CHAPTER – I

*Introduction*
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INTRODUCTION

Water demand continues to increase rapidly in India and other countries due to industrial development and human activities. Arsenic is the highly toxic chemical constituent thereby posing epidemiological problems to human health (Bagla, 1996). The intake of arsenic into the human body, approximately 50% of the arsenic is excreted in the urine (Das, 1995; Das et al., 1995), with small portions through the faeces, skin, hair, nails and lungs. Arsenic pollution has been seriously observed not only in various minerals and chemical process but also in some ground water or hot spring water over large areas in Bangladesh, West Bengal in India (Nickson, 1998), Inner Mangolia in China and Japan as well. A typical case in point is the State of West Bengal in India where ground water of at least six districts such as Malda, Murshidabad, Nadia, North 24 Parganas, and South 24 Parganas have been found to be contaminated with arsenic (Chakravarty and Dureja, 2002). Inorganic arsenic compounds particularly As$^{+3}$ are extremely toxic and have been described as sources of acute poisoning in humans and animals. Recent outbreaks of arsenic exposure in West Bengal have caused serious and fatal health hazards due to the consumption of ground water contaminated with concentrations of arsenic much above the WHO permissible limit of 50 µg/l. Most common arsenic species found in aqueous media are anionic species of arsenate and arsenite. The presence of toxic metals in ground water sources is an important issue of water and waste water treatment as their consequences on human health have been well established (Huang, 2000). Among them, arsenic contamination of ground waters concerns several countries around the world and has been recorded by WHO as a first priority issue. Arsenic is classified as one of the most toxic and carcinogenic chemical element (EPA, 2000), arsenic occurs in both inorganic and organic forms in naturals waters. Inorganic arsenic is the result of dissolution from the respecting mineral phase such as arsenic oxide (As$_2$O$_3$) or realgar (As$_2$S$_2$); it may be present in two oxidation states, as arsenate (As V) or arsenite (As III). Dominant arsenic species are a function of pH and redox potential. Arsenite is the thermodynamically stable form of inorganic species and generally predominates in surface water. Gao and Burau (1997) in a study about environmental factors affecting rates of arsine evolution from and
mineralization of arsenicals in soil reported that MMAA was not statistically detected from any DMAA treatment after incubation of soil. This indicated that MMAA was not an intermediate in DMAA demethylation and that DMAA degraded by simultaneously losing both methyl groups rather than by stages, first to MMAA and then to arsenate. In this study, MMAA was always the as species with the lowest concentration in the sludge solution, suggesting that MMAA was not an intermediate in the methylation of spiked-arsenite in sludge environments.

Methylation theoretically will not occur abiotically even if there is a supply of C, protein and other organic compounds because the C-C, C-N, and C-O bonds are more stable than C-As bonds (Williams, 1987; Gao and Burau, 1997). Thus, methylarsenic compounds (MMAA and DMAA) must be produced by microbial activity coupled to energy transfer system and the pH/Eh dependence of the observed speciation will be mainly related to pH/Eh range of tolerance of the native microbes. Toxicity of As to microorganisms is in the order (Carbonell-Barragancing et al., 2000):

**Arsenite > Arsenate > MMAA > DMAA**

In recent years, many researchers have applied iron oxide to the adsorption of heavy metals from metal bearing water. Adsorption is capable of removing metals over a wider pH range and lower concentrations than precipitation (Raji and Shubha, 1997). Most iron oxides are available only as fine powders or are generated in aqueous suspension as hydroxide floc or gel. In such forms, these oxides retain their desirable adsorptive properties for the trace metals, but they are limited to reactor configurations incorporating with large sedimentation basins or filtration unit. Under such conditions, the solid/liquid separation is fairly difficult. Besides, iron oxide alone is not suitable as a filter medium because of their low hydraulic conductivity (Theis, 1992).

The phenomenon is very common and finds useful applications for removal of unwanted or recovery of wanted materials from drinking water, are basically dependent on adsorption. The treatment of contaminant from water is carried out through conventional methods of treatment such as precipitation, coagulation, oxidation, biological technique (Khair, 1999) and by adsorption. Among these methods, adsorption is most attractive because of its high efficiency, low maintenance cost and ease of operation for treating drinking water. The common surface between the two phases where the adsorbed molecules concentrate is called the interface. Accumulation or retention of atoms, molecules or ions at a surface or interface between any two phases like gas-liquid, gas-solid, liquid-liquid or liquid-solid (Bailey and Bennett, 1992) is known as adsorption.
Hence, the existence of higher concentration of species at the surface of solid or liquid than in the bulk of the medium is known as adsorption. The substance that sticks or adheres to the surface is called adsorbate, and the surface on which the adsorbate settles is called adsorbent (Paige et al., 1997).

Recently, some researchers have developed the techniques for coating iron oxide on sand surface to overcome the problem of using iron oxide powders in water treatment process (Peryea, 1997; Theis, 1992). Iron-coated sands have been tested for removing of cations and anions from synthetic and real wastes (Satpathy and Chaudhary, 1995). The results from their studies confirm that the utilisation of iron-coated sand is worth developing for metal ions removal from water.

The study investigated the coating technology of iron oxide on the sand surface to use in water treatment. BET and SEM/EDX techniques of analysis were employed to investigate the properties of adsorption/desorption reactions for metals ions on the iron-coated sand surface in water. Results provide fundamentals of adsorption/desorption properties for the use of iron-coated sand (Manju and Raji, 1998). Attempts have been made to provide analytical methods that are routinely used together with other methods to detect and quantify arsenic at minute concentrations. The types of adsorption can be placed under two categories:

1.1 Physical Adsorption

Some adsorbates do not form strong chemical bonds with substrate atoms. This situation is called physical adsorption or physisorption (Scott and Green, 1995). It is due to the operation of forces between the solid surface and the adsorbate molecules, which are similar to the Vander Waals force, which exist between molecules. This type of adsorption is favored at low temperature and the heat of adsorption is of the order of 42 kJ mol\(^{-1}\) (10 kcal mol\(^{-1}\)) (Edwards, 1994).

1.2 Chemical Adsorption

The phenomenon is referred to as a chemisorption when the adsorbed molecules are held by chemical bonds to the molecules of the surface. In chemisorption, the adsorbate-adsorbate forces are usually small compared to the adsorbate-substrate binding forces, so that the adsorbate locations or sites are determined by the optimum adsorbate-substrate bonding. The heat of adsorption is greater than 83 kJ mol\(^{-1}\) (20 kcal mol\(^{-1}\)).
adsorption processes, whether physical or chemical in character, are accompanied by a decrease in free energy (Somorjai, 1994).

1.3 Theories of Adsorption

Various theories have been proposed to explain the mechanism involved in the adsorption process (Swedlund, 1999). The basic difference between the various theories of adsorption is mainly the nature of the interfacial forced domination. Some of the main theories which have been put forth to explain the adsorption from solutions on solid surface are chemical bond theory, residual valence theory, polarization theory, capillary condensation theory, thermodynamic potential theory, multimolecular theory, boundary layer theory, electron theory, and modern theory (Somorjai, 1994; Edwards, 1994).

The chemical bond theory explains successfully the chemical nature of the surface interactions between the adsorbent and adsorbate, the outer surface of the adsorbent being in a state of instauration exhibits residual valencies which can hold atoms, molecules or ions. Polarisation theory is helpful in explaining the adsorption of non-polar molecules on ionic adsorbents (Driehaus, 1998). Capillary condensation theory explains the adsorption on the basis of condensation of adsorbate species into the pores of the adsorbent and suggests that a thin layer of adsorbate molecules is formed inside the surface of the walls of the pores. Thermodynamic potential theory is based on the fact that adsorbent exerts a strong attractive force, which is responsible for the attraction of the adsorbate molecules in its vicinity and holds them at the surface of the adsorbent (Pokonova, 1998). B.E.T. theory is based on multilayer adsorption. According to boundary layer theory, the adsorption takes place as a result of electron transfer between the adsorbate and adsorbent (with semiconductor properties). Electron theory explains the process of adsorption in which charge transfer occurs and is accompanied by a change in conduction. The modern theory of adsorption is based on quantum and statistical mechanics (Pauling, 1993).

1.4 Adsorption Isotherms

Adsorption from aqueous solutions involves concentration of solute on the solid surface. When a solution is in contact with as solid adsorbent, molecules of adsorbate get transferred from the liquid to the solid until the concentration of adsorbate in solution is in equilibrium with adsorbent. No change in the concentration of the solute is observed when equal amounts of solute are being adsorbed and desorbed simultaneously. This is called adsorption equilibrium. The condition of equilibrium is
a characteristic of the entire system e.g., the solute, solvent, temperature, pH and so on. Adsorbed quantity at equilibrium increases with an increase in the solute concentration (Jain et al., 1997).

The equilibrium data at a given temperature are represented by adsorption isotherms and study of adsorption is of paramount importance in a number of chemical processes ranging from the design of heterogeneous chemical reactors to purification of compounds by adsorption (Prasad, 1994). The shape of the adsorption isotherms gives qualitative information about the adsorption process and the extent of the surface coverage by the adsorbent. All isotherms share a number of common features. In many chemical engineering operations both equilibrium and kinetic data are required to design an adsorption unit. As most adsorption processes are dynamic, equilibrium data for adsorbents are primarily of use for determining the absolute capacity of a particular adsorbent for a certain adsorbate (Ahmann, 2002).

Several mathematical relationships have been developed to describe the dynamic equilibrium distribution of adsorbate between the adsorbent and the bulk liquid phases (Vagliasindi, 1996). These relationships apply when the adsorption tests are conducted at constant temperature and are referred to as adsorption isotherms. Several workers have attempted to present mathematical models for describing the dynamic equilibrium of adsorption (Haron, 1999). Langmuir, Freundlich and B E T adsorption isotherms are the most commonly used models for describing the dynamic equilibrium.

Langmuir Adsorption Isotherm

Langmuir’s model assumed the surfaces of sorbents to be homogeneous and the sorption energies to be equivalent for each sorption sites. The basic assumption underlying the Langmuir’s model which is also called the ideal localized monolayer model, are:

* The molecules are adsorbed on definite sites on the surface of the adsorbent.
* Each site can accommodate only one molecule (monolayer). The area of the adsorbent site is fixed and the quantity of adsorbate is determined solely by the geometry of the surface, and
* The adsorption energy is the same at all active sites.

In addition, the adsorbed molecules can not migrate across the surface or interact with neighbouring molecules. The Langmuir equation was originally derived from kinetic considerations. Later it was derived on the basis of statistical mechanics, thermodynamics,
the law of mass action, the theory of absolute reaction rates and Maxwell-Boltzmann distribution law. The Langmuir isotherm can be represented by

\[ q_e = \frac{Q^0 b C_e}{1 + b C_e} \]

or

\[ \frac{C_e}{q_e} = \frac{1}{Q^0} C_e + \frac{1}{Q^0 b} \]

Where \( C_e \) (mg L\(^{-1}\)) is the equilibrium concentration, \( Q^0 \) and \( b \) are the Langmuir constants related to the capacity and energy of adsorption, respectively. A plot of \( C_e/q_e \) versus \( C_e \) gives a straight line with slope, \( 1/Q^0 \) and intercept, \( 1/Q^0 b \) (Stumm, 1987).

The Mass balance formula of this model is following-

\[ Q = (C_0 - C_{eq}) \times \frac{V}{M} \]

Where,

\( V \) = Volume of the solution (ml)
\( M \) = Sorbent Mass (gm)
\( C_0 \) = Initial Concentration (mg/lit)
\( C_{eq} \) = Equilibrium Concentration (mg of arsenic/ lit)

**Freundlich Adsorption Isotherm**

Freundlich based on the exponential distribution of the sorption sites as and energies, moreover, the molecules adsorbed on the surface can interact. It is developed an empirical equation for the adsorption isotherm, which encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies. Freundlich adsorption equation can be expressed as

\[ \frac{x}{m} = k_F C_e^{1/n} \]

\[ \log \frac{x}{m} = \log k_F + \frac{1}{n} C_e \]

Where \( x/m \) is the amount adsorbed in mg, g\(^{-1}\), \( k_F \) is a rough measure of the adsorption capacity and \( C_e \) is the equilibrium concentration of the arsenic solution. A plot of \( \log x/m \) versus \( \log C_e \) gives a straight line with intercept, \( \log k_F \) and slope, \( 1/n \) (Razakovic, 1992).

**B E T Adsorption Isotherm**
B E T adsorption isotherm was developed by Brunauer, Emmett and Teller for the generalization of the ideal localized treatment to account for multilayer adsorption. The B E T model is based on the assumption that each molecule in the first adsorbed layer serves as a site for adsorption of a molecule into the second and so on. The heat of adsorption, E of the second and subsequent layer is assumed to be equal to the heat of liquification of the bulk liquid and is therefore, different from the heat of adsorption of the first layer (Gupta, 1994; Glasstone, 1969).

The B E T equilibrium isotherm can be represented by

\[ q_e = \frac{a_B Q^0 C_e}{(C_S - C_e)[1 + (a_B - 1)C_e/C_S]} \]

or

\[ \frac{C_e}{q_e(C_S - C_e)} = \frac{a_B - 1}{a_B Q^0} \frac{C_S}{C_S} + \frac{1}{a_B Q^0} \]

Where \( C_s \) is the saturation concentration of solute, \( C_e \) is the measured concentration in solution at equilibrium, \( Q^0 \) is the number of moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface, \( q_e \) is the number of moles of solute adsorbed per unit weight of adsorbent and \( a_B \) is a constant signifying the energy of interaction with surface of the adsorbent. A plot of \( C_e/q_e(C_S - C_e) \) versus \( C_e/C_S \) should give a straight line having slope of \( (a_B-1)/a_B Q^0 \) and intercept, \( 1/a_B Q^0 \).

1.5 Factors Influencing Adsorption

Various parameters, which affect the rate and extent of adsorption, are given below:

(i) Nature of adsorbent
(ii) Nature of adsorbate
(iii) Concentration
(iv) Temperature
(v) pH

A brief account of all the above factors is given below:

**Nature of Adsorbent**

The extent of adsorption is largely dependent on the physico-chemical properties of the adsorbent such as surface area, particle size, porosity and residual charges on the surface of adsorbent. The nature of the adsorbent depends mainly on the chemical
composition of the solid, whereas, the surface that is responsible for adsorption is affected markedly by the presence of pores, edges, corners, cracks and any pretreatment, given to the adsorbent.

**Nature of Adsorbate**

The adsorption at a solid-solution interface is greatly influenced by the physico-chemical characteristics of the adsorbate, like molecular weight, molecular size, and electrical charge, capacity for aggregation, the degree of dissociation, solubilization and ionization. Solutes, which form the least soluble adsorption products or those exhibiting tendency for micelle formation, are usually adsorbed to the largest extent. Such excessive adsorption has been found in the adsorption of arsenic as micelles and in other substances such as heavier aggregates (Raghavan et al., 1998).

**Concentration**

The ionic concentration of an arsenic solution has remarkable effect on the uptake of ions by the surface of adsorbents. It is often observed that the process of adsorption at any particular temperature becomes complicated due to the formation and overlapping of mono and multilayer adsorption as well as capillary condensation. The extent of adsorption on a given adsorbent depends on the concentration of the adsorbate solution. It shows usually a regular increase to reach finally saturation.

**Temperature**

The temperature of the system significantly influences the rate and extent of adsorption. The rate of adsorption normally increases with decreasing temperature of the system, but in few cases the rise in temperature favours the rate of adsorption. The nature of adsorption and its thermodynamics have been studied by several investigators (Wasay, 1996).

**pH**

The pH of the solution is found to be very effective in deciding the amount of adsorption especially if the solid adsorbents are prone to surface alteration due to changes in the hydrogen ion concentration. The pH of the adsorbent-adsorbate system is one of the most important factors, which prominently affects the rate, extent, and mechanism of adsorption. The adsorption of cations generally increases at optimum pH of the solution.
The variation in adsorption with pH of the solution has been explained on the basis of competitive adsorption of H⁺/OH⁻ ions with the adsorbate species and also the aqua complex formation (Farrell, 2001).

1.6 Adsorption from Solutions

A solid surface in contact with a solution has the tendency to accumulate surface layer of solute molecules due to imbalance of surface forces. This accumulation of molecules at an interface is a vectorial function of the forces of attraction and repulsion to and fro solution and fro and to the adsorbent, respectively. Majority of the substance accumulated at the interface are adsorbed onto the large surface area within the pores of adsorbent and relatively a few are adsorbed on the outside surface of the particle (Alauddin, 2000). The affinity of adsorbate molecules for adsorbent varies with force field at liquid-solid interface. Adsorption of solutes from a solution is influenced largely by the competition between the solute and the solvent molecules for adsorption sites. The tendency of a particular solute to get adsorbed is determined by the difference in the adsorption potential between the solute and the solvent. When the solute-solvent affinity is large, the ability of the adsorbent to absorb solute is usually limited. The low adsorption capacity of polar adsorbents like zeolites for solutes in a polar solvent like water is an example of this phenomenon (Pal et al., 1996; Viraghavan, 1999). In general, lower the affinity of the adsorbent for the solvent, the higher will be the adsorption capacity for solutes. Activated carbon and polymeric adsorbents have high adsorption capacities in water primarily because a slow adsorption potential energy is needed on the part of an adsorbent. Conversely, adsorption from a non-polar medium would be most effectively accomplished using a polar solvent. Low affinity of the solvent for the adsorbent is not by itself sufficient to guarantee high adsorption capacity. The affinity of the solute for the surface must also be larger than the affinity of the solute for the solvent for adsorption to be highly favored. The solubility is a direct measure of the affinity of the solute for the solvent, and an inverse relationship between the adsorbate solubility and adsorption capacity has been observed. Less soluble solutes tend to adsorb more readily and more soluble ones tend to adsorb less readily (Vilyssider, 1998)

The influence of solubility on adsorption capacity is of great importance in adsorbent-solvent systems with low mutual affinity (such as coated sand and water) because the solute-solvent and adsorbent-solvent interaction potentials are not completely independent of each other. The attractive potentials between molecules that cause one
species to be soluble in another arise from the same forces (Vander Waals and electrostatic) that cause adsorption. Therefore, exactly those properties of a solute, which result in high solubility in the solvent, are likely to result in low affinity for the adsorbent and vice-versa (Franz, 2000).

Polarity is used here in a general sense of ability to engage in the hydrogen bonding of dipole-dipole interactions. Adsorption from solution is generally limited to monolayer coverage of the adsorbent surface. The mutual attraction of solutes in the first monolayer for unadsorbed solute molecules can be assumed to be equal to the attraction of a surface of pure liquid solute for dissolved solute molecules. However, the pure liquid solute will be dissolved spontaneously at below the saturation concentration. Therefore, adsorption from solution beyond the first monolayer rarely occurs (Ramaswamy, 2000).

1.7 Rate of Adsorption

The study of kinetics of adsorption is of great importance because it gives an idea about the feasibility of the process and applicability of the adsorbent in the wastewater treatment. The adsorption at the solid-solution interface mainly proceeds through the following three steps (Pal et al., 1996).

(i) Transfer of the adsorbate species from the bulk to the solid surface through the aqueous film that surrounds the adsorbent.
(ii) Diffusion of adsorbate species within the pores of the adsorbent particles, and
(iii) The uptake of the adsorbate species by the active surfaces, including formation of bonds between the adsorbate and adsorbent.

The third step is very rapid than other and is not a rate-limiting step in the adsorption process. Therefore, the first and second steps are generally considered as rate determining steps. However, in batch mode of operation, which provided a high degree of agitation or mixing, the pore diffusion is often the rate-determining step, while in case of continuous flow systems the rate-controlling step is the film diffusion due to low degree of agitation.

1.8 Modes of Operation

Several investigators have employed various experimental techniques in order to provide an intimate contact between adsorbate and adsorbent for the effective removal of pollutants from water and drinking water. The contacting systems may be of two types.
**Batch System**

In this type of operation, a fixed amount of adsorbent is shaken with a particular volume of natural or artificial contaminated water until the pollutant has decreased to a desired level. The quantity of adsorbent and time of contact are adjusted according to the needs. After a pre-selected interval of time the adsorbent is removed and either discarded or regenerated for reuse.

**Column Flow System**

In such type of operation, the adsorbent is always in contact with a fresh solution. The fresh adsorbent is added at the top of the column and the spent adsorbent is withdrawn from the bottom. The potable water flows upward through the column containing adsorbent at a velocity sufficient by gravitational force to suspend the solid particles.

The batch mode (Ramaswami, 2001) of adsorption has been used in the present investigation due to its simplicity and easy handling.