CHAPTER 4

SORPTION BEHAVIOUR
OF
DYES
USING
TiP AND TiHEDP
AS
SORBENTS
4.1 INTRODUCTION

Water is a vital natural resource, which is essential for a multiplicity of purposes. Its many uses include drinking and other domestic uses, industrial cooling, power generation, agriculture (irrigation), transportation and waste disposal. In the chemical process industry, water is used as a reaction medium, a solvent, a scrubbing medium, and a heat transfer agent. Billions of liters of waste water is generated every day from industries and domestic sources. The quality of water is of vital concern for mankind since it is directly linked with human welfare. With a growing population, the demand for fresh water is steadily increasing but as with all other resources, there is a limit to fresh water supply. In addition, the availability of high quality water is dwindling because of misuse, waste and pollution.

The paramount need of the hour is integrated planning, development and management of water. Industrial effluents have to be suitably treated for safe disposal into the environment. With positive approach, effluents may be suitably processed to obtain valuable products. They may be treated and used for resource regeneration. Many industrial units of the country are facing acute shortage of raw water and restrictions on the discharge of effluent, which are calling for costly effluent treatment systems. Therefore, water conservation is necessary for the industries.

Though scientists and technologists have been engaged in pollution abatement research and development for many years, they are still far away. The technologies developed for treatment of common/conventional wastewater are well established and can remove more than 90% of BOD and suspended solids. However, technologies developed for the treatment of non-conventional waste water are either underdeveloped and require lot of improvements and/or new ideas and inventions. There is thus a need for developing materials that are cost-effective and easy to handle. Major objectives for the removal of contaminants from aqueous solutions are (a) toxicity removal which entails an environmental aspect and (b) recovery of valuable materials which involves a technological aspect [1].
4.2 THE ENVIRONMENTAL CHEMISTRY OF DYES

Dyes are generally synthetic organic compounds with complex molecular structures and large molecular weight. Dyes are intensely coloured substances that can be used to produce a significant degree of coloration when dispersed in or reacted with other materials. Man has been fascinated by colour since prehistoric times. This is evident from the extensive use of colourants in paints and pigment industries, textile industries, plastics, food, paper, drugs, etc. Prior to the mid-nineteenth century, colourants were obtained from natural sources, which were mainly of vegetable and animal origin. Synthetic dyestuff industry has undergone phenomenal growth, resulting in over 8000 chemically different dyes having reached commercial significance on a world wide basis [2]. Amongst all industries, a major portion of the dyestuff production is consumed by the textile industry. The textile industry utilizes large volumes of water in its various wet processing operations and, thereby, generates substantial quantities of wastewater [3,4]. Wastewater is the principle route by which dyestuffs enter the environment. Dyes are highly dispersible aesthetic pollutants which contributes to aquatic toxicity. They are difficult to treat and interfere with municipal waste treatment operations. Soluble dyes present in the effluent, exhibit their colour in the stream and interfere with penetration of sunlight essential for photosynthesis. By design, dyes are highly stable molecules, made to resist degradation by light, chemical, biochemical and other exposures. Commercial dyes are usually mixtures of large complex dye molecules. Thus, several difficulties are encountered in removal of dyes from wastewaters. During the last twenty years, an increasing awareness has been observed on environmental issues concerning water pollution and waste disposal. These concerns have resulted in the development of more stringent environmental regulation and enforcement of the same. Pollution control board targets the textile industry to clean up the waste water that is being discharged from the textile mills. Regulators are looking closely at toxicity due to high salt, the ever present BOD, non destructible COD, heavy metals and colour of the effluent. Traditional industries, such as dye manufacturing and textile
processing, therefore have been forced to change their working culture from when effluents are discharged to disposal through: (1) Reduction of the volume and toxicity of the discharges, (2) Adoption of alternative processing methods and chemicals and (3) Recycling and reuse of water, chemicals, and colourants [5]. A large variety of dyestuffs such as acid, basic, reactive and direct dyes can be found in effluents. The problem posed in most cases is the high solubility of these dyes as well as resistance to biological and chemical degradation. It has been reported that dye wastewater is poisonous, carcinogenic and teratogenic to human beings [6]. It thus becomes essential to design a cost effective colour removal process which has attracted wide attention [7]. Literature [8-11] is available on the problem of colour, the search for solutions and currently available technologies/novel technologies. A review of these methods is presented below.
4.3 METHODS USED FOR REMOVAL OF COLOUR FROM WASTEWATER

The methods used for the removal of colour from wastewater may be classified into two main categories:

(1) Decomposition of the colour component.
(2) Separation of the colour component.

Colour decomposition involves methods such as

(i) Oxidative degradation
   (a) Chlorination
   (b) Ozonation
   (c) Use of Fenton’s reagent

(ii) Reductive degradation
   (a) Use of sodium hydrosulfite
   (b) Use of formamidine sulfonic acid

(iii) Biological degradation

Separation of colour component involves methods such as

(i) Filteration
   (a) Precipitation
   (b) Flocculation
   (c) Membrane technology.

(ii) Adsorption
   (a) Use of activated carbon
   (b) Use of ion exchangers

Oxidative degradation

Dyes may be effectively decolourized using ultraviolet light, corona discharge, permanganate, aerobic biological degradation and various chemical oxidizing gents such as chlorine, ozone, hydrogen peroxide, etc.
Chlorination

Chlorine added to solution oxidizes dye molecules. In some cases, chlorine bleaches the dye, and the color returns in a reducing environment. Additional biological treatment is necessary to reduce the organic matter, since chlorine rarely oxidizes the compounds completely. The most important consideration with respect to chlorine is the potential for toxic organic compounds resulting from the chemical reaction.

Ozonation

When introduced to solution, ozone oxidizes the dye molecules. The oxidizing power of ozone is estimated as approximately twice that of chlorine. Still, additional treatment generally is required to reduce organic matter following ozone treatment. Ozone generally works well on direct, acid, reactive, and basic dyes. Ozone may be appropriate for treatment of azo dyes. Disperse and sulfur dyes generally respond poorly to ozone treatment. Ozone treatment does not appear to be affected by pH or temperature. Ozonation does not remove COD well. The effectiveness of decolorization by the ozonation process reduces impurities in the wastewater.

Use of Fenton's reagent

The process not only possesses the advantages of both oxidation and coagulation processes, but can also increase the amount of oxygen in the water. Consequently, it is expected that the method could effectively decolorize all wastewater and could be ecologically safe.

Hydrogen peroxide and ferrous ions are usually more stable in a strong acid. But if hydrogen peroxide is added to an aqueous system containing an organic substrate and excess ferrous ions in a strong acid, a complex redox reaction, as in equations (1) – (4), will occur:

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{HO}^- \\
\text{HO}^- + \text{RH} & \rightarrow \text{H}_2\text{O} + \text{R}' \\
\text{R}' + \text{Fe}^{3+} & \rightarrow \text{R}^- + \text{Fe}^{2+} \\
\text{R}^- + \text{H}_2\text{O} & \rightarrow \text{ROH} + \text{H}^-
\end{align*}
\]
The hydroxyl radical generated would attack the organic substrate RH like the unsaturated dye molecule. So the chromophore or chromogen of the dye molecule would be destroyed and decolorized. Besides, the most likely side reactions in the redox system are equations (5) and (6), as follows:

\[
\text{HO}^\cdot + \text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{HO}_2^\cdot \quad (5)
\]

\[
2\text{R}^- \longrightarrow \text{R} - \text{R} \quad (6)
\]

The dimerization, as in equation (6), of such organic molecules as dyes, will be of advantage to decolorization. Ferric ions generated as above may form ferric hydroxide complexes with hydroxide ions, as in equations (7) and (8),

\[
[\text{Fe} (\text{H}_2\text{O})_6]^{3+} + \text{H}_2\text{O} \leftrightarrow [\text{Fe} (\text{H}_2\text{O})_5\text{OH}]^{2+} + \text{H}_3\text{O}^+ \quad (7)
\]

\[
[\text{Fe} (\text{H}_2\text{O})_5\text{OH}]^{2+} + \text{H}_2\text{O} \leftrightarrow [\text{Fe} (\text{H}_2\text{O})_5(\text{OH})]^+ + \text{H}_3\text{O}^+ \quad (8)
\]

and the complexes have a pronounced tendency to polymerize at pH 3.5 - 7 as equations (9) - (11).

\[
2[\text{Fe} (\text{H}_2\text{O})_5\text{OH}]^{2+} \leftrightarrow 2[\text{Fe} (\text{H}_2\text{O})_6(\text{OH})_2]^{4+} + \text{H}_2\text{O} \quad (9)
\]

\[
[\text{Fe}_2 (\text{H}_2\text{O})_6(\text{OH})_2]^{4+} + \text{H}_2\text{O} \leftrightarrow [\text{Fe}_2(\text{H}_2\text{O})_7(\text{OH})_3]^{3+} + \text{H}_3\text{O}^+ \quad (10)
\]

\[
[\text{Fe}_2 (\text{H}_2\text{O})_7(\text{OH})_3]^{3+} + [\text{Fe} (\text{H}_2\text{O})_5(\text{OH})]^2+ \leftrightarrow [\text{Fe} (\text{H}_2\text{O})_5(\text{OH})_4]^{5+} \quad (11)
\]

Thus, coagulation would probably exist. The remaining decolorized dye molecules in wastewater can be coagulated and precipitated [12]

**Reductive degradation**

It is widely known that, azo dyes undergo conversion to aromatic amines, via reductive cleavage of the azo bond, when subjected to a reducing environment [13] generating aromatic amines that, in theory are more amenable to subsequent aerobic biological treatment than the parent dye structures. The most commonly used chemical reducing agent is sodium hydrosulfite (also known as sodium dithionite). Thiourea dioxide [also known as formamidine sulfonic acid], sodium borohydride, sodium formaldehyde sulfoxylate and tin (II) chloride are additional reducing agents for treating dye wastewater. When evaluating the chemical decolourization of wastewater it is important to investigate the potential reversal of the reaction, upon exposure to oxygen, since colour may reappear upon discharging the wastewater to the environment. Reducing agents or the aromatic amines generated from
reductive cleavage of the azo bonds may have toxic effects on the microorganisms in the biological treatment plant.

**Biodegradation**

Since a large proportion of the biodegradable material in textile waste, is in the soluble form, the effluents are readily susceptible to biological treatment. Activated sludge systems (including extended aeration), trickling filters, anaerobic lagoons, anaerobic contract systems, aerobic lagoons and rotating biological contractors have all been successfully applied to textile effluents.

The conventional 5-day biochemical oxygen demand (BOD) test is commonly used to measure the biodegradability of a waste sample. When oxygen combines with partially degradable organic materials in an aerobic process, it is presented by following equation:

\[
\text{Biomass} \quad \text{Organics} + O_2 + \text{Nutrients} \rightarrow \text{New Biomass} + CO_2 + \text{Non reactive Ingredients}
\]

When biodegradation of different textile dyes were studied, the most interesting result discovered was that no significant colour loss (optical density) was observed after 30 days with any of the soluble reactive or direct dyes. The disperse and vat dyes are pigment dispersions. This was a result of the settling of the dispersed pigment on the bottom of the bottle rather than degradation. Therefore, biodegradation is not an effective process for removal of colour from the wastewater. There are two methods of biological treatment aerobic, and anaerobic.

**Aerobic biological treatment**

Typical wastewater treatment operations at large textile dyeing and finishing facilities include an aerobic biological treatment system. There are three main systems, (i) Stabilization Basins (ii) Aerated lagoons (iii) Trickling filters.

*Stabilization basins* are a common method of organic wastewater treatment where sufficient land area is available. Stabilization ponds have a water depth of 1-2 m and oxygen is supplied by surface entrainment or by
algae. The BOD loading must be low and the detention time 5-25 days. Aerated lagoons are 2-5 m liquid depth depending upon the aeration system and detention time is 2-10 days. They are mainly used because of their efficiency in removing BOD from textile effluents [14]. Trickling filters are cylindrical tanks packed either with stone or a synthetic medium [15]. The effluent flows onto the filter media by means of a rotating arm that distributes the waste load uniformly over the circular bed. The effluent trickles through the filter and over a slime of bacteria that adheres to the filter media. As bacteria die, they fall off the filter and are removed from the effluent throughout the secondary settling stage. The removal efficiency depends on the type of media used, the organic loading ratio, and the ratio of raw water to recycle waste water, and operating temperature.

**Anaerobic biological treatment**

Anaerobic decomposition involves the breakdown of organic wastes to gas (methane and carbon dioxide) in the absence of oxygen. Following biological treatment, the sludge containing adsorbed dyes may be digested under anaerobic conditions. Anaerobic processes are known to offer several advantages over aerobic treatment systems, for example (i) better waste stabilization, (ii) lower microbial yield, (iii) lower nutrient requirement, (iv) no oxygen requirement and (v) methane gas production. The disadvantages are poor process stability, a temperature requirement of 35°C, the inability to degrade various substrates and large reactor volume requirements because of slow reaction rates.

**Activated Sludge Process**

Activated sludge process is a continuous system in which aerobic biological growths (suspended growth) are mixed with influent waste water to allow development of an acclimated microbial population and then physically separated by gravity clarification (or by air floatation). A part of the concentrated sludge is recycled to the reactor to mix with incoming waste waters. Oxygen may be introduced either as air, oxygen or oxygen enriched air. The waste product from the process is excess sludge, which is a mixture of
dead and living organisms, flocculated by their slimy coats and also containing non biodegradable inorganics and refractory organics based on their adsorption capacity. This must be ultimately disposed off. As the concentration of organics in the waste water decreases, the rate of biological removal also decrease. Since the remaining organics are progressively more difficult to remove, thus BOD removal may be excellent but the removal of COD may be low.

The objective of the activated sludge process is to remove soluble and insoluble organic from a wastewater stream and to convert this material into a flocculent microbial suspension that is readily settleable and will permit the use of gravitational solid-liquid separation techniques. Although the activated sludge process is capable of providing high BOD, COD, TOC and TSS removal, it is less effective for colour removal. Since synthetic dyes used by the textile industry are specifically formulated to resist breakdown under oxidizing conditions, most dyes are resistant to biological degradation.

There are certain limitations of activated sludge process. The effluent is to be continuously monitored and adjusted for its COD/BOD values or heavy doses of COD will kill the biomass and one has to develop the biomass and begin again. Certain organics which are biostatic, cannot be treated by this method. Treatment of dyes and dye intermediate effluents by this method is not effective. It doesn’t help in complete removal of colour. For these reasons, an improvement in the biological treatment is needed for wastes containing dyes.

The efficiency of an existing bioaeration plant can be increased by the addition of activated carbon. One successful system patented by DuPont and further developed by Zimpro is the powdered activated carbon treatment (PACT) system[16]. The combined powdered activated carbon-activated sludge system (PACT® system) is a classic case of “Necessity is the mother of invention”.

PACT Process

The PACT system is a process for the treatment of organic materials in wastewater streams. The PACT system is used to treat aqueous waste streams
that are too dilute [50 and 50,000 mg chemical oxygen demand (COD) per liter of wastewater] for oxidation technologies, such as wet air oxidation or incineration, and for waste streams that are too strong to be economically treated with granular activated carbon. Depending upon the wastewater characteristic, carbon dosage, from 10 to over 5000 mg of powdered carbon is added per liter of the waste water flow.

The powdered activated carbon may be added to waste stream before treatment, to the recycle sludge, or to the aeration tank itself. Polyelectrolyte is often, but not always added to the overflow from the aeration tank to aid coagulation of fine particles in the clarifier where the solids are separated out of the treated water. Excess solids are usually removed from the PACT system by withdrawal of a small stream directly from the sludge recycle stream. Waste solids, being a mixture of powdered activated carbon, activated sludge, adsorbed organic material, and inert material, are then directed to solids processing.

Adding powdered activated carbon to the activated sludge process can be beneficial, i.e. more uniform operation and effluent quality, improved tendency for BOD, COD, and TOC removal, better removal of Phosphorous and Nitrogen, less tendency for foaming in the aerator because of the adsorption of detergents, adsorption of refractory solids and thicker sludges, greater treatment flexibility and enhanced colour removal of dye effluent.

This method is still not regarded as an excellent method due to the inherent disadvantages which include production of higher quantities of sludge, necessitating the installation and operation of sludge handling equipment, sensitive to shock loads of toxic and organic substances, requirement of careful attention for control of volume and concentration of return sludge and high cost of operation and maintenance.

Bioaugmentation

Bioaugmentation is obtaining maximum biodegradability by addition of microbial cultures in order to have optimum bacterial mass [17]. Several papers
have described the biodegradability of azo and triphenylmethane dyes using specific strain of bacteria.

The efficiency of these biological treatment methods are, however, mainly controlled by the initial pH of the waste. Expensive pH control, therefore, often limits the applicability of biological treatment methods.

**Filtration techniques**

**Coagulation**

Treatment by coagulation involves adding chemicals to create a floc incorporating the dye molecule. Concentration of the floc by sedimentation or floatation forms a sludge which is removed leaving clarified liquid.

A major disadvantage of coagulation is the production of relatively large quantities of sludge which must be handled and disposed.

Coagulants are of two types: inorganic salts and synthetic high-molecular weight organic compounds. Common inorganic salts are aluminum and iron salts, such as aluminum sulfate (alum) and ferric chloride. High-molecular weight cationic polyelectrolytes are popular synthetic organic coagulants. Organic coagulants were most successful at a facility utilizing approximately 75% vat dyes and 25% sulfur dyes.

**Membrane technology**

Commercially significant membrane – separation processes are: ultrafiltration, reverse osmosis and electrodialysis [18].

*Reverse osmosis* (RO) or *Ultrafiltration* (UF) can be used to concentrate toxic organic substances, depending on the type of compounds and the stability of the membrane against chemical attack. RO and UF are pressure driven membrane processes that remove solutes from solution based on particle or molecular size differentials. The separation mechanism characterizing ultra filtration, is based on membrane pore size and the difference in size between the solute and solvent.

RO can isolate a product water of comparatively high quality and a concentrate water containing 80 to 95% of the chemicals present in the original waste stream. Reverse osmosis is very effective for the removal of all
types of colour from dye house discharges. However, clogging of the membranes with concentrated dyes after prolonged use is a problem.

**Adsorption**

Amongst various techniques, adsorption is superior in simplicity of design, initial cost, ease of operation and insensitivity to toxic substances. Adsorption is an effective method for lowering the concentration of dissolved organics in an effluent. This technique depends on the properties of the compounds being removed and the regenerative capability of the adsorbent. Organic compounds are adsorbed on activated carbon, synthetic resins, specially prepared silica and activated alumina. Synthetic polymeric adsorbents have a high porosity, large surface area, and an inert hydrophobic surface. These resins can be regenerated chemically, which produces a concentrated waste stream requiring further treatment or disposal.

Factors such as dye structure, size and molecular shape, together with concentration and charge will all influence uptake and affect the extent and rate of the adsorption process. Other parameters such as pore structure, $pH$ of solution, particle size and temperature, affect the diffusion of the dye in solution and within the adsorbent structure. Surface chemistry and the distribution of adsorption sites on the surface of the adsorbent also play a significant role in the adsorption process.

**4.4 THEORETICAL ASPECTS ON ADSORPTION**

Adsorption is defined as “adhesion of a molecule to a surface”. Adsorption involves the interphase accumulation or concentration of substances at a surface or interface. The process can occur at an interface between any two phases, such as, liquid-liquid, gas-solid, gas-liquid, 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. The term *sorption*, which includes
both adsorption and absorption, 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 [19].

Adsorption is operative in most natural, physical, biological, and chemical systems, and is widely used in industrial applications.

As a result of adsorption, there is decrease in residual forces acting along the surface of the adsorbent. Consequently, there is decrease of surface energy, which appears as heat. Adsorption, therefore, is invariably accompanied by evolution of heat i.e. decrease in enthalpy of the system, i.e. $\Delta H$ of the process is invariably negative. Further, since the adsorbate changes from the more random gaseous (or solution) state to the less random adsorbed state on the surface of a solid, adsorption is also accompanied by decrease in entropy of the system, i.e., $T\Delta S$ of the process is also negative. Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system. The free energy change, $\Delta G$, for any feasible process, as given by the well-known thermodynamic equation,

$$\Delta G = \Delta H - T\Delta S$$

i.e., the value of $\Delta H - T\Delta S$ should be negative. This is actually the case. However, we know from experiment that the heat of adsorption per mole of the adsorbate goes on decreasing, i.e., $\Delta H$ become less and less negative, as adsorption proceeds further and further. Ultimately, $\Delta H$ become equal to $T\Delta S$ and $\Delta G$ becomes zero. This is the stage at which equilibrium is attained. Since adsorption is invariably accompanied by evolution of heat, therefore, in accordance with Le Chatelier’s principle, the magnitude of adsorption should increase with fall in temperature. Since adsorption is a surface phenomenon, it is evident that the greater the surface area per unit mass of the adsorbent, the greater is its capacity for adsorption under the given conditions of temperature and pressure.

Positive adsorption in a solid-liquid system results in the removal of solutes from solution and their concentration at the surface of the solid, to such time as the concentration of the solute remaining in solution is in a dynamic
equilibrium with that at the surface. At this position of equilibrium, there is a defined distribution of solute between the liquid and solid phases. The distribution ratio is a measure of the position of equilibrium in the adsorption process; it may be a function of the concentration of the solute, the concentration and nature of competing solutes, the nature of the solution, and so on. The preferred form for depicting this distribution is to express the quantity \( X/m \) as a function of \( C \) at fixed temperature, the quantity \( X/m \) being the amount of solute adsorbed per unit weight of solid adsorbent, and \( C \) the concentration of solute remaining in solution at equilibrium. An expression of this type is termed an *adsorption isotherm*. In general, the adsorption isotherm describes how adsorbates will interact with adsorbents and so is critical in optimizing the use of adsorbents [20]. Langmuir and Freundlich adsorption expressions are frequently used in the adsorption experiments. Langmuir and Freundlich adsorption isotherms are well described previously in Chapter III, Section 3.3).

### 4.5 ADSORBENTS USED IN WASTE WATER TREATMENT CONTAINING DYES

Activated carbon has been extensively studied in waste water treatment. Adsorption is defined as “adhesion of a molecule to a surface” and absorption as “to take in; engulf; assimilation”. Both definitions seem applicable to carbon in many cases. Activated carbon is non-polar type, hydrophobic, amorphous adsorbent with low affinity for water. Thus, it can mostly adsorb the non-polar compounds. Though activated carbon is hydrophobic in nature; its hydrophilicity increases when it comes in contact with water. Owing to such amphoteric characteristic, activated carbon selectively adsorbs the least polar compound and therefore cannot adsorb the pollutants having polarity more than water from the waste waters [21]. Thus, it can mostly adsorb the non-polar compounds. Adsorption using activated carbon in granulated form may be effective in removing colour, phenolics and host of other organic substances.
The development of a model on adsorption of some dye materials on activated carbon and its characterization were reported [22]. Activated carbon has been evaluated extensively for the waste treatment of the different classes of dyes, that is, acid, direct, basic, reactive, disperse, and so forth, and is now the most widely used adsorbent for dyes [23]. A group of basic and disperse dyes (cf. Basic Yellow 11, Basic Blue 3, Basic Blue 9, Disperse Red 78, and Disperse Blue 64) were studied to better define factors affecting the removal of textile dyes from wastewater by carbon adsorption. Based on results from the evaluation of 17 dyes, Horning [24] found that carbon treatment did not perform well with vat and disperse dyes but performed better than alum for reactive and basic dyes.

Carbon has been shown to be effective for reactive, basic, azo, and mordant dyes that are water soluble. Those dyes which have very low water solubility, such as dye pigments, are not effectively adsorbed by carbon at room temperature.

Chitin is the second most abundant natural carbohydrate polymer next to cellulose [25]. The major derivative of chitin is chitosan which refers to a family of polymers derived from chitin by deacetylation. Chitin and chitosan are adsorbents which can contain amine or amide nitrogen in varying proportions. It exhibits larger adsorption capacity for acid dyes or anionic dyes. Adsorption can occur by van der Waals attraction, hydrogen bonding and coulombic attraction [26, 27]. Chitin displays no significant attraction for basic dyes [28-31]. Diatomite is siliceous sedimentary rock consisting principally of the fossilized skeletal remains of the diatom [32]. The silanol group is a very active group, which can react with many polar organic compounds and various functional groups. This property makes it a possible adsorbent for many dyes. Fuller's earth is a natural clay which contains variable amounts of dioctahedral smectites, natural zeolites and other sepiolites. The main content is magnesium and aluminium silicates. Methylene blue, a cationic dye, is shown to adsorb strongly onto Fuller's earth [33]. In a comparison, the adsorption capacities of the Fuller's earth samples were higher than those of a commercial
activated carbon. In addition, the time to reach equilibrium is shorter. **Bentonite** is a fine powder clay which has been used for dye removal from water [34]. Acid, basic and disperse dyes were used and the results showed that the bentonite exhibited high basic dye removals. **Kudzu** (Pueraria lobata) is a rapidly growing, high climbing perennial leguminous vine. A study of basic dyes using Kudzu has been reported by Matthews [35]. Kudzu exhibits a good capacity for basic dyes, although the capacity was not as high as for a commercial carbon. Silica [36,37], perlite [38], lignite [39,40], dolomite [41], peat [42] have also been used as adsorbents.

### 4.6 LITERATURE SURVEY IN CURRENT AREA OF STUDY

Materials such as charred sawdust [43], carbonized wool waste [44], charred plant material [44], quaterinzed rice husk [45], and cassava peel char [46] have been found to be effective in the removal of a variety of dyes from water. Materials that have been used in their natural state for adsorption of dyes from solution include linseed cake [47], sunflower stalks [48], banana peel [49,50], orange peel [51,52], Fuller's Earth [53], chitin [54], eucalyptus bark [55], wood [56-58], maize cob [59,60], bio-gas waste slurry [61], water hyacinth roots [62], waste red mud [63], fly ash and coal [64,65]. Reviews of equilibrium and kinetic studies of dye adsorption by eggshell membrane [66], Rhyzopys oryzae [67], are reported. Neem leaf powder is reported to be an effective adsorbent for brilliant green dye [68]. Janos et al. tested brown coal fly ashes as adsorbents for both basic and acid dye [69]. Basic dye adsorption was increased at high pH values and the opposite was true for the anionic dyes. Microbial bio-mass is inexpensive and is shown to bind dyes [70]. Wood has been a source of adsorbent material both in its natural and modified state. The sawdust of soft spruce wood has been used for the adsorption of a basic and an acidic dye from solution. Spruce wood does have affinity for basic dyes rather than acidic dyes, although uptake is much less than for active carbon, peat and lignite. Recently, adsorption of Methylene Blue on zirconium phosphate by
means of ion exchange reaction has been reported. The dye is strongly retained and not easily leached from the matrix [71].

The use of novel alternative adsorbents continues to attract attention due to economic considerations, availability and adsorption efficiency. In particular there is a need for more research into tailoring the manufacture of specific adsorbents for particular applications together with more general adsorbents with wider applications.

Presently, there are several methods available to decolorize dye waste waters. For example, coagulation process effectively decolorizes insoluble dyes, but does not work well for soluble dyes. There is also a large volume of sludge formation. Oxidation processes such as ozonation decolorizes almost all dyes except disperse dyes, but does not remove COD well. The biological process does not effectively decolorize commercial dyes. It has been observed that ion-exchange systems have been ignored as a viable technology for treatment of dye effluents, probably due to the fact that ion exchangers cannot accommodate the wide diversity of dyes, the dye bath conditions or due to the poor performance, due to presence of other additives in the wastewater stream.

**Ion exchangers in adsorption**

Adsorption, ion exchange and chromatography are sorption processes in which certain adsorptives are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column. Normally, ion exchange phenomena has been used in industries for softening of water, for demineralization etc. Water soluble and ionic organic matter are also removed by this method. This is also a highly effective method for eliminating dissolved contaminants such as colourants and toxic metal ions.

There are few publications where ion exchange materials are used as sorbents for removal of dyes. Several works using zeolites, clays, and silica as supports for dye removal have been published [72,73,74]. Adsorption of basic dyes methylene blue and crystal violet has been carried out on montmorillonite [75]. Sorption of Methylene Blue on smectiltes have been studied [76]. The removal of Basic Blue 3 from a synthetic wastewater by adsorption using
bentonite was investigated [77]. Atun et al [78] investigated the adsorption behavior of methylene blue (MB) on four fuller's earth. Annadurai et al [79] have made use of activated carbon to remove Rhodamine 6G (Basic Red 1) from aqueous solutions. Meshko et al [80] compared the adsorption capacities of natural zeolite and granular activated carbon on some basic dyes from aqueous solutions. Arbeola et al [81] studied the adsorption of Rhodamine 6G (R6G) on sepiolite. Krupa and Cannon [82] studied the adsorption of three dyes, methylene blue, congo red, and crystal violet, onto six activated carbons. McKay et al [83] have carried out extensive work on adsorption of Basic, Acid, Direct and Disperse dyes using Coal, Bentonite and other natural sorbents.

**TMA salts as sorbents for dye removal**

Though the cation exchange characteristics of TMA salts are well established, not much work has been reported on the adsorption characteristics of these materials. However, earlier Varshney et al have used these materials as sorbents for the sorption of pesticides [84, 85].

Dyes in general contain one or more of the following functional groups in their structure (-OH, -COOH, -SO₂H, NO₂, NH₂, -N=N- etc.). When a cation exchange material is used as a sorbent it is believed that the interaction of the above functional groups with the matrix material (sorbent) being used, could be anywhere from covalent to coulombic, hydrogen bonding or the weak Van der Waals forces. The ability of the dye to be eluted out depends on the strength and type of interaction between the dye and sorbent. Due to the presence of structural hydroxyl groups in TiP and TiHEDP, it is expected that the dye could either be bound to the matrix material (TiP and TiHEDP) by hydrogen bonds or weak van der Waal's forces, making sorption and desorption easy and possible. It was therefore thought of interest to use TiP and TiHEDP as a sorbent for wastewater treatment containing dyes.

The sorption behaviour of dyes namely, Crystal Violet (CV), Methylene Blue (MB), Rhodamine 6G (R6G) and Pink FG (PFG) towards TiP and TiHEDP has been studied, based on thermodynamic parameters evaluated and
adsorption isotherms [Langmuir and Freundlich]. Breakthrough capacity and elution behaviour of dyes have also been studied and discussed.

4.7 MATERIALS AND METHODS

The synthesis and characterization of TiP and TiHEDP has been discussed in detail in Chapter – II. Crystal Violet (CV), Rhodamine 6G (R6G), Methylene Blue (MB) were procured from S.D. Fine chem. Ltd. and Pink FG (PFG) was procured from Coloutex Pvt. (India) Ltd. All reagents (H₂SO₄, HNO₃, HCl, KCl etc.) used were of AR grade. Double-distilled water was used for all the studies. The amount of dyes adsorbed and eluted was determined spectrophotometrically at the absorption maxima of the four dyes CV (590nm), R6G (525nm), MB (665nm) and PFG (532nm), using calibration curve for each individual dye. For sorption studies of dyes (CV, RG, MB and PFG) towards TiP and TiHEDP, a shaker bath having a temperature variation of ± 0.5 K was used.

For sorption studies, 1 g of sorbent material, TiP or TiHEDP as the case may be, were accurately weighed and transferred into a glass column (diameter 1.2 cm and length 2 cm).

**Sorption experiments**

**Optimization of pH and flow rate**

pH was optimized by passing 5 mL of feed solution containing 100 ppm dye solution through the sorbent material at a flow rate of 0.1 mL.min⁻¹, in the pH range 2-10 with increments of 2.

Optimization of flow rate was carried out by varying the flow rate of the feed solution from 0.1 to 1.0 mL.min⁻¹, maintaining pH of the solution, at which maximum sorption of respective dye takes place.

Percentage adsorption in both cases, was calculated using the formula 
\[ \frac{C_o - C_e}{C_o} \times 100 \], where \( C_o \) is initial dye concentration and \( C_e \) is the dye concentration in eluted solution.
**Adsorption isotherms**

The binding of the dyes onto surface of TiP or TiHEDP was studied using Langmuir and Freundlich adsorption isotherms. Adsorption isotherms were studied by taking 20 mL of each dye solution of varying concentration [10, 20, 30, 40, 50 ppm] and shaken with 200 mg of TiP or TiHEDP [30-60 mesh (ASTM)] for 90 mins, in stoppered conical flasks, at 313 K and 323 K, at optimum pH. The supernatant liquid was removed immediately after requisite time and the dye concentration evaluated.

**Breakthrough capacity (BTC)**

For this study, 5 mL fractions of each individual dye, containing (100 ppm in case of CV, R6G and PFG and 5000 ppm in case of MB) was passed through column containing the sorbent material, TiP or TiHEDP as the case may be, maintaining optimum flow rate and optimum pH. 5 mL fractions of the effluent was collected and dye concentration measured before and after elution. The process was continued till the amount of dye was same in feed and effluent. BTC is calculated using the ratio $C_e/C_0$, where $C_e$ is the concentration of the dye in the effluent and $C_0$ is the concentration of dye in the feed [85]. A breakthrough curve was obtained by plotting the breakthrough ratio $C_e/C_0$ against the effluent volume, where $C_o$ and $C_e$ are the concentrations of the initial solution and effluent respectively. Break through capacity is calculated using formula $(C_0V)/w$, where $C_0$ is concentration in mol.L$^{-1}$ of dye required for saturation and $w$ is the weight of the exchanger.

**Elution studies**

For elution studies, the sorbent material was loaded with 5 mL of each dye solution containing 100 ppm of CV, R6G, PFG and 500 ppm of MB and eluted with 0.01M solutions of HCl, HNO$_3$, H$_2$SO$_4$ and KCl. The amount of dye recovered was calculated as $(C_e/C_0) \times 100$ where $C_e$ is the concentration of the dye in the eluted solution and $C_0$ is initial concentration of dye.

**Case study**

In order to explore the utility of TiP and TiHEDP in waste water treatment containing dyes, an effluent sample containing MB was prepared.
having similar composition of textile waste water. The composition of prepared effluent is presented in Table 4.1.

Effluent sample was shaken with 500 mg of exchanger in stoppered conical flasks at constant temperature (303K) at different time intervals with increments of 15 min (15, 30, 45, 60, 75 min). The supernatant liquid was removed immediately and the COD measured each time to determine the extent of dye removal. COD was determined by the well known potassium dichromate method [87].

### Table 4.1 The composition of effluent sample

<table>
<thead>
<tr>
<th>Components/Parameters</th>
<th>Unit</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene Blue</td>
<td>ppm</td>
<td>200</td>
</tr>
<tr>
<td>pH</td>
<td>-</td>
<td>6.5</td>
</tr>
<tr>
<td>Total Alkalinity as CaCO₃</td>
<td>ppm</td>
<td>302</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>ppm</td>
<td>1215</td>
</tr>
<tr>
<td>COD</td>
<td>ppm</td>
<td>512</td>
</tr>
<tr>
<td>Chloride as Cl⁻</td>
<td>ppm</td>
<td>600</td>
</tr>
<tr>
<td>Sulphate as SO₄²⁻</td>
<td>ppm</td>
<td>120</td>
</tr>
<tr>
<td>Calcium (Ca⁺²)</td>
<td>ppm</td>
<td>68</td>
</tr>
<tr>
<td>Sodium (Na⁺)</td>
<td>ppm</td>
<td>2200</td>
</tr>
<tr>
<td>Potassium (K⁺)</td>
<td>ppm</td>
<td>52</td>
</tr>
</tbody>
</table>
4.8 RESULTS AND DISCUSSION

4.8.1 Sorption studies using TiP

The structures of dyes CV, R6G, MB and PFG have been presented in Figure 4a.

![Figure 4a. Structure of dyes](image)

Effect of pH on the sorption of dyes CV, R6G, MB and PFG (100 ppm), using TiP have been presented in Table 4.2.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Percentage adsorption</th>
<th>pH 2</th>
<th>pH 4</th>
<th>pH 6</th>
<th>pH 8</th>
<th>pH 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV</td>
<td>98.02</td>
<td>97.80</td>
<td>98.20</td>
<td>96.19</td>
<td>92.90</td>
<td></td>
</tr>
<tr>
<td>R6G</td>
<td>83.02</td>
<td>84.59</td>
<td>86.54</td>
<td>81.22</td>
<td>78.46</td>
<td></td>
</tr>
<tr>
<td>MB</td>
<td>94.72</td>
<td>96.94</td>
<td>99.09</td>
<td>93.96</td>
<td>90.20</td>
<td></td>
</tr>
<tr>
<td>PFG</td>
<td>90.53</td>
<td>82.72</td>
<td>83.71</td>
<td>81.20</td>
<td>100.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2 Effect of pH on the sorption of dyes using TiP
It is observed that, in case of CV, MB and R6G, maximum adsorption takes place at pH 6 and in case of PFG, at pH 10. Maximum adsorption of dyes is observed at a flow rate 0.1mL.min⁻¹.

Generally both Langmuir and Freundlich isotherms are used for explaining the adsorption on materials. This has been discussed in detail in chapter – III, Section 3A.3. If the adsorption process follows the Langmuir pattern, plot of \( \frac{1}{X/m} \) versus \( 1/C_e \) is a straight line. If it follows Freundlich pattern \( \log C_e \) versus \( \log(X/m) \) is straight line. Langmuir and Freundlich isotherms for each dye have been presented in Figures 4b. (1-4) and (5-8) respectively.
Figure 4b. Adsorption Isotherms of cationic dyes using TiP
Further, from Langmuir isotherms, $b$, $V_m$ and from Freundlich isotherms $(1/n)$ and $K$ have been calculated from the slope and intercept. All these parameters are presented in Table 4.3.

**Table 4.3 Langmuir and Freundlich constants evaluated for sorption of dyes towards TiP**

<table>
<thead>
<tr>
<th>Dye</th>
<th>Temp. (K)</th>
<th>Langmuir Constants</th>
<th>Freundlich Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$V_m$ (mg.g$^{-1}$)</td>
<td>$b$ (L.mg$^{-1}$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>323</td>
<td></td>
<td>29.67</td>
<td>0.029</td>
</tr>
<tr>
<td>R6G</td>
<td>313</td>
<td>217.39</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>33.11</td>
<td>0.010</td>
</tr>
<tr>
<td>MB</td>
<td>313</td>
<td>196.08</td>
<td>0.027</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>128.21</td>
<td>0.010</td>
</tr>
<tr>
<td>PFG</td>
<td>313</td>
<td>142.85</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>25.06</td>
<td>0.036</td>
</tr>
</tbody>
</table>

From Figures 4b (1-8), as well as $R^2$, correlation coefficient (Table 4.3), all dyes obey both Langmuir and Freundlich isotherms. It is observed that values of $V_m$ decrease with rise in temperature, indicating exothermic nature of the adsorption process [88]. Variation in $R^2$ with temperature is attributed to the fact that the surface adsorption is not a monolayer with single site. Two or more sites with different affinities may be involved in dye sorption [89].

In order to explain the effect of temperature on the sorption, thermodynamic parameters, standard free energy $\Delta G^0$, standard enthalpy $\Delta H^0$, and standard entropy $\Delta S^0$ were determined using the following equations [90],

$$\Delta G^0 = -RT \ln b,$$

$$\Delta H^0 = R\{T_1/T_2 - T_1\ln(b_2/b_1)\}$$

and

$$\Delta S^0 = (\Delta H^0 - \Delta G^0)/T,$$
where, $R$ is the gas constant, $b_1$ and $b_2$ are Langmuir constants at temperatures $T_1$ and $T_2$, respectively. Thermodynamic parameters for the sorption of CV, R6G, MB and PFG are presented in Table 4.4.

**Table 4.4 Thermodynamic parameters evaluated for sorption of dyes towards TiP**

<table>
<thead>
<tr>
<th>Dye</th>
<th>Temperature (K)</th>
<th>$\Delta G^\circ$ (kJ.mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ.mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (kJ.mol$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV</td>
<td>313</td>
<td>-0.521</td>
<td>-56.794</td>
<td>-0.1478</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>-9.042</td>
<td></td>
<td>-0.1478</td>
</tr>
<tr>
<td>R6G</td>
<td>313</td>
<td>-9.530</td>
<td>-82.192</td>
<td>-0.2300</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>-6.280</td>
<td></td>
<td>-0.2350</td>
</tr>
<tr>
<td>MB</td>
<td>313</td>
<td>-8.577</td>
<td>-112.75</td>
<td>-0.3870</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>-12.452</td>
<td></td>
<td>-0.3876</td>
</tr>
<tr>
<td>PFG</td>
<td>313</td>
<td>-5.939</td>
<td>-109.10</td>
<td>-0.3290</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>-9.615</td>
<td></td>
<td>-0.3080</td>
</tr>
</tbody>
</table>

Negative $\Delta G^\circ$ values indicate high affinity of dyes towards TiP and that the adsorption process is spontaneous. Negative $\Delta G^\circ$ values also indicate that the system reaches a more stable energy level after sorption. Negative $\Delta H^\circ$ values indicate sorption of dyes to be exothermic in nature. This is also supported by decrease in $V_m$ values with increase in temperature. The negative $\Delta S^\circ$ values in all cases, suggest favourable adsorption. A decrease in $\Delta S^\circ$ values, indicate higher uptake of the dyes, which is a result of high $S^\circ$ in the external aqueous phase and a lower $S^\circ$ in sorbent phase [91].

A breakthrough curve (plot of $C_e/C_0$ vs effluent volume) is presented in Figure 4c.
Breakthrough capacity for the sorption of the dyes, CV, R6G, MB and PFG using TiP are presented in Table 4.5.

**Table 4.5 Breakthrough capacity of CV, R6G, MB and PFG towards TiP**

<table>
<thead>
<tr>
<th>Crystal Violet $C_0 = 100$ ppm</th>
<th>Rhodamine 6G $C_0 = 100$ ppm</th>
<th>Methylene Blue $C_0 = 5000$ ppm</th>
<th>Pink FG $C_0 = 100$ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Through put (mL) $C_v/C_0$</td>
<td>Through put (mL) $C_v/C_0$</td>
<td>Through put (mL) $C_v/C_0$</td>
<td>Through put (mL) $C_v/C_0$</td>
</tr>
<tr>
<td>5 0.007</td>
<td>5 0.068</td>
<td>10 0.042</td>
<td>5 0.009</td>
</tr>
<tr>
<td>10 0.107</td>
<td>10 0.179</td>
<td>20 0.098</td>
<td>10 0.600</td>
</tr>
<tr>
<td>15 0.160</td>
<td>15 0.182</td>
<td>30 0.188</td>
<td>15 0.990</td>
</tr>
<tr>
<td>20 0.300</td>
<td>20 0.720</td>
<td>40 0.256</td>
<td></td>
</tr>
<tr>
<td>25 0.580</td>
<td>25 0.921</td>
<td>50 0.400</td>
<td></td>
</tr>
<tr>
<td>30 0.998</td>
<td></td>
<td>60 0.680</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>70 0.780</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>80 0.940</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>90 0.960</td>
<td></td>
</tr>
</tbody>
</table>
Breakthrough capacity is the maximum capacity of the sorbent to adsorb a particular solute. BTC is calculated by \( \frac{(C_0V)}{w} \), where \( C_0 \) is initial concentration in mol.L\(^{-1}\) required for saturation and \( w \) is the weight of the exchanger. The observed order of BTC is MB (1.47 mmol.L\(^{-1}\)) > CV (0.007 mmol.L\(^{-1}\)) > R6G (0.005 mmol.L\(^{-1}\)) > PFG (0.004 mmol.L\(^{-1}\)). This order reveals the sorption capacity of the dye towards TiP. All dyes exhibit good sorption which could be attributed to both cation exchange nature of sorbent and cationic nature of the dyes. The very high value observed in case of MB could be due to positive charge at the hetero atom. Though there is a positive charge in case of CV, R6G and PFG, breakthrough capacity is less which may be attributed to phenyl rings causing steric effects. Probably, even small changes in the dye structure may significantly influence the adsorption capacity. CV, R6G, MB and PFG (Figure 4a) possess -NR\(_2\) (where \( R = H \) or CH\(_3\)) as functional groups of varying basicity, the order of basicity being MB>CV>R6G>PFG. The sorbent TiP possesses structural hydroxyl groups. Therefore bonding of dyes onto the sorbents could be either hydrogen bonds or weak van der Waal’s forces. The sorption is expected to be MB>CV>R6G>PFG as per basicity order. Besides steric effects contributed by phenyl rings in case of PFG and R6G also plays an important role in the sorption. Elution behaviour of dyes CV, R6G, MB and PFG towards TiP have been presented in Table 4.6

**Table 4.6 Elution behaviour of dyes sorbed onto TiP**

<table>
<thead>
<tr>
<th>Eluting Agent</th>
<th>CV</th>
<th>R6G</th>
<th>MB</th>
<th>PFG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( E_v )</td>
<td>% E</td>
<td>( E_v )</td>
<td>% E</td>
</tr>
<tr>
<td>0.01M HNO(_3)</td>
<td>25</td>
<td>95.40</td>
<td>35</td>
<td>95.10</td>
</tr>
<tr>
<td>0.01M HCl</td>
<td>40</td>
<td>82.80</td>
<td>40</td>
<td>81.00</td>
</tr>
<tr>
<td>0.01M H(_2)SO(_4)</td>
<td>40</td>
<td>81.00</td>
<td>40</td>
<td>93.00</td>
</tr>
<tr>
<td>0.01M KCl</td>
<td>40</td>
<td>31.00</td>
<td>40</td>
<td>82.10</td>
</tr>
</tbody>
</table>

\( E_v = \) mL of eluting agent; \% E = percentage elution
It is observed from Table 4.6 that acids in general, are better eluants than electrolytes. However, 0.01 M HNO₃ is best eluant for all dyes. In case of PFG, there is 100% elution using 0.01 M HNO₃ as well as 0.01 M KCl. Due to presence of structural hydroxyl groups in TiP the dyes are probably bound by hydrogen bonds or the weak van der Waals forces making sorption and desorption (elution) easy and possible. In the present study, maximum sorption capacity of MB towards TiP is 196.08 mg·g⁻¹. Similar studies carried out on activated carbon made from Guava seeds towards sorption of MB is 0.667 mg·g⁻¹ [92]. Though activated carbon obtained from Guava seeds is a low cost material, TiP is more effective towards removal of dyes, probably due to its cation exchange property of both TiP as well as the dyes.

In the case study using an effluent sample containing MB it is observed that COD reduction at different time intervals is, 83.01% (15 min), 90.12% (30 min), 96.45% (45 min), 97.23% (60 min) and 98.65% (75 min) indicating good efficiency of TiP for removal of MB.

### 4.8.2 Sorption studies using TiHEDP

Effect of pH on the sorption of dyes CV, R6G, MB and PFG (100 ppm), using TiHEDP have been presented in Table 4.7.

<table>
<thead>
<tr>
<th>Dye (C₀=100 ppm)</th>
<th>Percentage adsorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 2</td>
</tr>
<tr>
<td>CV</td>
<td>98.50</td>
</tr>
<tr>
<td>R6G</td>
<td>24.45</td>
</tr>
<tr>
<td>MB</td>
<td>100.00</td>
</tr>
<tr>
<td>PFG</td>
<td>90.53</td>
</tr>
</tbody>
</table>

It is observed that, in case of CV, MB and R6G, maximum adsorption takes place at pH 6 and in case of PFG, at pH 10. Maximum adsorption of dyes is observed at a flow rate 0.1mL·min⁻¹.
Chapter IV – TiP and TiHEDP as Sorbents

Langmuir and Freundlich isotherm for each dye using TiHEDP have been presented in Figure 4d. (1-4) and (5-8) respectively.

Further, from Langmuir Freundlich isotherms, $b$, $V_m$ and from isotherms $(1/n)$ and $K$ have been calculated from the slope and intercept. All these parameters are presented in Table 4.8.
Figure 4d. Adsorption Isotherms of cationic dyes using TiHEDP
Table 4.8 Langmuir and Freundlich Constants evaluated for Sorption of dyes towards TiHEDP

<table>
<thead>
<tr>
<th>Dye</th>
<th>Temp. (K)</th>
<th>Langmuir Constants</th>
<th>Freundlich Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Vm (mg.g⁻¹)</td>
<td>b(mg.L⁻¹)</td>
</tr>
<tr>
<td>CV</td>
<td>313</td>
<td>79.37</td>
<td>0.0096</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>15.60</td>
<td>0.0490</td>
</tr>
<tr>
<td>R6G</td>
<td>313</td>
<td>56.49</td>
<td>0.0170</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>416.66</td>
<td>0.0043</td>
</tr>
<tr>
<td>MB</td>
<td>313</td>
<td>500.00</td>
<td>0.0382</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>454.54</td>
<td>0.0668</td>
</tr>
<tr>
<td>PFG</td>
<td>313</td>
<td>27.17</td>
<td>0.0282</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>25.64</td>
<td>0.0298</td>
</tr>
</tbody>
</table>

From Figures 4d (1-8), as well as R², correlation coefficient (Table 4.8), it is observed that CV (313 K), MB and R6G follow Freundlich pattern while PFG follows both patterns. Variation in R² with temperature is attributed to the fact that the surface adsorption is not a monolayer with single site. Two or more sites with different affinities may be involved in dye sorption [89]. In case of CV, MB, and PFG, the values of Vm decreases with rise in temperature, indicating exothermic nature of the adsorption process [88] whereas in case of R6G, values of Vm increases with rise in temperature, indicating endothermic nature of the adsorption process. The thermodynamic parameters for the sorption of CV, R6G, MB and PFG towards TiHEDP are presented in Table 4.9.
Table 4.9 Thermodynamic Parameters evaluated for sorption of dyes towards TiHEDP

<table>
<thead>
<tr>
<th>Dye</th>
<th>Temperature (K)</th>
<th>$\Delta H^0$ (kJ. mol$^{-1}$)</th>
<th>$\Delta G^0$ (kJ. mol$^{-1}$)</th>
<th>$\Delta S^0$ (kJ. mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV</td>
<td>313</td>
<td>-137.18</td>
<td>-5.90</td>
<td>-0.4194</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>-10.45</td>
<td>-0.3920</td>
<td></td>
</tr>
<tr>
<td>R6G</td>
<td>313</td>
<td>11.51</td>
<td>-7.37</td>
<td>0.0603</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>-3.92</td>
<td>0.0477</td>
<td></td>
</tr>
<tr>
<td>MB</td>
<td>313</td>
<td>-46.89</td>
<td>-9.48</td>
<td>-0.1801</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>-11.28</td>
<td>-0.1801</td>
<td></td>
</tr>
<tr>
<td>PFG</td>
<td>313</td>
<td>-4.64</td>
<td>-8.69</td>
<td>0.1290</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>-9.12</td>
<td>0.0138</td>
<td></td>
</tr>
</tbody>
</table>

It is observed that negative $\Delta G^0$ values in all cases indicate the sorption process is feasible and non spontaneous in nature. Negative $\Delta G^0$ values also indicate that the system reaches a more stable energy level after sorption. Negative $\Delta H^0$ values indicate sorption of dyes to be exothermic in nature. This is supported by decrease in $V_m$ values obtained in case of CV, MB and PFG. The positive entropy in case of R6G indicates an increased disorder of the system. Negative $\Delta S^0$ values in rest of the cases indicate absence of disorderliness in the system. A decrease in $\Delta S^0$ values indicates higher uptake of the dyes, which is a result of high $S^0$ in the external aqueous phase and a lower $S^0$ in sorbent phase [91].

A breakthrough curve (plot of $C/C_o$ vs effluent volume) is presented in Figure 4e.
Breakthrough capacity for the sorption of the dyes, CV, R6G, MB and PFG using TiHEDP are presented in Table 4.10.

**Table 4.10 Breakthrough capacity of CV, R6G, MB and PFG towards TiHEDP**

<table>
<thead>
<tr>
<th>Crystal Violet</th>
<th>Rhodamine 6G</th>
<th>Methylene Blue</th>
<th>Pink CFG</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_0 = 100$ ppm</td>
<td>$C_0 = 100$ ppm</td>
<td>$C_0 = 500$ ppm</td>
<td>$C_0 = 100$ ppm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Through Put (mL)</th>
<th>$C_r/C_0$</th>
<th>Through Put (mL)</th>
<th>$C_r/C_0$</th>
<th>Through Put (mL)</th>
<th>$C_r/C_0$</th>
<th>Through Put (mL)</th>
<th>$C_r/C_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.002</td>
<td>5</td>
<td>0.012</td>
<td>10</td>
<td>0.007</td>
<td>5</td>
<td>0.01</td>
</tr>
<tr>
<td>10</td>
<td>0.069</td>
<td>10</td>
<td>0.105</td>
<td>30</td>
<td>0.295</td>
<td>10</td>
<td>0.85</td>
</tr>
<tr>
<td>15</td>
<td>0.082</td>
<td>15</td>
<td>0.110</td>
<td>60</td>
<td>0.765</td>
<td>15</td>
<td>0.98</td>
</tr>
<tr>
<td>20</td>
<td>0.398</td>
<td>20</td>
<td>0.511</td>
<td>90</td>
<td>0.857</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.443</td>
<td>25</td>
<td>0.626</td>
<td>100</td>
<td>0.989</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.544</td>
<td>30</td>
<td>0.709</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>0.727</td>
<td>35</td>
<td>0.848</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.924</td>
<td>40</td>
<td>0.966</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The observed order of BTC is MB (0.156 mmol.L\(^{-1}\)) > CV (0.010 mmol.L\(^{-1}\)) > R6G (0.008 mmol.L\(^{-1}\)) > PFG (0.004 mmol.L\(^{-1}\)). This order reveals the sorption capacity of the dyes towards TiHEDP. All dyes exhibit good sorption which could be attributed to both cation exchange nature of sorbent and cationic nature of dyes. The very high value observed in case of MB could be due to positive charge at the hetero atom. Though there is a positive charge in case of CV, R6G and PFG, break through capacity is less which may be attributed to phenyl rings causing steric effects. Probably, even small changes in the dye structure may significantly influence the adsorption capacity. CV, R6G, MB and PFG (Figure 4a) possess -NR\(_2\) (where R = H or CH\(_3\)) as functional groups of varying basicity, the order of basicity being MB>CV>R6G>PFG. The sorbent TiHEDP possesses structural hydroxyl groups. Therefore bonding of dyes onto the sorbents could be either hydrogen bonds or weak van der Waal’s forces. The sorption is expected to be MB>CV>R6G>PFG as per basicity order. Besides steric effects contributed by phenyl rings in case of PFG and R6G also plays an important role in the sorption. Elution behaviour of dyes CV, R6G, MB and PFG towards TiHEDP have been presented in Table 4.11

<table>
<thead>
<tr>
<th>Eluting Agent</th>
<th>CV</th>
<th>R6G</th>
<th>MB</th>
<th>PFG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ev</td>
<td>%E</td>
<td>Ev</td>
<td>%E</td>
</tr>
<tr>
<td>0.01M HNO(_3)</td>
<td>25</td>
<td>80.00</td>
<td>50</td>
<td>95.70</td>
</tr>
<tr>
<td>0.01M HCl</td>
<td>35</td>
<td>96.00</td>
<td>50</td>
<td>83.00</td>
</tr>
<tr>
<td>0.01M H(_2)SO(_4)</td>
<td>40</td>
<td>83.50</td>
<td>50</td>
<td>82.90</td>
</tr>
<tr>
<td>0.01M KCl</td>
<td>35</td>
<td>100.00</td>
<td>45</td>
<td>87.70</td>
</tr>
</tbody>
</table>

Ev = mL of Eluting Agent; %E = Percentage Elution

It is observed that, acids, in general, are better eluants than electrolytes. 0.01 M HNO\(_3\) and 0.01 M HCl are found to be best eluants for all dyes,
whereas 0.01M KCl is best eluant for CV, R6G and PFG. However, 0.01M H$_2$SO$_4$ is not found to be so suitable for elution. Complete elution is observed in case of PFG, using 0.01 M HNO$_3$ as well as 0.01 M KCl. Due to presence of structural hydroxyl groups in TiHEDP the dyes are probably bound by hydrogen bonds or the weak van der Waal’s forces making sorption and desorption (elution) easy and possible. In the present study, maximum sorption capacity of MB towards TiHEDP is 500 mg.g$^{-1}$. Similar studies carried out on activated carbon made from Guava seeds towards sorption of MB is 0.667 mg. g$^{-1}$ [92]. Though activated carbon obtained from Guava seeds is a low cost material, TiHEDP is more effective towards removal of dyes, probably due to cation exchange property of both TiHEDP and the dyes.

In the case study using effluent sample containing MB, it is observed that COD reduction at different time intervals is, 45.69 % (15 min), 55.32 % (30 min), 72.32 % (45 min), 89.09 % (60 min) and 89.99 % (75 min) indicating good efficiency of TiHEDP for removal of MB.
4.9 CONCLUSIONS

- Both TiP and TiHEDP exhibit good chemical resistivity (acid and organic solvent media) and thermal stability which are important characteristics for materials to behave as sorbents.

- Being cation exchange materials, both TiP and TiHEDP exhibit good sorption for cationic dyes.

- Both TiP and TiHEDP also exhibit good elution behaviour. Due to presence of structural hydroxyl groups in TiP and TiHEDP, the dyes are bound by hydrogen bonds or weak van der Waal’s forces, making sorption and desorption easy and possible.

- The studies indicate TiP and TiHEDP to be promising candidates for removal and recovery of dyes.
REFERENCES

[21] Reife A, Waste Treatment of soluble Azo Acid, Direct and Reactive Dyes Using a Sodium Hydrosulfite Pretreatment Followed by Carbon


Chapter IV – TiP and TiHEDP as Sorbents


