CHAPTER - 1

GENERAL INTRODUCTION

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Contents Page

1.1 Introduction

Sorption phenomena play an important role in many fields of the natural sciences and underlie a number of extremely important processes e.g., separation of mixtures, industrial catalytic processes and purification of air, water and wastewater. One of the main sorption phenomenon is adsorption at different interfaces.

Molecular forces at the surface of a liquid or a solid are in a state of unbalance or unsaturation. Due to this unsaturation when the surface of a solid in contact with a gaseous, liquid or solution phase, attracts the gaseous molecules or dissolved substances to satisfy their residual forces. As a result, a higher concentration of a given species is present on the surface than that present in the bulk. This phenomenon of concentration of a substance on the surface of a solid is known as adsorption. The phenomenon is very common and has wide and useful applications in many chemical and industrial processes. Some such examples are the large scale production of various substances using heterogeneous catalysts, purification and drying of chemical substances, refining of vegetable oils, colour removal in sugar processing, separation of substances by chromatographic technique, treating of industrial wastewater, recovery of wanted materials from industrial waste, separation of metal ores from gangue by froth floatation processes and adsorption of toxic gases in the gas mask, etc.

The phenomenon of adsorption occurs at all interfaces, therefore, five types of interfaces can exist : (i) gas-solid (ii) gas-liquid (iii) solid-liquid (iv) solid-solid and (v) liquid-liquid. The solid-liquid interface has, however, received [1,2] much attention because of its importance in many electrochemical and biological systems.

1.2 Types of adsorption :

Depending on the nature of the forces involved, two types of adsorption processes may be distinguished (1) the physical adsorption or the physisorption, and (2) the chemical adsorption or chemisorption. A third type of adsorption which is referred to as activated adsorption is also known.

1.2.1 Physical adsorption :

Physical adsorption occurs when non-balanced physical forces appear at the boundary of the phases. The binding forces between the adsorbent and the adsorbate molecules are thought to be of the van der Waals type. There is no transfer or sharing of the electrons though new equilibrium adjustments take place without loosing the original association of the electrons with their respective interacting species. Presence of weak bond is characterised by a low heat of adsorption, usually less than 63-84 kJ mole^{-1} [3]. Physical adsorption is usually observed at low temperature or on relatively inert surfaces. It is reversible in nature and nonspecific with respect to the adsorbent.

1.2.2 Chemisorption :

In many cases, the adsorption of a substance at a surface involves the formation of chemical bonds between the adsorbate and the adsorbent due to the transfer or sharing of electrons. It is usually irreversible in nature, showing higher degree of specificity and characterised by large heat of adsorption, usually more than 84-126 kJ mole^{-1} [3].

1.2.3 Activated adsorption :

Adsorption in some cases requires an appreciable amount of energy of activation and therefore, proceeds above a characteristic minimum temperature. Such processes, named as activated adsorption, do not indicate that the adsorbed molecules are in an activated state though in a number of adsorbents which show this type of adsorption, the surface is seen to be catalytically active.

1.3 Methods for the measurement of adsorption :

The adsorption of gases on solid is generally measured either by volumetric or gravimetric method. But in the study of adsorption from the solution of a dissolved substance is somewhat complicated, because of the presence of the solvent. The methods which have been found convenient and successful for the measurement in such systems are summarised below.

In general a known amount of the adsorbent and the solution of the adsorbate are kept in contact with each other to attain equilibrium at a given temperature and the amount adsorbed is calculated either indirectly by measuring a decrease in the concentration of the solution or directly from the amount deposited on the adsorbent surface. For the former, conventional methods of analysis [4-9] e.g., titrimetric, gravimetric, calorimetric adsorptiometric and various electrometric techniques are employed. In the cases where dilute solutions are used or the adsorbents are poor, more sensitive methods [10-13] (e.g., use of spectrophotometer or radio isotopes) are used. In direct method changes in the weight of adsorbent give the extent of adsorption. Kipling [2] has reviewed the techniques which are commonly used for the analysis (e.g., titrimetric, calorimetric, interferometry, use of radio tracer etc.). Each has its own deficiencies which are particularly relevant when the adsorption is less and there is a need to measure very accurately the small concentration changes. Furthermore, if proper precautions are not taken, the effect of surface contamination can lead to irreproducible and erroneous results.

For solutions 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 acids and high polymers was studied by this method [14].

Study of adsorption using radio isotopes is convenient because of ease of the measurement from very dilute solutions as well as solids having less adsorption capacity. Thus determination of surface area of solid [15] and the study of adsorption of non ionic surfactant on various hydrophobic and hydrophilic solids [12] and also on nylon and polyester fibres [13] were studied by this method. The method is reliable but it is restricted to those systems only where suitable labelled compounds are available.

Study of the adsorption has also been carried out by measuring the refractive index [16,17] of the solutions. This method was found to be precise and relatively rapid.

Photometric adsorption methods have become very common over the years because of convenience of measurement and reliability of data. In these, the determination of selective absorption with coloured solutions (or in the case of colourless ones by converting into coloured species) gives the extent of adsorption.

1.4 Factors influencing adsorption :

The amount adsorbed from the solution on a solid depends on a number of factors. These are mainly the nature of the adsorbent and the adsorbate, the temperature of the system, the concentration and the pH of the solution, presence of foreign materials, the time duration allowed and the manner actually adopted for the systems. The nature of this dependence and its importance from the standpoint of present study are outlined below.

1.4.1 Role of adsorbent in adsorption process :

The nature of the 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 pretreatment, if given. Much work has been carried out with ill defined surfaces by various workers but a variation in the result was observed for similar materials. Contamination from exposure to the environment, variations in manufacturing conditions and lack of proper attention to remove surface impurities might be sufficient to cause significant variations in adsorption. The situation is similar for oxides, e.g., silica has been found in a variety of forms, i.e., porous and non porous, and the type and number of surface hydroxyl groups depend on the method of preparation and the treatment given before the adsorption experiments are carried out. Wright [18] has studied the adsorption of a series of dibasic acids from aqueous solutions at low concentrations by Spheron 6, 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 by Kiselev and Shikalova [19] of the adsorption of 6-methyl hept-1-ene and phenanthrene from dilute solutions in n-haptane by adsorbents having a wide range of polar character also demonstrates the role of surface.

Any pretreatment, if given to the adsorbent, such as heating, exposure to the radiation or treating with chemicals is also important. Pretreatment of the adsorbent with chemicals alters the nature of the surface considerably. Thus with the adsorption of acid orange II onto alumina, it was found that a pretreatment of the adsorbent with acid enhances the adsorption capacity [20]. Ganichenko et al. [21] used three non porous silica gels of different degree of hydration to study the adsorption of aliphatic alcohols from dilute carbon tetrachloride solutions and an enhanced adsorption was found with an increase in the degree of hydration of surface. Armistead et al. [22] have observed an increased adsorption of n-fatty acids ($C_6 - C_{16}$) from benzene solutions on fully hydroxylated surfaces. However, the removal of hydrogen bonded groups reduced the adsorption to a great extent. The effect of adsorbed water molecules on the adsorption behaviour of acids and alcohols on titanium dioxide has been reported. A decrease in the adsorption of octadecanol from p-xylene solutions onto rutile was observed as the amount of pre-adsorbed water was increased [23,24]. A similar result was noted for steric acid from benzene solution on anatage [25] and on commercial titanium dioxide pigments [26,27].

Irradiation with powerful rays in a similar way, introduces marked changes in the surface characteristics and thereby in actual adsorption. Thus gamma (γ) ray irradiated samples of platinum and stainless steel showed a large adsorption of cerium and phosphate ions [28,29]. A decrease in the amount adsorbed of crystal violet onto silica has been reported [30] when the sample was irradiated with neutron (n) and gamma radiation for 100 hours.

From the above discussion it is clear that the chemistry of surface plays an important role in the adsorption study.

1.4.2 Role of nature of solute (adsorbate) :

The adsorption of a soluble matter from its solutions depends on several factors such as its solubility in the experimental solvents, its chemical nature, physical state in solution, etc.

Solubility has, of course, an important role in the study of adsorption. For a given solvent less soluble substances are more strongly adsorbed than the more soluble ones. A relation between the extent of adsorption and chain length of the adsorbate has been recognised for a long time. Freundlich [31] established that the adsorption of lower n-fatty acids on charcoal from aqueous solutions increases with chain length. Similar results have also been observed in the adsorption of dicarboxylic acids (C_2 - C_6) from aqueous solutions on Spheron 6 and Graphon [18]. The trends are not always comparable. Crips [32] studied the adsorption of long chain alcohols on alumina from benzene solution and adsorption was found to be independent of the chain length.

The effect of increasing number of aromatic rings in the molecules was demonstrated by Kiselev and Shikalova [19]. They studied the adsorption of benzene, naphthalene and phenanthrene in n-haptane solution and found that the adsorption increases with the number of aromatic rings. Solutes which form least soluble adsorption products or those exhibiting tendency for micelles formation are usually adsorbed to the largest extent. Such excessive adsorption has been found in the adsorption of dyes [33]. Fatty acids 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 [4] but in perpendicular orientation on alumina and titaniumdioxide [34].

1.4.3 Role of the solvent on adsorption :

The solvent plays an important role in the adsorption study. Adsorption depends on the interaction of the solvent (i) with the solute in the solution, (ii) with the adsorbent, and (iii) with the solute present in the adsorbed layer [35]. Solvent effects are found to be important in adsorption onto polar surfaces, specially when the solvent is polar and/or contain aromatic rings. The solvent order of adsorption of lauric acid on alumina is n-pantane > benzene > diethyl ether [36] and on titaniumdioxide is n-haptane > benzene > acetone

[27]. With carbon blacks the polar surface sites also contribute to the solvent effect. In the adsorption of benzene and naphthalene onto Spheron 6 the solvent order is cyclohexane > carbon tetrachloride > cyclohexanone [37]. Furthermore, preferential adsorption of anthracene, at similar bulk concentrations, is more from cyclohexane and less from cyclohexanone but because of the much greater stability of anthracene in cyclohexanone, the highest adsorption value is obtained using cyclohexanone solutions [38].

1.4.4 Influence of temperature on adsorption :

Temperature is one of the chief determinant which plays an important role in the study of adsorption. Similar to the observation as in gaseous adsorption, the adsorption from liquid phase is also seen to depend on temperature. In general, a lower temperature is favourable for larger adsorption, i.e., the overall process is exothermic. In some cases, elevated temperature enhances the adsorption. Actually the variation depends on the nature of the adsorbate-adsorbent interaction. Mills and Hockey [39,40] demonstrated the increase in adsorption with temperature of lauric acid and ester of n-fatty acids (C_{10} and C_{14}) from benzene solutions 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 was also reported by Everett [16] for steric acid/benzene/Graphon and dodecanol/n-haptane/Graphon systems but in all cases, for which parallel orientation of the long chain molecules is probable, the adsorption decreased with increase in temperature [16,41,42].

The temperature range, possible for variation in the study with liquid solutions, is usually not so extended as that with gases, still the results obtained from various systems indicate almost conclusively the general nature of the behaviour. Sometimes in the study with solutions the actual variation becomes difficult, due to the large adsorption of solvent.

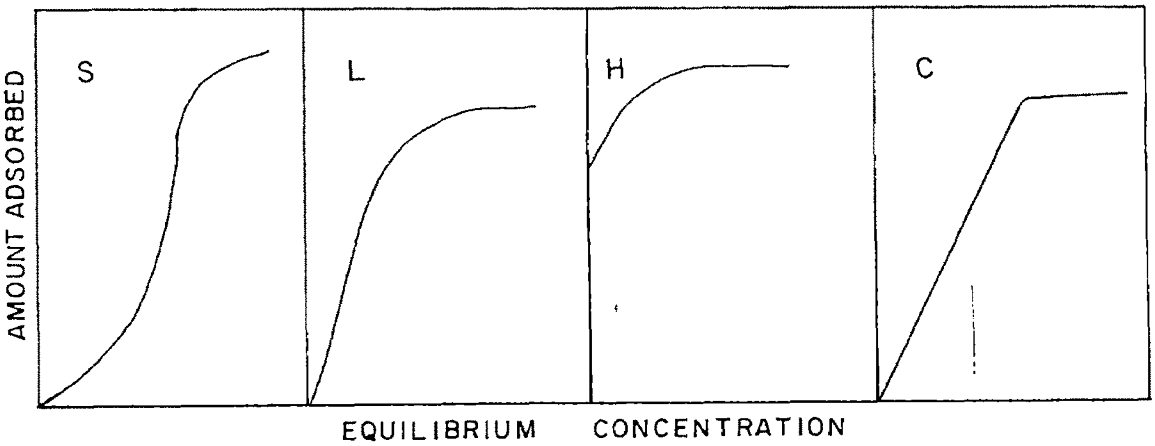
1.4.5 Influence of pH :

The pH of the solutions plays an important role in the study of adsorption. Generally when in contact with aqueous solutions oxide surfaces exhibit a surface charge which is dependent on the pH of the solutions. All oxides have a well defined pH at which this charge is zero [43]. 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 alterations due to changes in the hydrogen ion concentration. Large variations [44-48] have been found with metals, metal oxides and metal hydroxides as adsorbents. A rise in the pH value generally favours the adsorption of cationic dyes whereas with anionic ones, the reverse is true. Similar results have been reported by Podlesnyuk and Levchenko [49] in the study of adsorption of crystal violet onto polysorb and found that adsorption increases with pH. However they observed a decrease in adsorption with the pH in the case of anionic dyes bromcresol green and bromthymol blue. In a similar way, adsorption of basic dye on Spheron 6 and Graphon was found to be favourable at the pH value of 10 although between 7.0 and 9.2 it did not show any appreciable alteration [50]. The actual amount adsorbed by a given solid, when plotted against the pH of the medium, showed in several cases, a maximum at a particular pH value; a minimum in some cases has also been reported [44,45].

1.4.6 Role of concentration of the solution :

For a given adsorbate-adsorbent system, adsorption largely depends on the concentration of the adsorbate solution. Generally adsorption increases with the increase of concentration and then reaches to a saturation. In some cases, definite breaks are observed, which may be due to the transition in the adsorbed phase or an onset of the formation of further layers. The actual variation of adsorption with concentration at a given temperature, is represented by an isotherm. A classification of these, as observed in adsorption from liquid phase has been given by Giles et al.

[51] and later a theoretical concept was given to the classification adopted [52]. The important isotherm shapes considered are shown below :



Four characteristics classes are identified, based on the initial part of isotherm. They are S, L, H, and C curves.

For the S type isotherm, the initial slope is convex to concentration axis, and this is frequently followed by a point of inflection leading to an S shaped isotherm. This type of isotherm is obtained when (i) the solvent is strongly adsorbed, (ii) there is strong intermolecular interaction, and (iii) the adsorbate is monofunctional. The L type isotherm is the most common and is characterised by an initial region which is concave to the concentration axis. In L type isotherm, the competition of the solvent for sites is not very appreciable. The H (high affinity) curves are observed when the affinity between the adsorbate and adsorbent is very high. In this type, adsorption takes place at a very low concentration giving an intercept on the ordinate. The C (constant partition) curve has an initial linear portion which indicates the constant partition of the adsorbate between the solution and the adsorbent and occurs with micro porous adsorbents.

In the theoretical concept of various isotherm shapes Giles et al. [52] indicated that much useful information can be obtained about the adsorption mechanism and this is illustrated with examples from the literature [53]. The analysis is similar as stated by Langmuir for gas adsorption and the constant in Langmuir equation is related to the energy of activation required to remove the solute from the surface. If the interaction between the adsorbed molecules is negligible, the energy of activation will be independent of coverage, and as a result L or H type isotherm are formed. When the force of interaction is significant compared to that between solute and adsorbent, the activation energy will be higher, and cooperative adsorption occurs corresponding to the S isotherm. In this case, the solute molecules tend to be packed in rows or clusters on the surface and this situation is favoured when the solute is monofunctional and is strongly adsorbed. Some dyes form aggregates in solution and when adsorbed give the S isotherm. The C curve is found with microporous adsorbents and is consistant with the conditions that the number of sites remain constant throughout the concentration range. Numerous examples of these shapes have been given by Kipling [2] and Giles et al. [51]. It is thus evident that the variation depends on the actual system and the concentration range studied.

1.5 Theories of adsorption

A lot of efforts have been made by various workers to develop methods for systematic interpretation of different types of adsorption. As a result, many theories have been developed over the years, a brief description of some important ones are given below.

1.5.1 Langmuir Theory

Langmuir [54] suggested a theory to describe the adsorption of gaseous molecules on metal surfaces. The Langmuir adsorption isotherm has been found suitable to many sorption processes and it can be used to explain the sorption of dyes onto solid surfaces. According to this theory, it is assumed that the surface of a solid is made up of elementary sites and each site is capable to adsorb one molecule of a gas, therefore a saturation value is reached beyond which no further adsorption takes place. For the solid/liquid interface the saturated monolayer can be represented by the following expression :

$$q_e = \frac{x}{m} = \frac{Q^o bC_e}{1+bC_e}$$

Where x is the amount adsorbed on the surface, m is the mass of the adsorbent and Q^o and b' are constants. A linear form of this expression is

$$\frac{Ce}{q_e} = \frac{1}{K} + \frac{b}{K} C_e$$

K and 'b' are isotherm constants for a particular solule-solvent combination and $\overset{o}{Q}b$ is represented by K.

1.5.2 Freundlich Theory

A fairly satisfactory empirical isotherm which can be applied to adsorption of gases with considerable success but has been used principally for adsorption from solution, has been discussed by H.Freundlich [55]. He suggested that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of the solute in the solution is not constant at different concentrations of solution. If q_e is the amount of solute adsorbed per gram of adsorbent and C_e is the concentration in the solution, the empirical relation is :

$$q_e = K_F C_e^{1/n}$$

where K_F and n are empirical constants. The linear form of this expression is :

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

1.5.3 The Redlich-Peterson Theory

Redlich and Peterson [56] proposed a theory based on Langmuir and Freundlich theories. Later Jossens et al.[57] incorporated the features of the above mentioned theories and proposed a modified form. The expression for the above isotherm is as follows.

$$q_e = \frac{x}{m} = \frac{KC_e}{1 + a_R C_e^b}$$

Where K, a_R and b are isotherm constants and can be calculated from the linear plot represented by the following equation

$$\ln(K\frac{C_e}{q_e} - 1) = b\ln C_e + \ln a_R$$

1.5.4 Thermodynamic (Potential) Theory

Potential theory of adsorption was first suggested by Polanyi [58,59] and later modified by several workers [60,61]. According to this theory, the existance of adsorption potential is considered to be responsible for the phenomenon. This potential is effective over short distances from the surface and decays as a function of distance from the surface. The expression is given below :

$$\varepsilon = -\frac{RT}{D} \log P_s/P$$

Where D is the diffusion coefficient, P_s is the saturation pressure of the gas and P, the adsorption equilibrium pressure at temperature T. According to this theory, the sorbed penetrant is considered as a homogeneous film of definite thickness.

1.5.5 Residual Valence Theory

This theory postulated by Haber [62], assumes that every atom on the surface of a solid is in a state of unsaturation or is having residual valencies. The adsorbate molecules when come in contact, adhere to it. As each residual valency can accomodate only one molecule, the maximum adsorption, therefore, corresponds to a complete saturation of these valencies. The theory presents the phenomenon in a very simple way but lacks in the consideration of various types of interaction and the corresponding complications involved during adsorption.

1.5.6 BET Theory

A significant advance in the interpretation of the physical adsorption process was made by Brunauer, Emmett and Teller [63] starting with the basic concepts of Langmuir, the multilayer adsorption was included. It was assumed that the rate of evaporation from the nth adsorbed layer is equal to the rate of condensation of the (n-1)th layer. Though the theory has undergone several modifications [64-66], still its importance lies in its wide utility for the determination of surface area of the adsorbents. The expression is :

$$\frac{p}{v(p_o - p)} = \frac{1}{v_m c} + \frac{(c-1)p}{v_m c p_o}$$

Where v is the total volume adsorbed at pressure p, v_m is the volume adsorbed in the monolayer, p_o is the saturation vapour pressure of the adsorbate and c is a constant related to the heat of adsorption and of liquefaction of the adsorbate. This multilayer approach had a profound influence on experimental approaches to physical adsorption and is known as BET theory.

1.5.7 Modern approaches regarding adsorption

The modern theories of adsorption developed on the basis of quantum and statistical mechanics [67,68] have been found successful in explaining to a large extent the chemisorption of gases taking place on solid adsorbents. The molecular orbital model for surface adsorbed species has been proposed and modified by several workers [69,70]. The boundary layer theory of chemisorption are very successful in explaining the adsorption in some cases but suffers several drawbacks. On the otherhand, electron theory of catalysis, being wider in scope, finds applicability in several types of adsorption. The details of these two theories are given below.

1.5.8 The Boundary Layer Theory of Chemisorption

According to this theory, adsorption takes place as a result of electron transfer between adsorbent and adsorbate. It is assumed that the adsorbent is a semiconductor. Thus in case of n-type semiconductor, the electron is transferred from the adsorbent surface to the adsorbate molecules which results in making the latter negatively charged. As the process proceeds, a positive space charge develops in the semiconductor underneath the surface; the surface simultaneously accumulates negatively charged adsorbate molecules. As a result a definite negative field is set up which repells the electrons and thus prevents the transfer process from proceeding any further. Because of this and also because of the fact that the electrons available from upper conduction bands are depleted, the adsorption remains confined to a monolayer. This type of adsorption is known as "depletive chemisorption". According to this the adsorbent should exhibit a decrease in the conductivity with the progress of adsorption. On the otherhand, in the p-type semiconductors, (on the basis of similar mechanism) an increase of the conductivity is expected with the progress of adsorption. This type of adsorption is known as "cumulative chemisorption".

This theory has been verified by using n-type and p-type semiconductors [71]. The theory fits well with the observation of monolayer adsorption and explains successfully the modification in the adsorption behaviour due to the presence of impurities in the adsorbents [72-74]. In addition, it is possible to predict the nature of the adsorption process from the knowledge of the electron donor or acceptor properties of the adsorbate molecules and the type of the semiconductor. The serious drawback of the theory is the assumption that the charge transfer is necessary for the process. Furthermore, it is difficult to explain such adsorption processes which show no appreciable change in the conductivity values.

1.5.9 Electron Theory of Chemisorption

According to this theory, the overall process comprises of both weak and strong chemisorption processes. In weak process there is no change in the number of electrons in the conduction band or the positive holes in the valence band of the adsorbent; the chemisorbed particles being practically neutral indicates that the interacting forces are weak van der Waals forces, or ion dipole interaction etc. In strong chemisorption, electrons play an important role similar to that described in the case of the boundary layer theory. As a result, the number of electrons in the conduction band or positive holes in the valence band changes. Due to the involvement of a free electron or a hole, two types of strong chemisorption bonds can be formed. The first one is donor bond in which the chemisorbed particles donate the electrons. The second one is acceptor bond in which the chemisorbed particles capture free electrons from the adsorbent. Thus the chemisorbed particles have been classified as radical or valence saturated species. In general, the participation of a free electron (or hole) leads to the transformation of a radical into a valence saturated species or vice versa..

Wolkenstein [75] on the basis of above mechanism assumed that the chemisorbed particles exist in equilibrium with the adsorbent either as charged or neutral species; the former being due to the weak chemisorption. Thus, availability of electrons or holes is responsible for weak or strong chemisorption which in turn is governed by the corresponding energy level (e.g., the Fermi, acceptor or donor levels, the valence band etc.). Making use of the Boltzmann distribution for the availability of electrons from various levels, the following expression for adsorption isotherm has been obtained :

$$P=\text{constant}\{1+\exp(-\varepsilon_s^-/kT)+\exp(-\varepsilon_s^+/kT)\}N^0\exp(-q^0/kT)$$

Where P is the amount of adsorbate adsorbed per unit mass of the adsorbent, q^0 is the heat of desorption of a particle held in a state of weak chemisorption, N^0, the chemisorbed particles in a state of weak bonding and ε_s^+ and ε_s^- are the energy differences respectively between the Fermi level and the valence band, and the Fermi level and the conduction band.

The main advantage of this theory is that it is capable of explaining adsorption process involving the participation of both the charged species as well as the neutral one. Additionally, it also explains satisfactorily the adsorption process which proceeds without change in the conductivity.

1.6 Use of Photometers in the Study of Adsorption

In the study of adsorption of dyes from solution, photometric method is very useful and reliable and frequently has been used by many workers [76-80]. In the use of spectrophotometer (equipped with electronic devices) the possibility of personal error is avoided which helps in maintaining the accuracy of the results. Further, spectrometric measurements are possible even in very dilute solutions. Thus using such instruments, adsorption isotherms(complete from very low to saturation values of concentration) have been determined. On the basis of isotherm study various interpretations, such as the nature of the interaction involved during the process, coverage factor, surface area, pore size of the adsorbent and the aggregation of dye molecules, can be made. Kipling and Wilson [81] estimated the surface area of finely divided solid from the measurement of adsorption of methylene blue. Similar method was followed by various workers [82-83] for the determination of surface area of graphite, alumina, silica, zinc oxide etc. From the study of adsorption of basic dye Allen et al. [84] have proposed cylindrical pore structure of peat. Similar measurements have also been helpful to compute coverage factor [85], aggregation number of the dye molecule, adsorption capacity etc.[86]. The particle size of silver powder [87] was determined using adsorption of crystal violet and malachite green and in a similar way that of thoria [88] using methylene blue as adsorbate. In some measurements with oxide surfaces,large adsorption, much more than expected for a monolayer covering was found, the results are indicative of the adsorption of the dye micelles [83], in which dye molecules are assumed to be packed face to face, and not as multilayers of monodisperse ions [85].

Graphite, activated carbon and coal samples adsorbed both types [33,85] (anionic as well as cationic) of dyes and in several cases the results were utilized to determine the surface area of the adsorbent and were compared with that obtained from gaseous (N_2) measurement. Similar measurements made in other cases also have been helpful to compute the surface coverage, coverage factor and corresponding surface area of a number of common adsorbents [89-92] e.g., $BaSO_4$, silica, alumina etc. and also the naturally occuring ones such as bentonite, vermiculite, feldsper etc.

In some studies, it is found that the amount of dye adsorbed is dependent on the nature of the adsorbent, the procedures adopted for its prior processing and the presence of electrolytes in the solution. Thus the adsorption of disperse dyes on textured polyester fibres was found to increase when the dyebath contains a carrier [93]. The effect due to prior treatment given to the adsorbent with chemicals have been studied by several workers. Thus the removal efficiency of basic dyes from wastewater was found to increase by silica which was treated with $ClMe_3Si$ [94]. Activation of hydrolytic lignin with sodium hydroxide increases the sorption capacity for the basic dyes [128]. In the adsorption of cationic dyes by hydrated zirconium dioxide it is found for the maximum adsorption capacity, the hydrated ZrO_2 needed precipitation by the addition of excess of sodium hydroxide; although a decrease in the adsorption capacity of hydrous oxide was observed with aging [95]. The adsorption of methylene blue onto bentonite was measured after the treatment of the adsorbent with salts such as NH_4Cl, KF, $MgCl_2$, $CaCl_2$ etc; adsorption capacity was found to increase with NH_4Cl and KF while with others a decrease was observed [96]. The adsorption capacity of kaolin for above dye was found to enhance when it was treated with 2% HCl [97].

The importance of the presence of the additional ions [98] in regulating the adsorption has been illustrated specially using chlorazol sky blue FF as the adsorbate and a number of adsorbents including silica and titania. In a similar way, adsorption of thymol blue on active carbon was seen to increase on addition of electrolytes such as $CaCl_2$ and KCl to the dye solution [99]. The other aspect i.e., the removal of adsorbed dyestuff from the surface by using chemicals has also been studied in some cases. For example, for the removal of adsorbed crystal violet and malachite green from the asbestos surface, cationic type of substances were found to be effective [100].

Large amount of work on adsorption of dyes includes the use of textile fibre as the adsorbent. Its importance is evident from the standpoint of the dyeing process and fading of the dyed fabric [101]. The fabric in contact with aqueous solutions swells upto such an extent that the meaning of surface area as understood for other substances can not be applied. Consequently, the understanding of availability of active adsorption site, needs differentiation from that of the common adsorbents.

In the use of dyestuffs two points of special importance required careful consideration. The first one is that the dye ion carries a small charge associated with a heavy particle and the second is the existance of aggregates [49,102] in solution above a characteristic concentration known as critical micelle concentration (c.m.c). The nature of the adsorbed phase thus depends on the concentration of the solution from where adsorption takes place. Further, the dyes which are adsorbed as a result of some type of chemical and quasi-chemical interaction are held tenaciously with the surface and resist removal whereas those adsorbed by physical forces are usually reversible. Results of adsorption belonging to both the above types have been found in the study with dyes. The references to these and the important conclusions derived are indicated at the relevant places concerning the particular parameter of study in the present work.

1.7 Time rate studies of adsorption of dyes

The rate of adsorption of dyes depends on various factors such as contact time, pH of the media, concentration of the solution, temperature of the system etc. The adsorption of dyes on solid surfaces is usually fast process and equilibrium is obtained within a short interval of time, though with other substances, time intervals varying very widely have been found [103]. These ranges starting from few minutes to several hours and in some cases the final equilibrium is found to reach after several days. For example, in the adsorption of cibacron violet 2R by kaolinite, the equilibrium was attained in 15 minutes [104], while in the adsorption of phenols by activated carbon, the equilibrium was reached in about 24 hours [105].

Time required to attain equilibrium for a system also depends on the agitation rate. Thus the equilibrium with the adsorption of mono-, di-, and tri-, chloracetic acid onto silica was established within 2 minutes with regular agitation whereas it took 12 to 30 minutes when the agitation was intermittent [106]. This is interpreted as follows. The increase in agitation rate causes a decrease in the external surface film resistance allowing the dye molecules to reach the particle surface rapidly. Similar is the findings of Allen et al. in the study of adsorption of basic dyes onto peat [84]. Factors like the pore size of the adsorbent, size of the adsorbate molecules, solute-adsorbent interaction also play an important role in the time required to attain the final equilibrium. It may also be influenced by the presence of foreign materials in the adsorbate solutions. From the above discussion it is thus evident that several factors should be taken into consideration in deciding the time needed for attainment of equilibrium. A precise correlation to express the behaviour is evidently difficult, though isolated attempts have been made in simple cases [107,108].

Fava and Eyring [109] derived a rate expression for the sorption of dodecyl benzene sulphonate onto cotton. It is represented as :

$$\frac{d\Phi}{dt} = 2k_1 (1-\Phi) \sinh b (1-\Phi)$$

Where Φ is the fraction adsorbed, k_1 is rate constant for adsorption and b is a constant.

Another rate expression on the basis of Langmuir concept, which was successful in interpreting the adsorption of poly(vinyl acetate) from benzene onto chrome plate [110] is :

$$\frac{d\theta}{dt} = k_1 (1-\theta) c - k_2$$

Where k_1 and k_2 are the rate constants for adsorption and desorption respectively, c is the concentration of the solution and θ is the fraction of the surface covered by polymer. Lindstrom et al. [111] have also suggested a rate expression on the basis of Langmuir's interpretation which gives a kinetic parameter for both adsorption and desorption processes. The expression is represented as :

$$\frac{d\Phi}{dt} = k'_1 \left\{ (1-\Phi)(1-\frac{\Phi}{2}) e^{-b\Phi} \right\} + k'_2 \left\{ (1-\frac{\Phi}{2}) e^{b(2-\Phi)} - \frac{\Phi}{2}^{\gamma}) e^{b\Phi} \right\}$$

Where Φ is the fraction of amount adsorbed; k'_1, k'_2 and b are real non negative constants. The equation was found to be applicable in the study of adsorption of some sparingly soluble, biologically active organic compounds onto illite clay and silica gel.

1.8 Scope and Object of the Present Work

Environmental considerations are today imposing greater restriction and closer control on the disposal of industrial effluents. The development of new industries has increased the demand from environmentalists to ensure proper control over the effluents introudced to the environment. Industrial effluents mostly the textile effluents contain a large number of metal complex dyes. The high concentration of such dyes causes many waterborne diseases and also increases the BOD of the receiving water [112-114]. Because of their complex structure and larger molecular size, most of the dyestuffs are considered as nonoxidisable substances by environmental, biological and chemical treatment methods [115,116] and hence disposal of such effluents is a major environmental problem. The prime consideration to an industrialist is the cost of treating effluents to reduce specific pollutant levels to below the accepted standards. The technology required to meet the standards is still being developed. Adsorption at the solid/liquid interface is an effective method for controlling the extent of water pollution due to dyes and metallic species [117-120]. Adsorption phenomenon at the solid/liquid interface is important from biological, environmental and technological points of view. A large amount of work has been carried out over the years for the removal of dyes from the textile effluents. The investigations, however, have been confined to the study of adsorption isotherms [121-127] and their interpretation [51,53] without much emphasis on time rate study of the adsorption process.

The main objective of the present work is to investigate the time rate study of removal of various types of dyes from aqueous solutions using inorganic oxides and graphite as adsorbents. The oxides selected for the present work are alumina (neutral and basic) and silica gel. The adsorbates chosen for the present work are cationic dyes (Basic Brown 4, Basic Green 1, Basic Violet 1 and 2, and Basic Blue 3) and anionic dyes (Acid Green 25, Acid Black 1 and Ketone Blue A). The work presented in the thesis includes the measurement of adsorption as a function of time, nature of adsorbent, concentration of dye solution, pH and temperature. The energy of activation was calculated using Arrhenius equation. The values of energy of activation was used in computing the values of entropy of activation. On the basis of isotherm study, Langmuir and Freundlich adsorption isotherms have been tested and various thermodynamic parameters such as ΔG, ΔH and ΔS have been calculated. The influence of surfactants, electrolyte and alcohol on the adsorption behaviour has also been seen. An elution process is introduced in order to regenerate the adsorbents by using the electrolyte solution.

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