

INTRODUCTION

Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. Heavy metal ions do not degrade into harmless end products so the presence of heavy metal ions is a major concern due to their toxicity to many life forms. Contamination of water with toxic metal ions such as Hg(II), Cr(III), Ni(II), Cu(II), Cd(II), As(III) is becoming a severe environmental and public health problems. In order to remove toxic metal ions from water and achieve environmental detoxification various techniques such as adsorption, precipitation, ion exchange, reverse osmosis, electrochemical treatments, membrane filtration, evaporation, floatation, oxidation and biosorption processes are extensively used. Among these adsorption is an efficient technique to remove toxic metal ions from water.

To date, considerable research attention has been paid to the removal of heavy metals from contaminated water via adsorption process. Adsorption process can offer flexibility in design and operation and in many cases will produce high-quality treated effluents. At present, adsorption is widely accepted in environmental treatment applications throughout world. Liquid-solid adsorption systems are based on the ability of certain solid to preferentially concentrate specific substances from solution to their surfaces. This principle can be used for the removal of pollutants such as metal ions and organics from wastewater.

Adsorption plays an important role in many fields and facilitate multifarious applications in chemical and industrial processes, e.g. separation of mixtures, purification of air, water and waste water, industrial catalytic process, heterogeneous catalysis, purification and drying of chemical substances, color removal in sugar processing, refining of vegetable oils, recovery of useful materials from industrial waste, separation of metal ores and adsorption of toxic gases in the gas mask, etc.

The adsorption phenomenon occurs at all interfaces. The following types of interfaces can exist:

- 1) Solid-Gas
- 2) Liquid-Gas
- 3) Solid-Liquid
- 4) Solid-Solid
- 5) Liquid-Liquid

However, the solid-liquid Interface has found greater application in many electrochemical, chemical, and biological processes.

Types of adsorption

Depending upon the nature of the forces involved, two main types of adsorption process may be distinguished,

- 1) Physical adsorption or the Physisorption
- 2) Chemical adsorption or Chemisorption

The third type of adsorption, which is referred to, as activated adsorption is also known.

1) Physisorption

It is assumed that the weak Van-der Waal's forces bind the adsorbent and adsorbate together. There is no transfer or sharing of electron though new equilibrium adjustment takes place without losing the original association of electron with their respective interacting species. Presence of these weak bonds is characterized by low heat of adsorption usually less than 10 Kcal/mole [63-84 KJ/mol]⁹. This adsorption is appreciable only at temperature below the boiling point of adsorbate. It is reversible in nature and non-specific with respect to the adsorbent. In keeping with idea that physical adsorption may be leading to the formation of multilayer, these lead to more dependence on the nature of the adsorbate than that of solid adsorbent.

2) Chemisorption

In many cases, the adsorption of a substance at a surface involves the formation of chemical bonds between the adsorbate and adsorbent due to transfer or sharing of electron. It is generally characterized by high degree of heat of adsorption i.e. more than 20-150 Kcal/mole and can occur at high temperatures. It is usually irreversible in nature and nonspecific with both adsorbate and adsorbent. Due to high initial heat which leads to large amount of adsorption is a indicative of chemical adsorption to form something like monolayer, followed by the formation of multilayer that are bound by physical forces.

3) Activated adsorption

When an appropriate amount of energy is required to activate and conduct the process of adsorption, and named as activated adsorption. For this type, the surface is seemed to be catalytically active.

Methods for the measurements of adsorption

Adsorption of gases on solids is generally measured either by volumetric or gravimetric method. But in the study of adsorption from solution of dissolved substance is somewhat complicated because of presence of solvent.

In general a known amount of the adsorbent and the solution of adsorbate are kept in contact with each other to offer the equilibrium at given temperature and the amount adsorbed is calculated either indirectly by measuring a decrease in the concentration of solution or

directly by the amount deposited on the adsorbent surface. For the former, conventional method of analysis e.g. titrimetric, gravimetric, calorimetric, adsorptiometric and various electronic techniques are employed. But in case of dilute and moderate solution or when the adsorbents are poor, more sensitive methods e.g. use of radioisotope and spectrophotometer. In indirect method change in the weight of adsorbent gives the extent of adsorption. The most method used for determining the amount of adsorbate adsorbed by substrate is the use of spectroscopy in the visible region. Because of their intense color it is easily possible to follow the change in concentration of dyes in solution by any standard adsorptiometer. By this means the effect of change in common variable of interest time, temperature and concentration of dye or the other reagent and pH of the solution can readily be studied. This method has been found almost exclusively available for some three to four decades ago.

For solution containing non-volatile solutes dissolved in volatile solvents, the amount adsorbed can be measured by evaporating the solvent and weighing the residual solute. The adsorption of fatty acid on high polymer can be studied by this method. Study of adsorption has also been carried out by measuring the refractive index of the solution.

Use of spectrophotometer in the study of adsorption

In the study of adsorption of dyes and metal ions from solution Spectrophotometric method is very useful, reliable and mostly used by various workers. With the help of spectrophotometer the possibility of personnel error is avoided which helps in maintaining the accuracy of results. The most important feature of this instrument is that it can be applied to very dilute solutions. Using this instruments adsorption isotherm has been determined. Hence on the basis of isotherm studies various interpretations can be given, such as nature of interaction involved during the process, coverage factor, surface area and pore size of adsorbent and the aggregation of dye molecules. Kipling and Wilson estimated the surface area of finely divided solid from the measurement of adsorption of methylene blue. Similar method was followed by various workers for determination of surface area of graphite, alumina, silica, zinc oxide, carbon etc.

In some studies it is found that the amount of dye and heavy metal ions adsorbed is dependent on the nature of adsorbent, the procedure adopted for the adsorption of disperse dyes on textured polyester fibers was found to be increase when the dye bath contain a carrier when the prior treatment is given to the adsorbent with some chemicals. Such types of effect have been studied by several workers.

Factors influencing adsorption

The amount adsorbed from the solution on a solid depends upon the number of factors such as nature of adsorbent and adsorbate, interfacial tension between solution and adsorbent, temperature of the system, concentration. pH of the solution, porosity of the adsorbent, presence of the foreign material, time duration allowed and the procedure adopted for the systems. The important factors are discussed below.

1) Nature of adsorbent

The nature of adsorbent depends mainly on the chemical composition of the adsorbent but the surface which is responsible for the adsorption is affected due to the presence of pores, edges, corners, cracks and pre-treatment, if given. As most of the adsorption studies are carried out on the solid adsorbent such as alumina, activated carbon, cellulose, starch, polymer and many others, sufficient data are available on these investigations. Contamination from exposure to environment, variation in manufacturing conditions and lack of proper attention to remove surface impurities might be sufficient to cause significant variation in adsorption. Wright has studied the adsorption of series of dibasic acid from aqueous solution at low concentrations by Spheron 6 heated at 1000°C and Graphon (Spheron 6 heated at 2700°C) to demonstrate the effect of removal of oxygen complexes. A study of Kiselav and Shikalova et.al of the adsorption of 6-methyl hept-1-one and phenanthrene from dilute solution in n-heptane by adsorbent having a wide range of polar character also demonstrates the role of surface.

Any pre-treatment, if given to the adsorbent, such as heating, exposure to radiation or treating with chemicals is also important. Pre-treatment of the adsorbent with chemicals alters the nature of the surface considerably. Thus in the adsorption of the acid orange II onto alumina, it was found that pre-treatment of the adsorbent with acid enhances the adsorption capacity of the adsorbent¹⁵. The adsorption of thiram (ITS) on bentonite, acid treatment with H₂SO₄ and heat treated at 110°C or at 200°C from aqueous solution at 20°C has been studied by E. Gonzalez et.al. They found that adsorption increases by acid wash and also by heating. Ganichenko and co-workers used three non-porous silica gels of different degree of hydration to study the adsorption of aliphatic alcohols from dilute carbon tetrachloride solution and found an enhanced adsorption with an increase in the degree of hydration of surfaces.

The effect of adsorbed water molecule on the adsorption behaviour of acids and alcohols on titanium dioxide has been reported. Irradiation with powerful rays in similar way introduces marked changes in the surface characteristic and thereby in actual adsorption as stainless steel shows a large adsorption if cerium and phosphate ion¹⁶ are present there. It is clear, therefore, that the chemistry of surface plays an important role in the adsorption study.

2) Nature of solute (adsorbate)

The adsorption of soluble matter from its solutions depends upon several factors such as its solubility in the experimental solvents, its chemical nature, physical state in solution, etc. Solubility has an important role in the study of adsorption. For a given solvent less or slightly soluble adsorbate are more strongly adsorbed than the much soluble ones. The relation between the extent of adsorption and chain length of adsorbate has been recognized for a long time. Freundlich established that the adsorption of lower n-fatty acid on charcoal from aqueous solution increases with chain length. Similar results have also been observed in the adsorption of dicarboxylic acids from aqueous solution. Trends are not comparable. Crip studied the adsorption of long alcohols on alumina from benzene solution and adsorption was found to be independent of the chain length.

The effect of increasing number of aromatic ring in the molecule was demonstrated by Kiselev and Shikalova. They studied the adsorption of benzene, naphthalene and phenanthrene in n-heptane solution and found that the adsorption increases with number of aromatic rings. Solutes which form least soluble adsorption products are those exhibit tendency for micelles formation are usually adsorbed to the largest extent. Fatty acids and many other compounds exist mainly in the dimeric form in organic media, but their configuration in an adsorbed layer depends on the relative strength of their interaction with the surface and of the association. Hence on non-polar solids (such as Graphon) they are probably adsorbed as dimers with the major axis parallel to the surface but in perpendicular orientation on alumina and titanium dioxide¹⁷. It is also found that most of the solutes are generally toxic in nature. Increase in concentration of heavy metal ion in receiving media or water creates health hazard to human being.

Industrial and mining waste waters are the major source of pollution of heavy metals furthermore, in developing countries, many industries are operated at a small or medium scale or even as a family business within the residential premises of the owner. These smaller units can generate a considerable pollution load which in many cases, is discharged directly into the environment without any facilities for waste water treatment. This is because the capital investment, turnover and profit for these industries are also small. In India, such a situation exists and the discharge of waste water containing chemicals and metallic ions into nearby water courses. Heavy metals can pose health hazards if their concentration exceeds allowable limits. Even with the concentration of metal does not exceed these limits, there is still a potential for long term contamination.

3) Nature of Solvent

Solvent plays an important role in the adsorption study. Adsorption depends upon the interaction of solvent with the solute present in the adsorbed layer.

Solvent effects are found to be important in adsorption onto polar surfaces, especially when the solvent is polar and/or contain aromatic ring. The solvent order of adsorption of lauric acid on alumina is n-pentane, benzene, diethyl ether, with carbon blacks; the polar surface sites also contribute to the solvent effect.

4) Influence of temperature

Temperature is one of the chief determinants, which plays an important role in the study of adsorption. Similar to gaseous adsorption, the adsorption from liquid phase is also seen to depend on temperature. In general, a lower temperature is favorable to larger adsorption i.e. overall process is exothermic. In some cases, elevated temperature enhances the adsorption. Actually the variation depends on the nature of adsorbate-adsorbent interaction.

Mills and Hockey demonstrated the increase in adsorption with temperature of lauric acid and ester of n-fatty acids from benzene solution onto silica. From infrared and calorimetric data they concluded that the hydrocarbon chains do not displace adsorbed benzene, hence are oriented perpendicular to the surface and the solvated hydrocarbon chains form an ordered layer. Structuring at the interface has also been reported by Everett. Bajpai and Vishakarma suggested the increased adsorption with increase in temperature of polyacrylamide onto fuller earth surface. From the data they justify the increased adsorption as the temperature of the adsorption system rises, the intermolecular forces between the water molecules which are adsorbed at the interlayer portion of the montmorillonite. But in many cases adsorption decreases with increased in temperature.

5) Influence of pH

The study of adsorption is very much depending on pH of the solution. Generally the oxides surface exhibits a surface charge, which is dependent on the pH of solution. All oxides have a well-defined pH at which this change is zero. The pH of the solution is found to be very effective in deciding the amount of adsorption especially if the solid adsorbent are prone to surface alternation due to changes in the hydrogen concentrations, large variation have been found with metal, metal oxides and metal hydroxides as adsorbents.

