ADSORPTION OF HEAVY METALS ON RIVER SEDIMENT

A DISSERTATION

Submitted in partial fulfilment of the
requirements for the award of the degree
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CHEMICAL ENGINEERING
(With Specialization in Industrial Pollution Abatement)

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CANDIDATE'S DECLARATION

I here by declare that the work which is being presented in the dissertation entitled **"ADSORPTION OF HEAVY METALS ON RIVER SEDIMENT"** in partial fulfillment of the requirement for the award of the degree of **MASTER OF ENGINEERING** in **CHEMICAL ENGINEERING** with specialization in **INDUSTRIAL POLLUTION ABATEMENT** submitted in the Department of Chemical Engineering, University of Roorkee, Roorkee, is an authentic record of my own work carried out from July 2000 to February 2001 under the supervision of **Dr. S.D. Bhattacharya**, Professor in the Department of Chemical Engineering, University of Roorkee, Roorkee.

The matter presented in this dissertation has not been submitted by me for the award of any other degree or diploma.

Dated: February,26,2001
Place: Roorkee

(MANU GUPTA)

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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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 behavior.

The adsorption characteristics of the bed sediments collected from river Hindon near village Sishki 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 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 increased in pH value.

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

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

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NOMENCLATURE

C_o	Initial metal ion concentration (mg/L).
C_t	Metal ion adsorbed (mg/L).
C_e	Equilibrium metal ion concentration (mg/L).
	Contact time (min).
W_s	Adsorbent dose (g/L).
q_e	Amount of solute adsorbed per unit weight of adsorbent (mg/g).
Q^0	Solid phase concentration corresponding to all available sites being filled or maximum adsorption (mg/g).
b	Adsorption coefficient $(mg/L)^{-1}$.
K_f	Characteristic constant indicates adsorption capacity.
n	Characteristic constant indicates adsorption intensity.

INTRODUCTION

1.1 ADSORPTION PROCESSES

The term adsorption refers strictly to the existence of a higher concentration of any particular 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 present concepts of adsorption, this surface phenomenon may be categorized as:

Exchange adsorption
Physical adsorption
Chemical adsorption.

Exchange adsorption is a process in which ions of one substance concentrate at a surface as result of electrostatic attraction to charged sites at the surface. Adsorption occurring as a result of Vander Waal 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 transnational 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 named as activated adsorption or 'chemisorption'. Chemical sorption involves electronic interactions between specific sites on the sorbing surface and solute molecules. Chemically adsorbed molecules are considered not to move freely on the surface, or within the interface.

Physical adsorption is usually predominant 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 favored by higher temperature, because a chemical reaction proceeds 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 solid-liquid system results in the removal of solutes from solutions and their concentration at the surface of the solid, to such time as concentration of the solute remaining in solution is in a dynamic equilibrium with that at the surface. Equal amounts of solute eventually are being adsorbed and described simultaneously.

Consequently, the rates of adsorption and desorbed 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 equilibrium 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 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 includes 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. Significance of metals studied are :

Lead : Lead is a non-essential toxic heavy metal. It enters the human body primarily via inhalation had 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 is 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. Lead poisoning is associated with the problems of anaemia, damage, and damage to the central nervous system and kidney damage.

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.

Zinc: Zinc is one of the most abundant essential elements 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 may life forms. Excessive amount of zinc, however, may be toxic especially to the aquatic biota. Moderately increased concentrations in water resulting from galvanized 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.

The guideline value for zinc in drinking water is 5.0mg/L base 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 manmade sources during their transport are distributed between the aqueous phase and the suspended sediments. The fraction in the sediment is expected not to present direct danger, if the metal ions are tightly bound to it and subsequently settled to bottom in course of time. This state of affairs is maintained until there is remobilization from the sediment due to changing conditions in the system.

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

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 until 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 where upon 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.

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 derbies 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 additionally influenced by climatic regime (weathering and hydraulic conditions), land form and land use and time in transit.

LITERATURE REVIEW

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.

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

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

Hildebrand and Blum [12] determined that at pH > 7, the lead ion adsorption process on clay minerals follow the same pattern as a chemical sorption.

Jenne. et.al.[16] The zero point 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.

Forstner et. al.[7] 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 in inert positions.
Heavy metal -hydroxides -carbonates -sulfides		Precipitation as a result of exceeding the solubility product in the area of the water course
Hydroxides and oxides of Fe/Mn	pH-dependent	Physio-sorption Chemical sorption (exchange of H+ in fixed positions
Bitumen, lipids humic substances Residual organics		Physio-sorption chemical sorption (exchange of H+ in COOH-,OH-groups)
Calcium carbonate	pH-dependent	Physico-sorption Pseudomorphosis (dependent on supply and time)

Soong et. al. [27] 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, et. al. [17] Since the ionization potential of copper and zinc are quite similar (Cu: 2.71; Zn: 2.70; Pb: 1.66 eV), the different adsorption behavior 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.

Jenne et. al. [16] 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 affinities involve mechanisms of adsorption and co-precipitation.

Benjamin and Lackie [2] The adsorption or heavy metal ions on oxides, another potential adsorberin sediments, are studied extensively, reported the adsorption of Cd, Cu and Pb on a number of hydrous oxides and indicated source surface sites for adsorption.

Dempsey and Singer [4] 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.

Hildebrand and Blum [12] The mechanism of heavy metal sorption on hydrous oxides has been demonstrated by 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 hydroxy 1 group of the Fe0 (OH) crystal.

Gadde and Laitinen [10] 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 .

Jeffries and stumm [15] 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 et. al. [28] found that a combination of exchange reactions and solid solution could satisfactorily explain the observed chemistry of natural Ferro-manganese material.

Gibbs et. al. [11] Chemical leaching of trace elements in carbonate-free sediments from the Amazon and Yukon Rivers indicate 4-50% of Cu, Cr, Pb, and Ni to be present in the form of hydrous Fe/Mn oxide coatings.

Perhac et. al. [20] 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.

Singer [29] 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. He summarized the influence of dissolved organic 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 et.al. [25] 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 form the solubilization of minerals by natural waters containing organic ligands with respect to the direct association of metal-organic species to sedimentary material, the association with clay minerals is of particular significance.

Curtis et. al. [3] has proposed a simplified scheme to explain why certain metals (Cr, Cu, Mn, Pb, Ni, U, V) shows a positive association with organic carbon in a sediment, while other elements exhibit no significant correlation, or may even be negatively correlated with organic carbon.

SORPTION MODELS

In practice, sorption 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 equilibrium 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 mode.

4.1 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 localized 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 with 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-θ, 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:

$$K_d \theta = k_a P (1-\theta) \qquad (1)$$

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

$$.\theta = \frac{k_a P}{k \quad + k_a P} = \frac{bP}{{}_d1 + bP} \qquad (2)$$

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

$$b = b_0 \exp. (-\Delta H/RT) \qquad (3)$$

Where b_0 is a constant related to the entropy. Equation (2) can also be derived using methods of statistical thermodynamics.

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

$$q_o = \frac{Q^o b \, C_0}{1 + b \, C_0} \qquad (4)$$

Where q_o 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_o is the liquid-phase concentration at equilibrium. Equation (4) can be written in a variety of linear forms:

$$\frac{C_o}{q_o} = \frac{1}{Q^o b} + \frac{C_o}{Q^o} \quad (5)$$

$$\frac{1}{q_o} = \frac{1}{Q^o} + \frac{1}{b Q^o C_o} \quad (6)$$

$$q_o = Q^o - \frac{q_o}{b C_o} \quad (7)$$

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 .

4.2 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 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:

$$q_0 = \frac{BC_0Q^0}{(C_s - C_0)[1 + (B-1)(C_0 / C_s)]} \quad (8)$$

Where C_s is the saturation concentration of the solute, C_0 is the liquid-phase concentration at equilibrium, Q^0 is the solid-phase concentration corresponding to a complete monolayer, and q_o is the solid-phase equilibrium concentration. B is constant expressive of the energy of adsorption:

$$B = \frac{d_2 C_1}{d_1 c_2} \exp(E_1 - E_2)/RT \tag{9}$$

Where E_1 is the average heat of adsorption of the first layer, E_2 is the heat of condensation, and d_{2c1} / d_{1c2} is the ratio of evaporation-condensation coefficients for the adsorbed layers, which are often nearly, equal to unity.

Equation (8) can be linearized to facilitate its application:

$$\frac{C_e}{(C_s - C_e)q_e} = \frac{1}{BQ_0} + \frac{B-1}{BQ_0} \cdot \frac{C_e}{C_s} \tag{10}$$

4.3 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 could be better described by the relationship:

$$q_e = K_F C_e^{1/n} \tag{11}$$

Where K_F and n are characteristic constants, Equation (11) linearizes in logarithmic form:

$$\text{In } q_e = \text{In } K_F + 1/n \text{ In } C_c \tag{12}$$

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 relative indicator of sorption capacity, while 1/n is indicative of the intensity of the reaction.

EXPERIMENTAL METHODOLOGY

5.1 SAMPLING AND STORAGE

For the adsorption studies of heavy metal ions (lead and zinc) on the bed sediments of river Hindon, freshly deposited sediments from shallow water nearer to bank were collected from the upstream section of the river (near village Shirki) 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.

The size distribution of the sediment samples was done by dry sieving method using ASTM standard sieves to obtain various fractions. Five fractions viz. 75-150, 150-212, 212-250 250-325 & 325-425 micron were separated for absorption studies. Sieved sediments were oven dried overnight at 105^0C and after cooling in dissecator, stored in airtight containers for adsorption studies.

5.2 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 sulfate respectively. Double distilled water prepared in All Quartz Double Distiller was used through out the study. All glass wares and other containers were thoroughly cleaned by soaking in detergent followed by soaking in 10% nitric acid for 48 hrs. And finally rinsed with demonized 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) HCl.

5.3 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 25^0C for the desired duration's 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 analyzed for residual concentration of respective metal ions. All the adsorption experiments were conducted at 25^0C.

5.4 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:

RESULTS AND DISCUSSION

6.1 EFFECT OF OPERATING VARIALBES

6.1.1 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 Hindon studies were conducted with initial metal ion concentration of 4,8,10,15,20 and 25mg/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 utilisation of the adsorptive capacities of the adsorbent is expected due to a greater driving force (by a higher concentration gradient pressure).

6.1.2 Effect of pH

The adsorption of two metal ions viz.pb^{2+} and Zn^{2+} on the bed sediments of river Hindon 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.

From the results it is evident that the pH for maximum uptake of lead ion (478 µg/g) is 6.0 (Fig.3a). At this pH the concentration of lead ion in solution is quite low (reduced to 7.61 mg/L from 10.0 mg/L due to pH adjustment). Further, it is apparent form Fig.4 (a) that the adsorption of lead rises form 2.8% at pH 4.0 to 23.9% 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 294 µg/g (Fig.3b). At this pH the concentration of zinc ion in solution decreased from 10.0 mg/L to 8.03 mg/L due to pH adjustments. In this case adsorption of zinc rises form about 3.1% at pH 3.0 to 19.7% at pH 6.0 (fig.4b).

6.1.3 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 a fixed particle size of adsorbent (212-250 µm), are presented in Table 4 and graphically shown in Fig. 5-7. These plots indicated 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 empirically found functional relationship, common to the most adsorption processes, is that the uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time, t. Therefore in, fig . 8-10 , plots of metal 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 bed sediments of river Hindon follows three distinct phases, viz. 1) instantaneous extremely fast uptake; 2) transition phase and 3) extremely slow uptake.

6.1.4 Adsorbent does (W_S)

The effect of adsorbent dose on the adsorption properties of bed sediments of river Hindon has been studied at pH 5.0 with different adsorbent does varying from 2 to 10 g/L and at a fixed initial metal ion concentration of 10mg/L. Fig. 11 & 12 (showing plots of adsorption 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.

From 355 μg/g to 227 μg/g in the case of lead and from 340μg/g to 155μg/ 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 7.1 to 22.7 percent in the case of lead and from 6.8 to 15.5 percent in the case of zinc (fig12 Table 5) with increasing adsorbent dose (2 to 10 g/L) for both the metal ions under study.

6.2 ADSORPTION ISOTHERMS

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

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

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

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. Where $1/q_e$ 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. 13 shows the Langmuir adsorption isotherms for the two metal ions, lead and zinc, adsorbed by sediments of size 212-250 μm. The Langmuir parameters calculated from isotherm (Fig. 13) for adsorption of lead and zinc are shown below:

Metal ion	Adsorption Maxima 'Q^0' (mg/g)	Bonding Energy Constant 'b' $(\text{mg/L})^{-1}$
Lead	0.5966	0.1554
Zinc	0.7173	0.0517

6.2.2 Freundlich Isotherm

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

$$\text{Log } q_e = \log K_F + 1/n \log C_e$$

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. The adsorption data for lead and zinc have also been utilized to draw the Freundlich isotherm plot depicted in Fig. 14. In these plots, log q_e has been plotted against log C_e, in respect of sediments of size 212-250 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	0.1235	0.4456
Zinc	0.047	0.6968

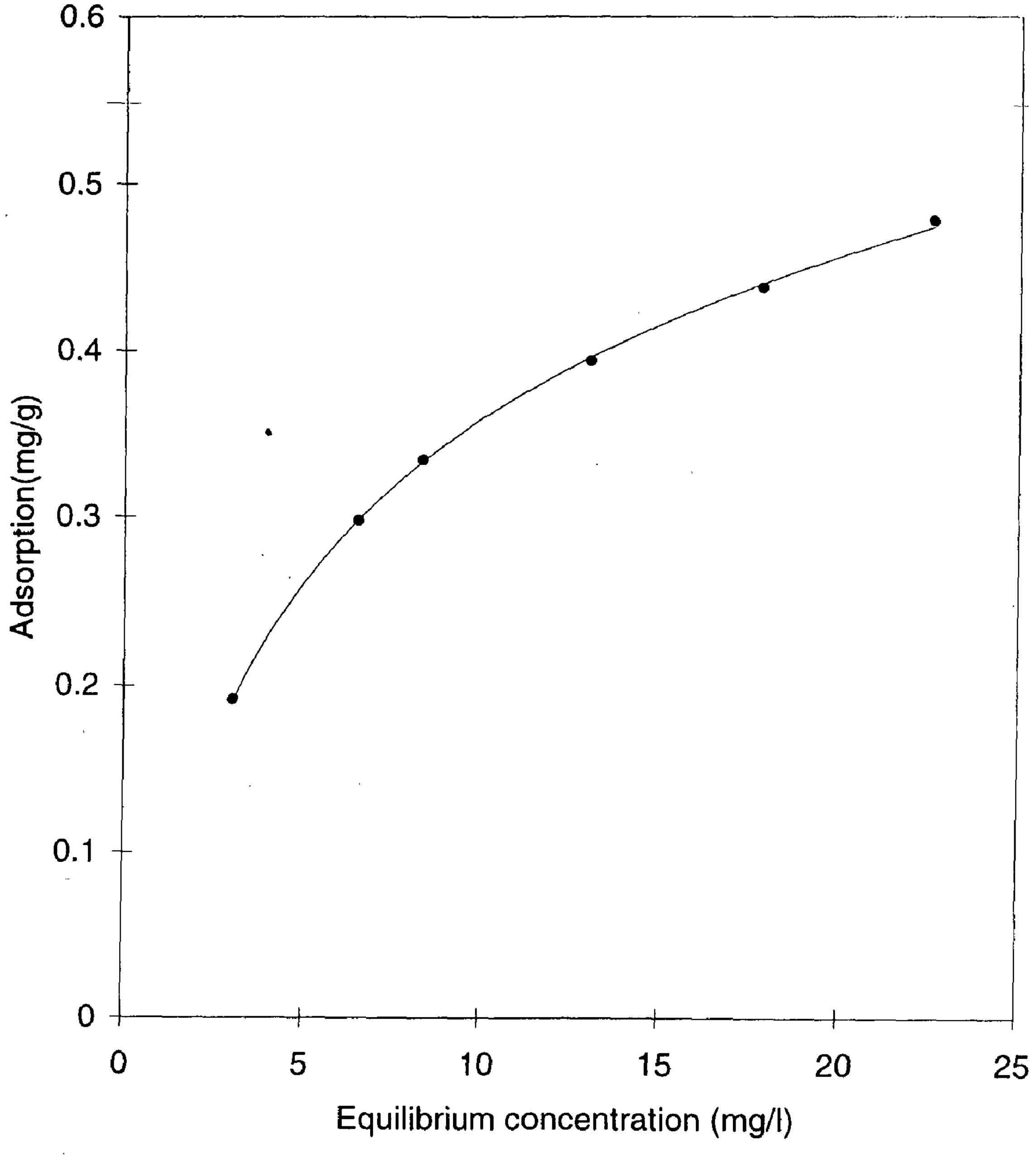

Fig. 1a Adsorption of lead on bed sediments of river Hindon(Adsorption size 212-250micron; pH - 5.0; Adsorption dose - 5g/l; Temperature -25^{0}C.)

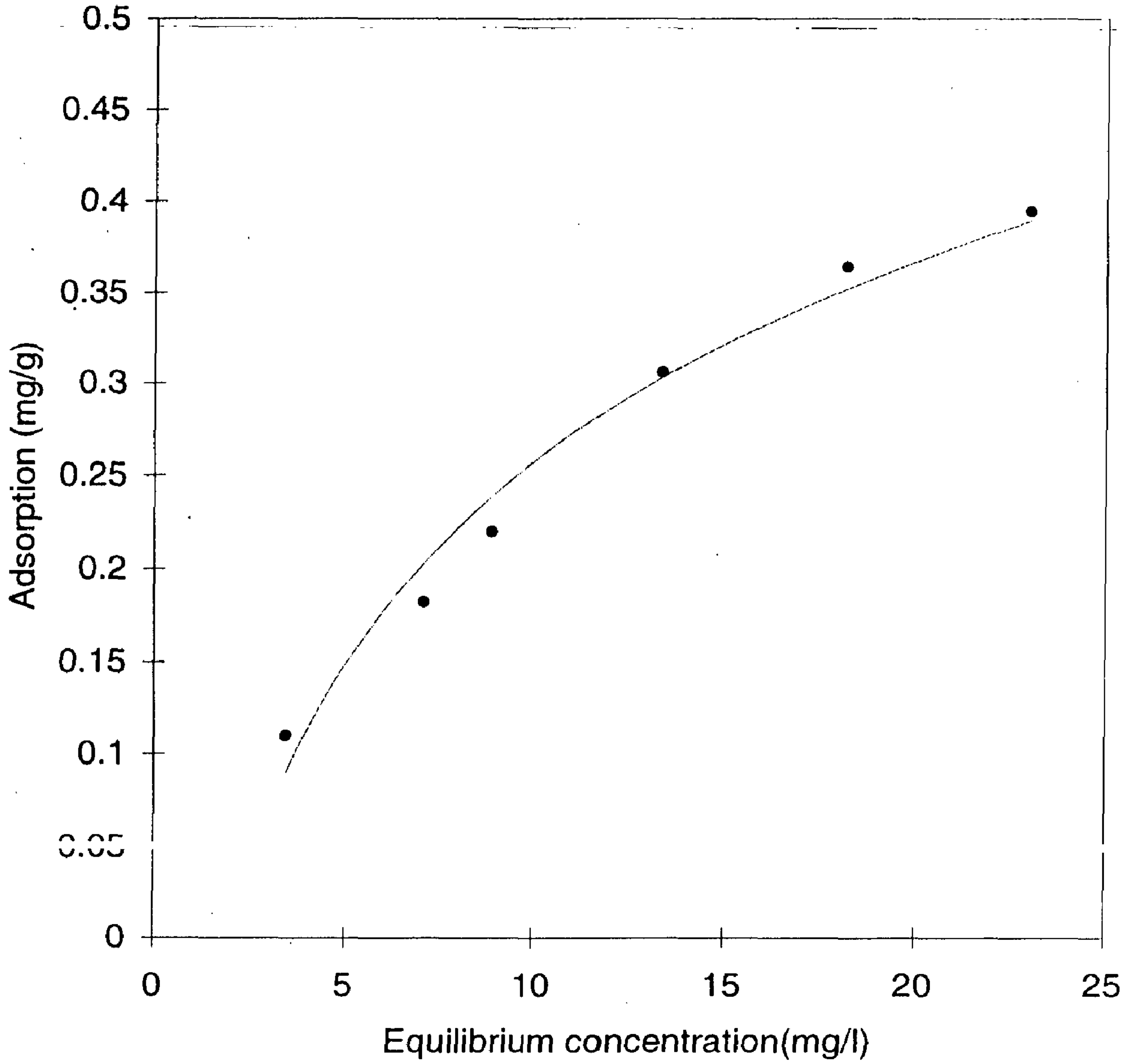

Fig.1b Adsorption of zinc on bed sediments of river Hindon(Adsorbent size 212-250micron; pH-5.0; Adsorbent dose - 5g/l; Temperature-25^{0}C)

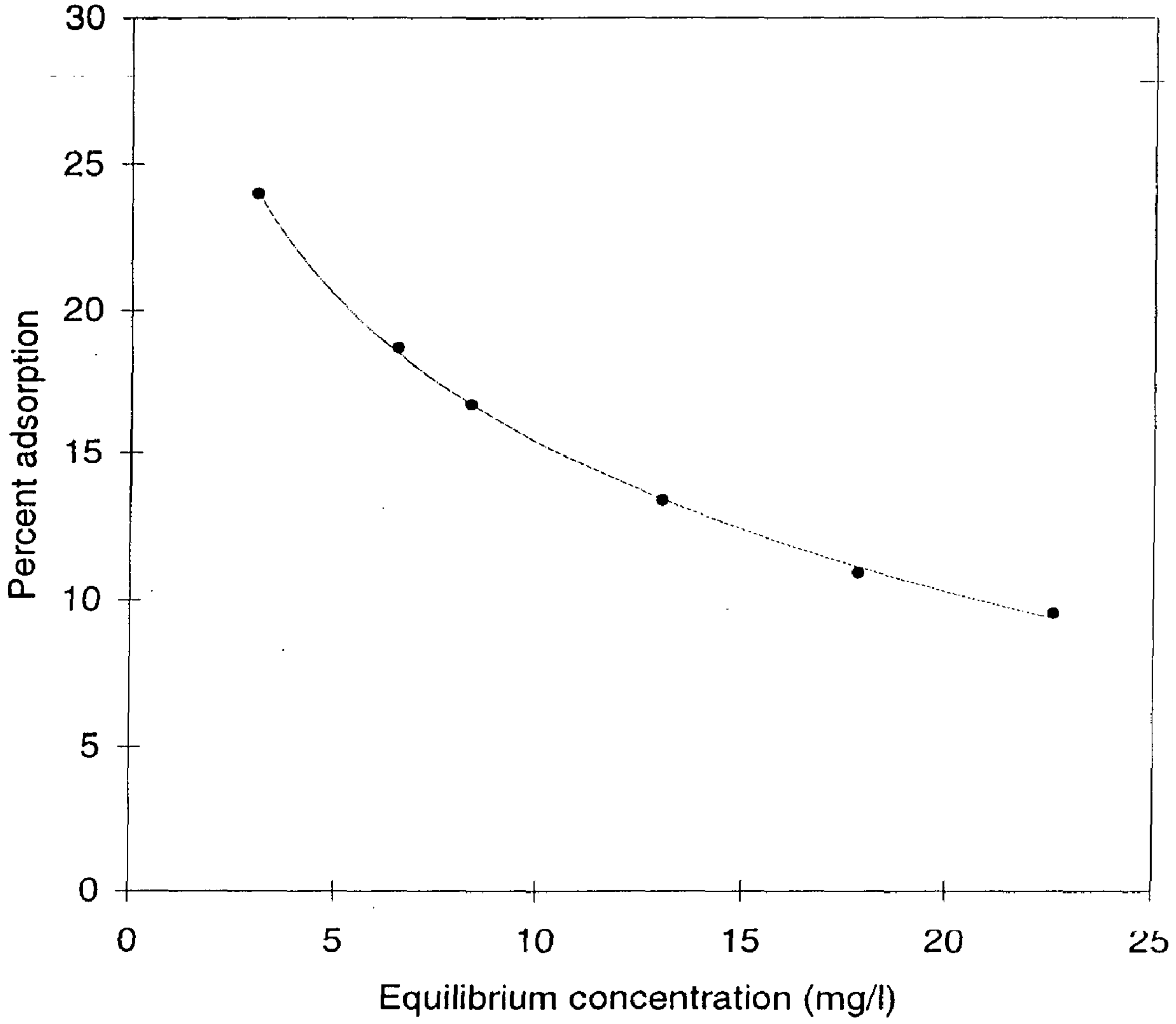

Fig.2a Percent adsorption of lead on bed sediments of river Hindon(Adsorbent size 212-250micron; pH - 5.0; Adsorbent dose - 5g/l; Temperature -25^{0}C)

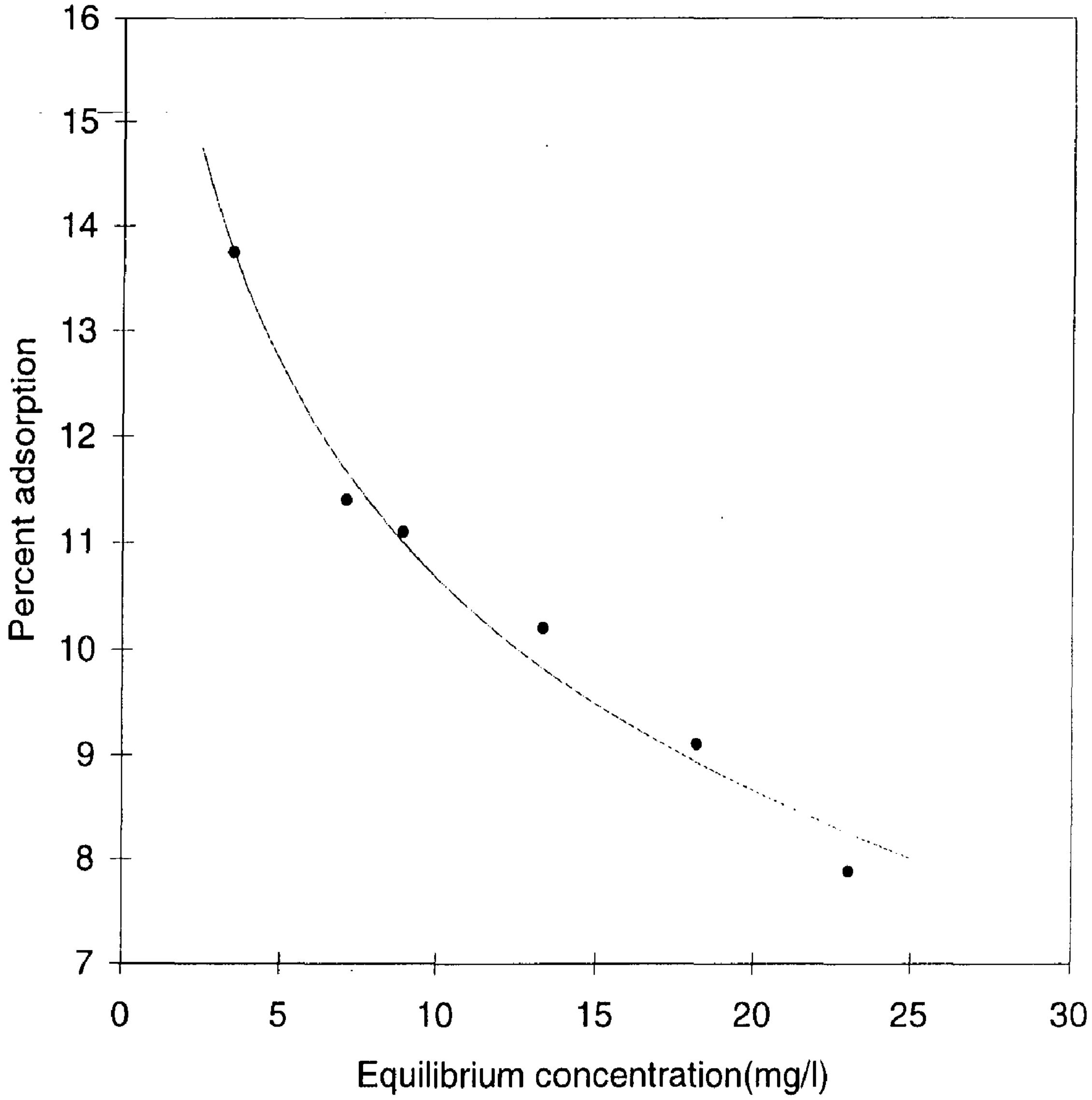

Fig.2b Percent adsorption of zinc on bed sediments of river Hindon(Adsortption size 212-250micron; pH - 5.0; Adsorbent dose - 5g/l; Temperature - 25^0C)

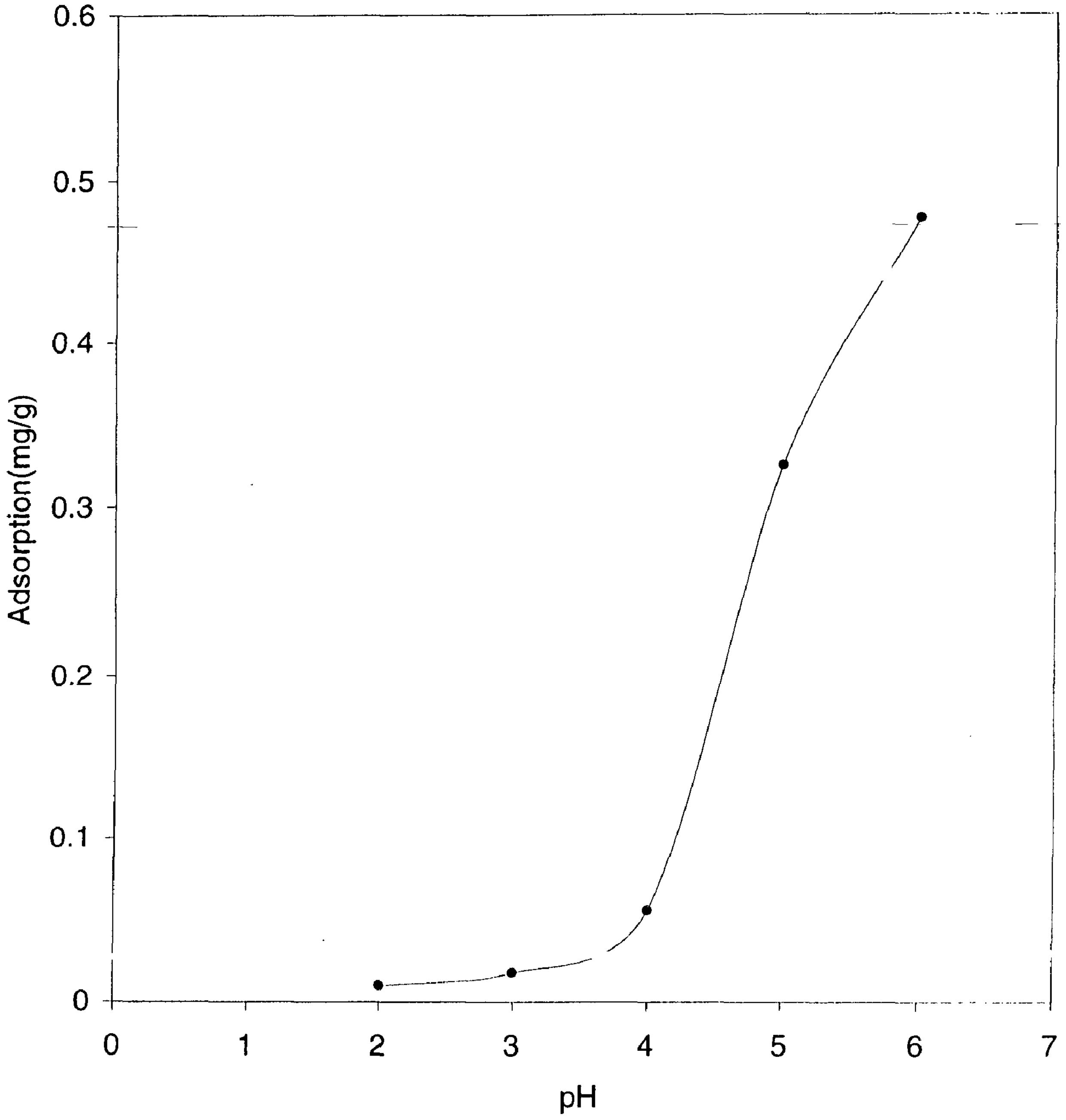

Fig.3a Effect of adsorption of lead on bed sediments of river Hindon (Adsorbent size 212-250 micron; Adsorbent dose – 5g/l; Temperature –25^{0}C)

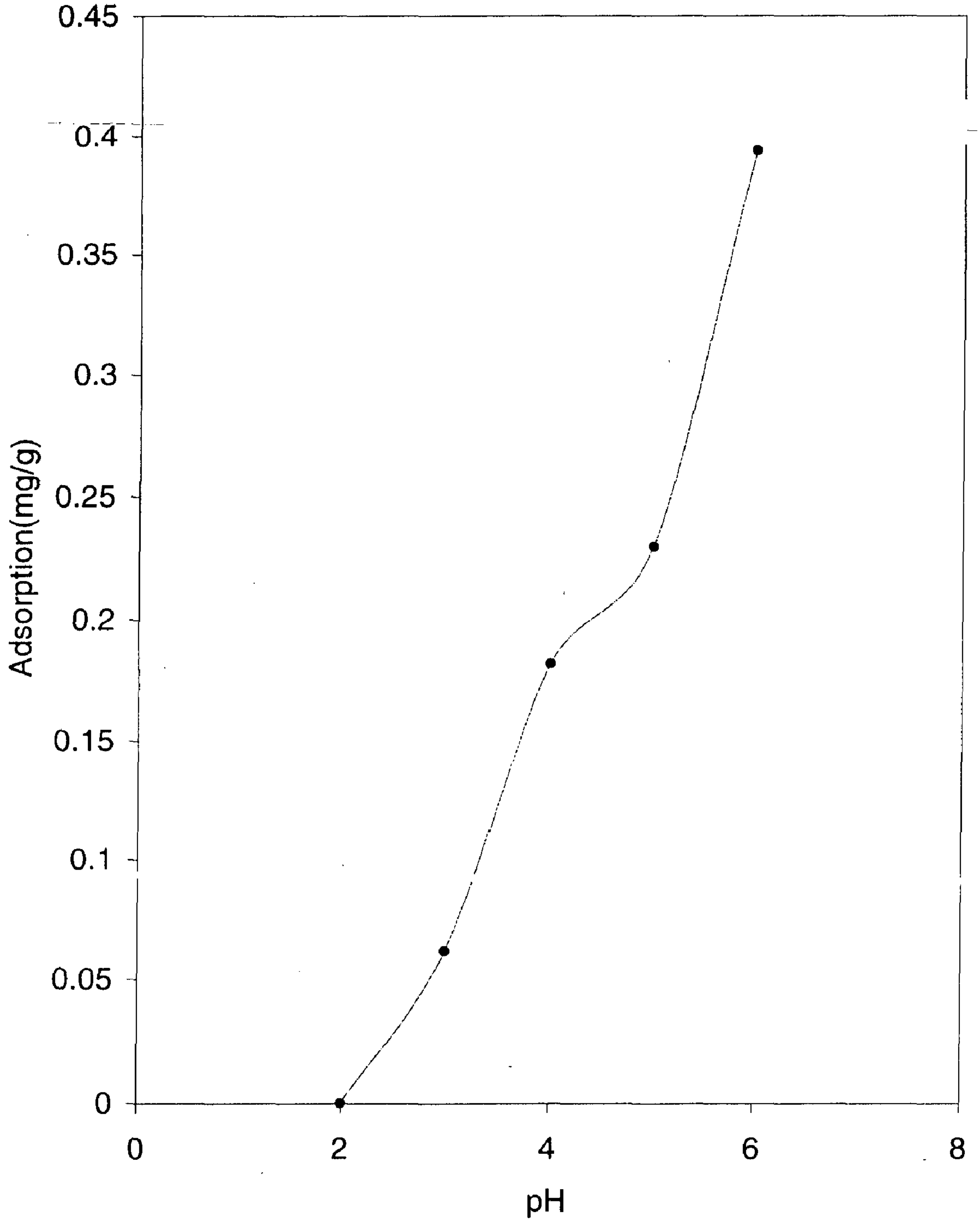

FIg.3b Effect of pH on adsorption of zinc onbed sediments of riverHindon (Adsorbent size 212-250 m; Adsorbent dose – 5g/l;Temperature –250C)

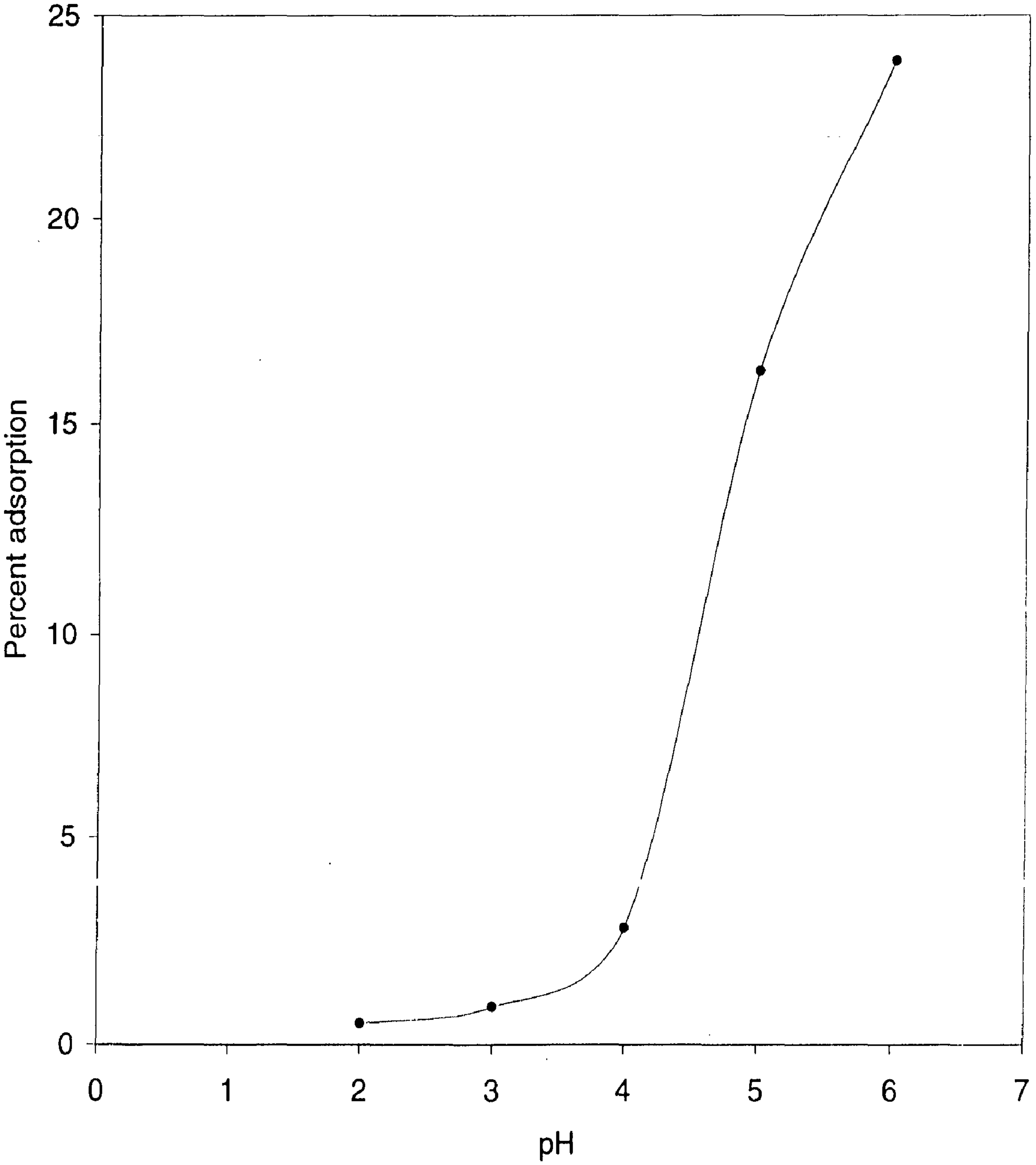

Fig.4a Effect of pH on percent adsorption of lead on bed sedimentsof river Hindon (Adsorbent size 212-250 micron; Adsorbent dose – 5g/l; Temperature –25^{0}C)

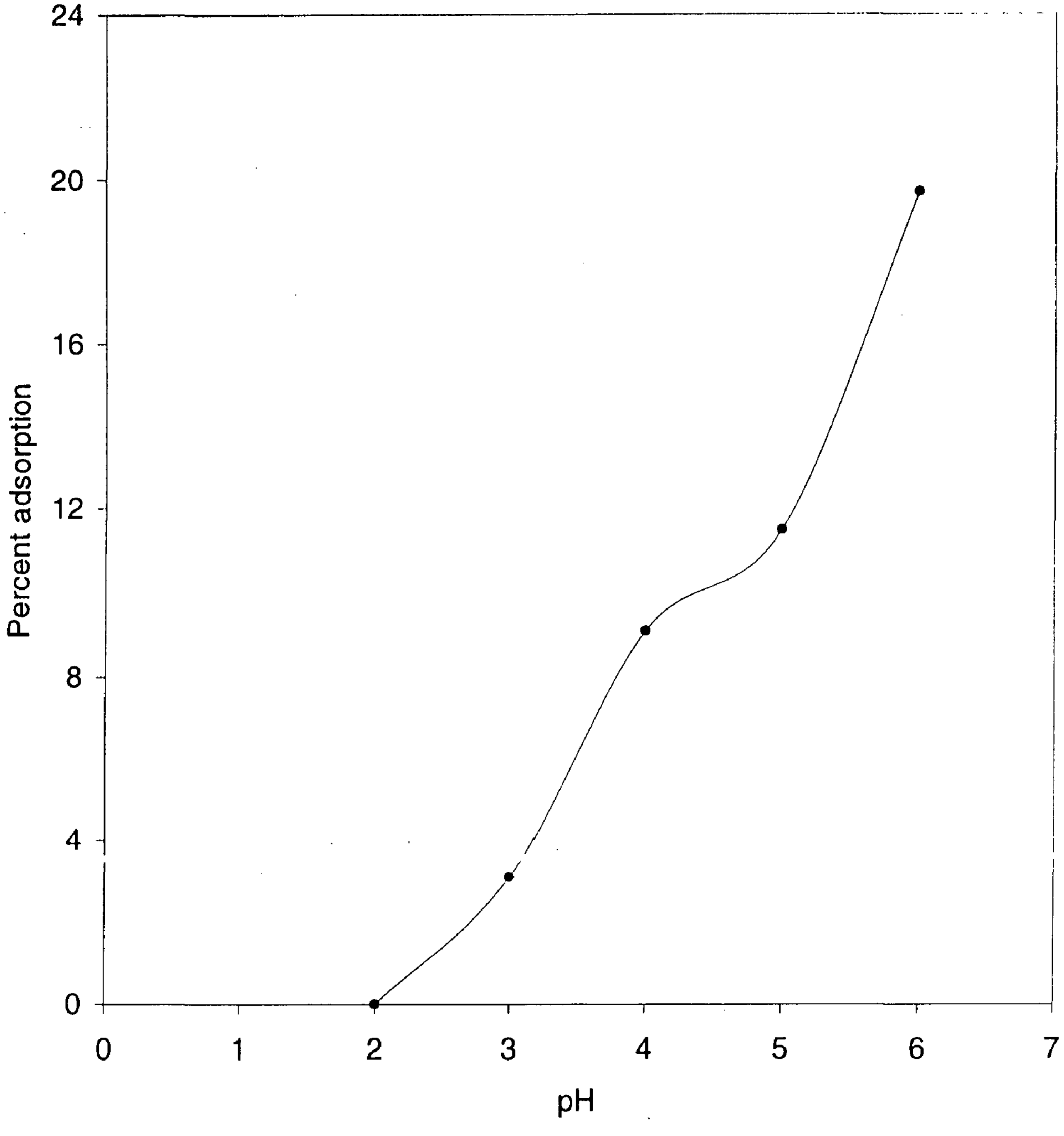

Fig.4b Effect of pH on percent adsorption of zinc on bed sediments of river Hindon (Adsorbent size 212-250 m; Adsorbent dose – 5g/l; Temperature –25^{0}C)

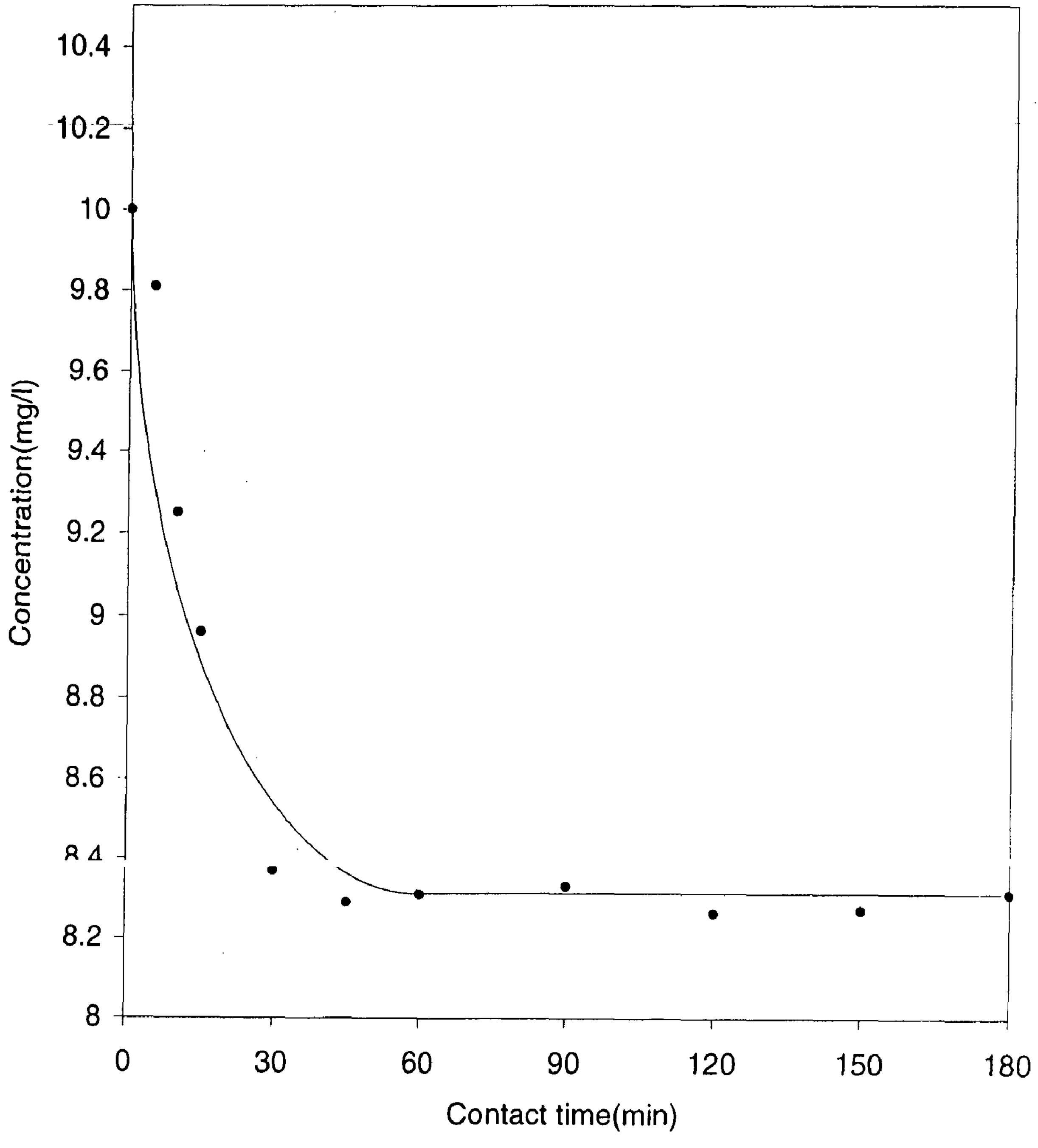

Fig5a Effect of contact time on adsorption of lead on bed sediments of river Hindon(Adsorbent size 212-250 micron; Adsorbent dose – 5g/l; pH – 5.0; Temperature –25^{0}C)

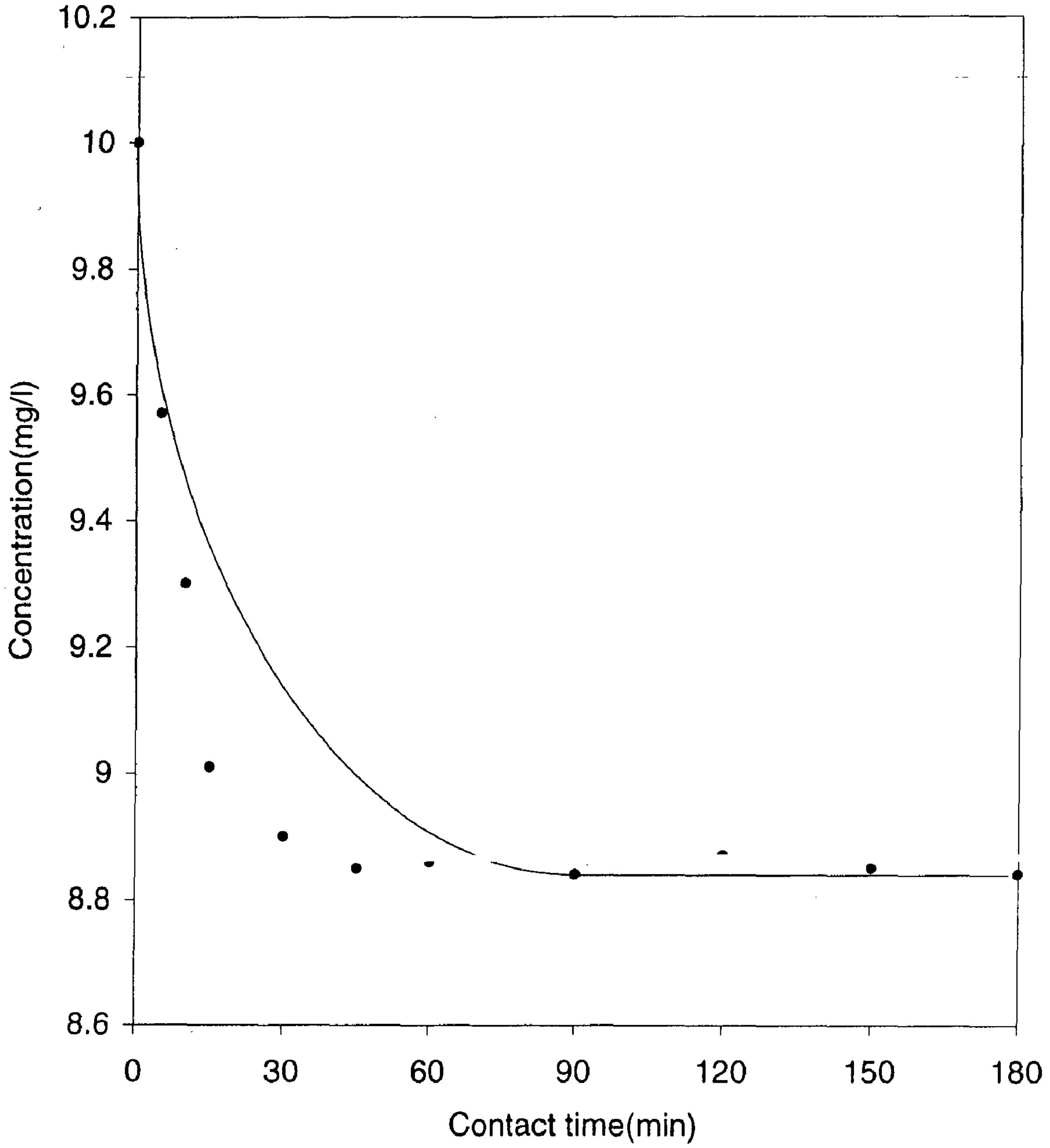

Fig.5 Effect of contact time on adsorption of zinc on bed sediments of river Hindon(Adsorbent size 212-250micron; Adsorbent dose – 5g/l; pH – 5.0; Temperature –25^{0}C)

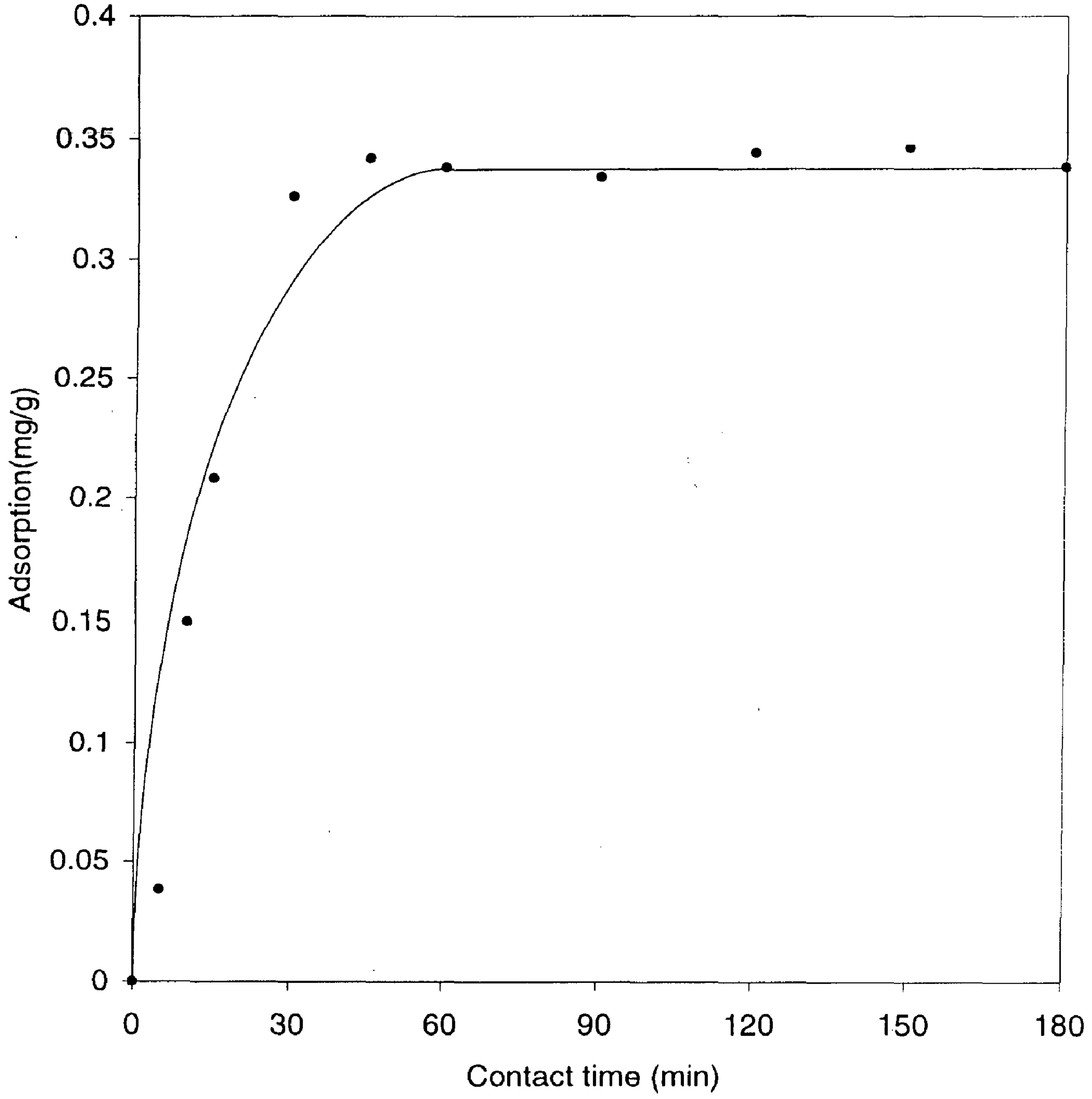

Fig.6a Effect of contact time on adsorption of lead on bed sediments of river Hindon(Adsorbent size 212-250 micron; Adsorbent dose – 5g/l; pH – 5.0; Temperature –25^{0}C)

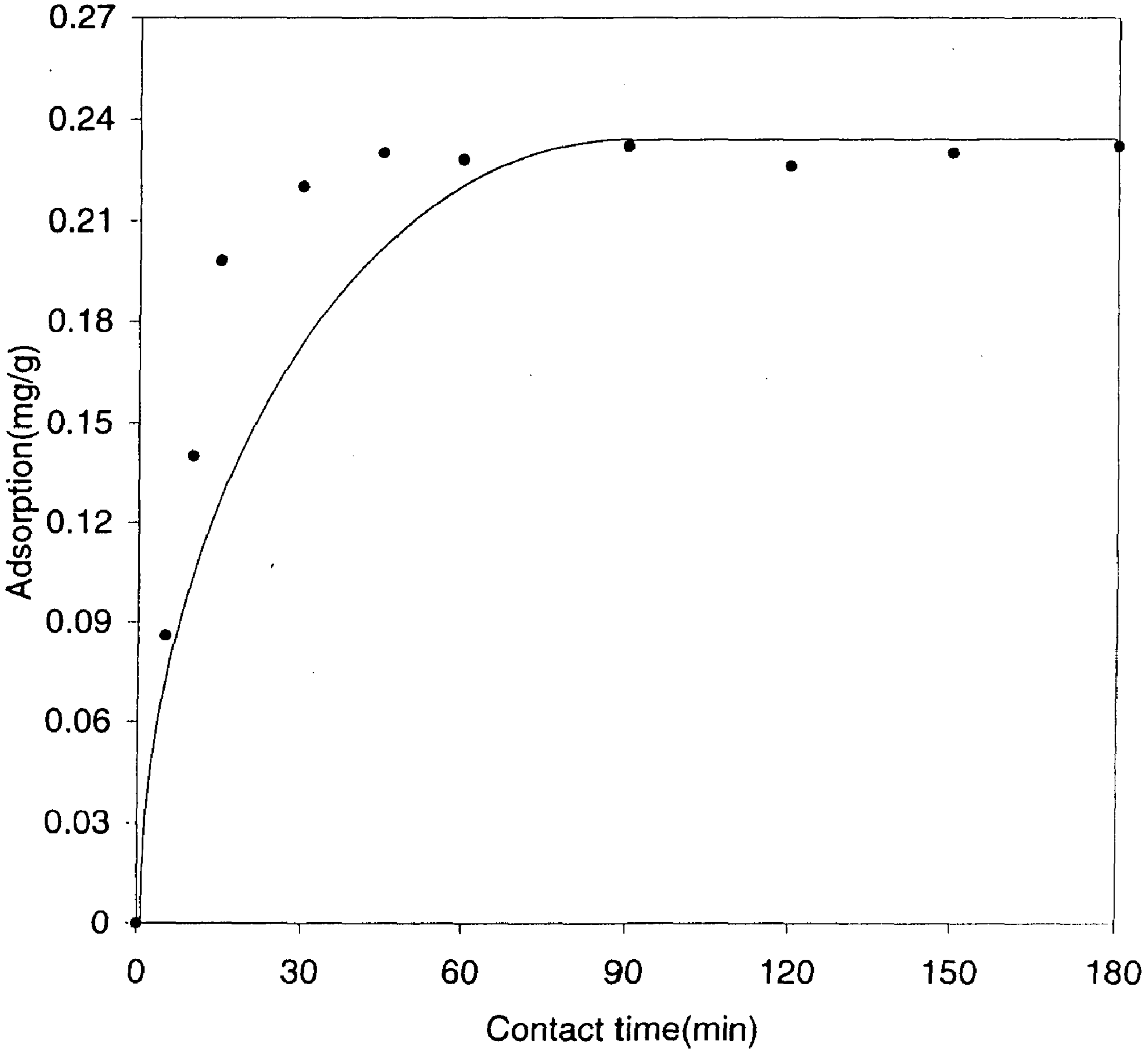

Fig6 Effect of contact time on adsorption of zinc on bed sediments of river Hindon(Adsorbent size 212-250micron; Adsorbent dose – 5g/l; pH – 5.0; Temperature –25^{0}C)

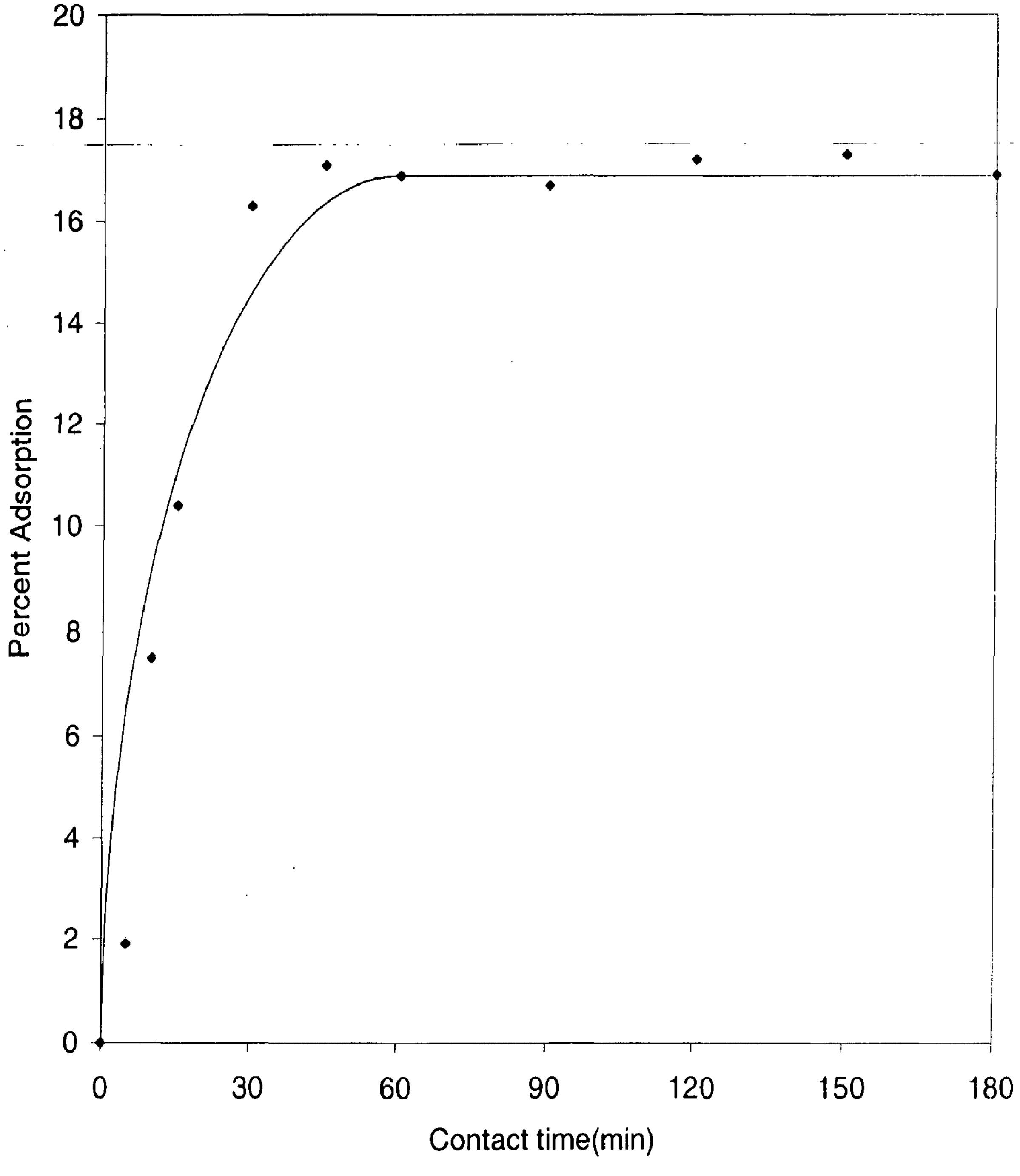

Fig.7a Effect of contact time on percent adsorption of lead on bed sediments of river Hindon(Adsorbent size 212-250 micron; Adsorbent dose – 5g/l; pH – 5.0; Temperature –25^{0}C)

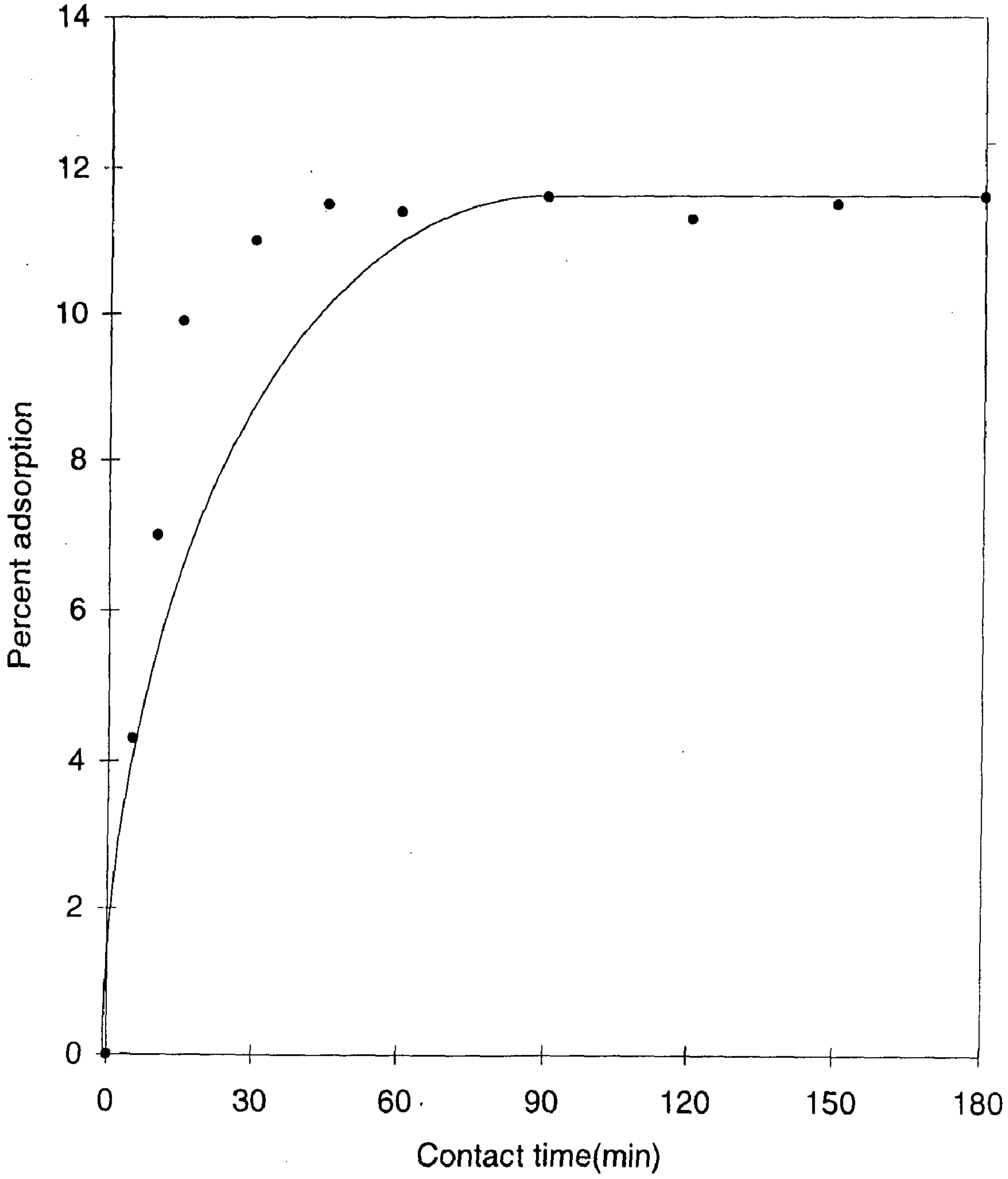

Fig.7. Effect of contact time on percent adsorption of zinc on bed sediments of river Hindon(Adsorbent size 212-250 micron; Adsorbent dose – 5g/l; pH – 5.0; Temperature –25^{0}C)

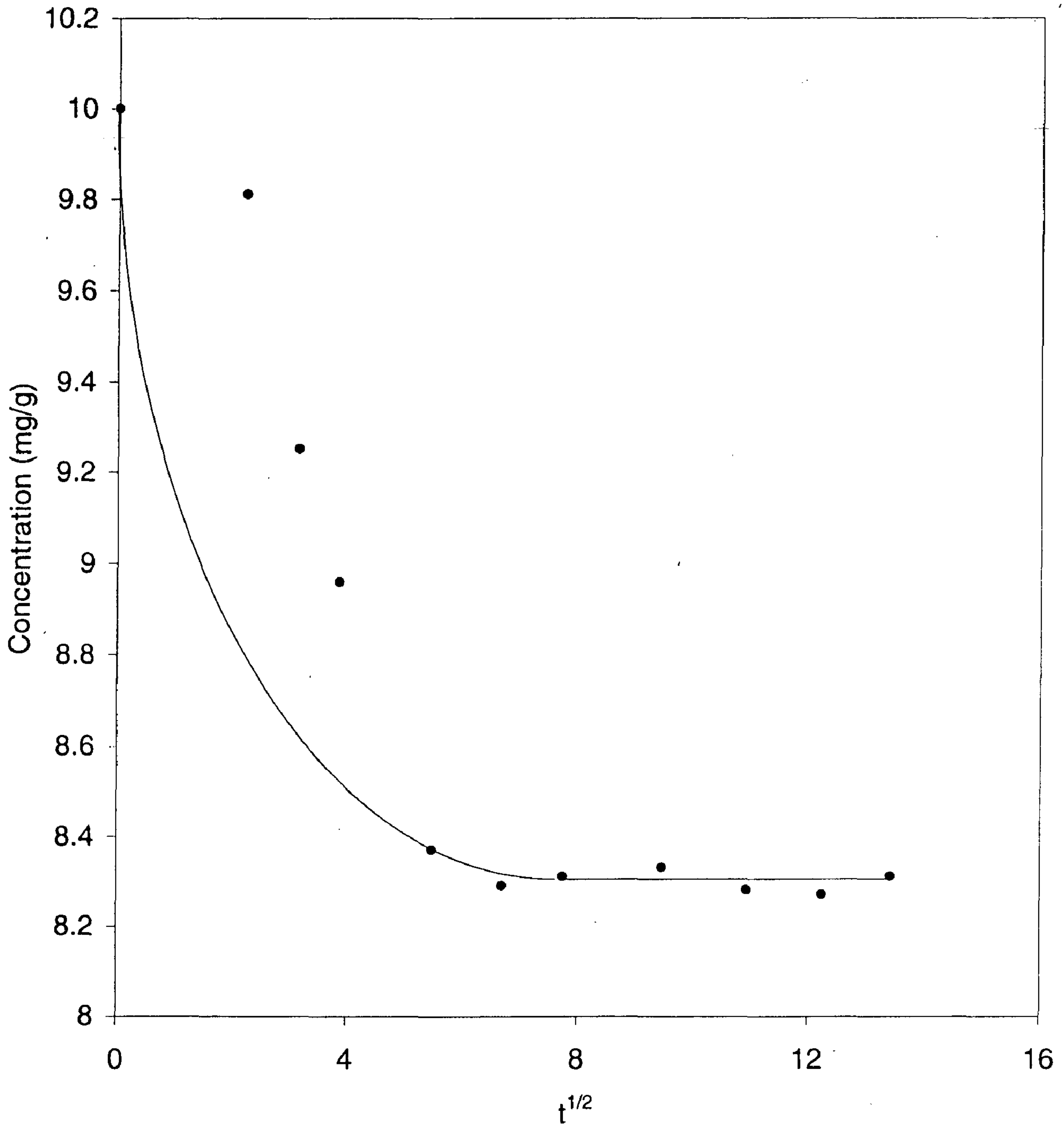

Fig.8a Effect of $t^{1/2}$ on adsorption of lead on bed sediments of river Hindon(Adsorbent size 212-250 micron; Adsorbent dose – 5g/l; pH – 5.0; Temperature –25^0C)

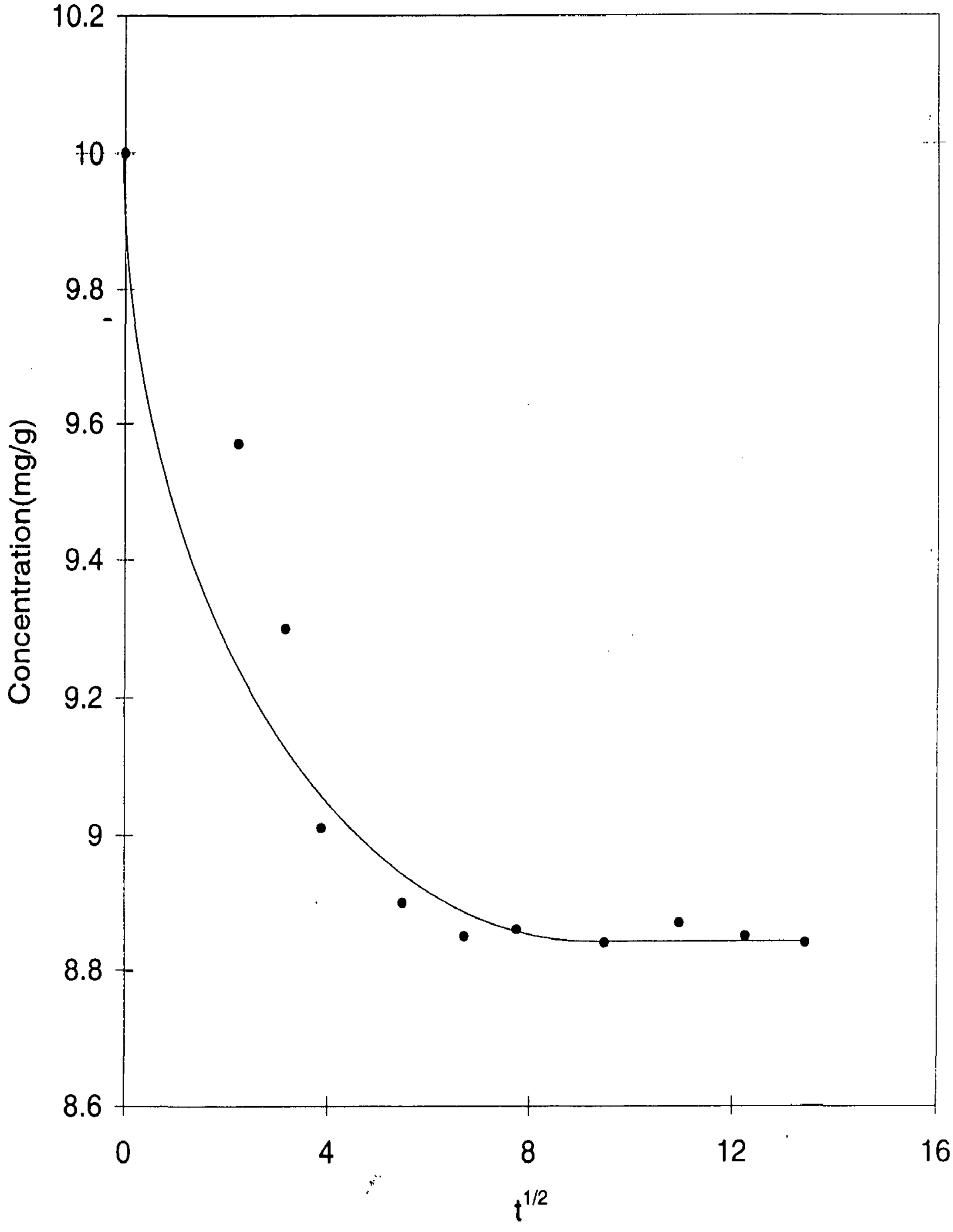

Fig8b Effect of $t^{1/2}$ on adsorption of zinc on bed sediments of river Hindon(Adsorbent size 212-250 micron; Adsorbent dose – 5g/l; pH – 5.0; Temperature –25^{0}C)

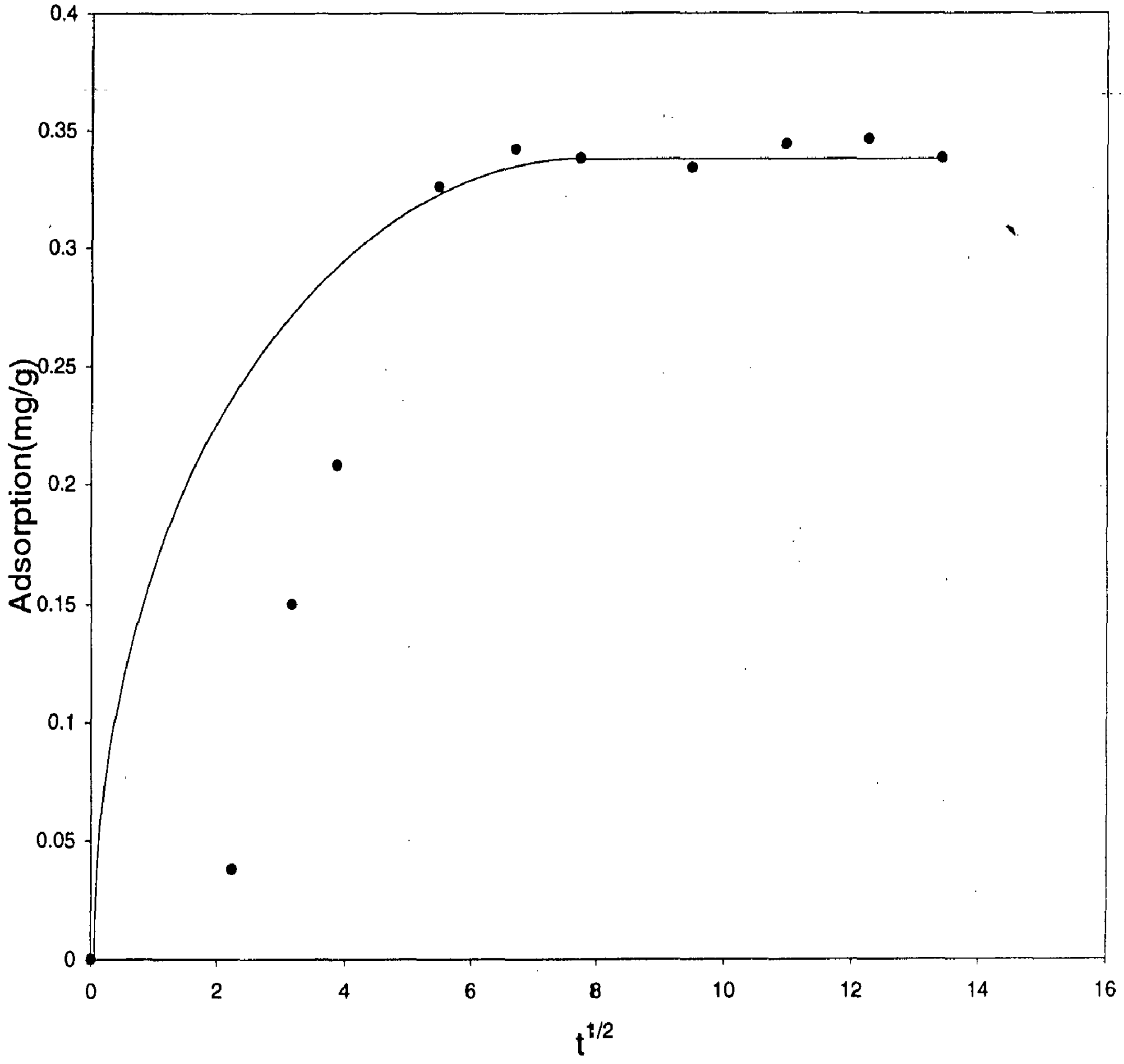

Fig.9a Effect of $t^{1/2}$ on adsorption of lead on bed sediments of river Hindon(Adsorbent size 212-250 micron; Adsorbent dose – 5g/l; pH – 5.0; Temperature –25^{0}C

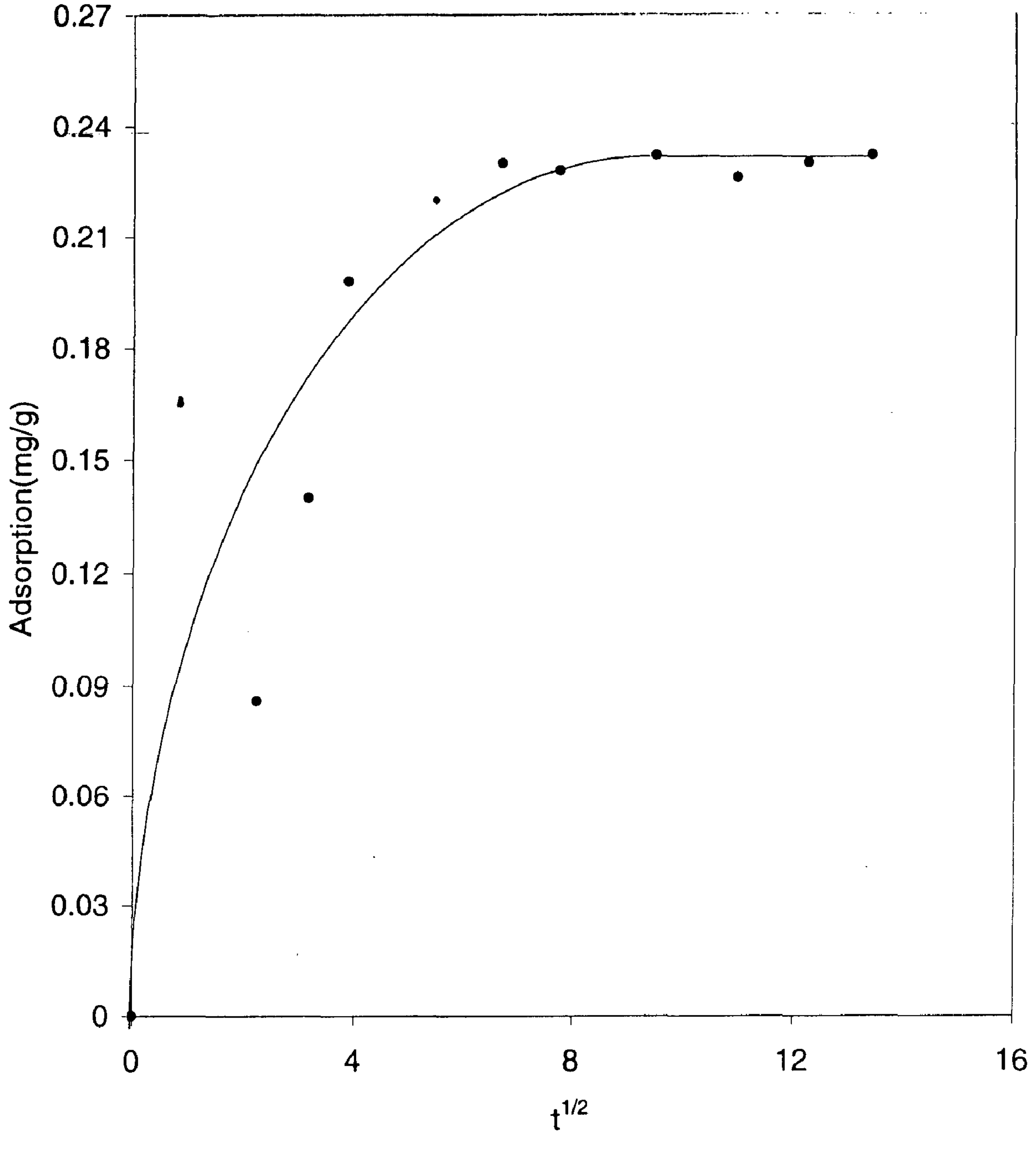

Fig.9b Effect of $t^{1/2}$ on adsorption zinc on bed sediments of river Hindon(Adsorbent size 212-250 micron; Adsorbent dose – 5g/l; pH – 5.0; Temperature –25^{0}C)

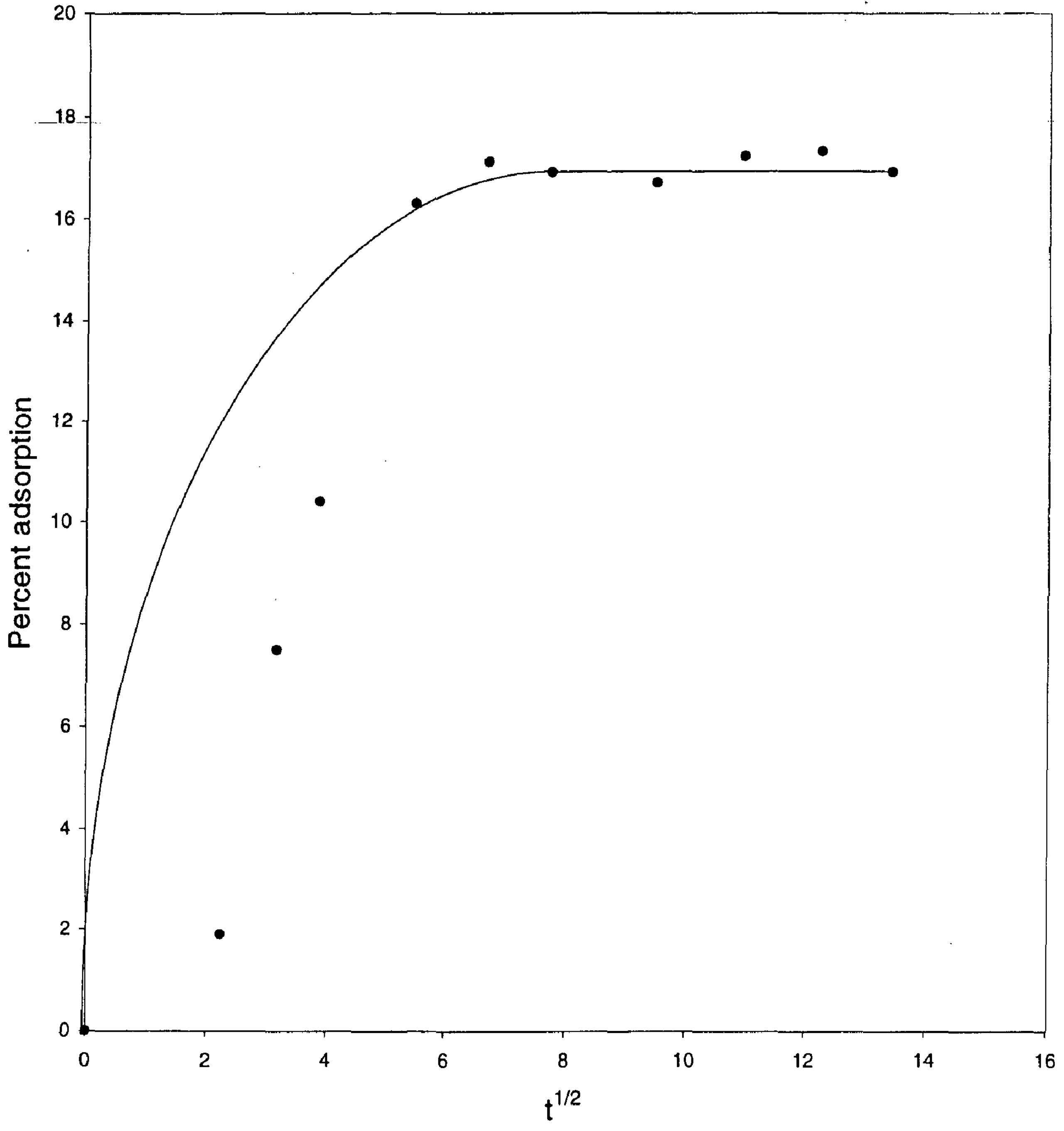

Fig.10a Effect of $t^{1/2}$ on percent adsorption of lead on bed sediments of river Hindon(Adsorbent size 212-250micron; Adsorbent dose – 5g/l; pH – 5.0; Temperature –25^{0}C)

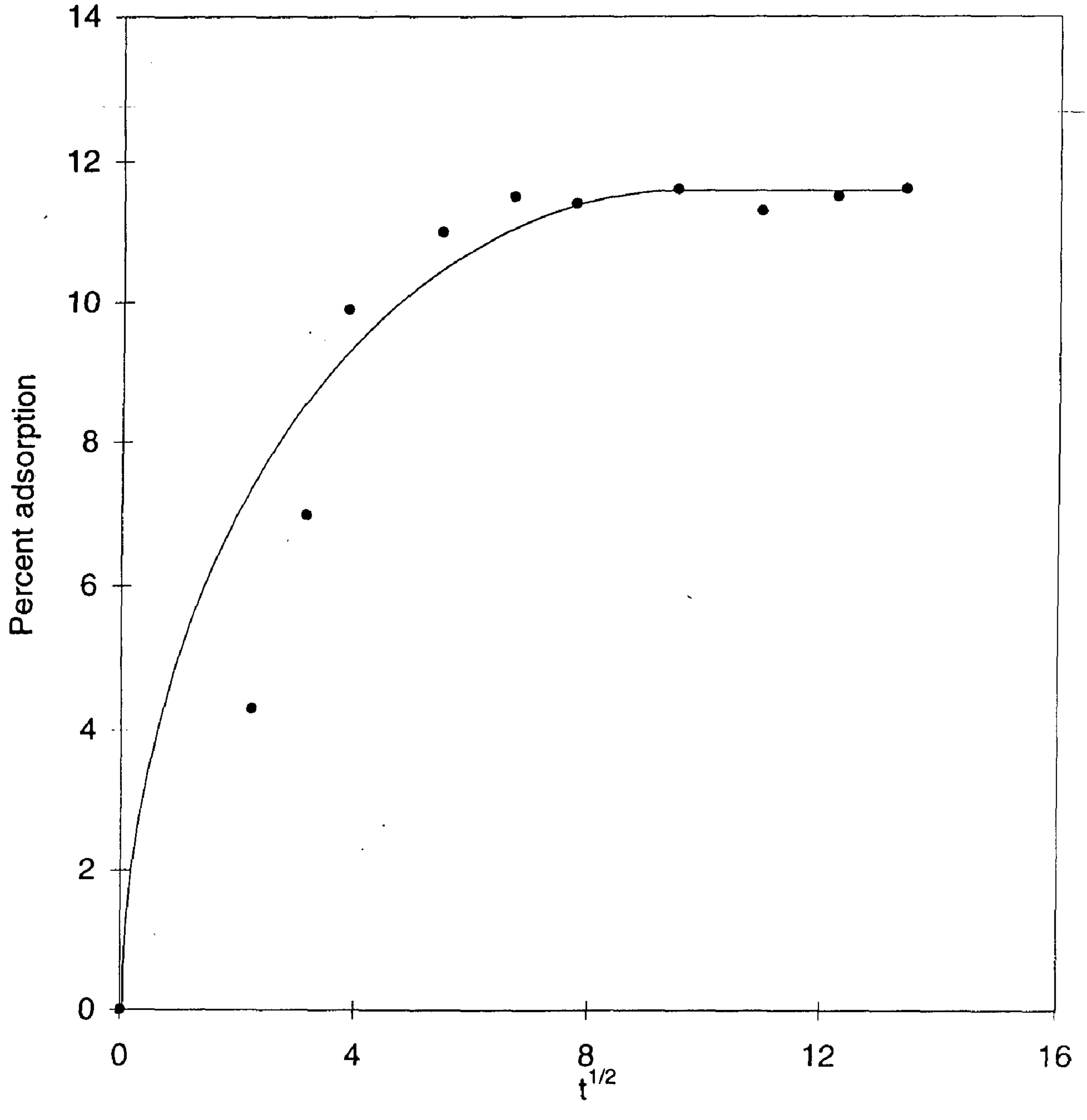

Fig.10b Effect of $t^{1/2}$ on percent adsorption of zinc on bed sediments of river Hindon(Adsorbent size 212-250 micron; Adsorbent dose – 5g/l; pH – 5.0; Temperature –25^{0}C)

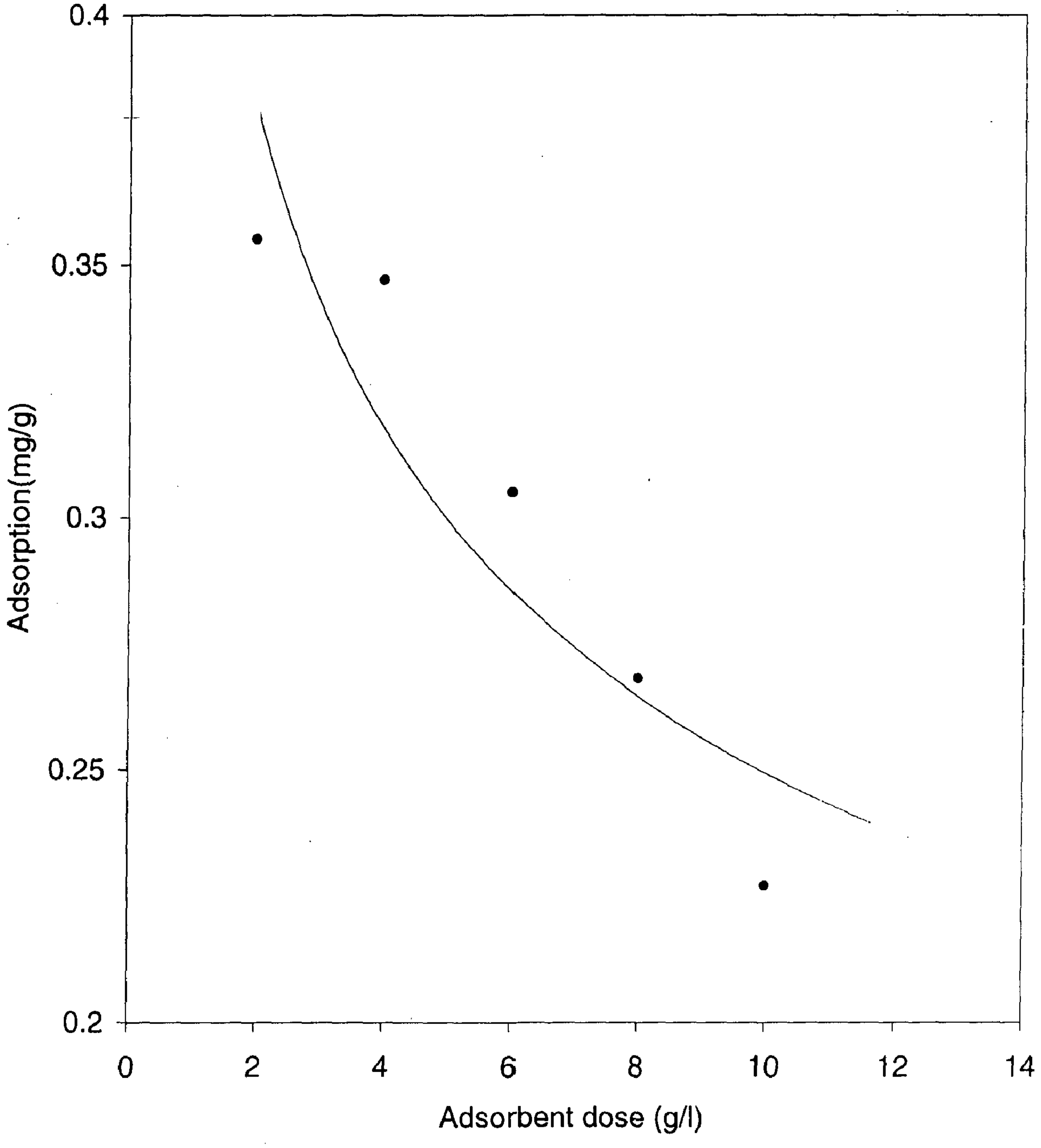

Fig.11a Effect of adsorbent dose adsorption of lead on bed sediments of river Hindon (Adsorbent size 212-250 micron; pH-5.0; Temperature-25^{0}C)

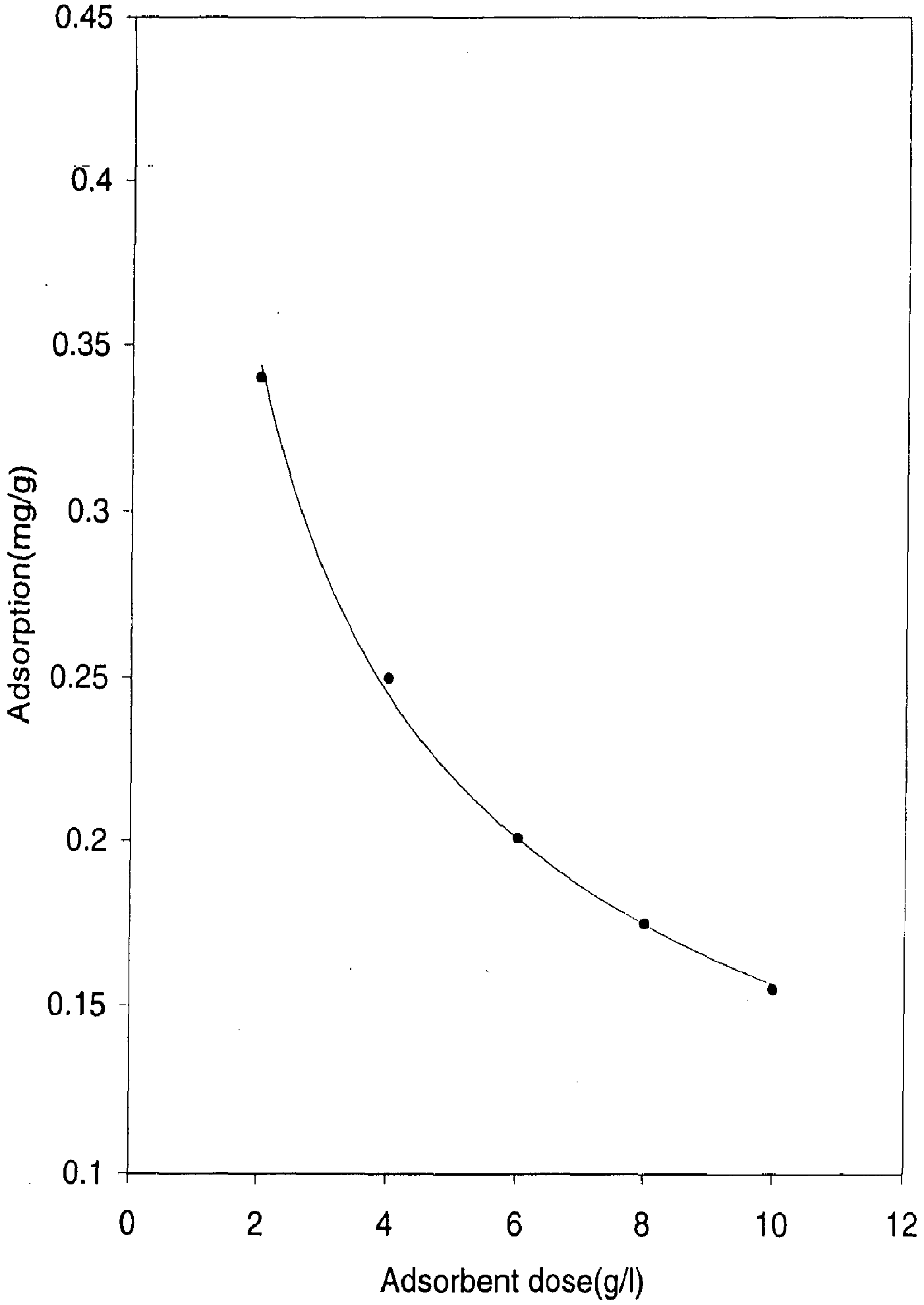

Fig.11b Effect of adsorbent dose on adsorption of zinc on bed sediments of river Hindon (Adsorbent size 212-250 micron;; pH-5.0; Temperature –25^{0}C

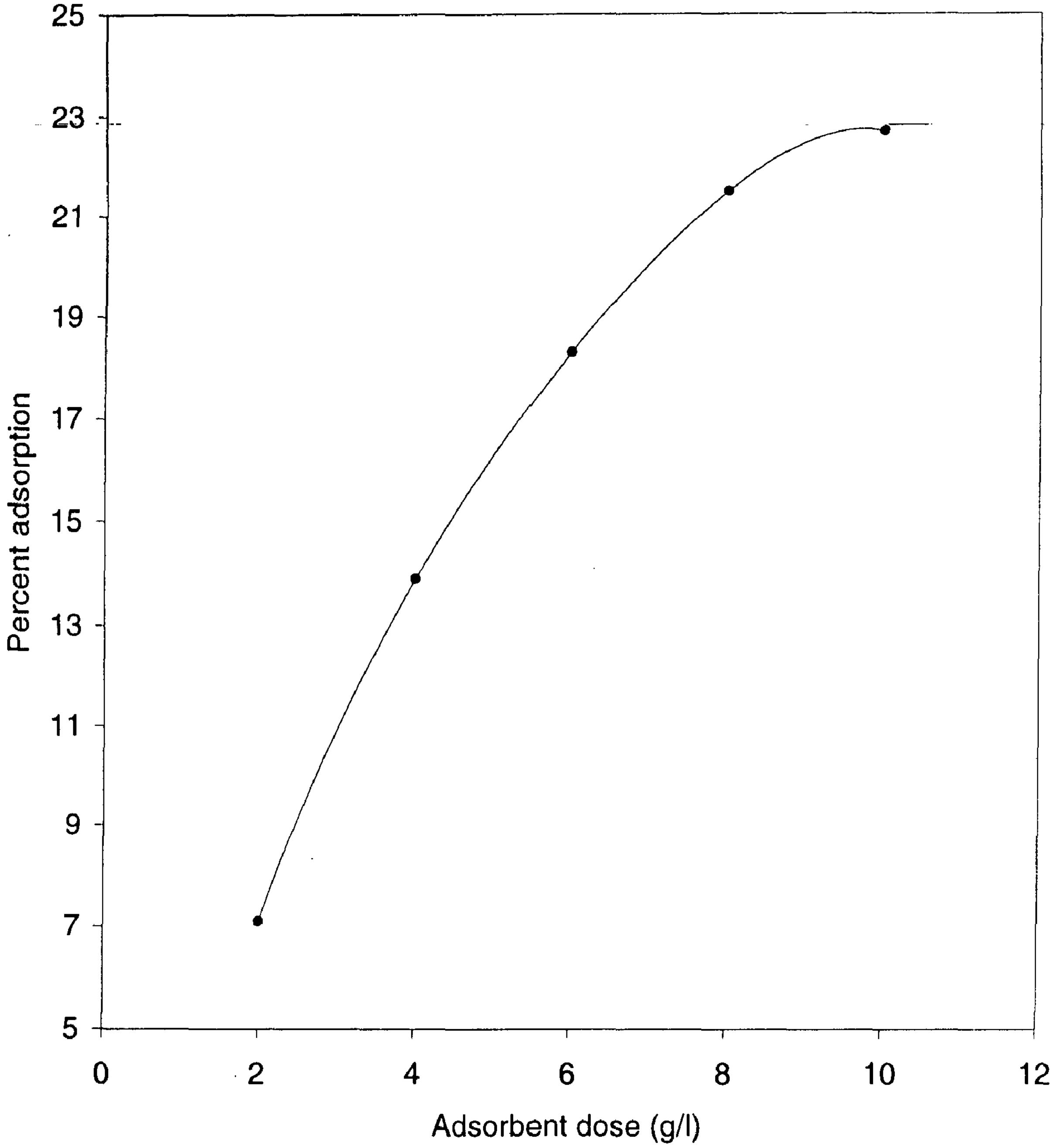

Fig.12a Effect of adsorbent dose on percent adsorption of lead on bed sediments of river Hindon (Adsorbent size 212-250 micron; pH – 5.0; Temperature –25^{0}C

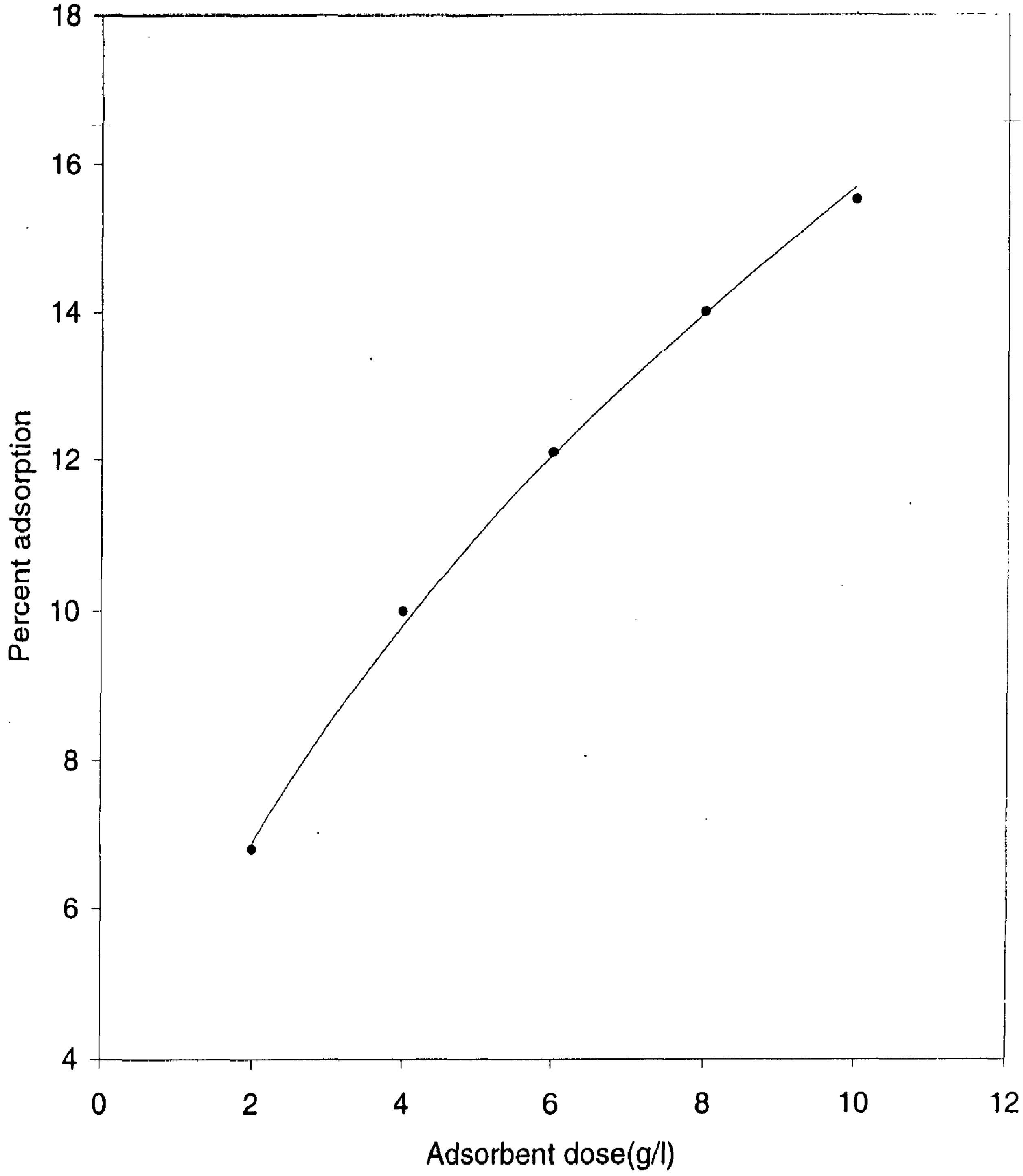

Fig.12b- Effect of adsorbent dose on percent adsorption of zinc on bed sediments of river Hindon (Adsorbent size 212-250 micron; pH – 5.0; Temperature –25^{0}C)

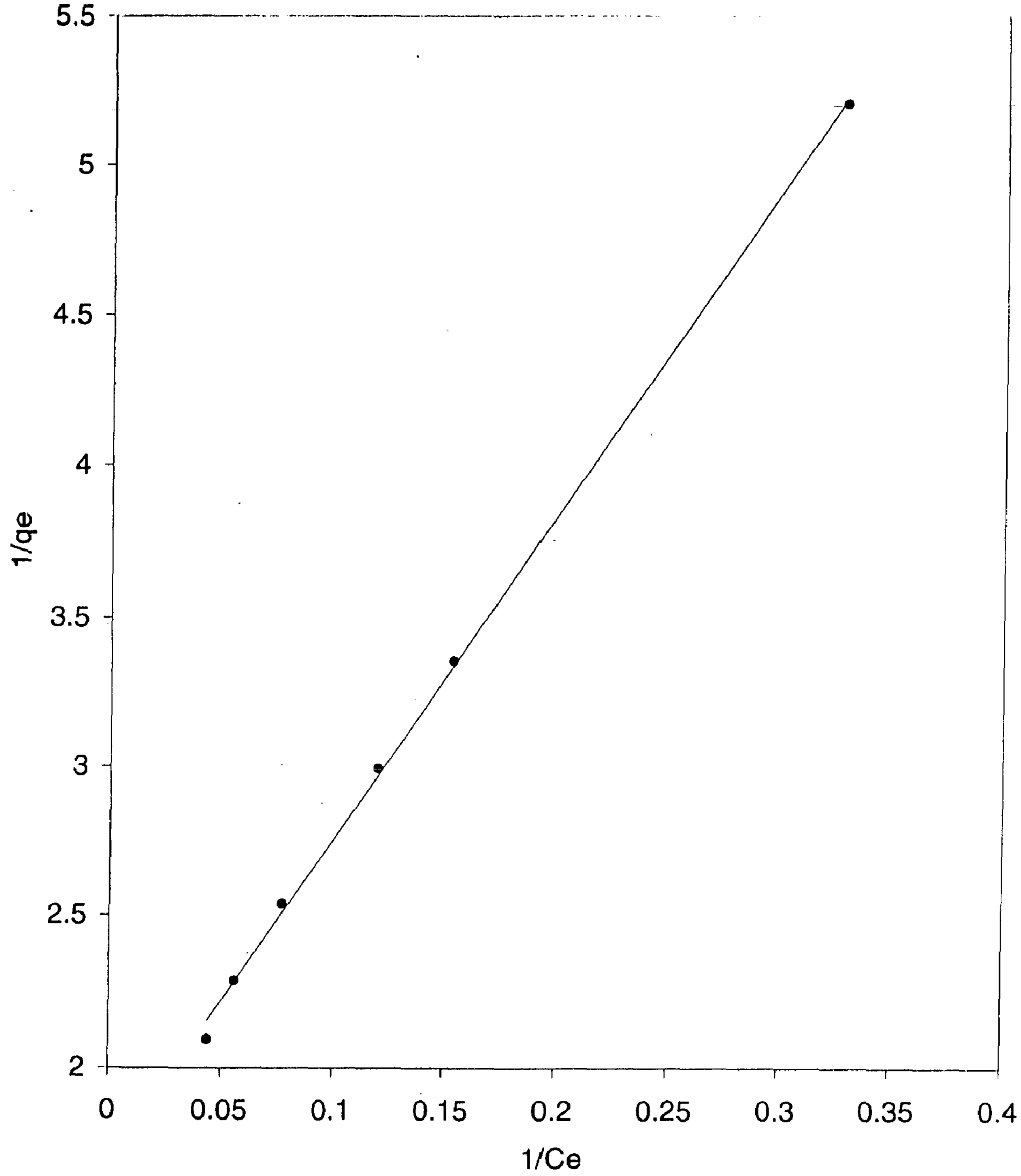

Fig.13a Graphical representation of langmuir isotherm for lead

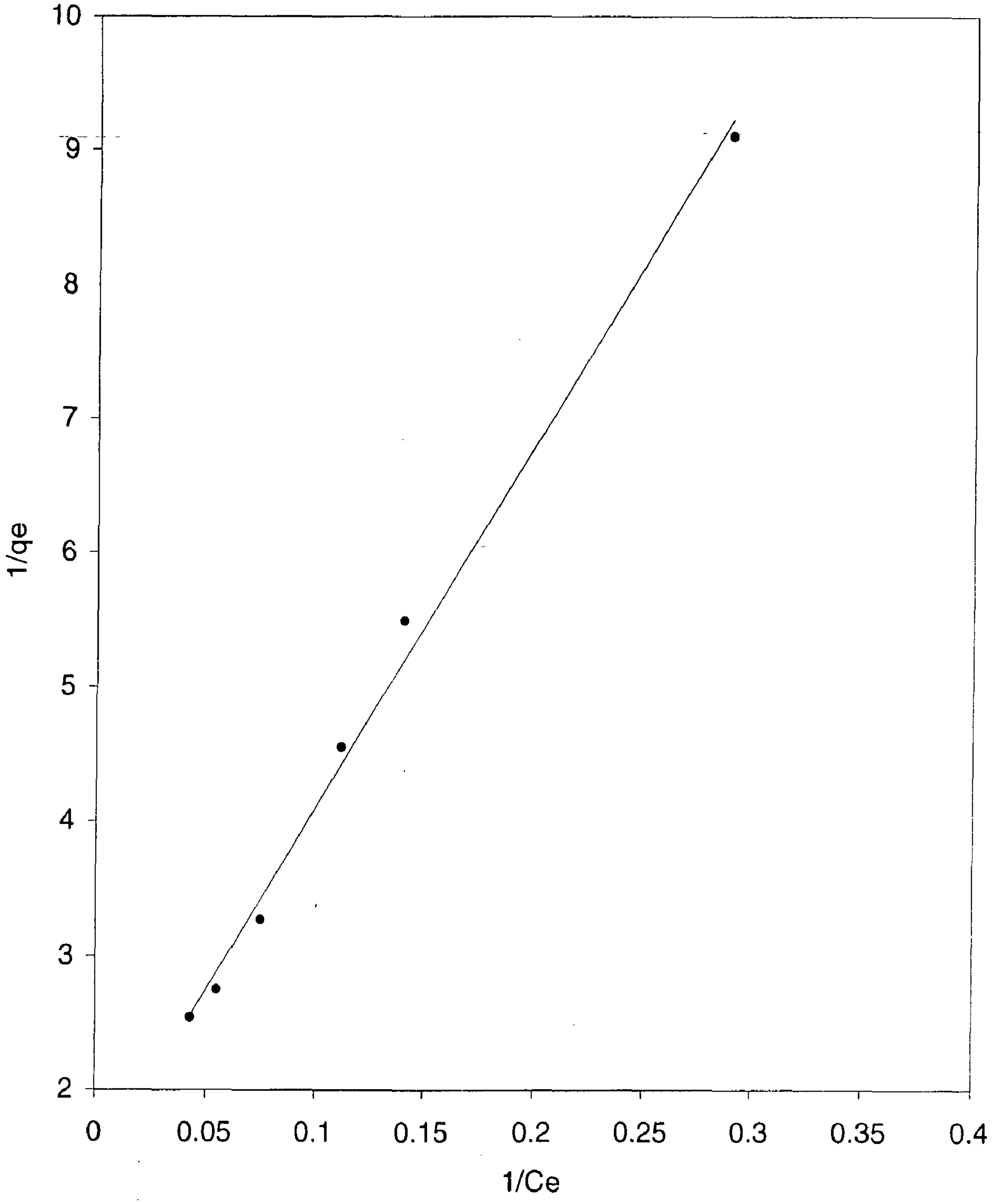

Fig.13b Graphical representation of Langmuir isotherm for zinc

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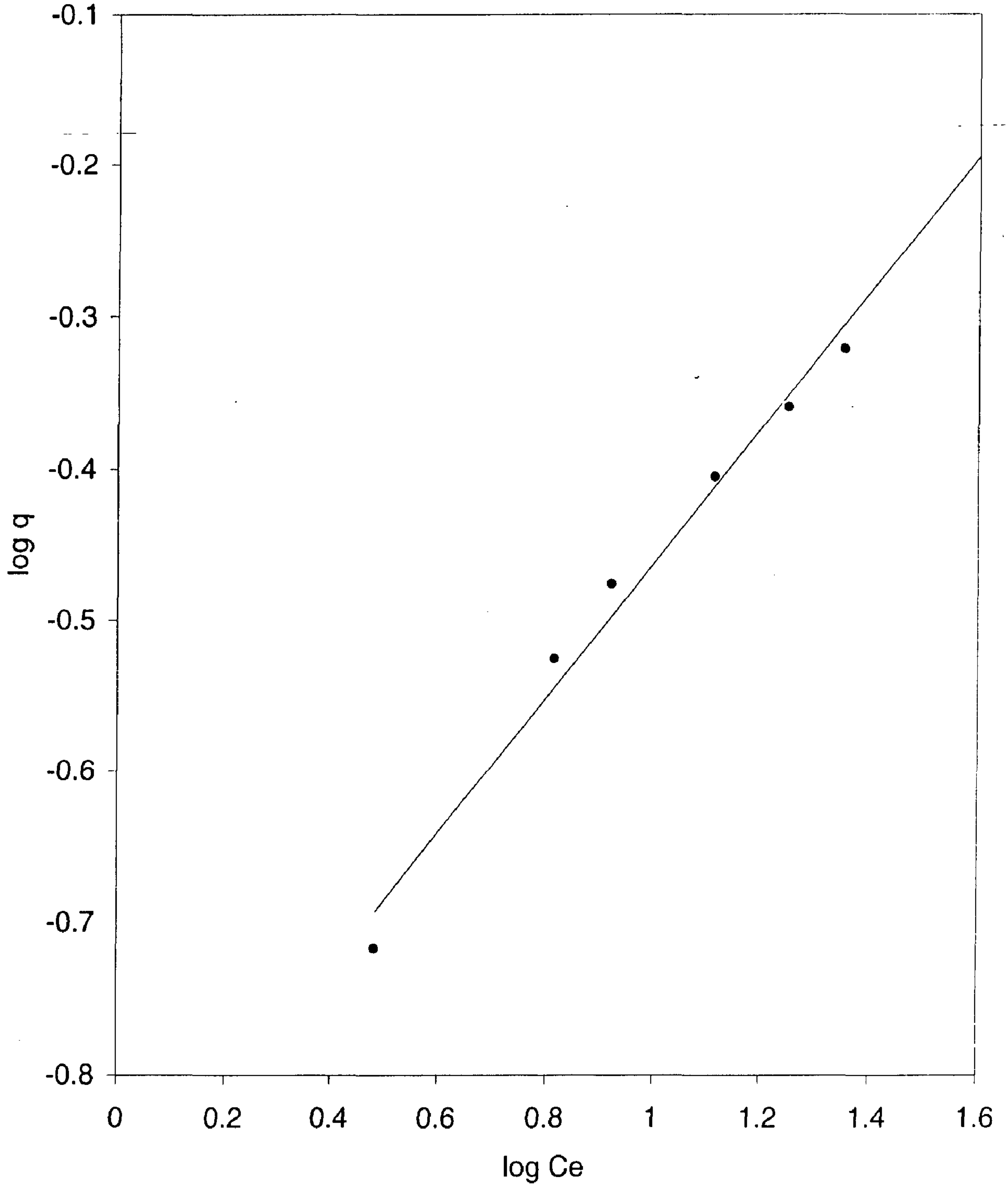

Fig.14a Graphical representation of Freundlich isotherm for lead

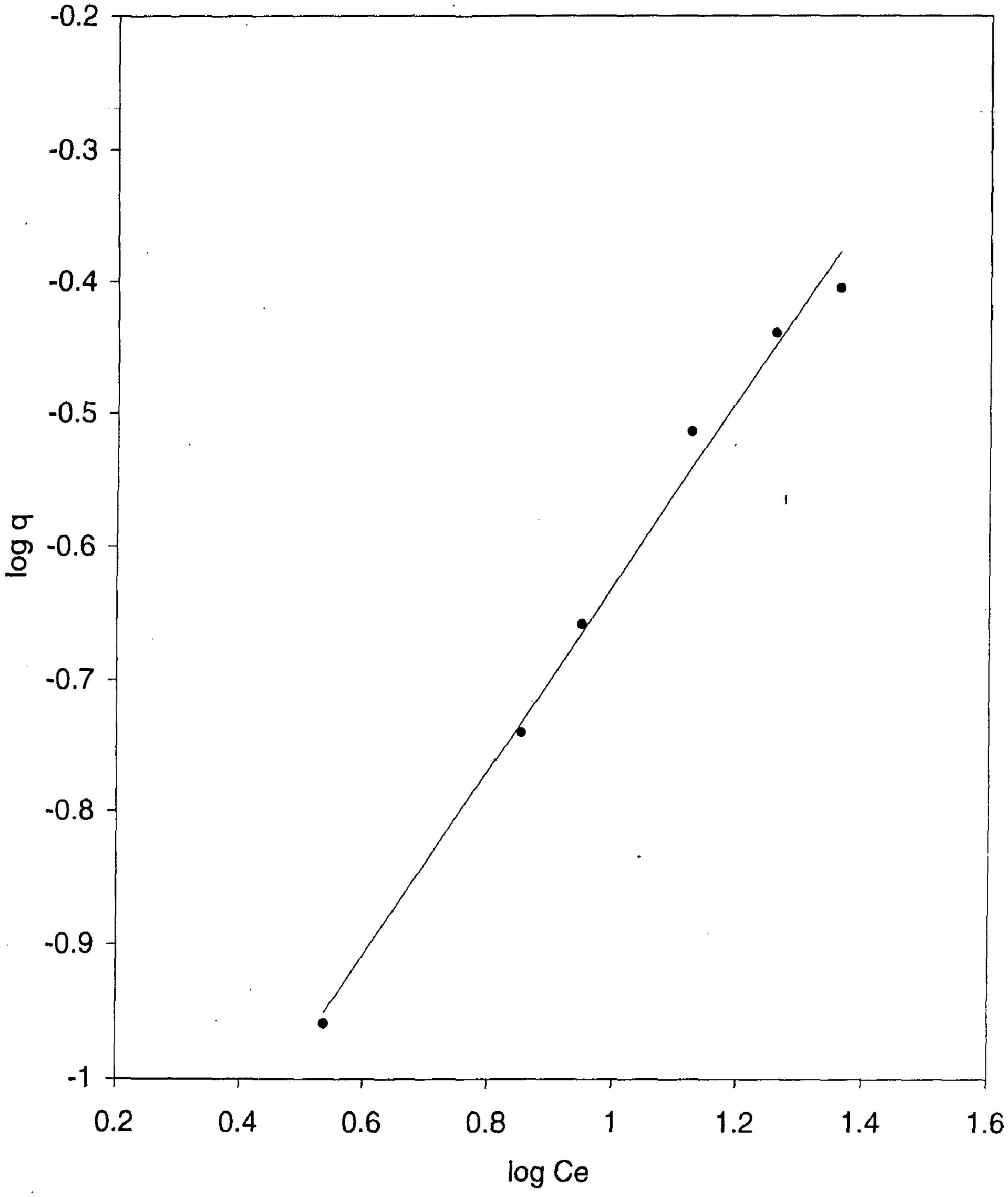

Fig.14b Graphical representation of Freundlich isotherm for zinc

CONCLUSIONS AND RECOMMENDATIONS

Adsorption of heavy metals on sediments represent an important control on their speculation and hence on their bioavailability and mobility in the aquatic environment. The most important parameter in the control of metal ion adsorption onto the riverbed sediments is the pH. The percent metal ion removal at equilibrium increases with increasing adsorbent doses. Among the two ions studied, it is concluded that the bed sediments of river Hindon 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.

Following are the recommendations for further work:

1. As it a rainy season river, study can be conducted at different seasons.
2. Similar study can be carried out for other metals also.
3. Sampling may be done from various locations upstream & downstream the river & the results can be compared.
4. Samples can be taken from different depths of the sediment & results be compared.

APPENDIX

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

Table2: Adsorption data for lead and zinc on bed sediments of river Hindon; Adsorbent size = 212 - 250 µm; pH = 5.0; Adsorbent dose = 5 g/L; Temperature = 25^{0}C.

Metal Ion	Initial conc. C_0 (mg/L)	Conc. Remaining at equilibrium C_e (mg/L)	Metal ion adsorbed		
			Mg/L	(µg/g)	(Percent)
Pb	4.00	3.04	0.96	192	24.0
	8.00	6.51	14.9	298	18.7
	10.00	8.33	1.67	334	16.7
	15.00	13.03	1.97	394	13.4
	20.00	17.81	2.19	438	10.95
	25.00	22.61	2.39	478	9.56
Zn	4.00	3.45	0.55	110	13.75
	8.00	7.09	0.91	182	11.4
	10.00	8.90	1.10	220	11.1
	15.00	13.37	1.53	306	10.2
	20.00	18.18	1.82	364	9.1
	25.00	23.03	1.97	394	7.88

Table3: Adsorption of lead and zinc on bed sediments of river Hindon at different pH values; Adsorbent size = 212-250 μm; Adsorbent does = 5 g/L; Temperature = 25^0C.

Metal ion	Initial conc. C_o (mg/l)	pH	Conc. After pH adjustment (mg/l)	Metal ion adsorbed	
				μ μg/g	Percent
Pb	10.00	2.0	9.95	10	0.5
		3.0	9.91	18	0.9
		4.0	9.72	56	2.8
		5.0	8.37	326	16.3
		6.0	7.61	478	23.9
Zn	10.00	2.0	Nil	Nil	Nil
		3.0	9.69	62	3.1
		4.0	9.09	182	9.1
		5.0	8.85	230	11.5
		6.0	8.03	294	19.7

Table 4: Adsorption of lead and zinc on bed sediments of river Hindon at different duration's of contact time; Adsorbent size = 212-250μm; Adsorbent does = 5 g/L; pH = 5.0; Temperature = 25^0C.

Metal ion	Initial conc. C_0 (mg/l)	Contact time, (min)	Conc. At time t (mg/l)	Metal ion adsorbed		
				mg/l	μg/g	Percent
Pb	10.0	5	9.81	0.19	38	1.9
		10	9.25	0.75	150	7.5
		15	8.96	1.04	208	10.4
		30	8.37	1.63	326	16.3
		45	8.29	1.71	342	17.1
		60	8.31	1.69	338	16.9
		90	8.33	1.67	334	16.7
		120	8.28	1.72	344	17.2
		150	8.27	1.73	346	17.3
		180	8.31	1.69	338	16.9
Zn	10.0	5	9.57	0.43	86	4.3
		10	9.30	0.70	140	7.0
		15	9.01	0.99	198	9.9
		30	8.90	1.10	220	11.0
		45	8.85	1.15	230	11.5
		60	8.86	1.14	228	11.4
		90	8.84	1.16	232	11.6
		120	8.87	1.13	226	11.3
		150	8.85	1.15	230	11.5
		180	8.84	1.16	232	11.6

Table5: Adsorption of lead and zinc on bed sediments of river Hindon at different adsorbent doses; Particle size = 212-250μm; Temperature = 25^0C pH = 5.0.

Metal ion	Initial conc. C_0 mg/l	Adsorbent dose, W_s (g/l)	Metal ion adsorbed	
			μg/g	Percent
Pb	10.0	2.0	355.00	7.1
		4.0	347.50	13.9
		6.0	305.00	18.3
		8.0	268.75	21.5
		10.0	227.00	22.7
Zn	10.0	2.0	340.00	6.8
		4.0	250.00	10.0
		6.0	201.67	12.1
		8.0	175.00	14.0
		10.0	155.00	15.5

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