ADSORPTION OF METAL IONS ON SEDIMENTS

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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 untill 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 heavy metal ions on bed sediments of river Kali have been taken-up in their natural state of occurrence.

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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. Heavy metals today have a great significance due to their toxicity and adsorption behaviour.

The adsorption characteristics of the bed sediments collected from river Kali near village Malira have been studied for the uptake of lead and zinc ions. The parameters controlling the uptake viz. initial metal ion concentration, the 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. It is observed that the extent of adsorption increases with the increase of pH of the solution but on the other hand, metal ion concentration decreases with increase in pH value.

The adsorption of metal ions on the bed sediments follows three distinct phases viz. i) instantaneous extremly fast uptake, ii) transition phase and iii) extremly slow uptake. Further, the adsorption of metal ions increases with increasing adsorbent doses and decreases with adsorbent particle size.

The adsorption data of the two metal ions by sediments of river Kali has also been analysed with the help of Langmuir and Freundlich models to evaluate the mechanistic parameters associated with the adsorption process. Some parameters viz., monolayer capacity and sorption intensity have been evaluated for the system.

1.0   INTRODUCTION

1.1   Adsorption Processes

The term adsorption refers strictly to the existence of a higher concentration of any partiuclar component at the surface or interface than is present in the bulk. The process can occur at an interface between any two phases, such as, liquid-liquid, gas-liquid, gas-solid, or liquid-solid interfaces. The material being concentrated or adsorbed is the adsorbate, and the adsorbing phase is termed the adsorbent.

Absorption, conversely, is a process in which the molecules or atoms of one phase interpenetrate nearly uniformly among those of another phase to form a solution with the second phase. In actual fact it is practically impossible to separate the effect of adsorption from those of absorption, particularly for systems of gases and solids, and hence the term sorption is more frequently employed. It is a general expression for a process in which a component moves from one phase to be accumulated in another, particularly for cases in which the second phase is solid.

1.2   Types of Adsorption

According to the most plausible present concepts of adsorption, this surface phenomenon may be categorised as:

- Exchange adsorption
- Physical adsorption
- Chemical adsorption

Exchange adsorption is a process in which ions of one substance concentrate at a surface as a result of electrostatic attraction to charged sites at the surface. Adsorption occuring

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as a result of van der Waals forces is generally termed as 'physical adsorption'. In this case adsorbed molecule is not affixed to a specific site at the surface but is, rather, free to undergo translational movement within the surface. Adsorption of this type is in general referred as 'ideal adsorption'. If the adsorbate undergoes chemical interaction with adsorbent, the phenomenon is referred as 'chemical adsorption'. This may also be named as 'activated adsorption' or 'chemisorption'. Chemical sorption involves electronic interactions between specific sites on the sorbent surface and solute molecules. Chemically adsorbed molecules are considered not to move freely on the surface, or within the interface.

Physical adsorption is usually predominent at low temperature, and is characterized by relatively low energy of adsorption, that is, the adsorbate is not held as strongly to the adsorbent as for chemical adsorption. Chemical interaction between the adsorbent and the adsorbate is favoured by higher temperature, because chemical reactions proceed more rapidly at elevated temperature than at lower temperature.

Most adsorption phenomena are combination of the three forms of adsorption; that is, the several forces which influence the different types of adsorption often interact to cause concentration of a particular solute at an interface. Thus it is generally not easy to distinguish between physical and chemical adsorption.

1.3 Adsorption Equilibria

Positive adsorption in a solid-liquid system results in the removal of solutes from solutions and their concentration at the surface of the solid, to such time as the concentration of the solute remaining in solution is in a dynamic equilibrium with that at the surface. Equal amounts of solute eventually are being

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adsorbed and desorbed simultaneously. Consequently, the rates of adsorption and desorption will attain an equilibrium state, called adsorption equilibrium . At equilibrium, no change can be observed in the concentration of the solute on the solid surface or in the bulk solution. The position of euilibrium is characteristic of the entire system, the solute, adsorbent, solvent, temperature, pH, and so on. The presentation of the amount of solute adsorbed per unit weight of solid adsorbent as a function of equilibrium concentration in bulk solution, at constant temperature, is termed the adsorption isotherm'. The adsorption isotherm is a functional expression for the variation of adsorption with concentration of adsorbate in bulk solution at constant temperature. In general, the amount of adsorbed material per unit weight of adsorbent increases with increasing concentration, but not in direct proportion.

The shape of adsorption isotherm gives qualitative information about the adsorption process and the extent of the surface coverage by the adsorbate.

1.4   Metals Under Consideration

The definition of heavy metal is perhaps one of the most ill defined nomenclature in the entire chemical literature. One most frequently used definition include all metals which have atomic weight greater than sodium or density higher than 4 gm/cm^3. This definition covers a number of metals, but in the present investigations only two heavy metals of environmental significance viz lead and zinc have been considered.

Literature[*] on heavy metals, their toxicity and environmental impact is quite voluminous. Sittig (1976) has elaborated eighteen metals in his review on toxic metals relating to pollution control. Train (1979) in his quality criteria for water has also reviewed a number of metals of environmental

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importance. The quality criteria for drinking water and also for irrigation water have been decided with certainty (WHO, 1984; Shainburg, 1978). Significance of metals studied are:

Lead : Lead is a non-essential toxic heavy metal. It enters the human body primarily via inhalation and through the ingestion of contaminated food and water. It is retained more efficiently in the lungs than the gastro-intestinal tract. Once absorbed into the blood stream it is transported to all parts of the body primarily by the red blood cells although its incorporation into tissues apparently occurs through the blood plasma. Lead begins to appear in liver and kidneys within few hours after absorption, but ultimately about 90 % of the inorganic lead in the body is deposited in the bones where it replaces calcium. Once incorporated in the bone-structure, lead is released back to the blood stream at a steady but very slow rate. In contrast to inorganic lead, organic lead (e.g. lead alkyls) does not accumulate into bones but tends to concentrate in lipid tissues, including those of central nervous system. The highest concentration of organic lead is often found in the brain and liver (Waldron and Stofen, 1974). Lead poisoning is associated with the problems of anaemia, damage to the central nervous system and kidney demage.

The WHO guidelines for lead in drinking water is 0.05 mg/L. The recommended maximum concentration of lead in irrigation water for continuous use is 5.0 mg/L on all soils and for use upto 20 years on fine textured soil at pH 6.0 to 8.5 is 10 mg/L (Shainberg and Oster, 1978).

Zinc : Zinc is one of the most abundant essential element required by the human body. Zinc is essential for the normal activity of DNA polymerase and for protein synthesis, and thus plays vital role in the healthy development of many life forms. Excessive amount of zinc, however, may be toxic,

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especially to the aquatic biota (Nriagu, 1980). Three types of toxic reactions of zinc to human beings have been reported by Prasad (1976)

Moderately increased concentration in water resulting from galvanised pipes do not induce any clinical manifestations. The results of laboratory tests on animals indicate, however, that the metabolism of humans may be effected, especially of children and patients already suffering from irregular metabolism (Forstner and Wittman, 1983).

The guideline value for zinc in drinking water is 5.0 mg/L based on taste considerations (WHO, 1984). The tolerance for zinc in irrigation water is 5.0 mg/L on a continuous basis and 10.0 mg/L on a short term basis.

1.5   Scope of the Study

Heavy metals added to a river system by natural or man-made 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 untill there is remobilizaton 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.

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2.0 SORPTIVE PROPERTIES OF SEDIMENTS

2.1 Importance of Sediment Sorption

The heavy metals added to a river system by natural or man made 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 untill there is remobilization from the sediment due to changing conditions in the system resulting from:

- elevated salt concentration, whereby the alkali and alkaline earth cations can compete with the metal ion sorbed on to the solid particles;

- change of redox conditions usually due to advanced eutrophication whereupon ferric and manganese hydroxides are partially or completely released;

- lowering of pH which leads to dissolution of carbonates and hydroxides as well as the increased desorption of metal cations due to competition with hydrogen ions; and

- increased use of synthetic and natural complexing agents which can form soluble metal complexes, some times of high stability, with heavy metals that are otherwise adsorbed to solid particles.

Thus, in the natural conditions of river water suspended load and sediments have the important functions of buffering higher metal concentrations of water particularly by adsorption or precipitation (Forstner and Muller, 1973).

2.2   Nature of Sediments

The nature of sediments is briefly described .(UNESCO, 1983) as consisting of inorganic and organic compounds both of which come from sources outside or within the river. The organic matter consists of microorganisms (phyto-planktons, zooplanktons, benthos and bacteria), the remains of micro-phytes and large size organisms together with detritus derived from the decaying materials. The inorganic matter consists of erosion products from the rocks in the watershed together with compounds such as FeOOH or Fe(OH)$_3$, SiO$_2$, CaCO$_3$ which may be brought into the water or form within it. In broad sense, natural sediments may be described as a mixture of different compositional types:

- mineral and small pieces of rocks derived from the fragmentation of source material;
- clay minerals;
- precipitates and coatings; and
- organic materials.

A typical bulk composition is cited as: mineral and rock fragments > clay > organism> precipitates/coatings.

Man-made debries may also contribute to the formation of sediments of similar characteristics. In general the sediment composition is largely controlled by the composition of source rock and additionaly influenced by climatic regime (weathering and hydraulic conditions), land form and land use and time in transit.

2.3   Sorption Active Ingredients of Sediments

Despite the wide variability of composition of the sediments depending upon the prevailing conditions, they are characterized by some inherrent structural and surface properties

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favouring heavy metal sorption. A number of ingredients present in sediments are identified as sorption active compounds and are studied and reported by different authors.

Fors⁺ner (1977) compiled the most association of heavy metals in particulate form in sediments, where he described the active constituents with the nature of association:

Minerals of natural
rock debris
e.g., heavy minerals   Metal bonding predominantly
Heavy metal   in inert positions
-- hydroxides   Precipitation as a result of
   carbonates   exceeding the solubility product
   sulfides   in the area of the water course.
Hydroxides and oxides   Physico-sorption
of Fe/Mn   pH-dependent   Chemical sorption (exchange of H^+
                                                    in fixed positions)
                                                    Coprecipitation as a result of
                                                    exceeding the solubility product
Bitumen, lipids   pH-dependent   Physico-sorption
Humic substances   Chemical sorption (exchange of H^+
Residual organics   in COOH-, OH-groups)
                                                   Complexes
Calcium carbonate   pH-dependent   Physico-sorption
                                                   Pseudomorphosis (dependent on
                                                   supply and time)
                                                   Coprecipitation (incorporation by exceeding
                                                   the solubility product)

Jenne (1976) in the review, 'Trace element sorption by sediments and soils - sites and processes' discussed the role played by clay size minerals in trace element sorption by soils and sediments during trace element transport by fluvial system.

A number of sediment forming materials with a large surface area - particularly clay minerals, freshly precipitated iron hydroxide, amorphous silicic acids, as well as organic substances - are capable of sorbing cations from solutions and releasing equivalent amounts of other cations into the solution, i.e., by cation exchange. The mechanism which results in cation exchange is based on the sorptive properties of negatively charged anionic sites - SiOH-, $AlOH_2$-, and AlOH-group in clay minerals, FeOH-group in iron hydroxide, carboxyl and phenolic OH-group in organic substances - towards positively charged cations. The balancing of negative charges of the lattice is a selective process which accounts for preferential adsorption of specific cations and the release of equivalent charges associated with other species. Furthermore, all fine-grained materials with a large surface area are capable of accumulating heavy metal ions at the solid-liquid interface as a result of intermolecular forces.

With clay minerals, which are particularly common in pelitic sediments and suspended material, the exchange capacity increases markedly in the order kaolinite < chlorite < illite < montmorillonite. This increase corresponds accordingly with the reduction of particle size and the related increase of surface area. A low percentage of organic material can thus cause a marked increase in the exchange capacity of the total sediment.

The pH value play an important role in the adsorption processes of heavy metals onto clay minerals. The H^+ ions compete with heavy metal catioons for exchange sites in the system, thereby partially releasing the latter. The heavy metal cations are completely released under circumsstances of extreme acidic

conditions. From infrared absorption spectra, Hildebrand and Blum (1974) determined that at pH > 7, the lead ion adsorption process on clay minerals follow the same pattern as a chemical sorption.

The zeropoint charge (ZPC is the pH at which the solid surface charge from all sources is zero) of the clay minerals, kaolinite (4.6) and montmorillonite (2.5), indicate that at pH = 8 the particles have negative charge and as such will exhibit the electrostatic affinity for cations such as heavy metal ions (Jenne, 1976).

Soong (1974) has performed a series of experiments on the competitive sorption of heavy metals (lead, copper and zinc) onto clay mineral and reported that lead has a special affinity for the clay mineral structures due to its ionic radius, which is very similar to that of potassium (a metal primarily incorporated onto clay minerals). At the same time, lead is also capable of replacing potassium in the montmorillonite lattice (Marshall, 1964). Since the ionization potential of copper and zinc are quite similar (Cu: 2.71; Zn: 2.70; Pb: 1.66 eV), the different adsorption behaviour of these two elements were attributed to polarization effects. Cu^{2+} does in fact posses an unpaired electron in the 3d-orbitals and is therefore more strongly polarized than Zn^{2+} (with no unpaired 3d electrons) and exhibits a greater affinity to anionic sites.

Investigations carried out by Bittell and Miller (1974), and Lagerwerff and Browner (1972 and 1973) on lead, cadmium and calcium to establish selectivity coefficients for sorption on montmorillonite, illite and kaolinite indicate that Pb^{2+} and Cd^{2+} may compete with common divalent ions in the soil e.g., with Ca^{2+}, for clay adsorption sites. Whereas Cd^{2+} competes more or less on an even basis with Ca^{2+} for such sites, the adsorption of Pb^{2+} is favored by a factor of 2 to 3 over Ca^{2+}.

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Very little is known about the specific interaction of the wide range of ionic complexes that occur in natural aquatic systems. In river systems, for example, different hydroxo-, carbonato- and aquo-inorganic metal complexes occur. The adsorption of complexed ions by anionic sites is often more stable than the affinity for less hydrated cations of soil.

Jenne (1976) reported 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 afinities involve mechanisms of adsorption and coprecipitation.

The adsorption of heavy metal ions on oxides, another potential adsorberin sediments, are studied extensively. Benjamin and Lackie (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 ion on hydrous ferric and manganese oxides which may in turn be associated with clays and effect of calcium ions on the adsorption. Loganathan (1973) reported the sorption of heavy metal ions by hydrous manganous oxide.

The hydrous oxides of aluminum, iron, and manganese, particularly the redox-sensitive Fe- and Mn-hydroxides and oxides under oxidizing conditions, constitute significant sinks of heavy metals in aquatic systems. These hydroxides and oxides readily sorb or coprecipitate cations and anions; even a low percentage of $Fe(OH)_3$ and MnO_2 has a controlling influence on the heavy metal distribution in an aquatic system. Practical application of the sorption ability of hydrous metal oxides has been made in water and waste water treatment, particularly by the use of iron and aluminium salts for the removal of phosphorus compounds,

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organic contaminants and trace metals. Under reducing conditions the sorbed heavy metals are readily mobilized; accumulations of hydrous Fe/Mn oxides can therefore act as a major source of dissloved metals in natural waters. The latter mechanism is particularly effective in the presence of higher concentrations of dissolved organic material. Observations from heavily polluted waters indicate that both actions frequently coincide in these systems (Jenne, 1976).

The mechanism of heavy metal sorption on hydrous oxides has been demonstrated by Hildebrand and Blum (1974) from the example of the Pb^{2+} interactions with Fe hydroxides. Pb is incorporated in the Stern layer of the hydroxide structure and hydrogen ions are exchanged, so that lead exhibits a strong affinity for the hydroxyl group of the FeO(OH) crystal. Gadde and Laitinen (1973) observed in their investigation that the sorption of Pb^{2+} at pH values between 5 and 7 steadily decreases. In this pH range FeOOH is positively charged: lead therefore appears specifically sorbed. Similar results were obtained by Lockweed and Chen (1973, 1974) for the sorption of Hg^{2+} by hydrous manganese oxides and ferric hydroxide. Jeffries and stumm (1976) studied the sorption characteristics of a defined Mn mineral species and found that data did not agree with a simple 1:1 (Cu:H) exchange model of adsorption; this discrepancy may be due to some degree of 1:2 surface exchange and/or specific adsorption. Subramanian (1976) found that a combination of exchange reactions and solid solution can satisfactorily explain the observed chemistry of natural ferro-manganese material. Studies of Hohl and Stumm (1976), Schindler et al. (1976) and James and McNaughton (1972 and 1977) have formulated the adsorption of hydrolysable metals as a surface complex with electrostatic interactions.

Investigations on the trace metal content in manganese coatings of stream deposits were first performed by Smith (1960),

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and Canney and Nowlan (1964). Jenne and Wahlberg (1965) studied the enrichment of trace metals in iron oxide compounds of stream sediments. Cutshall (1976) found iron oxides to be the most important single sediment component in the retention of chromium-51 in sediments from the Columbia River.

Chemical leaching of trace elements in carbonate-free sediments from the Amazon and Yukon Rivers by Gibbs (1973) indicate 4-50 % of Cu, Cr, Co, and Ni to be present in the form of hydrous Fe/Mn oxide coatings. Perhac (1972 and 1974) determined 5-50 % of Co, Cu and Zn in the dithionite-reducible fraction (or hydrous iron and manganese oxide fraction) in fluviatile sediments containing principally carbonate and primary silicates.

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

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minerals by natural waters containing organic ligands. With respect to the direct association of metal-organic species to sedimentary material, the associatioon with clay minerals is of particular significance. Curtis (1966) has proposed a simplified scheme to explain why certain metals (Cr, Cu, Mn, Mo, Ni, U, V) shows a positive associatioon with organic carbon in a sediment, while other elements exhibit no significant correlation, or may even be negatively correlated with organic carbon.

The extent of heavy metal sorption on carbonates has been a source of conflicting opinion for many years. Considering the relatively low contents of most of the heavy metals in carbonates, Krauskopf (1956) suggested that sorption does not play a very significant role. Currently, more has become known about the processes of carbonate sorption; it appears that the surface energy of the substances is generally sufficient to effect adsorption, at least in the order of magnitude observed for clay minerals such as kaolinite (Suess, 1973). Data obtained by Deurer et al. (1978) from lake sediments imply that coprecipitation with carbonate minerals may be an important mechanism for a number of metals e.g., zinc and cadmium.

It has been stressed by Jenne (1976) in his review on "trace element sorption by sedtment and soils - sites and processes", the armoring of sediment particles is of great importance to their sorption characteristics as it slows down rates of reactioon and prevents portions of the various sinks from equilibrating with their associated waters. While the clay minerals themselves are relatively unimportant as trace element sinks, their role as a mechanical substrate for the precipitation and flocculation of organics and of hydrous iron oxides has been pointed out in many studies. In some cases, carbonate coatings on clays and hydrous iron oxides exert a characteristic influence on the sorption properties that sediment particles exercise on trace elements.

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3.0   SORPTION MODELS

In practice, sorpiton studies are conducted by equilibrating known quantities of a solid with solutions of the compound of interest. A plot of the variation of solid phase concentration - the amount of the compound sorbed per unit mass of solid - vs the solution phase concentration under quilibrium conditions, is termed an isotherm. Several models have been developed to describe this relationship. A particular, model may describe experimental data accurately under one set of conditions, but fail entirely under another set of conditions. No single model has been found to be generally applicable, a fact that is easily understood in light of the derivative assumptions made for each model.

3.1   Langmuir Model

Langmuir model was developed for adsorption of gases onto solids and makes the following assumptions (Langmuir, 1918):

i) The energy of adsorption is constant and independent of surface coverage;

ii) Adsorption occurs on localised sites and there is no interaction between adsorbate molecules; and

iii) The maximum adsorption possible is that of a complete monolayer.

The relationship can be derived by considering equilibrium between gas molecules striking the surface and those which evaporate off after the lapse of a certain time.

The relationship can be derived by considering the kinetics of condensation and evaporation of gas molecules at a solid surface. If θ is the fraction of complete monolayer coverage that exists at a given time, then the rate of

evaporation from the surface is proportional to θ. Similarly, the rate of condensation of gas phase molecules onto the surface is proportional to the number of sites remaining, or $1 - \theta$, and to the rate at which molecules contact the surface. The latter term is proportional to P, the absolute pressure of the gas. Equating these two rates for equilibrium conditions yields:

$$k_d \ \theta = k_a \ P(1 - \theta) \tag{1}$$

where k_d is the rate constant for evaporation and K_a is the constant for condensation. The fraction of surface covered, θ, is then

$$\theta = \frac{k_a \ P}{k_d + k_a \ P} = \frac{b \ P}{1 + bP} \tag{2}$$

The adsorption coefficient, $b = k_a/k_d$, is related to the enthalpy of adsorption (ΔH) by

$$b = b_o \ \exp(-\Delta H/RT) \tag{3}$$

where b_o is a constant related to the entropy (Weber, 1972). Equation (2) can also be derived using methods of statistical thermodynamics (Hill, 1960).

In solid-liquid systems equation (2) is usually written:

$$q_e = \frac{Q^o \ b \ C_e}{1 + b \ C_e} \tag{4}$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent; Q^o is the solid-phase concentration corresponding to all available sites being filled, or the maximum adsorption, and C_e is the liquid-phase concentration at equlibrium. Equation (4)

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can be written in a variety of linear forms:

$$\frac{C_e}{q_e} = \frac{1}{Q^o\,b} + \frac{C_e}{Q^o} \qquad (5)$$

$$\frac{1}{q_e} = \frac{1}{Q^o} + \frac{1}{b\,Q^o\,C_e} \qquad (6)$$

$$q_e = Q^o - \frac{q_e}{b\,C_e} \qquad (7)$$

While all are equivalent, one particular form may be more desirable than the others depending on the range and spread of the data to be described (Weber, 1972; Reinbold et al., 1979)

3.2   BET MODEL

Brunauer et al. (1938) extended the Langmuir model to include the adsorption of multiple molecular layers. They assumed that any given layer need not be complete before subsequent layers can form. The first molecules to adhere to the surface do so with an energy comparable to the heat of adsorption for monolayer attachment, while subsequent layers are treated essentially as condensation reactions. If it is assumed that all layers beyond the first have equal energies of adsorption, the BET equation takes the simplified form:

$$q_e = \frac{B\,C_e\,Q^o}{(C_s - C_e)\,[1 + (B - 1)(C_e/C_s)]} \qquad (8)$$

where C_s is the saturation concentration of the solute, C_e is the liquid-phase concentration at equlibrium, Q^o is the solid-phase concentration corrsponding to a complete monolayer, and q_e is the solid-phase equilibrium concentration. B is a constant expressive of the energy of adsorption:

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$$B = \frac{d_2 \, c_1}{d_1 \, c_2} \, \exp \, (E_1 - E_2)/RT \qquad (9)$$

where E_1 is the average heat of adsorption of the first layer, E_2 is the heat of condensation, and d_2c_1/d_1c_2 is the ratio of evaporation-condensation coefficients for the adsorbed layers which is often nearly equal to unity (Bailey and White, 1970). Equation (8) can be linearized to facilitate its application:

$$\frac{C_e}{(C_s - C_e)q_e} = \frac{1}{B \, Q^o} + \frac{B - 1}{B \, Q^o} \frac{C_e}{C_s} \qquad (10)$$

3.3   Freundlich Model

Despite the sound theoretical basis of the Langmuir and BET models, these isotherms fail to describe sorption data adequately. Freundlich (1926) found that such data can be better described by the relationship:

$$q_e = K_F \, C_e^{1/n} \qquad (11)$$

where K_F and n are characteristic constants. Equation (11) linearizes in logarithmic form:

$$\ln q_e = \ln K_F + 1/n \ln C_e \qquad (12)$$

Freundlich attempted to attach rigorous physical significance to the constants K_F and n, but was, for the most part, unsuccessful. The value of K_F can, however, be taken as a relative indicator of sorption capacity, while 1/n is indicative of the intensity of the reaction (Weber, 1972).

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4.0 EXPERIMENTAL METHODOLOGY

4.1 Sampling and Storage

For the adsorption studies of heavy metal ions (lead and zinc) on the bed sediments of river Kali, freshly deposited sediments from shallow water nearer to bank were collected from the upstream section of the river (near village Malira) 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 seiving method using ASTM standard sieves to obtain various fractions. Five fractions viz. 75-150, 150-210, 210-250, 250-325 and 325-425 micron were separated for adsorption studies. Seived sediments were oven dried overnight at 105° C and after cooling in dessicator, stored in air-tight containers for adsorption studies.

4.2 Materials and Reagents

All chemicals used in the study were of AnalaR grade. Aqueous solutions of lead and zinc were prepared from lead nitrate and zinc sulphate respectively. Double distilled water prepared in All Quartz Double Distiller was used through out the study. All glasswares and other containers were thoroughly cleaned by soaking in detergent followed by soaking in 10 % nitric acid for 48 hrs. and finally rinsed with deionized water several times prior to use. Stock solutions of 1000 mg/L were prepared as follows :

Zn stock solution : Zn stock solution was prepared by dissolving 1.0 g zinc metal in a minimum volume of (1+1) HCl and diluting to 1 liter with 1% (v/v) HCl.

Pb stock solution : Pb stock solution was prepared by dissolving 1.598 g lead nitrate in 1% (v/v) HNO_3 and diluting to 1 liter with 1% (v/v) HNO_3.

4.3   Adsorption Experiments

Adsorption experiments for the sediments were performed in Erlenmeyer flasks with ground-glass stoppers. 50 mL of the chosen desired concentration of the metal ion solutions 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 Whatman No. 1 filter paper and analysed for residual concentration of respective metal ions. All the adsorption experiments were conducted at 25° C.

4.4   Metal Ion Analysis

Metal ion (Zn and Pb) concentrations were determined by flame atomic absorption spectrometry using Perkin-Elmer Atomic Absorption Spectrometer (Model 3110) using air-acetylene flame. The operational conditions were adjusted to yield optimal determination Quantification of the metals was based upon calibration curves of standard solutions of respective metals. The instrumental parameters for the analysis of metal ions under consideration are as follows:

Table 1. Instrumental Parameters for Measurement of Lead
and Zinc by Atomic Absorption Spectrometer

Metal ion	Light source	Lamp current (mA)	Wave length (nm)	Slit width (nm)	FLame gases	Sens. check (mg/L)	Linear range (ug/mL)
Pb	Hollow Cathode	12	283.3	0.7	A-Ac	20.0	20.0
Zn	Hollow Cathode	20	213.9	0.7	A-Ac	1.0	1.0

5.0   RESULTS AND DISCUSSION

5.1   Effect of Operating Vaiables

5.1.1   Initial metal ion concentration (C_0)

To evaluate the effect of initial metal ion concentration (C_0) on adsorption behaviour of lead and zinc on bed sediments of river Kali, studies were conducted with initial metal ion concentration of 2, 4, 6, 8, 10, 15, 20 and 25 mg/L. Based on the adsorption data (Table 2), plots were prepared between the metal ion adsorbed (C_t) versus equilibrium metal ion concentration (Fig. 1 & 2). These plots indicate that the total metal ion adsorbed increases sharply in the beginning and then slowly towards the end of the run. A perusal of the Fig. 1 reveals that for the same equilibration time, the metal ion adsorbed is higher for greater values of initial metal ion concentration (C_0). 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).

5.1.2   Effect of pH

The adsorption of two metal ions viz. Pb^{2+} and Zn^{2+} on the bed sediments of river Kali was studied over the pH range 2-6 and the same has been presented in Table 3. Graphical representation of the adsorption data for the two metal ions over the studied pH range have been shown in Fig. 3 & 4.

A general increase in adsorption with increasing pH of solution has been observed, for both the metal ions upto pH value 6.0, beyond this pH the determination could not be performed due to low solubility of both the metal ions. A similar behaviour has been reported by many authors (Farrah and Pickering, 1976, 1979; Netzer and Wilkinson, 1976; Benzamin and Leckie, 1980) for the uptake of

Table 2. Adsorption data for lead and zinc on bed sediments of river Kali; Adsorbent size = 210-250 μm; pH = 5.0; Adsorbent dose = 5 g/L; Temperature = 25^0C.

Metal Ion	Initial concn. C_0 (mg/L)	Concn. remaining at equilibrium C_e (mg/L)	Metal ion adsorbed		
			mg/L	(μg/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

Table 3. Adsorption of lead and zinc on bed sediments of river
Kali at different pH values; Adsorbent size = 210-250
μm; Adsorbent dose = 5 g/L; Temperature = 25^{0}C.

Metal Ion	Initial concn. C_0 (mg/L)	pH	Concn. after pH adjustment (mg/L)	Metal ion adsorbed	
				μg/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
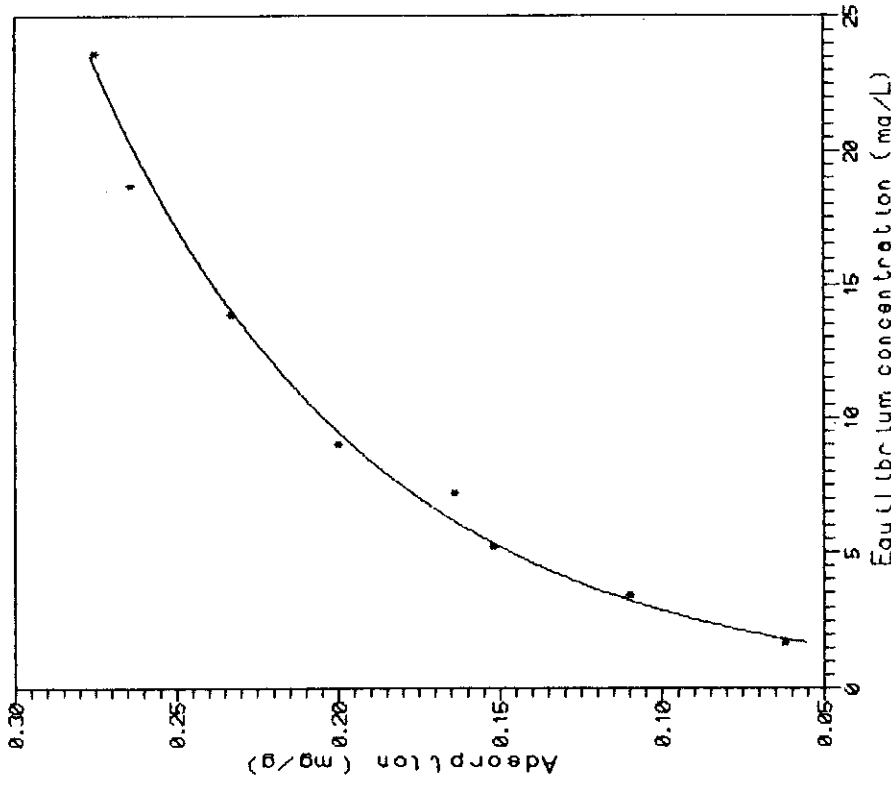
Fig. 1(b) Adsorption of zinc on bed sediments of river Kali

Fig. 1(a) Adsorption of lead on bed sediments of river Kali

Fig. 2(b) Percent adsorption of Zinc on bed sediments of river Kali

Fig. 2(a) Percent adsorption of lead on bed sediments of river Kali

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Fig. 3(b) Effect of pH on adsorption of zinc
on bed sediments of river Kali
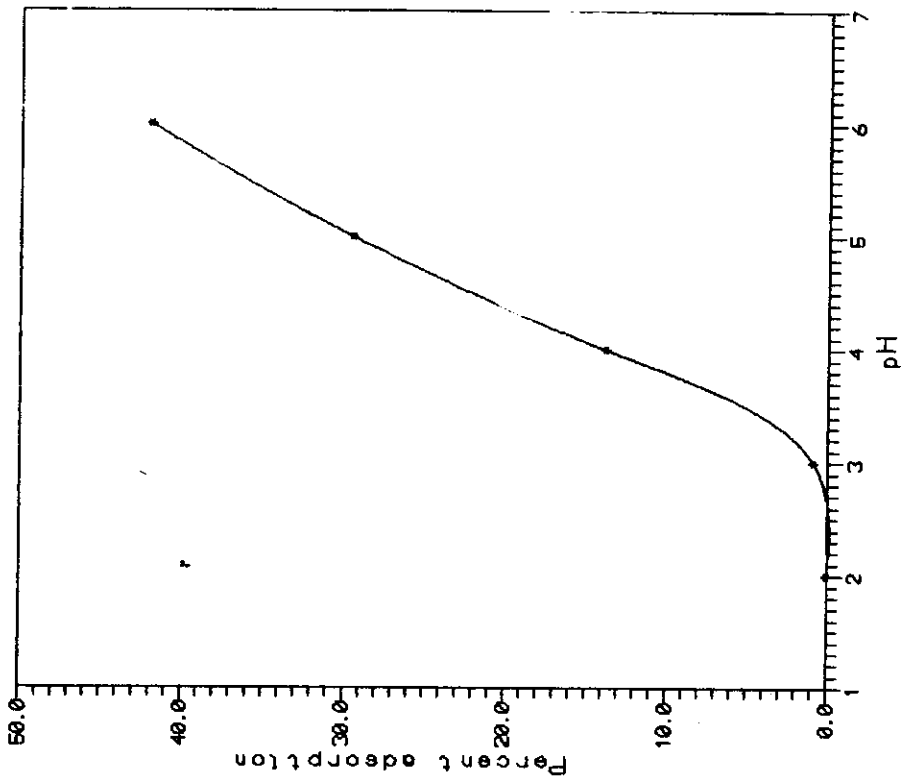
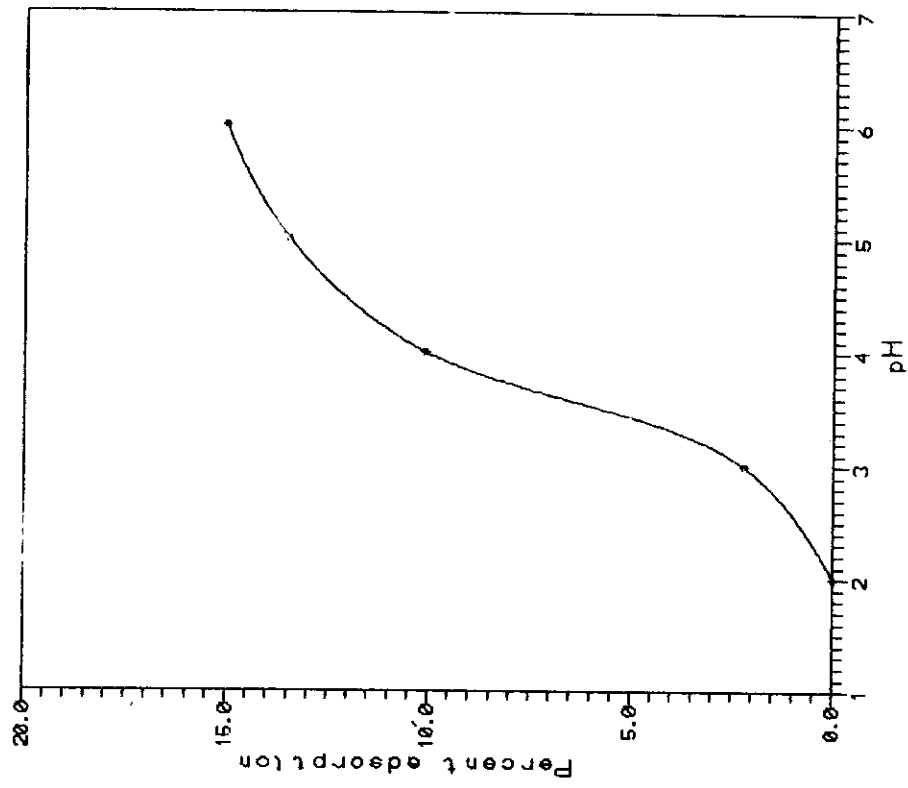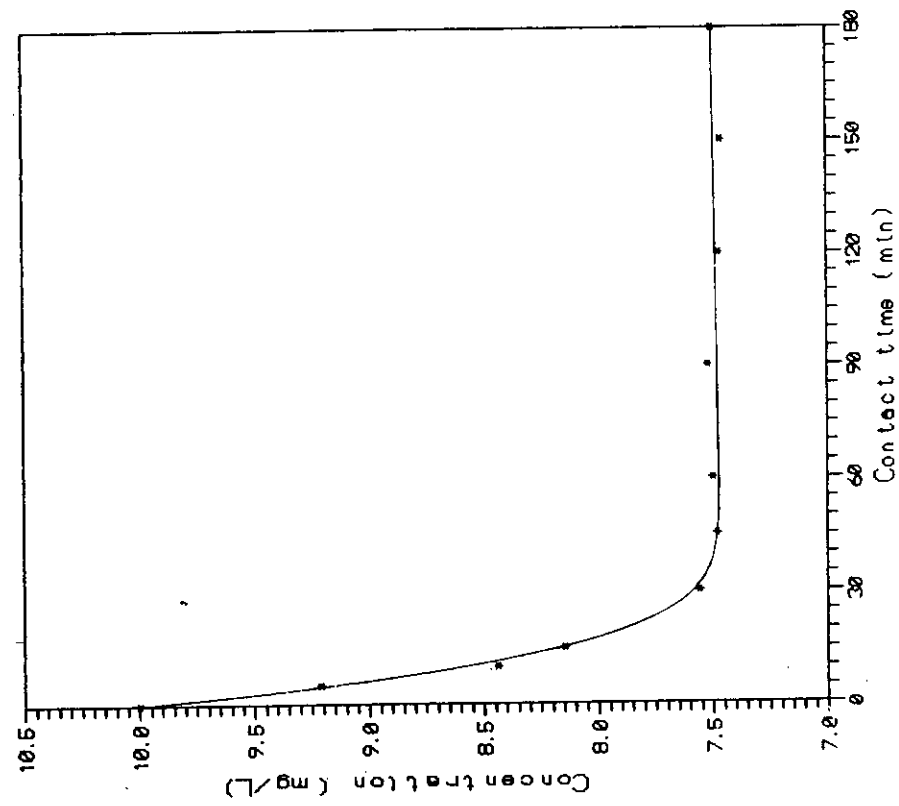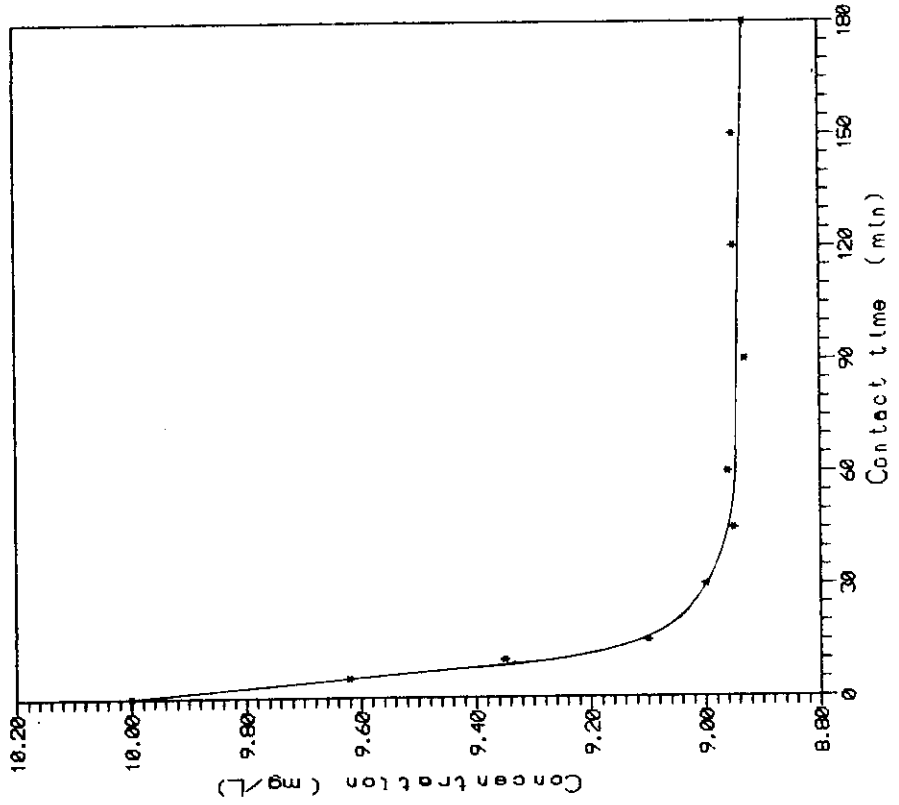Fig. 3(a) Effect of pH on adsorption of lead
on bed sediments of river Kali

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Fig. 4(b) Effect of pH on percent adsorption of zinc on bed sediments of river Kali

Fig. 4(a) Effect of pH on percent adsorption of lead on bed sediments of river Kali

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metal ions on various adsorbents.

From the results it is evident that the pH for maximum uptake of lead ion (530 µg/g) is 6.0 (Fig. 3a). At this pH the concentration of lead ion in solution is quite low (reduced to 6.31 mg/L from 10.0 mg/L due to pH adjustment). Further, it is apprent from Fig. 4(a) that the adsorption of lead rises from 13.8% at pH 4.0 to 42% at pH 6.0 (Table 3) which reveals the sediment's capacity for adsorbing lead ions even in acidic freshwaters.

The maximum removal of zinc is also observed to take place at pH 6.0 with corresponding adsorption value being 206 µg/g (Fig. 3b). 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 (Fig. 4b).

5.1.3   Contact time (t)

The adsorption data for the uptake (C_t) of metal ions versus contact time (t) for a fixed adsorbent dose (W_s = 5 g/L) with initial metal ion concentration (C_0) of 10 mg/L and at a fixed particle size of adsorbent (210 -250 µm), are presented in Table 4 and graphically shown in Fig. 5 - 7. 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. This time presumed to represent the equilibrium time at which an equilibrium metal ion (lead and zinc) concentration (C_e) is presumed to have been attained.

An emperically found functional relationship, common to the most adsorption processes, is that the uptake varies almost proportionalty with $t^{1/2}$ rather than with the contact time, t (Weber and Morris, 1963). Therefore, in Fig. 8 - 10, plots of metal

Table 4. Adsorption of lead and zinc on bed sediments of river
Kali at different durations of contact time; Adsorbent
size = 210-250 μm; 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	μg/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
		1 0	7.47	2.53	506	25.3
		1 50	7.46	2.54	508	25.4
		180	7.50	2.50	500	25.0
Zn	10.0	5	9.62	0.38	76	3.8
		0	9.35	0.65	130	6.5
		5	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. 5(b) Effect of contact time on
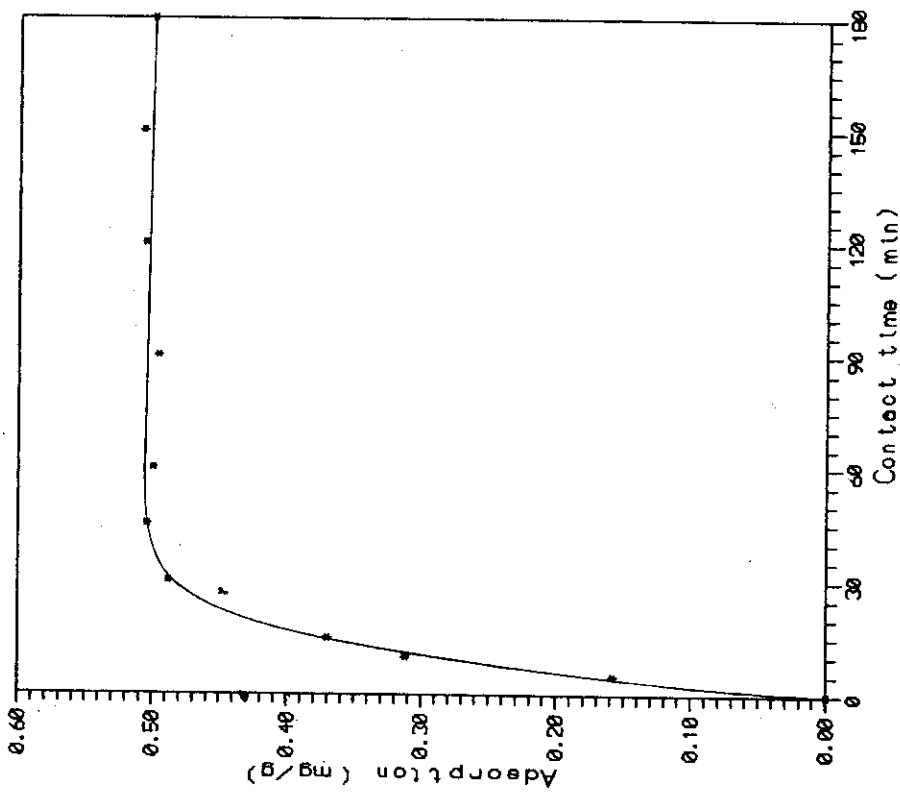adsorption of zinc on bed
sediments of river Kali

Fig. 5(a) Effect of contact time on
adsorption of lead on bed
sediments of river Kali

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Fig. 6(b) Effect of contact time on
adsorption of zinc on bed
sediments of river Kali

Fig. 6(a) Effect of contact time on
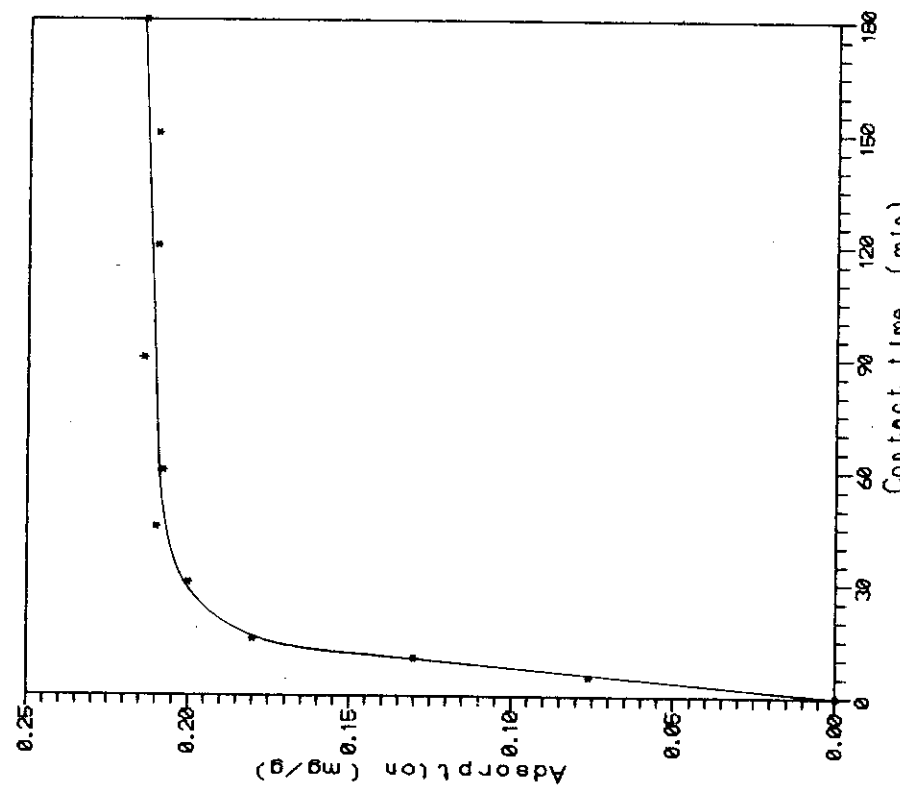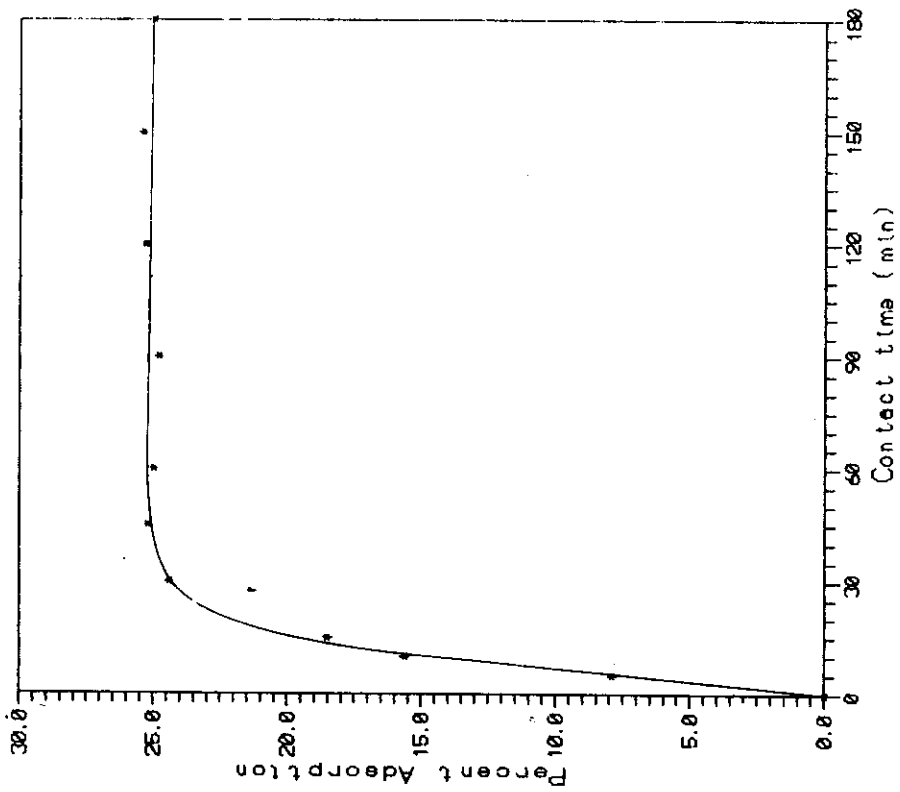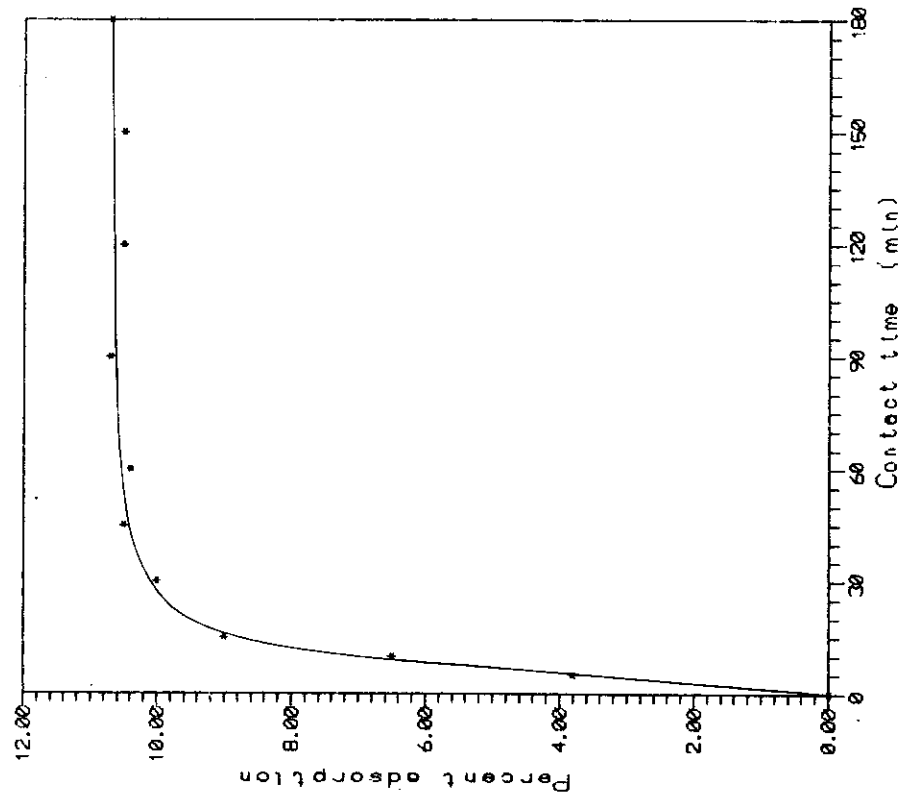adsorption of lead on bed
sediments of river Kali

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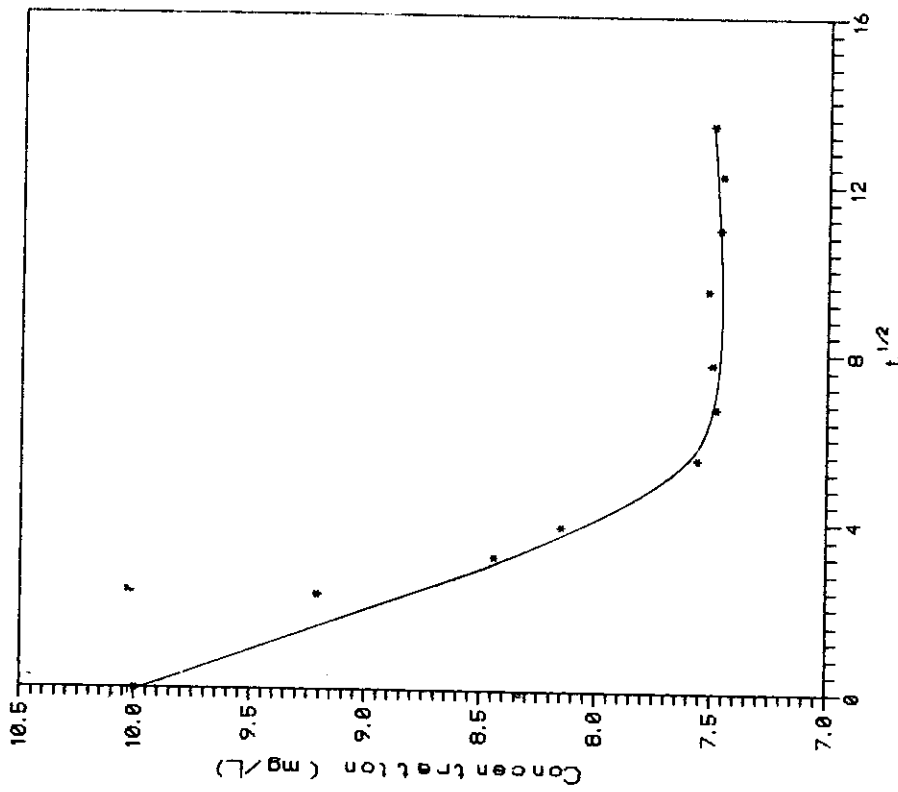Fig. 7(b) Effect of contact time on percent adsorption of zinc on bed sediments of river Kali

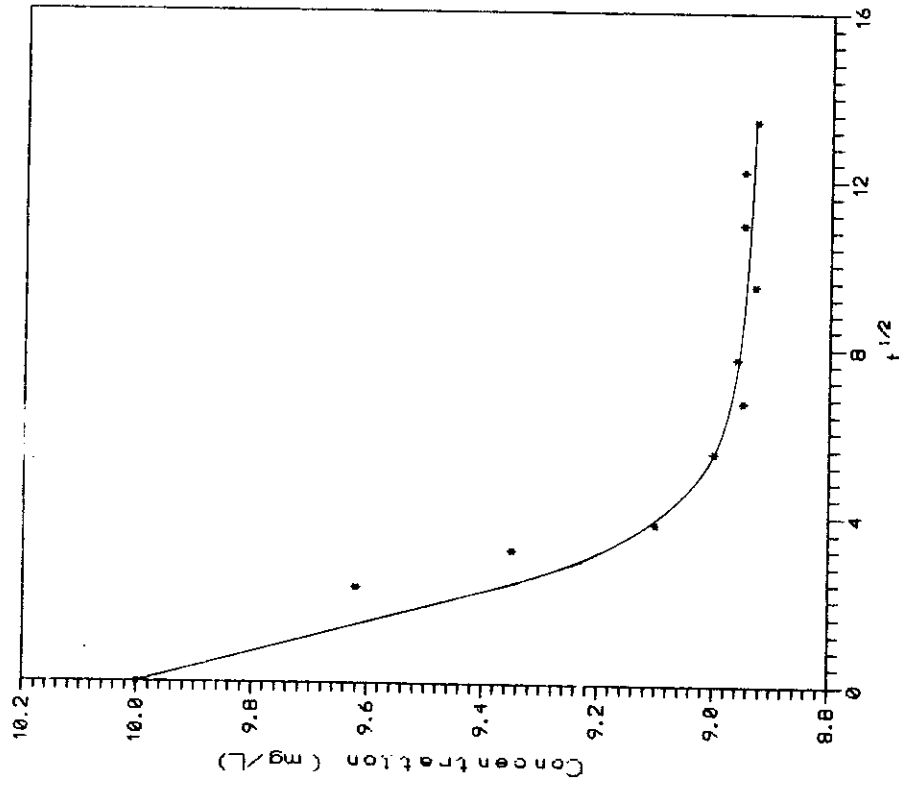Fig. 7(a) Effect of contact time on percent adsorption of lead on bed sediments of river Kali

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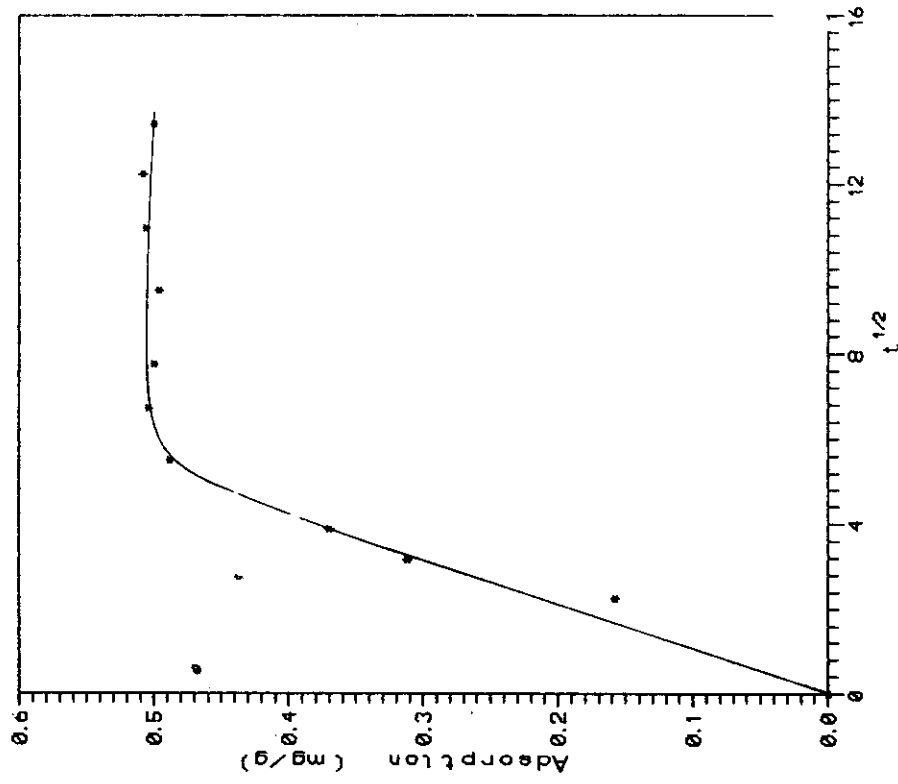Fig. 8(b) Effect of $t^{1/2}$ on adsorption of zinc on bed sediments of river Kali

Fig. 8(a) Effect of $t^{1/2}$ on adsorption of lead on bed sediments of river Kali

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Fig. 9(b) Effect of $t^{1/2}$ on adsorption of zinc on bed sediments of river Kali

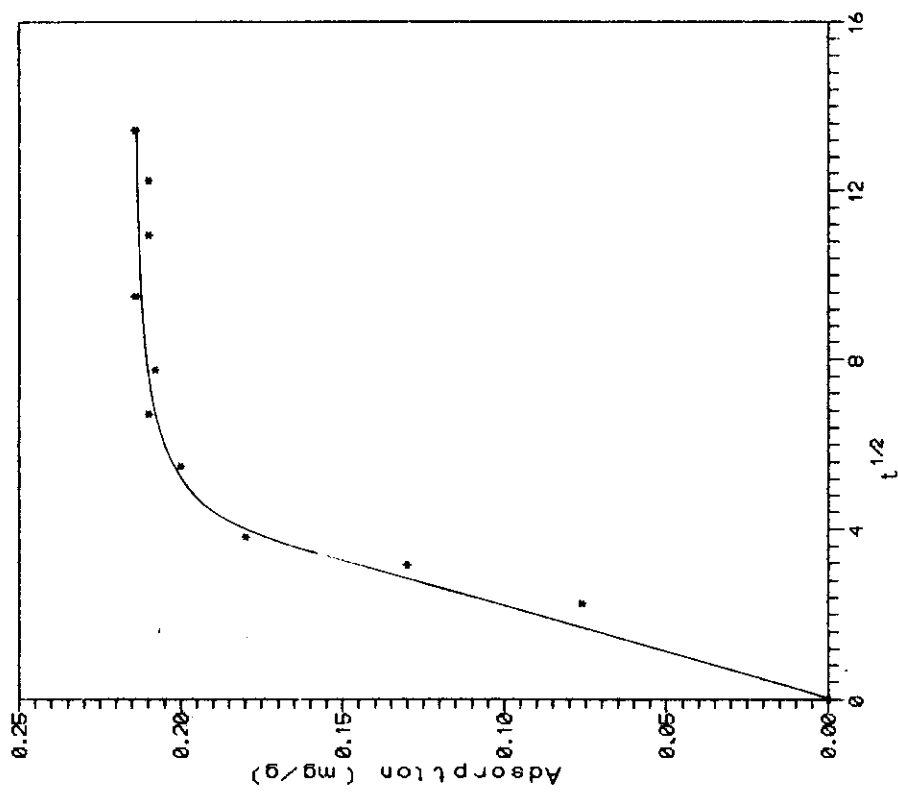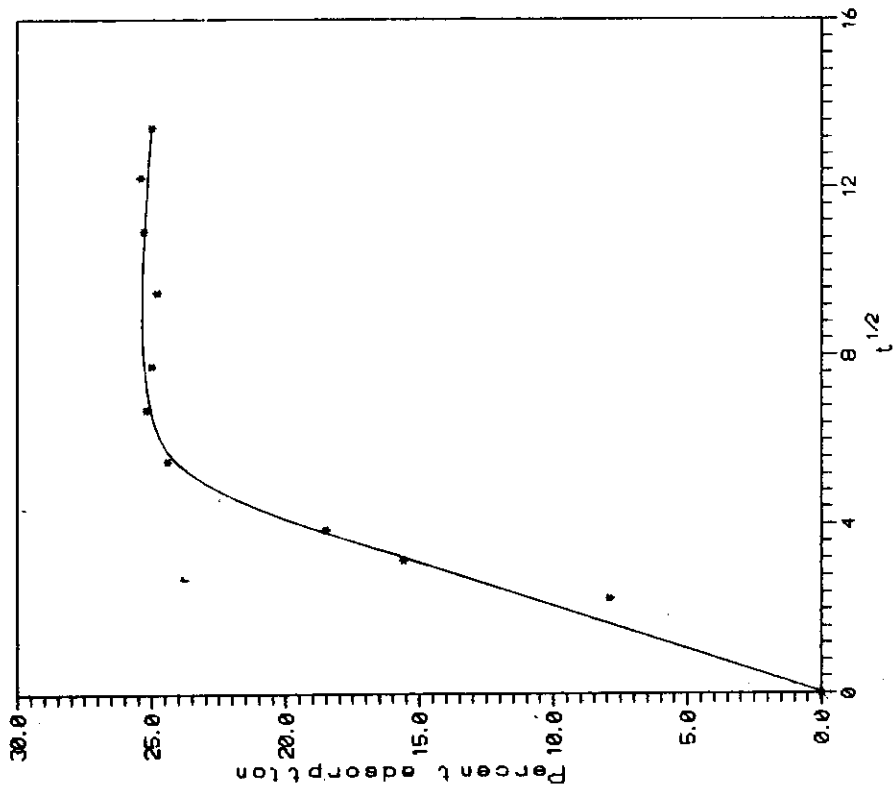Fig. 9(a) Effect of $t^{1/2}$ on adsorption of lead on bed sediments of river Kali

Fig. 10(b) Effect of $t^{1/2}$ on percent adsorption of zinc on bed sediments of river Kal

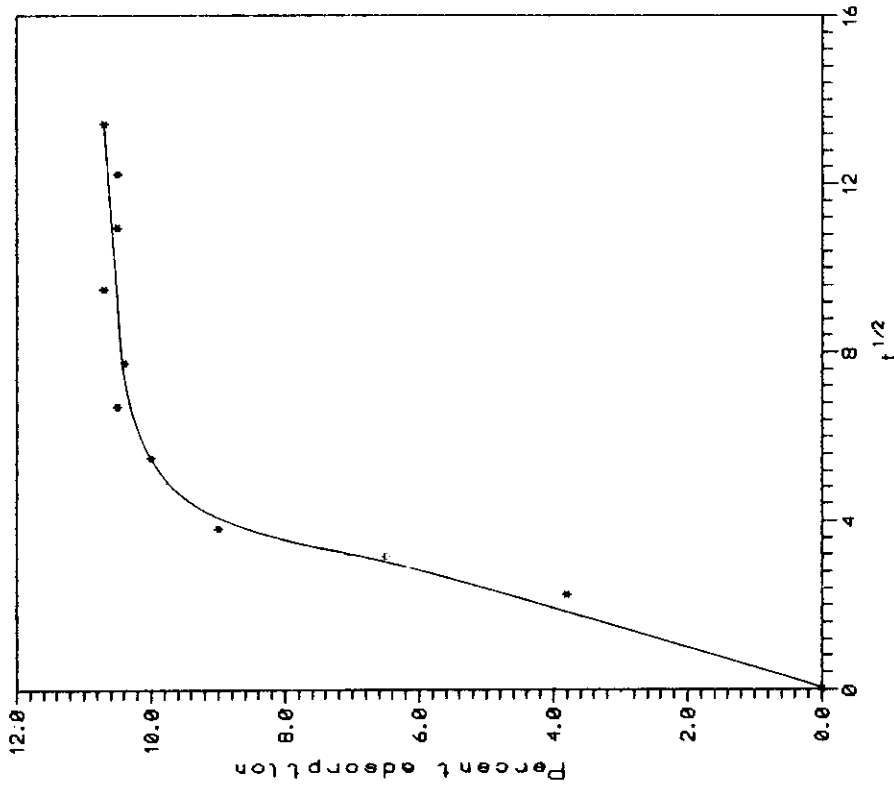Fig. 10(a) Effect of $t^{1/2}$ on percent adsorption of lead on bed sediments of river Kali

ions adsorbed, C_t vs $t^{1/2}$ are presented for both the metal ions under consideration. It is evident from Fig. 9 that adsorption of two metal ions on the bed sediments of river Kali follows three distinct phases, viz. i) instantaneous extremly fast uptake; ii) transition phase and iii) extremely slow uptake.

In phase I, about 18 % of the lead is uptaken with in a $t_{1/2}$ value of 3.5 min and manifests an average rate of uptake of about 100 µg/g min$^{-1/2}$. This is attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface. In the case of zinc, about 8 % of the zinc is uptaken with in a $t^{1/2}$ value of 3 min and manifests an average rate of uptake of about 70 µg/g min$^{-1/2}$

The visual observation clearly indicate the absence of any precipitation from ion exchange. Phase II, exhibiting additional removal is attributed to the diffusion of the adsorbate from the surface film into the micropores of the adsorbent (pore diffusion), stimulating further migration of metals from the liquid phase on to the adsorbent surface. Phase III, shows an extreamely small uptake. This slow rate is attributed to a very slow diffusion of the adsorbed metals from the surface film into the micropores which are the least accessible sites of adsorption. This also stimulates a slower rate of migration of metals from the liquid phase on to the adsorbent surface.

5.1.4   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. Fig. 11 & 12 (showing plots of adsorption of metal ions vs adsorbent dose) indicate that for a fixed initial metal ion concentration (C_0 = 10 mg/L), the adsorption of metal ions per unit weight of adsorbent decreases

Table 5. Adsorption of lead and zinc on bed sediments of river Kali at different adsorbent doses; Particle size = 210-250 µm; pH = 5.0; Temperature = 25^{0}C.

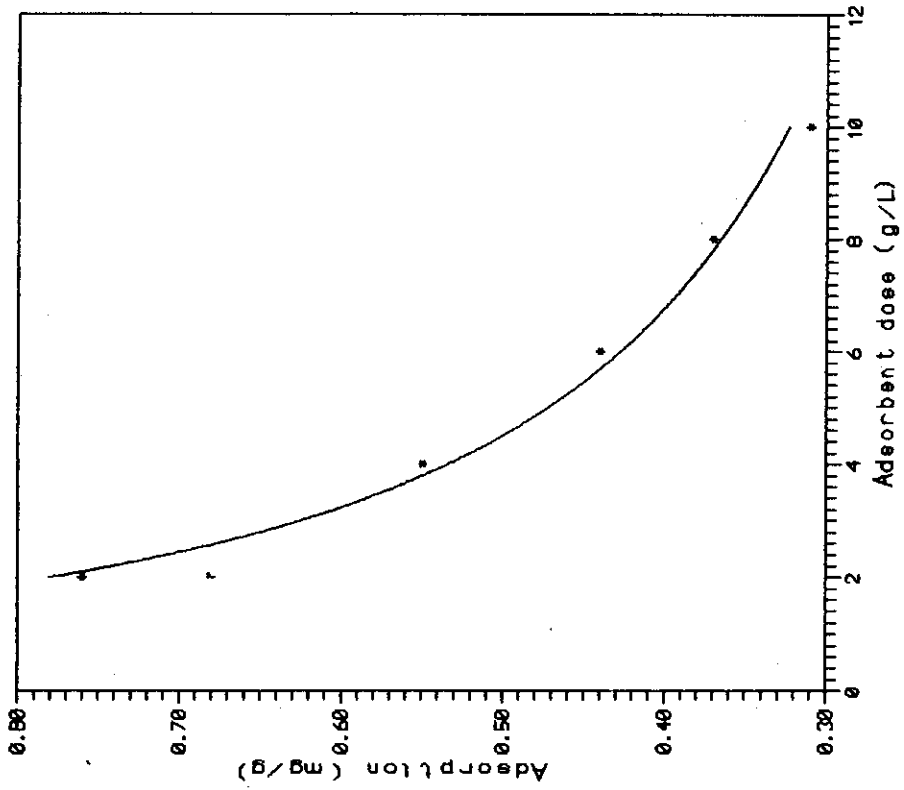| Metal Ion	Initial concn., C_0 (mg/L)	Adsorbent dose, W_s (g/L)	Metal ion adsorbed	
			µg/g	Percent
Pb	10.0	2.0	760	15.2
		4.0	550	22.0
		6.0	440	26.4
		8.0	370	29.6
		10.0	310	30.8
Zn	10.0	2.0	290	5.8
		4.0	225	9.0
		6.0	185	11.1
		8.0	163	13.0
		10.0	155	14.5

Fig. 11(a) Effect of adsorbent dose on adsorption
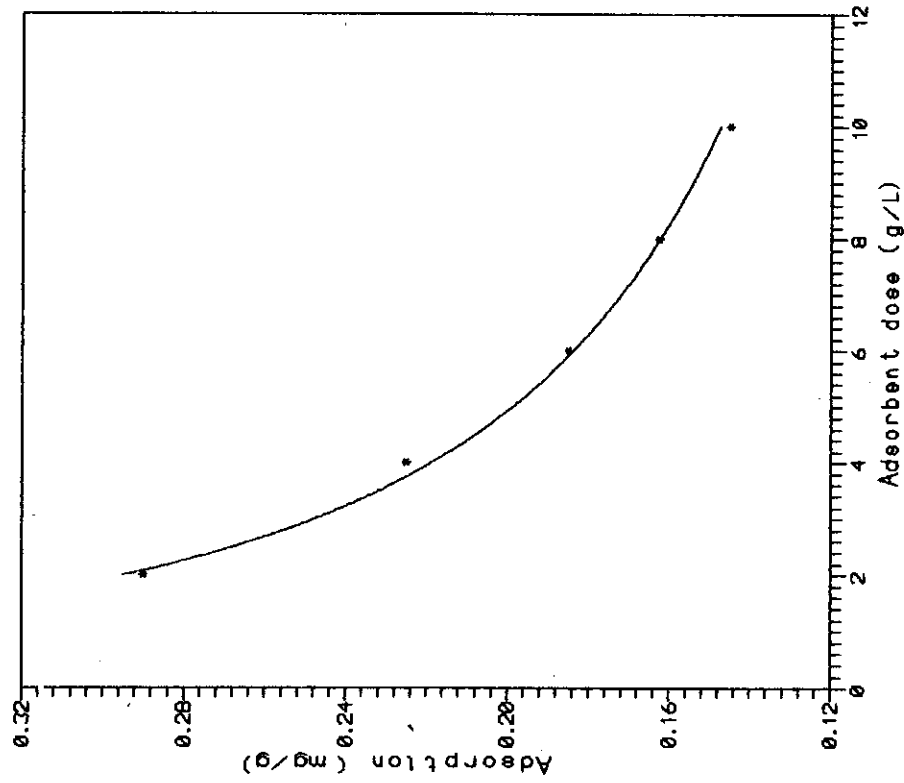of lead on bed sediments of river Kali

Fig. 11(b) Effect of adsorbent dose on adsorption
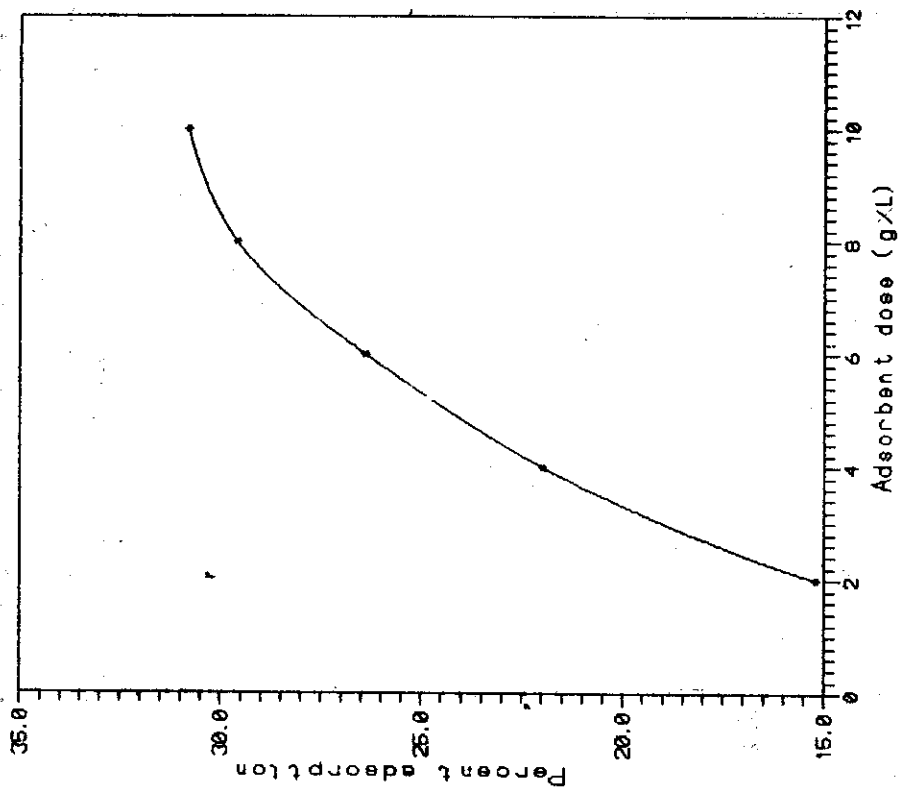of zinc on bed sediments of river Kali

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Fig. 12(b) Effect of adsorbent dose on percent adsorption of zinc on bed sediments of river Kali

Fig. 12(a) Effect of adsorbent dose on percent adsorption of lead on bed sediments of river Kali
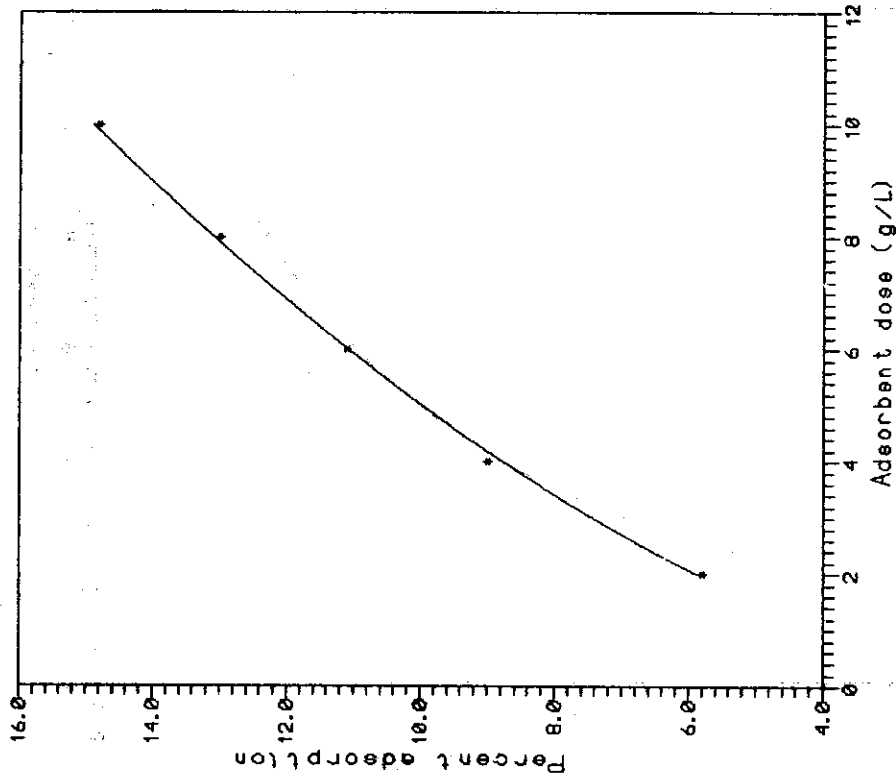
from 760 µg/g to 310 µg/g in the case of lead and from 290 µg/g to 155 µg/g in the case of zinc with increasing adsorbent dose (from 2 to 10 g/L). However, the percent adsorption (or removal) of metal ions increases almost linearly from about 15 to 31 percent in the case of lead and from 6 to 15 percent in the case of zinc (Fig. 12, Table 5) with increasing adsorbent dose (2 to 10 g/L) for both the metal ions under study.

5.1.5   Particle size (d_p)

The experimental data for the adsorption of metal ions at different sizes of adsorbent are shown in Fig. 13 & 14. The plots between percent adsorption of metal ions at equilibrium vs adsorbent sizes (Fig. 14) reveals that for a fixed adsorbent dose the metal ion adsorbed is higher for smaller adsorbent size. Further, it is observed that the percent metal ion adsorbed decreases linearly from 30 to 20 percent in the case of lead and 11 to 8 percent in the case of zinc with the increasing geometric mean of adsorbent size (Table 6). This is because, adsorption being a surface phenomenon, the smaller adsorption sizes offered comparatively larger surface area and hence higher adsorption occurs at equilibrium.

5.2   Adsorption Isotherms

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

5.2.1   Langmuir isotherm

Langmuir's isotherm has been extensively used by many authors for the sorption of heavy metals on clays, metal oxides, soils etc. In the present study for the adsorption of lead and

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^{0}C.

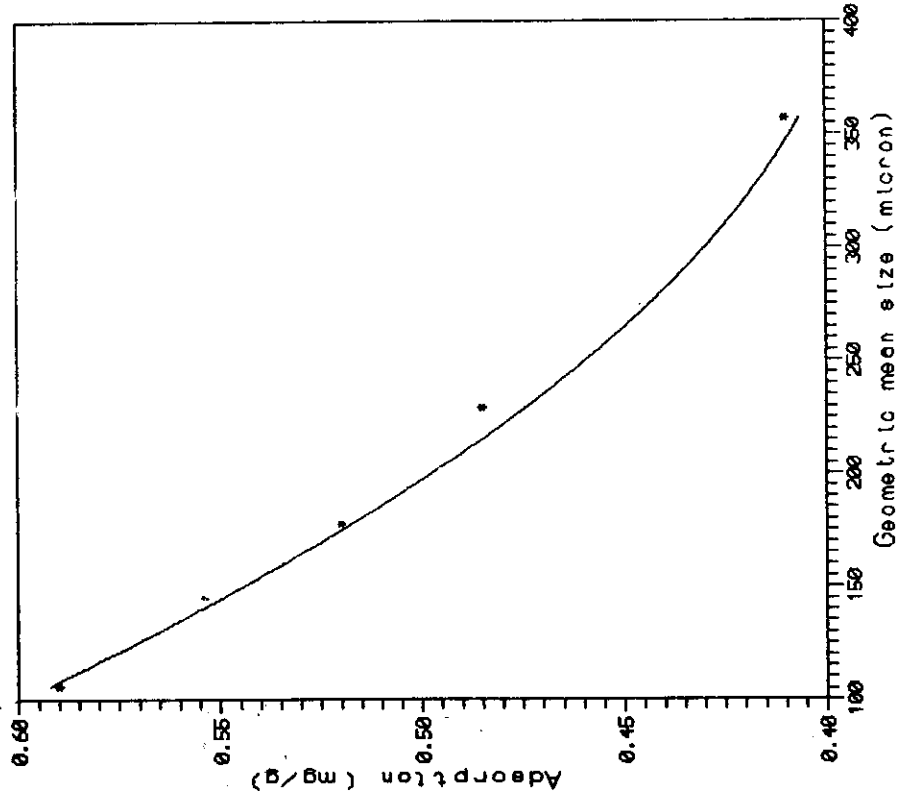| Metal Ion	Initial concn., C_0 (mg/L)	Particle size, d_p (µm)	Metal ion adsorbed	
			µg/g	Percent
Pb	10.0	106.1	590	29.5
		177.5	520	26.0
		229.1	485	24.3
		273.8	430	21.5
		357.1	410	20.5
Zn	10.0	106.1	220	11.0
		177.5	205	10.3
		229.1	195	9.8
		273.8	188	9.4
		357.1	168	8.4

Fig. 13(b) Effect of adsorbent size on adsorption
of Zinc on bed sediments of river Kali

Fig. 13(a) Effect of adsorbent size on adsorption
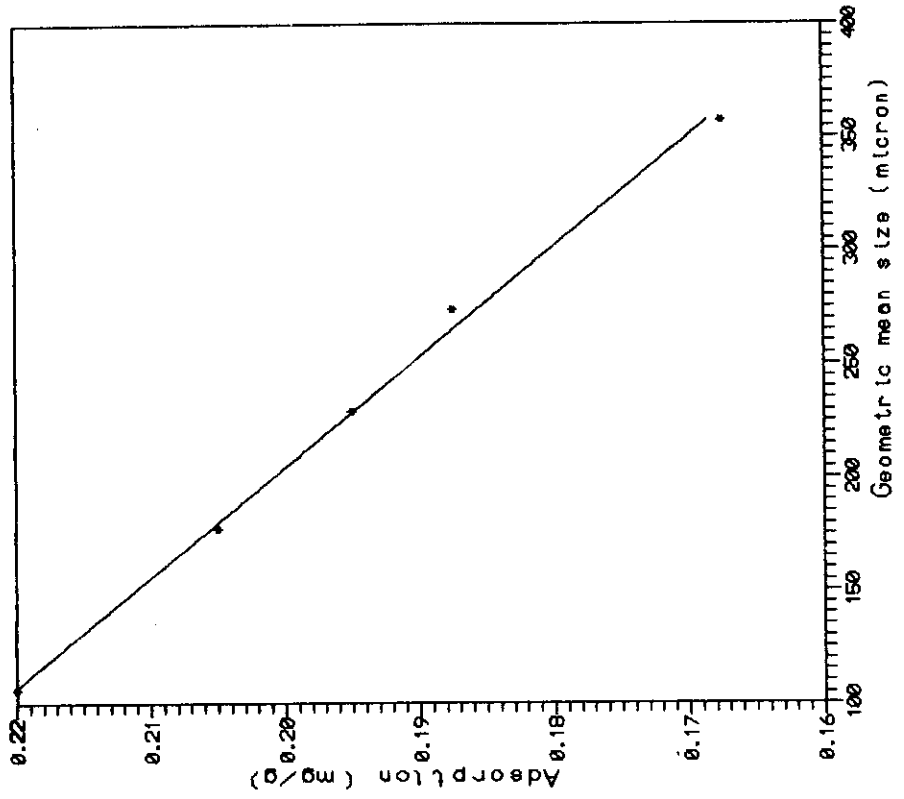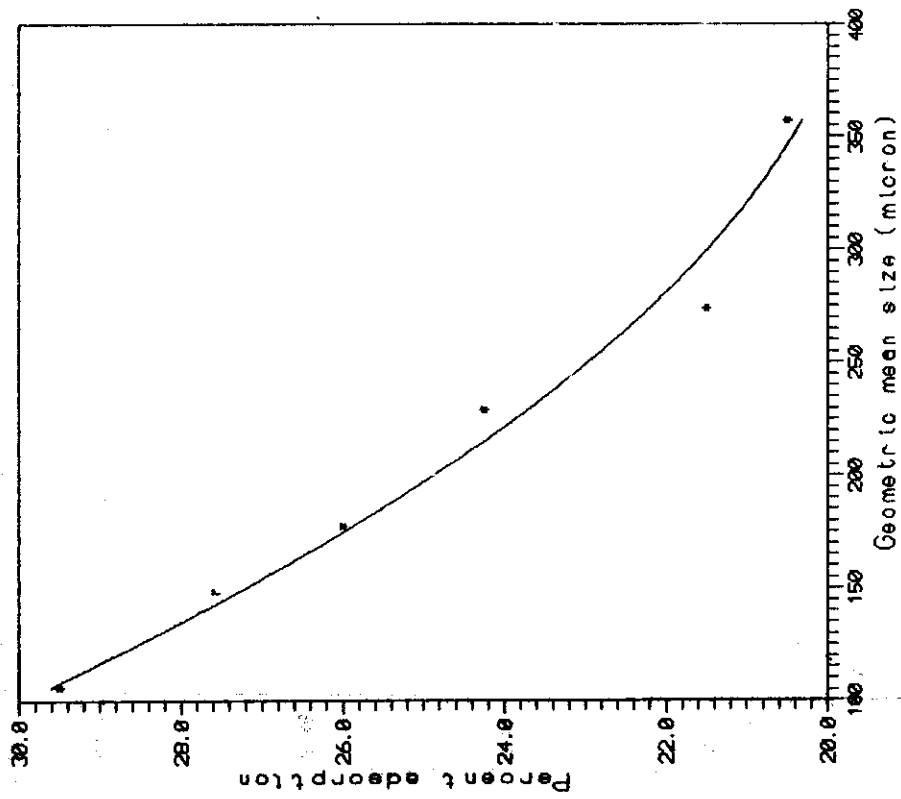of lead on bed sediments of river Kali

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Fig. 14(b) Effect of adsorbent size on percent
adsorption of zinc on bed sediments
of river Kali

Fig. 14(a) Effect of adsorbent size on percent
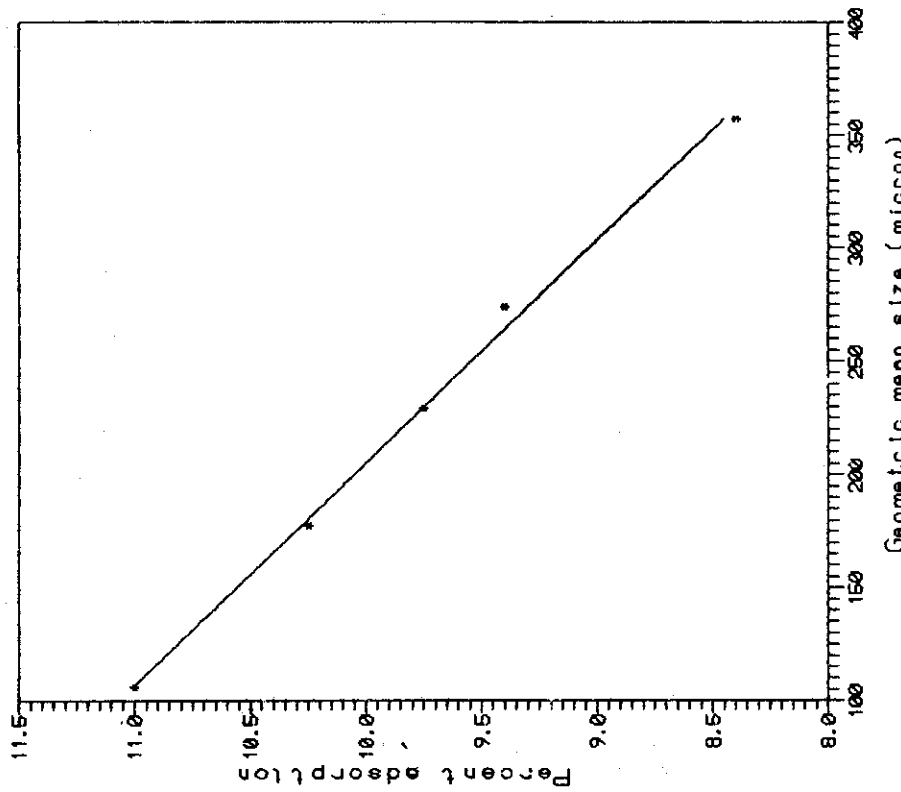adsorption of lead on bed sediments
of river Kali

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zinc, the linear form of Langmuir equation has been utilised.

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

Where q_e is the amount of uptake in mg per gm of adsorbent and C_e is the equilibrium concentration in mg/L of the adsorbate ions. When $1/q_e$ is plotted against $1/C_e$ values, a straight line with slope $1/bQ^0$ and intercept $1/Q^0$ is obtained.

The Langmuir parameters i) maximum sorption capacity 'Q^0'(monolayer capacity) and ii) parameter related to energy of adsorption 'b' are calculated from the graph. These values are used for comparison and correlation of the sorptive properties of the sediments. Fig. 15 shows the Langmuir adsorption isotherms for the two metal ions, lead and zinc, adsorbed by sediments of size 210-250 μm. The Langmuir parameters calculated from isotherm (Fig. 15) for adsorption of lead and zinc are shown below:

Metal ion	Adsorption Maxima 'Q^0' (mg/g)	Bonding Energy Constant 'b' $(mg/L)^{-1}$
Lead	0.613	0.639
Zinc	0.384	0.118

5.2.2   Freundlich isotherm

The adsorption data for lead and zinc has also been analysed using logarithmic form of Freundlich isotherm as shown below:

$$\log q_e = \log K_F + 1/n \, \log C_e$$

The intercept of line, $\log K_F$, is roughly an indication of the adsorption capacity and the slope, $1/n$, is an indicator of the adsorption intensity, as observed by Weber (1972).
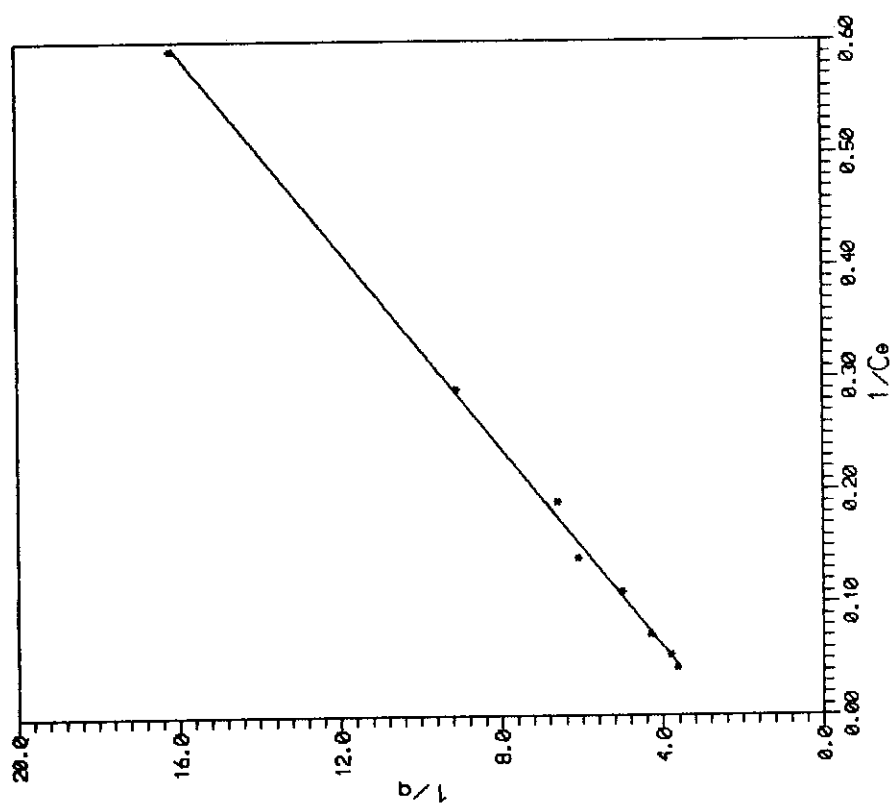
45

Fig. 15(b) Graphical representation of Langmuir
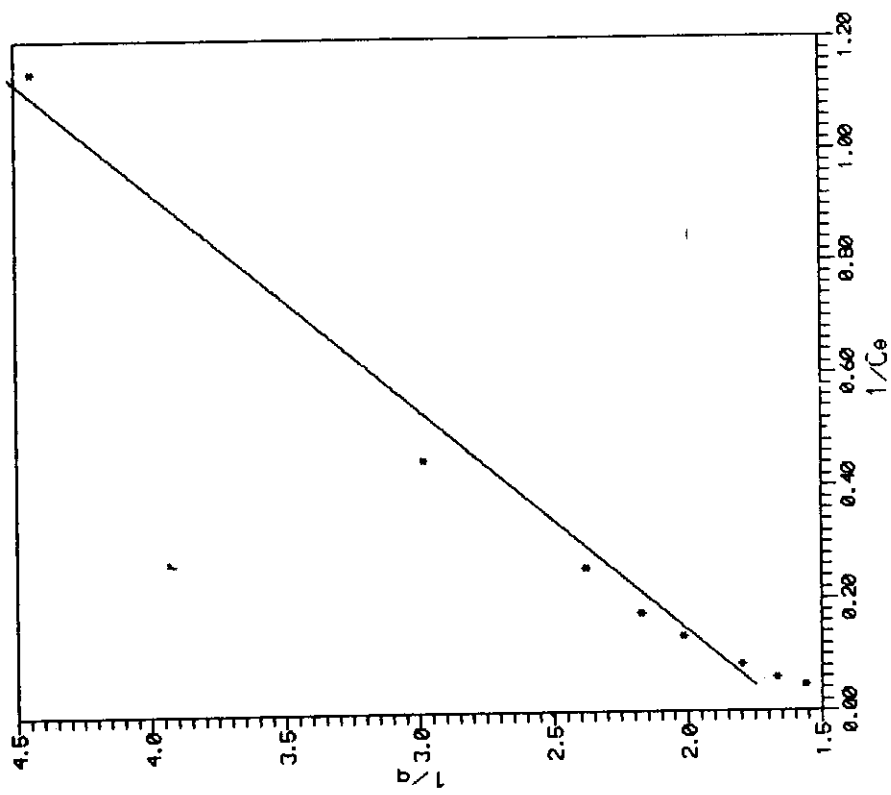isotherm for zinc

Fig. 15(a) Graphical representation of Langmuir
isotherm for lead

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Fig. 16(b) Graphical representation of
Freundlich isotherm for zinc

Fig. 16(a) Graphical representation of
Freundlich isotherm for lead

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The adsorption data for lead and zinc have also been utilised to draw the Freundlich isotherm plot depicted in Fig. 16. In these plots, log q_e has been plotted against log C_e, in respect of sediments of size 210-250 µm.

The graph reflects the satisfaction of freundlich equation. The values for sorption capacity, K_f, and adsorption intensity, 1/n, are shown below:

Metal ion	Adsorption Capacity 'K_f' (mg/g)	Adsorption Intensity '1/n'
Lead	0.259	0.309
Zinc	0.053	0.558

6.0 CONCLUSION

Adsorption of heavy metals on sediments represent an important control on their speciation and hence on their bioavailability and mobility in the aquatic environment. The most important parameter in the control of metal ions adsorption onto the riverbed sediments is the pH. 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, it is concluded that the bed sediments of river Kali have greater potential for the removal of lead as compared to zinc ions.

The sediments existing at the bottom of the water column play a major role in pollution studies due to their specific adsorption capacity. They reflect the quality of the water system and can be used to detect the presence of contaminants that do not remain soluble after discharge into surface waters. Therefore, the analysis of heavy metals in sediments and their adsorption behaviour permits us to detect pollution that could escape water analysis, and also provide information about the critical sites of the water system under consideration.

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