi is one of them originating at Gaumukh in Gangotri galcier, 3129 m above mean sea level, while the other one is Alaknanda with its origin in Sapta Tal glacier. After covering a distance of about 220 km in the Himalayas it enters the plains at Hardwar and after meandering over a distance of about 2290 km in the plains in the states of Uttar Pradesh, Bihar and West Bengal, it joins the Bay of Bengal through a large number of branches flowing in India and Bangladesh (Fig. 1).

Physiographically the area is generally flat except Siwalik hills in the north and north east. The area is devoid of any relief features of provinces except from deep garges cut by nalas and rivers flowing through the area. The drainage pattern is dominated by the river Ganga, which is the only major river flowing through the area. Since the Ganga is fed by the water of the melting glaciers in the upper Himalayas, it has a perennial supply of water.

The climate of the region is characterized by moderate type of subtropical monsoonal climate. It has a cool dry winter season from October to March, a hot dry summer season from April to June and a warm rainy season from July to September. The average annual rainfall in the area is about 1000 mm, a major part of which is received during monsoon period. It has been observed that the rainfall is heaviest in the northern region of Hardwar district, close to the foothills of Himalayas and become lesser southward. The major land use is agriculture and there is no effective forest cover.

Geologically, the area is a part of the west Indogangetic plain, which is mainly composed of Pleistocene and subrecent alluvium brought down by the river action from Himalayan region. At Hardwar, the sequence of sandstone and shales along with gravel beds and clays are grouped within the upper and middle Siwaliks. The soils of the area are loam to silty loam and are normally free from carbonates.
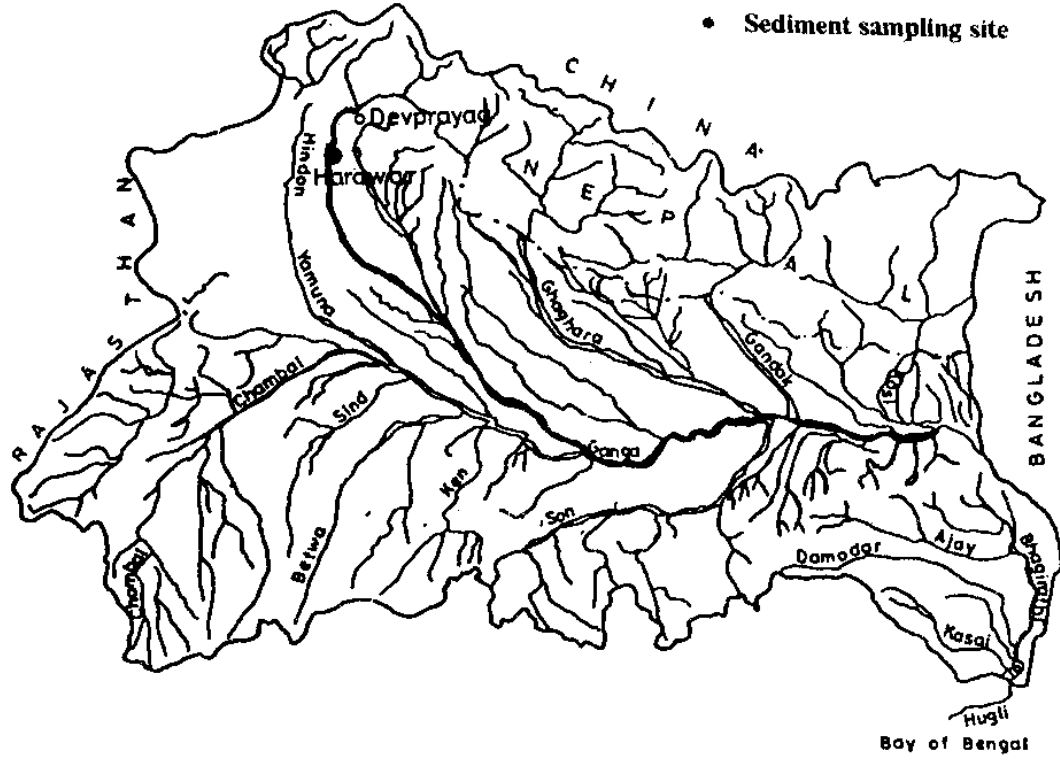
Fig. 1. The river system showing location of sediment sampling site

3.0 POLLUTION STATUS OF RIVER GANGA

The river Ganga occupies a unique position in our country. It has served as the cradle of Indian civilization and is interwoven with India's history, culture, religion and philosophy. A large number of tributaries of varying dimensions merge their identity with this mighty river, which is respectfully worshipped by millions of Indians. Ganga and its tributaries constitute one of the largest riverrine systems in the world. Besides being a source of supply of drinking water to the people inhabiting the cities, towns and villages situated on its banks, it is also being used for navigation, irrigation, bathing, washing, fishing and for industrial purposes.

However, during the last few decades, the water of this river, which has been considered as 'nectar' and carried to far places for drinking and religious purposes, has become polluted. Despite the mineral ingredients and micro-flora and fauna present in it, the self-purification power of the Ganga is not limited. Depleted every day by our need for irrigation and drinking water, assailed constantly by the discharge of industrial effluents and municipal waste, the dumping of human and animal bodies and the residues of burning ghats, the river has developed dangerous levels of toxicity in certain stretches. At several places the river has been converted into a network of cesspools and drains by the industries and municipalities of the region.

It is paradox that a river which is a part of cultural heritage of India was put to abuse by discharging untreated effluents from tanneries, distilleries, sugar factories, paper mills and domestic sewage all along its course. Identifying the magnitude of pollution, the Central Pollution Control Board together with State Board and fourteen universities started an in-depth study of the river and presented a unique report titled "Basin, sub-basin inventory of water pollution - Ganga basin" (CBPCWP, 1984). Based on this report, Ganga Action Plan was envisaged to mitigate pollution load of this river system. This mighty river flows through Uttar Pradesh, Bihar, and West Bengal, finally joining Bay of Bengal as Bhagirathi-Hooghly system near Ganga Sagar. Near Farakka the main river divides into two arms. The left arm knows as Padma, runs towards Bangladesh while the right arm Bhagirathi flows in southern direction. From Nabdweep onwards, it is known as Hooghly which, ultimately flows into Bay of Bengal about 145 km downstream of Calcutta.

The Bhagirathi Hooghly riverine system has been the lifeline of west Bangal which, helped urbanization and industrialization of the twin cities, Calcutta and Howrah on either side. There are hundreds of industries located along the banks of the Hooghly. Besides, a number of drains collecting sewage joins to this river. Near Calcutta and howrah, the rivers receives 346 outfalls which carry 120 million and 50 million gallons of domestic and industrial waste (Datta, 1984). The total pollution load by industrial waste indicates that 1.41 lakh kg per day BOD entered into the river Hooghly in 1970 as compared to the value of 1.18 lakh per day in the year 1969 (NEERI, 1970). Realising the magnitude of pollution load due to urbanization and industrial growth, Calcutta Metropolitan Development Authority has taken up studies in stretch between Kalyani and Birlapur regarding physico-chemical features and major groups of plankton (CMDA Reports 1978-82). Besides, there are some notable works carried out on this river by various investigators concerning physico-chemical features, plankton and heavy metal toxicity on fish populations (Ghosh et at., 985; Data, 1984; Nandy et al., 1983). A perusal of the data reveal that no attempt has been made to interrelate various limnological features on the biological or functional aspects of the river system.

Studies on water quality of river Ganga in various stretches have been conducted by several workers. Out of the 2525 km length, ranging from the Gangotri in the Himalayas to the Ganga Sagar where the Ganga empties into the Bay of Bengal, the worst polluted stretch is almost 600 km long. In the plains the main sources of pollution are urban liquid waste, large scale wallowing of cattle and throwing of dead bodies into the river. In addition the increasing surface run-off from cultivated land on which the cultivators use pesticides, insecticides, fertilizers and manure and a similar run-off from grounds where urban solid wastes and industrial wastes have been dumped, are responsible for the degradation of the river. The untreated city sewage remains the worst pollution. The cultural and religions factors in polluting Ganga and its main tributary Yamuna is also note worthy. This is increased especially during Kumbh and other auspicious occasions when millions of people believing in Ganga's perpetual sacredness bath in Ganga. The staggering increase in the coliform count during such mass bathing is to be seen to be believed. This phenomenon, defiling of the sacred river by the very people who worship her, is ironic.

It is recognized that the reach of the river Ganga from Kannauj to Buxar in the lean season is not even fit for bathing purposes at several places. From Hardwar to Kannauj and from Buxar to Farakka it is not fit for drinking water purposes in the lean season. This is due to various reasons including the fact that the cities located near the banks of the Ganga and its principal tributaries are not adhering to the sewage disposal regulations by effective treatment to render it harmless. Many industries located along the river are not treating the effluents before these are discharged into the river. There are some 100 cities located on the river Ganga, with over 30 having a population of more than one lakh. These contribute heavily to the pollution load. Ecology of river Ganga from Patna to Farakka was studied by Bilgrami and Dutta (1985).

Some pollution specific studies conducted on river Ganga include physico chemical characteristics of river Ganga in Kanpur region (Pande and Pande, 1980), effect of tannery waste disposal on the quality of river in the region (Chandra and Krishna, 1984), chemical quality of Ganga water and their effect on water use (Handa et al., 1993). A short term study on the pollution status of river Ganga in Kanpur has been conducted by Chattopadhya et al. (1984). A similar study was also conducted earlier by Saxena et al. (1966). Characterization of waste water of Kanpur city was carried out by Sehgal and Siddiqi (1969) to evaluate the design criteria for waste management programme. Ray and David (1966) made an attempt to see the effect of industrial wastes and sewage upon the chemical and biological composition of the river Ganga while David and Ray (1960) described the processes responsible for tannery and textile wastes and their effect on the quality of water of river Ganga.

In the city limit of Allahabad again degradation in water quality is observed due to the discharge of untreated waste. The quality of water is quite unsatisfactory and treatment is necessary before using for drinking and other domestic purposes. Pollution studies of river Ganga at Sangam during Ardha Kumbha has been reported by Upadhyay et al. (1982) and status of pollution at Sangam and its adjoining rivers at Allahabad by Singh et al. (1988, 1989). The effect of mass bathing on water quality of Sangam before, during and after Maha Kumbh mela at Allahabad have been studied by Singh et al. (1989). The studies on water quality of Ganga river from Kare-Manikpur to Phaphmau (Allahabad) have been reported by Sinha et al. (1989).

Agarwal et al. (1976) studied the physico-chemical and bacteriological

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characteristics of the river Ganga at Varanasi. Bacteriological studies conducted near the ghats of Varanasi indicated the BOD ranges between 2.1-7.8 mg/L and fecal coliform counts between 500-23000 per 100 mL. This state of affairs caused concern in the people who understood the risks of the rising level of river pollution. Mathur et al. (1987) conducted a study on river Ganga at Varanasi with special emphasis on heavy metal pollution. Recently Mishra and Upadhyay (1993) have reported that about 85% of the total pollution of the river at Varanasi is due to the disposal of sewage into the river. The major amount of the wastewater flows through the main sewer outfall downstream of the city whereas most of the remaining flow enters through other major outlets. From the point of view of industrial pollution, the situation has not been very bad at Varanasi because toxic pollutants are stated to be either absent or present only in insignificant quantities in the water of the bathing areas (Mishra et al., 1992). Ecological studies of the Ganges river at Varanasi were studied by Rai (1978) and Sikandar et al. (1989).

The quality of river Ganga at Patna, the most populated city of Bihar state, has been reported by Rao et al. (1990) with special reference to domestic waste and major industries of the area. The over all values of DO and BOD indicate that the river water in Bihar could be used as drinking water source without conventional treatment but with disinfection and also suitable for bathing, swimming and recreation. They further reported that the amount of dissolved oxygen throughout the river in Bihar was above 70% saturation and well within the requirements of propagation of fish. Further detailed studies on Physico-chemical characteristics of river Ganga from Mirzapur to Ballia have been studied by Shukla et al. (1989). Their study reveals that the Ganga water quality was quite good at the point where it enters the city and get highly polluted at midstream as a result of assimilation from a number of sewage and industrial drains. The downstream water at Varanasi was observed highly polluted in comparison to all other sites, this is due to discharge of sewage mixed with industrial effluents through Rajghat nala, however the water quality at Ballia was recorded fairly clean. Ecology of river Ganges from Patna to Farakka was studied by Bilgrami and Datta (1985).

Sinha et al. (1993) conducted some studies in Rae-Bareli district and reported that deterioration in water quality of the river Ganga in Rae-Bareli district is due to ageold practice of mass bathing, washing of cloths, cremation and dumping of garbage into the river. Other studies on river Ganga include pollution status of the river water in West Bengal (Sinha and

Banerjee, 1987; Sengupta et al., 1988). A comprehensive survey of the Ganga basin conducted by Central Pollution Control Board, New Delhi revealed that the river, despite its extra ordinary resilience, is heavily polluted at several places. Such a situation calls for immediate action, specially, because of the fact that 80% of the diseases are water borne.

The literature available on the studies of heavy metals speciation in water-sediment system is relatively scanty. The research initiative in this direction started only a decade back (Jha et al., 1990). Subramanyam et al. (1987) studied distribution of heavy metals in sediments of Ganga and Brahmaputra rivers while Ajmal et al. (2987) analysed heavy metals in water and sediments of the Ganga river. Modak et al. (1992) determined the concentrations of mobile and bound trace metals associated with sediment components of the lower reaches of river Ganga.

Saikia (1987) and Saikia et al. (1988) studied the incidence and transport of heavy metals (Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb) in water and sediments of upper regions of river Ganga) and reported that suspended load is the prominent mode of transport of these metals. The study also showed that adsorption of Cu, Zn and Pb on the bed sediments is quite significant. Thus, in the present study, detailed adsorption characteristics of bed sediments of river Ganga have been studied in their natural state of occurrence to demonstrate the role of bed sediments in controlling metal pollution.

4.0   EXPERIMENTAL METHODOLOGY

Freshly deposited sediments from shallow water near the bank of river Ganga at Hardwar were collected 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. 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 ($HF + HClO_3 + HNO_3$) 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 zinc were prepared from zinc nitrate. Deionized water was used throughout the study. All glass wares 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 zinc ion solution (100-1000 µg L^{-1}) were transferred in the flasks together with desired adsorbent doses (W_s in g L^{-1}), and placed in a water bath shaker maintained at 30°C. The pH of 6.5 ± 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 zinc 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 zinc ion was 0.002 mg L^{-1}. Operational conditions were adjusted to yield optimal determinations. Quantification of the metals was based upon calibration curves of standard solutions of zinc ion. These calibration curves were determined several times during the period of analysis.

5.0   RESULTS AND DISCUSSION

The sediment under study has a rather coarse texture, composed of more than 90% sediment of size >75 μm and <10% silt and clay. The organic content of the sediment was of the order of 0-1%. The background zinc 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 zinc particulate attached to the sediment particles.

The content of two important geochemical phases (iron and manganese) in different particle size fractions alongwith 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 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. The content of iron in the sediment fractions is relatively higher and indicates 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 150-210 μm particle size constitute 68.6% of the total sediment load. Therefore, it was considered appropriate to study the adsorption of zinc ions on this fraction (150-210 μm) and to compare with the clay and silt fraction (<75 μm particle size) to demonstrate the relative importance of the coarser fraction in controlling metal pollution.

5.1   Operating Variables

5.1.1   Equilibrium time (t)

In order to determine the equilibrium time for the adsorption process, adsorption experiments were performed for the uptake of zinc ions for different duration of contact times

Table 1. Characteristics of sediments			
Sediment fraction (µm)	Weight (%)	Total Mn (mg/g)	Total Fe (mg/g)
<75	9.8	1.570	68.2
75-150	13.5	1.420	62.0
150-210	68.6	1.199	58.0
210-250	6.6	0.844	55.1
250-300	0.7	0.830	52.1
300-425	0.6	0.823	52.0
425-600	0.2	0.824	52.0

for a fixed adsorbent dose of 0.5 g L^{-1} and with an initial metal ion concentration of 1000 μg L^{-1} (Table 2, Fig. 2&3) for the two particle size of adsorbent (0-75 and 150-210 μm) at a pH value of 6.5. 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 zinc ions becomes asymptotic to the time axis such that there is no appreciable change in the remaining concentration after 60 minutes for both the fractions. 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 zinc adsorbed, C$_t$ vs t$^{1/2}$, are presented for the two particle size of adsorbent in Fig. 4&5. It is clearly evident that adsorption of zinc ions on the bed sediments follow three phases, an instantaneously extremely fast uptake, transition phase and an almost flat plateau section. Phase I, is attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface (bulk diffusion). Phase II, exhibiting additional removal, is attributed to the diffusion of the adsorbate from the surface film into the macro-pores of the adsorbent (pore diffusion or intraparticle diffusion), stimulating further migration of adsorbate from the liquid phase onto the adsorbent surface. Phase III, plateau section shows equilibrium state. The visual observation indicates the minor importance of any precipitation from ion exchange.

5.1.2   Adsorption isotherm

The adsorption isotherms for the zinc adsorption on the bed sediments are shown in Fig. 6 with a fixed adsorbent dose of 0.5 g L^{-1} at a pH of 6.5 ± 0.1. The adsorption data (Table 3) indicate linear distribution in the range 0 to 1000 μg L^{-1}. It is evident that for the same equilibration time, the zinc adsorbed is higher for greater values of initial concentration of zinc ions or the percentage adsorption is more for lower concentration of zinc and decreases with increasing initial concentration (Fig. 7). 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 zinc is more for <75 μm fraction, i.e., clay and silt as compared to coarser fraction. It is also

Table 2. Adsorption of zinc on bed sediments of River Ganga at different durations of contact times.						
Adsorbent dose = 0.5 g/L; pH = 6.5; Temperature = 30°C.						
Sediment fraction	Initial concn.	Contact time	Concn. at	Metal ion adsorbed		
(μm)	C_o, μg/L	t, min	time t, μg/L	μg/L	μg/g	%
0-75	1000	5	248	752	1504	75.2
	1000	10	220	780	1560	78.0
	1000	15	204	796	1592	79.6
	1000	30	187	813	1626	81.3
	1000	45	178	822	1644	82.2
	1000	60	173	827	1654	82.7
	1000	90	171	829	1658	82.9
	1000	120	170	830	1660	83.0
	1000	150	171	829	1658	82.9
	1000	180	169	831	1662	83.1
150-210	1000	5	322	678	1356	67.8
	1000	10	300	700	1400	70.0
	1000	15	280	720	1440	72.0
	1000	30	253	747	1494	74.7
	1000	45	244	756	1512	75.6
	1000	60	238	762	1524	76.2
	1000	90	236	764	1528	76.4
	1000	120	236	764	1528	76.4
	1000	150	234	766	1532	76.6
	1000	180	232	768	1536	76.8

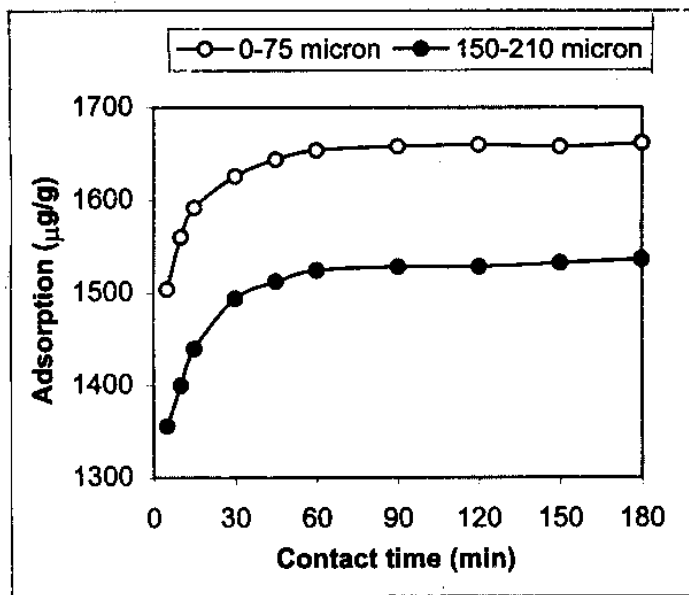| Table 3. Adsorption of zinc on bed sediments of River Ganga at different concentrations.					
Contact time = 60 min; Adsorbent dose = 0.5 g/L; pH = 6.5; Temperature=30°C.					
Sediment fraction	Initial concn.	Equil. concn.	Metal ion adsorbed		
(µm)	C_o, µg/L	C_e, µg/L	µg/L	µg/g	%
0-75	200	32	168	336	84.0
	400	65	335	670	83.8
	600	99	501	1002	83.5
	800	134	666	1332	83.3
	1000	175	825	1650	82.5
	1200	268	932	1864	77.7
	1400	380	1020	2040	72.9
	1600	520	1080	2160	67.5
	1800	680	1120	2240	62.2
	2000	850	1150	2300	57.5
150-210	200	44	156	312	78.0
	400	90	310	620	77.5
	600	139	461	922	76.8
	800	188	612	1224	76.5
	1000	239	761	1522	76.1
	1200	325	875	1750	72.9
	1400	440	960	1920	68.6
	1600	560	1040	2080	65.0
	1800	730	1070	2140	59.4
	2000	900	1100	2200	55.0

Fig. 2. Effect of contact time on adsorption of zinc ions
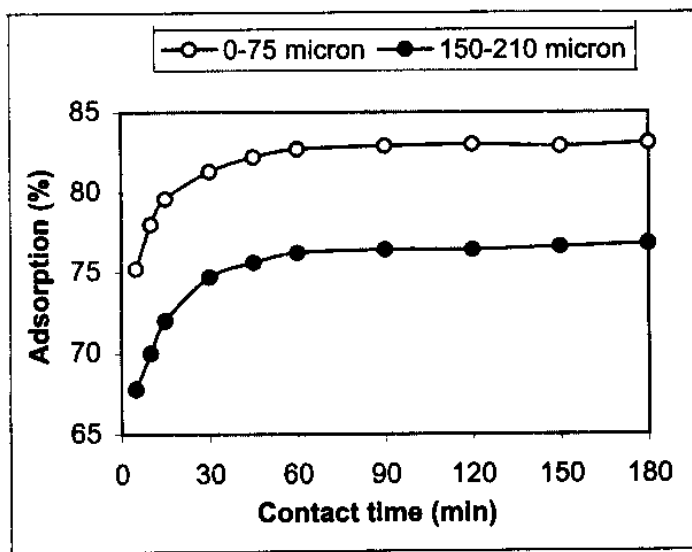

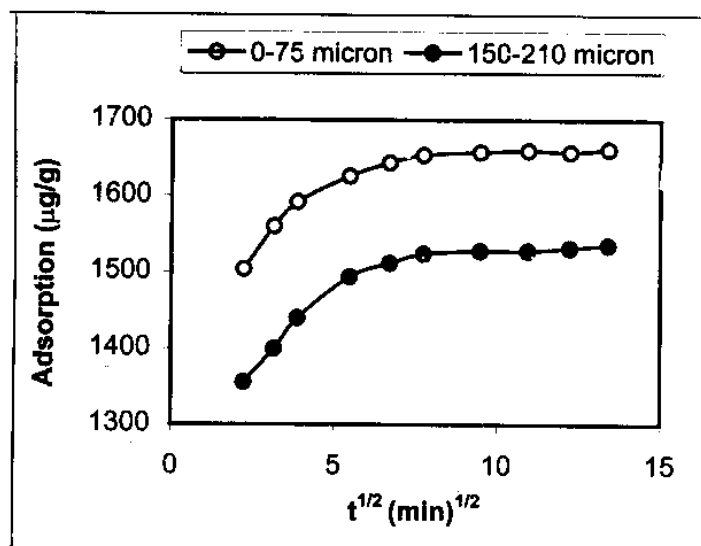Fig. 3. Effect of contact time on percent adsorption of zinc ions

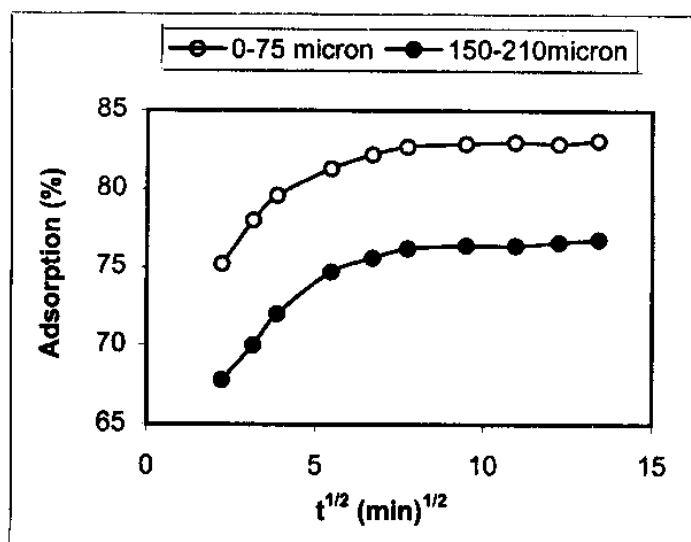Fig. 4. Effect of $t^{1/2}$ on adsorption of zinc ions

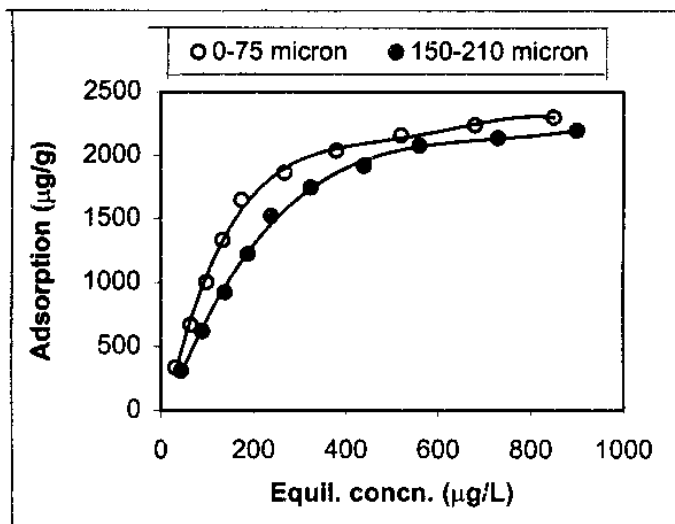Fig. 5. Effect of $t^{1/2}$ on percent adsorption of zinc ions

Fig. 6. Adsorption of zinc ions on bed sediments at
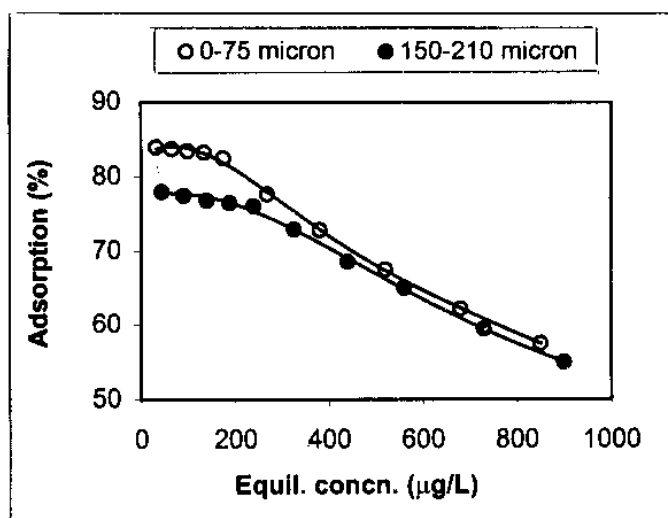different concentrations

Fig. 7. Percent adsorption of zinc ions on bed sediments
at different concentrations

evident from Table 1 that <75 µm fraction contain more iron and manganese content than that of 150-210 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 zinc adsorption. However, due to paucity of data correlation statistics could not be attempted to confirm this statement. The clay and silt constitute <10% of the total sediment load and therefore, comparing the two weight percentage of the two fractions and their corresponding adsorption capacities for zinc ions, it is clear that the contribution of coarser sediment is more in controlling zinc 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).

5.1.3   Effect of pH

The adsorption of zinc on the riverbed sediments was studied over the pH range 2-7 for a fixed initial concentration of zinc (C_i = 1000 µg L^{-1}) and adsorbent dose of 0.5 g L^{-1} at a particle size of 0-75 and 150-210 µm (Table 4, Fig. 8&9). 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 5.0 for both the fractions of the sediment. From the results it is evident that the pH for maximum uptake of zinc ion is 5.0. Further, it is apparent that the adsorption of zinc rises from 0.5% at pH 2.0 to 82% at pH 5.0 in the case of clay and silt fraction (0-75 mm) and from 0.4% at pH 2.0 to 75% at pH 5.0 in the case of coarser sediment fraction (150-210 µm). Almost similar trend with pH was reported by Palheiros et al. (1989) for the adsorption of cadmium on riverbed sediment.

5.1.4   Adsorbent dose (W$_s$)

The effect of adsorbent dose on the adsorption properties of bed sediments of river Ganga has been studied at pH 6.5 with different adsorbent doses varying from 0.2 to 2.5 g L^{-1} and at a fixed initial zinc concentration of 1000 µg L^{-1} (Table 5, Fig. 10&11). The experiments were conducted in a water bath shaker to disperse the sediment particles in the

Table 4. Adsorption of zinc on bed sediments of River Ganga at different pH values.						
Contact time = 60 min; Adsorbent dose = 0.5 g/L; Temperature=30°C.						
Sediment fraction (μm)	pH	Initial concn. C_o, μg/L	Equil. concn. C_e, μg/L	Metal ion adsorbed		
				μg/L	μg/g	%
0-75	2	1000	995	5	10	0.5
	3	1000	805	195	390	19.5
	4	1000	255	745	1490	74.5
	5	1000	180	820	1640	82.0
	6	1000	174	826	1652	82.6
	7	1000	173	827	1654	82.7
150-210	2	1000	996	4	8	0.4
	3	1000	837	163	326	16.3
	4	1000	323	677	1354	67.7
	5	1000	256	744	1488	74.4
	6	1000	236	764	1528	76.4
	7	1000	235	765	1530	76.5

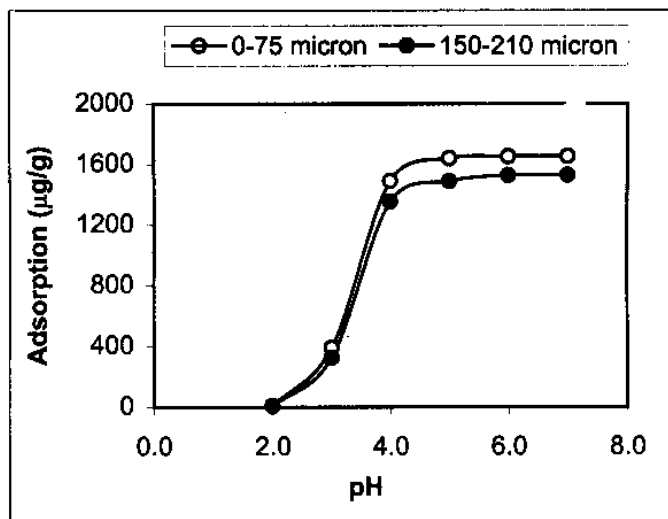| Table 5. Adsorption of zinc on bed sediments of River Ganga at different adsorbent doses.						
Contact time = 60 min; pH = 6.5; Temperature = 30°C.						
Sediment fraction	Initial concn.	Adsorbent dose	Equil.concn.	Metal ion adsorbed		
(μm)	C_o, μg/L	W_s, g/L	C_e, μg/L	μg/L	μg/g	%
0-75	1000	0.5	175	825	1650	82.5
	1000	1.0	136	864	864	86.4
	1000	1.5	115	885	590	88.5
	1000	2.0	107	893	447	89.3
	1000	2.5	87	913	365	91.3
150-210	1000	0.5	237	763	1526	76.3
	1000	1.0	189	811	811	81.1
	1000	1.5	154	846	564	84.6
	1000	2.0	119	881	441	88.1
	1000	2.5	100	900	360	90.0

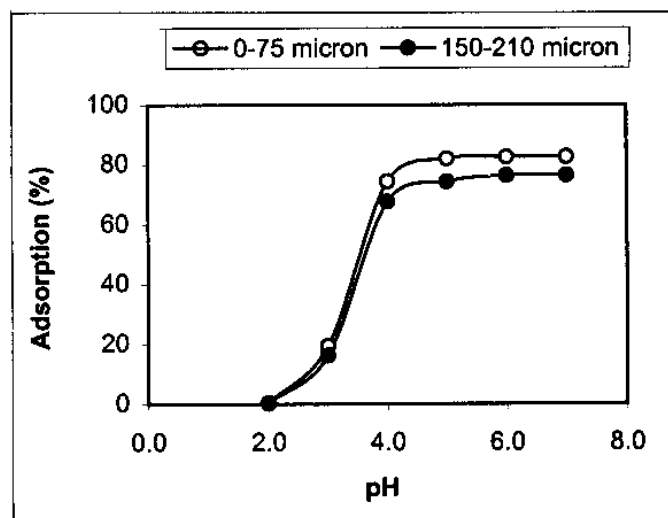Fig. 8. Effect of pH on adsorption of zinc ions

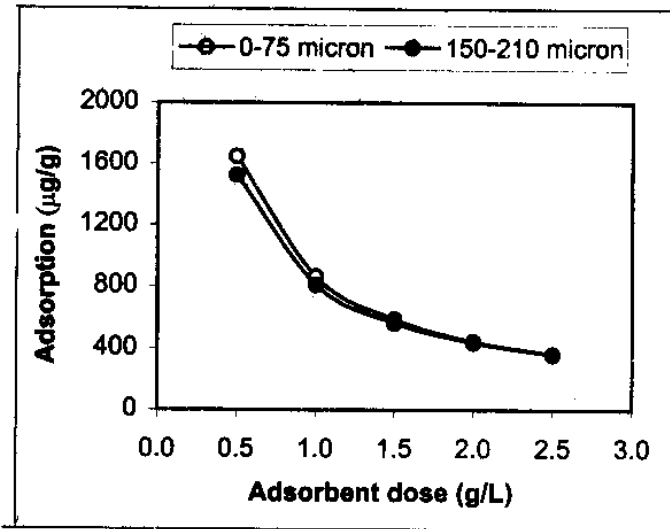Fig. 9. Effect of pH on percent adsorption of zinc ions

Fig. 10. Effect of adsorbent dose on adsorption of zinc
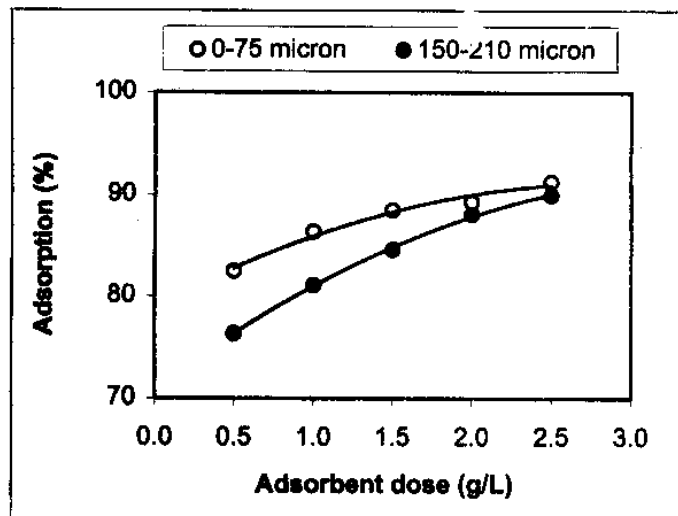ions

Fig. 11. Effect of adsorbent dose on percent adsorption
of zinc ions

aqueous media. It is observed that for a fixed initial concentration of zinc (C_o = 1000 μg L^{-1}), the adsorption of zinc per unit weight of adsorbent decreases with increasing adsorbent load. On the other hand percent adsorption increases from 82.5 to 91.3% for the 0-75 μm fraction with increasing adsorbent load from 2 to 2.5 g L^{-1}. The adsorption of zinc was higher for the 0-75 μm fraction as compared to 150-210 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 zinc ions.

5.1.5   Particle size (d_p)

The effect of particle size of adsorbent on zinc adsorption are shown in Fig 12&13 for a fixed initial concentration of zinc (C_i = 1000 μg L^{-1}) and adsorbent dose of 0.5 g L^- and at a pH value of 6.5 (Table 6). These plots reveal that for a fixed adsorbent dose, the zinc adsorbed is higher for smaller adsorbent size. Further, it is observed that the percentage of zinc adsorbed decreases from 82.5% on 0-75 μm fraction to 68% on 425-600 μm fraction, with the increasing geometric mean of adsorbent size. This is because, adsorption being a surface phenomenon, the smaller particle sizes offered comparatively larger surface area and hence higher adsorption occurs at equilibrium. The higher content of iron and manganese in the 0-75 μm sediment fraction also accounts for higher adsorption of zinc in this fraction as compared to higher fractions of the sediment.

5.2   Adsorption Models

Adsorption data for wide range of adsorbate concentrations are most conveniently described by adsorption models, such as the Langmuir or Freundlich isotherm, which relate adsorption density q_e (metal uptake per unit weight of adsorbent) to equilibrium adsorbate concentration in the bulk fluid phase, C_e. The adsorption data of zinc on the bed sediments of the River Ganga has been analysed with the help of Langmuir and Freundlich models to evaluate the mechanistic parameters associated with the adsorption process.

| Table 6. Adsorption of zinc on bed sediments of River Ganga at different adsorbent sizes.					
Contact time = 60 min; Adsorbent dose = 0.5 g/L; pH = 6.5; Temperature = 30°C.					
Adsorbent size*	Initial concn.	Equil. concn.	Metal ion adsorbed		
d_p, μm	C_o, μg/L	C_e, μg/L	μg/L	μg/g	%
8.7	1000	175	825	1650	82.5
106.1	1000	210	790	1580	79.0
178.3	1000	235	765	1530	76.5
230.2	1000	256	744	1488	74.4
273.9	1000	270	730	1460	73.0
357.1	1000	294	706	1412	70.6
505	1000	320	680	1360	68.0
* Geometric mean					
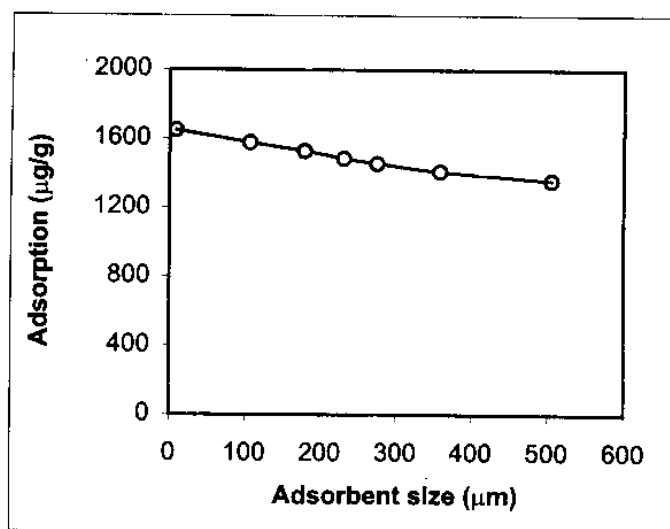
Fig. 12. Effect of adsorbent size on adsorption of zinc io
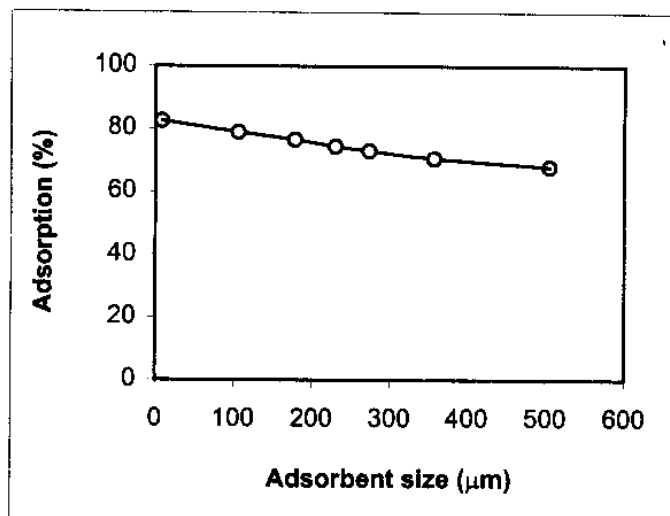

Fig. 13. Effect of adsorbent size on percent adsorption
of zinc ions

5.2.1   Langmuir model

Langmuir's isotherm model is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The Langmuir treatment is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface.

The linear form of Langmuir isotherm equation is represented by the following equation:

$$\frac{1}{q_e} = \frac{1}{Q^o} + \frac{1}{bQ^o C_e} \qquad \ldots (1)$$

Where q_e is the amount adsorbed at equilibrium time ($\mu g/g$), C_e is the equilibrium concentration of the adsorbate ions ($\mu g/L$), and Q^o 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 $1/bQ^o$ and intercept $1/Q^o$ is obtained (Fig. 14), which shows that the adsorption of zinc ions follow Langmuir isotherm model. The Langmuir parameters, Q^o and b, are calculated from the slope and intercept of the graphs and are given in Table 7. These values may be used for comparison and correlation of the sorptive properties of the sediments.

5.2.2   Freundlich model

The Freundlich equation has been widely used for many years and is applicable for isothermal adsorption. This is a special case for heterogeneous surface energies in which the energy term, b, in the Lagmuir equation varies as a function of surface coverage, q_e, strictly due to variations in heat of adsorption (Adamson, 1967). The Freundlich equation has the general form:

$$q_e = K_F C^{\frac{1}{n}} \qquad \ldots (2)$$

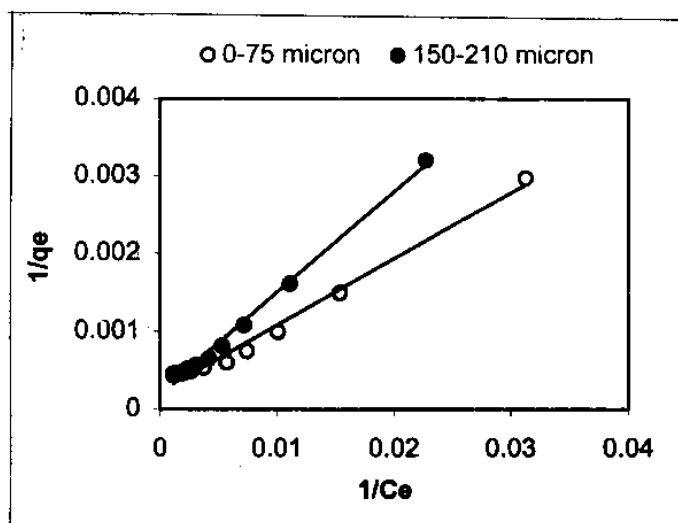| Table 7. Langmuir parameters for the adsorption of zinc ions		
Sediment fraction	Adsorption maxima	Bonding energy constant
(μm)	Q^o (mg/g)	b (mg/L)$^{-1}$
0-75	5.0	2.35
150-210	5.0	1.55

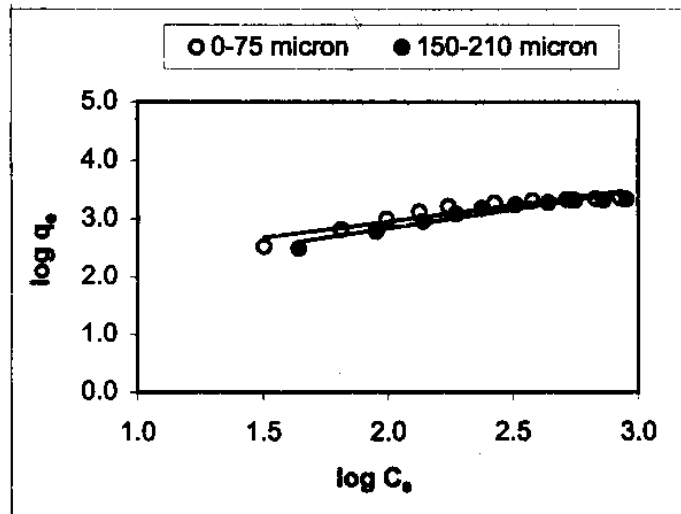Fig. 14. Graphical representation of Langmuir isotherm

Fig. 15. Graphical representation of Freundlich isotherm

The Freundlich equation is basically empirical but is often useful as a means for data description. Data are usually fitted to the logarithmic form of the equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad \qquad \ldots (3)$$

Where q_e is the amount adsorbed ($\mu g/g$), C_e is the equilibrium concentration of the adsorbate ions ($\mu g/L$), 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. 15). This reflects the satisfaction of Freundlich isotherm model for the adsorption of zinc 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 8.

The freundlich type adsorption isotherm is an indication of surface heterogeneity of the adsorbent while Langmuir type isotherm corresponds to surface homogeneity of the adsorbent. This leads to the conclusion that the surface of the bed sediments of the river Ganga is made up of small heterogeneous adsorption patches which are very much similar to each other in respect of adsorption phenomenon (Ajmal et al., 1998).

5.3 Adsorption Kinetics

5.3.1 Themodynamic parameters

Fig. 16&17 shows that increasing contact time increased the zinc adsorption and it remained constant after 60 min for the two particle size (0-75 and 150-210 μm) of the adsorbent. The equilibrium time was also found to be independent of initial concentration of zinc ions. The adsorption curves are smooth and continuous leading to saturation, suggesting the possible monolayer coverage of zinc ions on the surface of the adsorbent. The temperature range used in the study was from 20 to 40°C. Adsorption increased with temperature (Fig. 18&19).

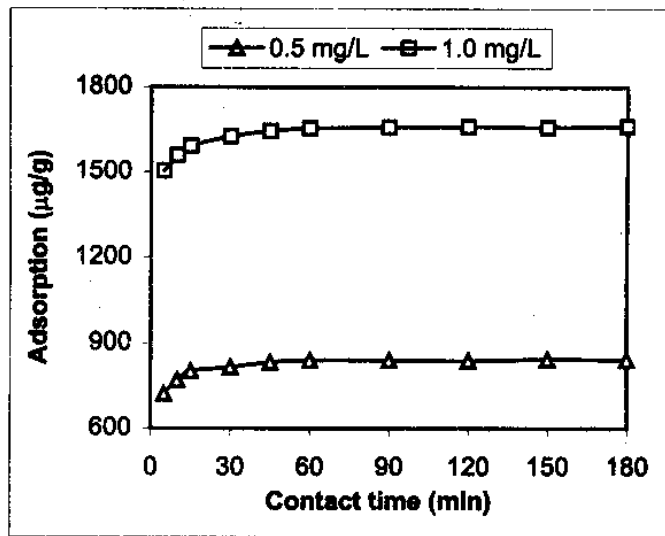| Table 8. Freundlich parameters for the adsorption of zinc ions		
Sediment fraction (μm)	Adsorption capacity K_F (mg/g)	Adsorption intensity $1/n$
0-75	0.069	0.5565
150-210	0.035	0.6428

Fig. 16. Effect of contact time and initial concentration o adsorption of zinc ions. Sediment fraction = 0-75 μm.
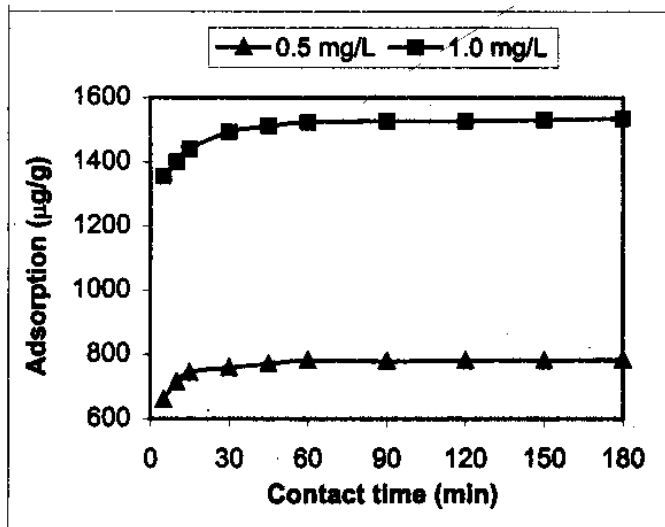

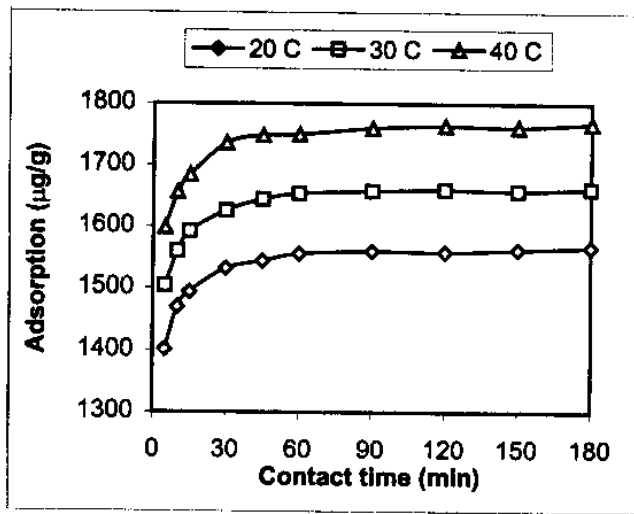Fig. 17. Effect of contact time and initial concentration o adsorption of zinc ions. Sediment fraction = 150-210 μm.

Fig. 18. Effect of contact time and temperature on adsorption of zinc ions. Sediment fraction = 0-75 μm; Initial concn. = 1000 μg/L.
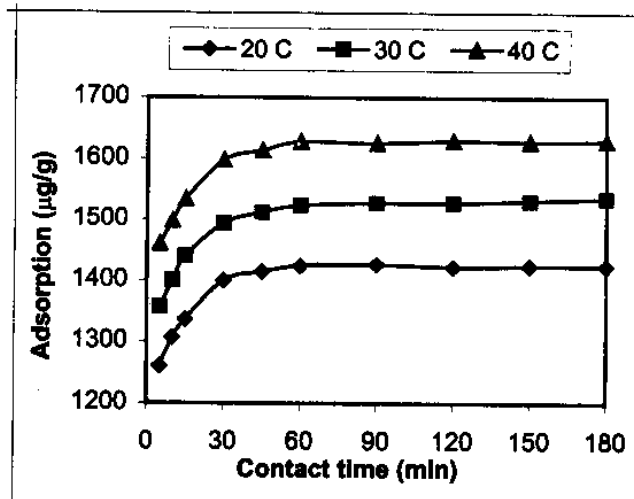

Fig. 19. Effect of contact time and temperature on adsorption of zinc ions. Sediment fraction = 150-210 μm Initial concn. = 1000 μg/L.

Thermodynamical parameters such as free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were determined using the following equation (Singh et al., 1988; Catena and Bright, 1989; Fraiji et al., 1992).

$$\Delta G^\circ = -RT \ln K_c \qquad \ldots (4)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad \ldots (5)$$

where:

ΔG° = change in free energy, kJ/mol

ΔH° = change in enthalpy, kJ/mol

ΔS° = change in entropy, J/mol/K

T = absolute temperature, K

R = gas constant = 8.314×10^{-3}

K_c = equilibrium constant. This may be defined as:

$$K_c = \frac{C_{Ae}}{C_e} \qquad \ldots (6)$$

where C_{Ae} and C_e are the equilibrium concentration ($\mu g/L$) of the metal ion on the adsobent and in the solution respectively.

From equation (4) and (5) it can be rewritten as:

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \qquad \ldots (7)$$

When $\log K_C$ is plotted against $1/T$, a straight line with slope $\dfrac{\Delta H^\circ}{2.303R}$ and intercept $\dfrac{\Delta S^\circ}{2.303R}$ is obtained (Fig. 20&21). The values of ΔH° and ΔS° were obtained from the slope and intercept of the van't Hoff plots of log K_c vs $1/T$ (Fig. 20&21). The thermodynamic parameters for the adsorption process are given in Table 9.

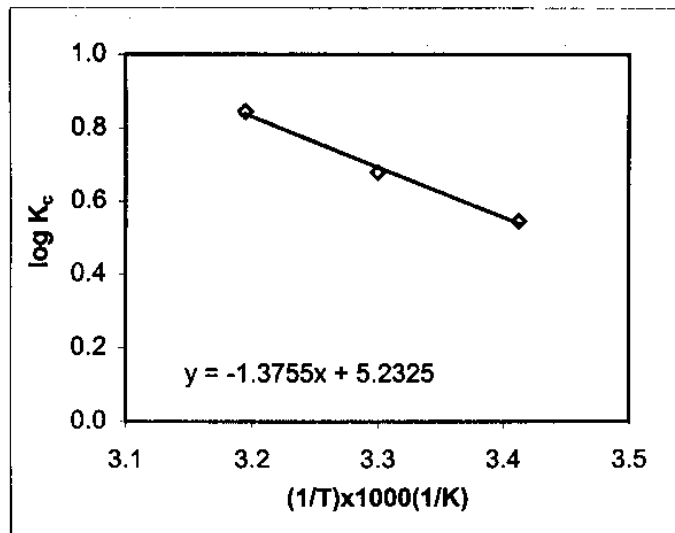| Table 9. Thermodynamic parameters for the adsorption of zinc on bed sediments					
Sediment fraction	Temp.	K_c	ΔG^o	ΔH^o	ΔS^o
(μm)	°C		kJ/mol	kJ/mol	J/mol/K
0-75	20	3.505	-3.055	26.337	100.187
	30	4.780	-3.942		
	40	7.000	-5.065		
150-210	20	2.472	-2.206	21.745	81.647
	30	3.202	-2.930		
	40	4.376	-3.842		

Fig. 20. Van't Hoff plot for adsorption of zinc ions.
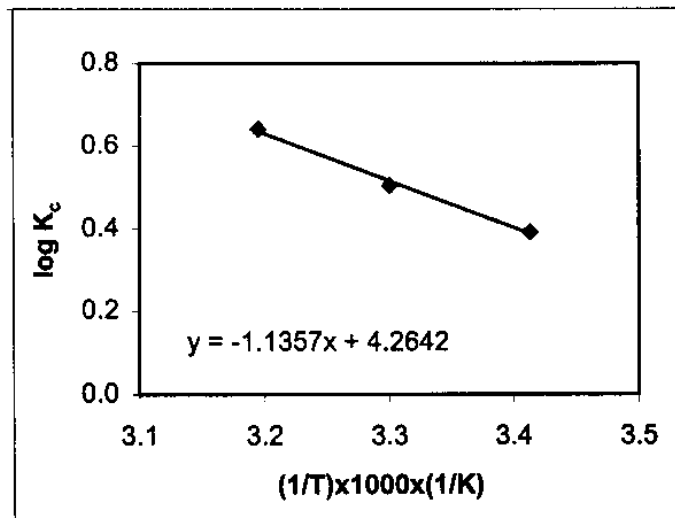Sediment fraction = 0-75 μm.

Fig. 21. Van't Hoff plot for adsorption of zinc ions.
Sediment fraction = 150-210 μm.

Positive values of ΔH° suggest the endothermic nature of the adsorption. The negative values of ΔG° indicate spontaneous nature of the adsorption process. However, the negative value of ΔG° decreased with an increase in temperature, indicating that the spontaneous nature of adsorption is inversely proportional to the temperature. The positive values of ΔS° show the increased randomness at the soild/solution interface during the adsorption process. The adsorbed water molecules, which are displaced by the adsorbate species, gain more translational energy than is lost by the adsorbate ions, thus allowing the prevalence of randomness in the system. Enhancement of adsorption capacity at higher temperatures may be attributed to the enlargement of pore size and/or activation of the adsorbent surface (Vishwakarma et al., 1989).

5.3.2 Adsorption dynamics

The rate constant of adsorption is determined using Lagergren first order rate expression (Singh et al., 1989; Namasivayam and Ranganathan, 1995; Zhang et al., 1998):

$$\log(q_e - q) = \log q_e - \frac{k_{ad}}{2.303} \times t \qquad \dots (8)$$

Where q and q_e are amounts of metal adsorbed ($\mu g/g$) at time, t(min) and at equilibrium, respectively and k_{ad} is the Lagergren rate constant for adsorption (1/min). The straight line plots of $\log(q_e - q)$ vs t for different concentrations (Fig. 22&23) and temperatures (Fig. 24&25) indicate the applicability of the above equation. Values of k_{ad} were calculated from the slope of the linear plots and are presented in Table 10 and 11 for different concentrations and temperatures, respectively. The rate constant was higher at higher temperature.

5.3.3 Intraparticle diffusion

The rate constant for intraparticle diffusion (k_{id}) is given by Weber and Morris

Table 10. Rate constants at different concentrations			
Sediment fraction (μm)	Concn. of Zinc (μg/L)	Lagergren rate constant k_{ad} (1/min)	Intraparticle rate constant k_{id} (μg/g/min$^{1/2}$)
0-75	500	6.84×10^{-2}	10.857
	1000	6.52×10^{-2}	17.333
150-210	500	5.71×10^{-2}	9.23
	1000	6.68×10^{-2}	13.27

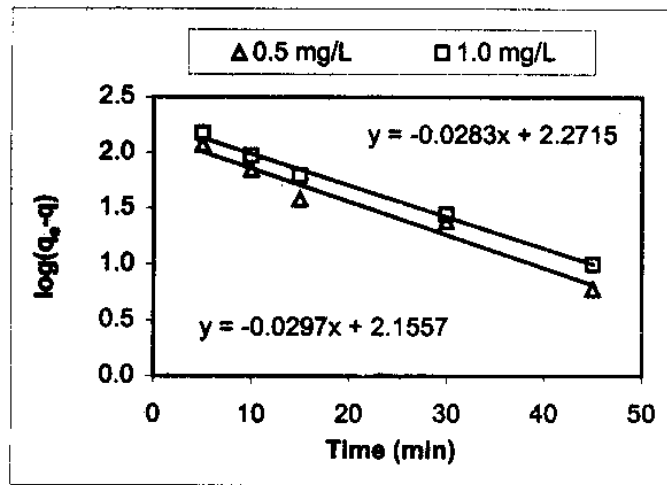| Table 11. Rate constants at different temperatures			
Sediment fraction (μm)	Temperature ($^\circ$C)	Lagergren rate constant k_{ad} (1/min)	Intraparticle rate constant k_{id} (μg/g/min$^{1/2}$)
0-75	20	5.83×10^{-2}	20.37
	30	6.52×10^{-2}	20.55
	40	10.76×10^{-2}	20.86
150-210	20	7.21×10^{-2}	20.37
	30	6.68×10^{-2}	20.55
	40	10.76×10^{-2}	20.86

Fig. 22. Lagergren plots at different initial concentrations
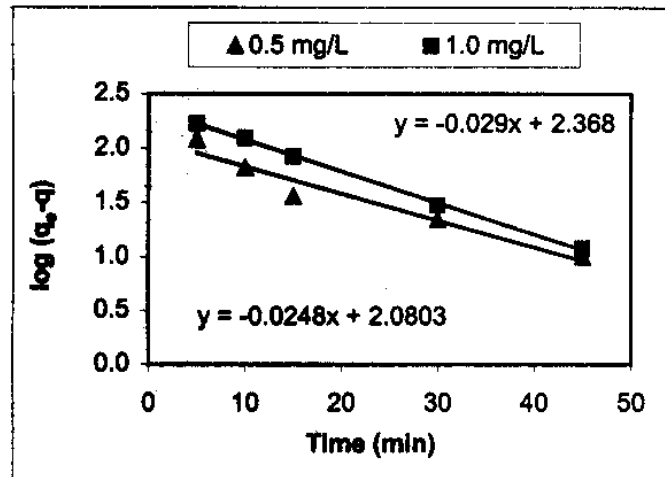Sediment fraction = 0-75 μm.

Fig. 23. Lagergren plots at different initial concentrations
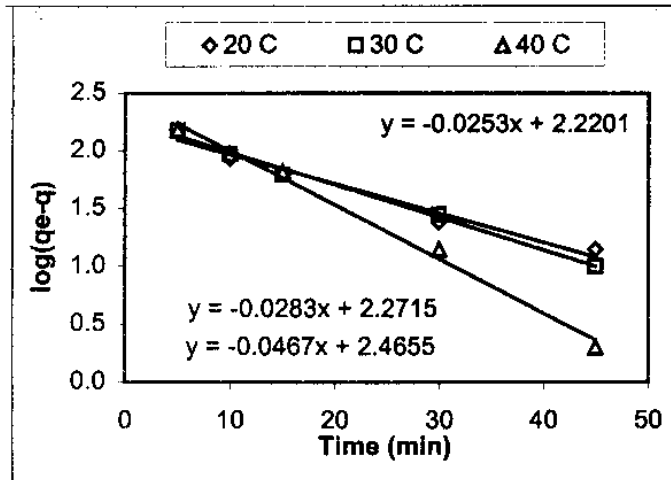Sediment fraction = 150-210 μm.

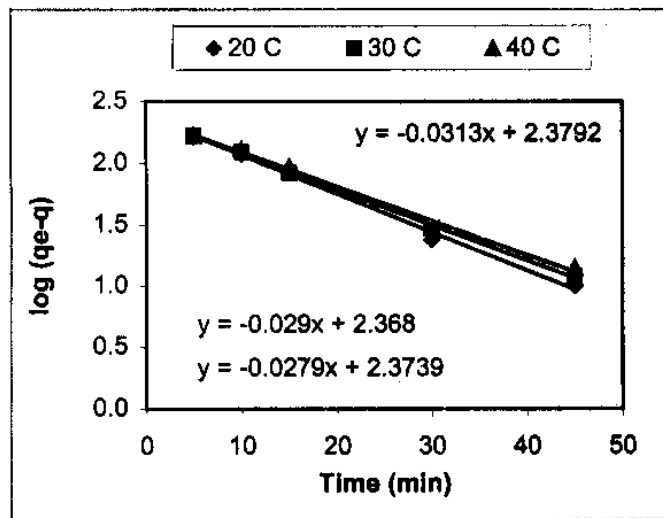Fig. 24. Lagergren plots at different temperatures.
Sediment fraction = 0-75 μm.

Fig. 25. Lagergren plots at different temperatures.
Sediment fraction = 150-210 μm.

(1962):

$$q = k_{id} t^{1/2}$$
... (9)

Where q is the amount adsorbed (µg/g) at time, t (min). Plots of q vs $t^{1/2}$ are shown in Fig. 26&27 and 28&29 for different initial concentrations and temperatures, respectively. All the plots have the same general features, initial curved portion followed by linear portion and a plateau. The initial curved portion is attributed to the bulk diffusion, the linear portion to the intraparticle diffusion and the plateau to the equilibrium. This indicates that transport of zinc ions from the solution through the particle solution interface, into the pores of the particle as well as the adsorption on the available surface of sediment are both responsible for the uptake of zinc ions. The deviation of the curves from the origin also indicates that intraparticle transport is not the only rate limiting step (Kishk and Hassan, 1973). The values of rate constants (k_{id}) were obtained from the slope of the linear portion of the curves for each concentration of metal ions (Table 10) and temperatures (Table 11). The value of intraparticle rate constant (k_{id}) was higher at higher concentration. Increasing temperature slightly improved the k_{id}, but did not have any significant effect.

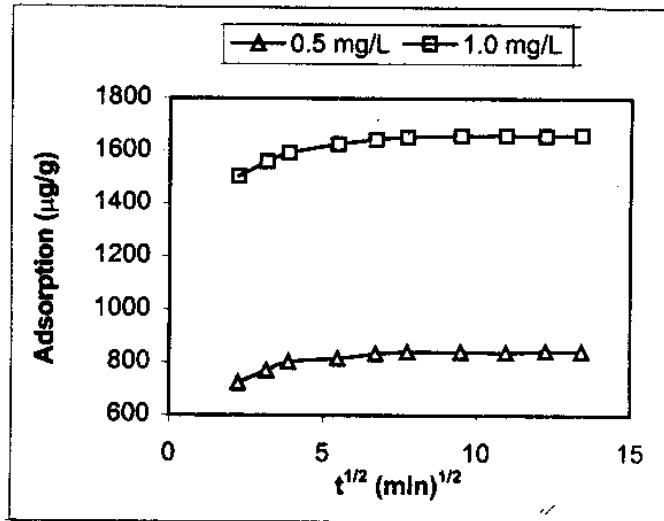Fig. 26. Intraparticle diffusion plots at different initial
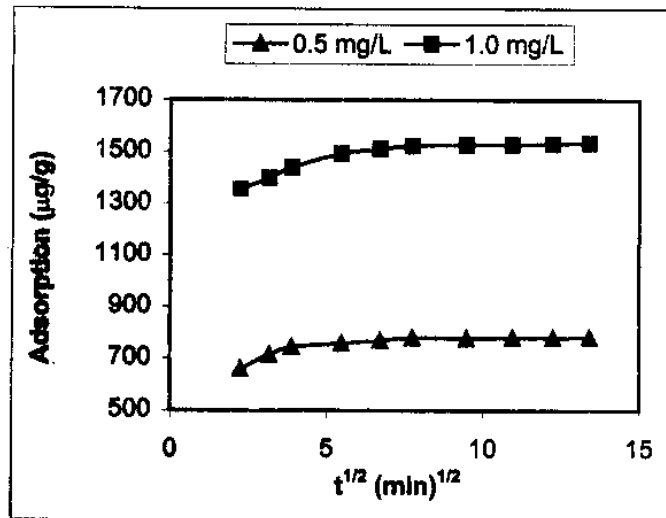concentration. Sediment fraction = 0-75 μm.

Fig. 27. Intraparticle diffusion plots at different initial
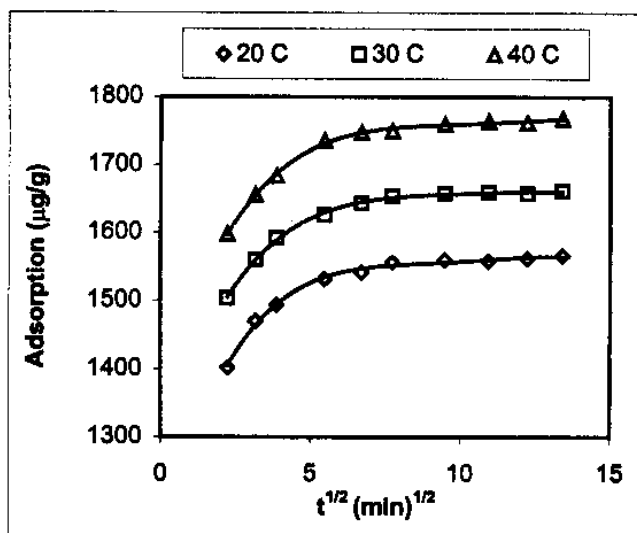concentration. Sediment fraction = 150-210 μm.

Fig. 28. Intraparticle diffusion plots at different
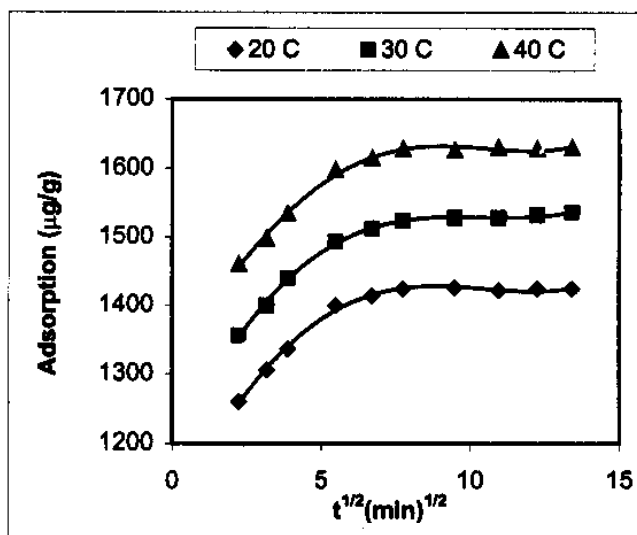temperatures. Sediment fraction = 0-75 μn

Fig. 29. Intraparticle diffusion plots at different
temperatures. Sediment fraction = 150-210 μm.

6.0   CONCLUSION

The present study has shown the potentiality of freshly deposited sediments to adsorb zinc 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 zinc 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 zinc pollution. 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. 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 150-210 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 zinc adsorption. The results of the experimental study obtained from this study are highly useful and may be extended for other rivers with coarser sediments. 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. The equilibrium data describe the Langmuir and Freundlich isotherm models satisfactorilly. The kinetic data suggest that the adsorption of zinc on bed sediments is an endothermic process, which is spontaneous at low temperature. The uptake of zinc is controlled by both bulk as well as intraparticle diffusion mechanisms.

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