Colored materials and dyes constitute the focus of much environment concern nowaday. Dyes are used in many industries like textile, paper, leather, plastics, cosmetics, pharmaceuticals etc. These industries uses a considerable amount of water for dyeing and their effluent mainly consist of colored waste water. Color is the first observable parameter for checking the quality of water and according to WHO recommendations the water used for drinking purpose should be colorless. In industrial waste water color is the first apparent pollutant. The presence of very small amount of color hampers the penetration of sunlight and affects aquatic flora and fauna. The presence of dyes impart excess organic load in waste water.

Around 10,000 different types of dyes are available worldwide with an annual production of $7 \times 10^5$ metric tones. According to an estimate 10% dyes are discharged out after dyeing textiles and 2% dyes are left in waste water even after treatment in primary treatment plants. The effluent treatment by aerobic processes is insufficient for removing color of the effluent. The synthetic dyes are xenobiotic and the microbes in natural ecosystem are unable to degrade these as they do not have the enzymes required for their biodegradation. Due to toxic nature of many dyes several microbes are unable to degrade them at appreciable concentrations. In the dye molecules there are two important components: chromophore, responsible for producing the color and auxochromes which enhances the affinity of the dye toward the fibers. Generally, the dyes used in the textile industry are basic dyes, acid dyes, reactive dyes, direct dyes, azo dyes, mordant dyes, vat dyes, disperse dyes and sulfur dyes. Dyes can be classified into the main categories of cationic, anionic and nonionic dyes. Cationic dyes are basic dyes while the anionic dyes are acid dyes. The dyes are very soluble in water thus their removal needs some specific techniques before discharge at water outlets. The high solubility of dyes in water makes processes like coagulation and flocculation difficult. These processes are usually carried out by the use of Fe (III) salts or alums which causes secondary chemical load in water after treatment. In addition to this, these processes produces a large amount of sludge thus the treatment by this method causes a big sludge disposal problem. Some other physical methods are common for color removal like membrane separation, electrochemical removal and photochemical degradation. Membrane separation involves the use of micro porous or nano porous membranes at high pressure for reverse osmosis. The synthesis and maintenance of such membranes at industrial scale is not so easy. In developing Asian countries like
India the membrane recharge is not economically feasible. Electrochemical removal requires large amount of energy for generating sufficient threshold energy, several toxic by-products are generated in the process thus technically and economically the process is not feasible at industrial scale. Photochemical degradation is usually carried out in the presence of catalyst but the degradation products of certain dyes are colorless but mutagenic e.g. the photochemical degradation of azo dyes containing naphthalene nucleus undergo oxidation to give naphthaquinone which appears colorless in bulk effluent and is carcinogenic. Biological treatment of effluents is also an attractive mean of color removal. Recently a lot of work is going on fungal decolorization, microbial degradation and adsorption on dead biomass. Many microorganisms have been found capable of dye degradation. The biological degradation requires a large area for water treatment and the treatment may not eliminate complex dyes with synthetic origin. The temperature variation in region may also affect the growth of microorganisms. The microbes can be used only in batch mode and not in column as the growth inside the column may block the operation. Amongst several physical, chemical and biological techniques, adsorption is a procedure of choice due to its efficiency and economical viability. For about past two decades, adsorption technique has been well explored to removes hazardous pollutants including dyes from waste water. Commercially available activated carbon has yielded excellent results in the dye removal. However taking into account the high costs involved in the preparation and regeneration process, the feasibility of alternate adsorbents has been studied recently by the scientists. These include agricultural as well as industrial by-products. Adsorption is an age old sorption process for water decontamination applications. This is better than any other process due to its simplicity, economic viability, application in batch and column mode, flexibility and efficiency for toxic pollutants. After adsorption, no harmful, toxic and unwanted chemicals are generated. Adsorbent can also be desorbed using suitable recovery agent. The adsorbate can be trapped to small volume solid instead of huge volume of effluent. When dyes are removed using this process, the spread area of effluent and colored contaminant decreases. The dye loaded adsorbent decomposes after the process and the sludge volume decreases from 100 to 1.

For the facility of the presentation, the results of our finding have been divided into seven chapters.
Chapter 1: Introduction and Literature Review

This chapter deals with the introduction and review of literature showing the application of various adsorbents for dye removal in the last decade. From the detailed literature review, the following conclusions were drawn:

- Activated carbon (AC) has been efficiently used for the removal of anionic and cationic dyes. Activated carbon normally has very porous structure with a large surface area ranging from 500-2000 m$^2$g$^{-1}$. Adsorption on AC is not selective as it takes place through Vander Waal’s interactions.

- The literature survey revealed that several wood by-products and agricultural wastes offer a renewable source of activated carbon. These waste materials have no virtual economic importance; their carbonization offers disposal solution and activated carbon obtained after the process adds up an economic value. Several carbon materials from wastes have been used for removal of acid and basic dyes.

- Several agricultural wastes like hazelnut shell, low-cost banana and orange peels, tree fern, neem saw dust, date pits, barley husk and corncob, wheat straw, wood chips and corn-cob shreds etc. opened new ventures for the dye removal by low cost adsorbents derived waste materials.

- Industrial solid wastes are generated in huge amounts in industries and such materials have been used for dye removal from textile effluents sulphuric acid-modified bagasse, hen feathers i.e. poultry waste, Lignin-a paper industry waste, blast furnace dust and deoiled soya-an oil mill waste etc. Thus several industrial by products are being explored for their adsorption capacities for dye removal.

- Natural clays are abundant on most of the continents of the world. Clay materials possess layered type of structure and they are also classified on the basis of their layered structures. These clays are cheaper than activated carbon.
Some mesoporous materials like mesoporous carbons, microporous zeolites, TiO₂, nano porous materials derived from peels of jack fruit, nano porous silica, clay minerals of halloysite nano tubes etc. have been used as adsorbents for dye removal.

Chapter 2: Material and Experimental Methods

Preparation of Eucalyptus bark, Eucalyptus bark carbon, Tea waste, Tea waste carbon, Bagasse and Bagasse carbon as adsorbent

Eucalyptus bark (EB), Tea waste (TW), Bagasse (BG) have been treated with suitable reagent to remove color and were then completely dried in an oven at 353 K for 24 h. The dried bark was then cut into small pieces, crushed, and sieved to eliminate fine particles. The obtained material was washed repeatedly with DDW. Finally, the obtained material was dried in an air circulating oven at 353 K and stored in the dessicants until further use.

The materials EB, TW and BG were carbonized in sulphuric acid followed by and dipping in 1% NaHCO₃ and washing with DDW. The materials were then completely dried in an oven at 353 K for 24 h and stored in the desiccators until further use. These carbonized materials were EBC, TWC and BGC.

Preparation of Surfactant modified adsorbents

We have studied the specific modifications of EB, EBC, TW, TWC, BG and BGC with SDS (Sodium dodecyl sulfate), TX (Triton X-100) and CPC-EB (Cetyl pyridinium chloride). SDS, TX and CPC are anionic, non ionic and cationic surfactants respectively and were used as model surfactants belonging to different classes. The adsorbent were mechanically stirred with adsorbent below their critical miceller concentration (CMC). The modified adsorbent was filtered and washed with double DDW thrice and then material was dried in hot air oven at 343 K for 24 h. The adsorbents derived were EB, SDS EB, CPC EB, TX EB, EBC, SDS EBC, CPC EBC, TX EBC, TW, SDS TW, CPC TW, TX TW, TWC, SDS TWC, CPC TWC, TX TWC, BG, SDS BG, CPC BG, TX BG, BGC, SDS BGC, CPC BGC, TX BGC were prepared for use as adsorbents for dye removal.
Cellulose extraction and surface modification by grafting and carboxylation

Cellulose was extracted from EB as it contained around 40% cellulose. The extraction was carried out by a standard protocol. White fluffy cellulose is obtained which was grafted by acrylamide using K₂S₂O₈ as initiator. Polyacrylamide grafted cellulose; PAG-Cell was carboxylated by treating with succinic anhydride in 1, 4-dioxane at pH 4.0 to give carboxylated polyacrylamide grafted cellulose (PAG-Cell-COOH). The material obtained was dried in hot air oven at 353 K and stored in dessicator till further use. The adsorbents prepared were Cell, PAG-Cell and PAG-Cell-COOH.

Preparation of Microporous adsorbents and their derivatives

Zeolite-4A (Z-4A); (SiO₂)₂(Al₂O₃)(Na₂O)₅H₂O was procured from National drugs and chemicals, India. This was crushed into fine powder of size fraction <0.25 mm. Surfactant modification of Z-4A was carried out by treating Benzyl trimethyl ammonium chloride (BTMAC). The Surfactant modified zeolite (SMZ) was dried at 353 K and stored in air tight container till further use.

Preparation of Mesoporous adsorbents

Vermiculite (VC), a 2:1 type aluminosilicate clay mineral was obtained from Tamil Nadu Minerals limited, Dharampuri. This was crushed and finally powdered and particle size <0.5 mm was separated for adsorption study. This was activated by washing with DDW and filtration using vacuum pump and drying at 353 K for 24h and stored in air tight container for further study.

Bentonite (BT) i.e. (Al₂O₃)(SiO₂)₄ xH₂O was procured from Loba chemie. This was crushed, ground and sieved through a mesh to get a particle size <0.25 mm and dried at 393 K for 2h before use. This was then stored in air tight container for further use.

10.0 g Bagasse fly ash (BFA) was dipped in 10% v/V of 20 V H₂O₂ for 24 hours to oxidize the organic matter. This was then filtered and washed with distilled water several times till the washings attain neutral pH and negligible conductance and dried in a hot air oven at 80° for 12 hours and sieved to get the particle size less than 250 μm and was stored in an air tight container for further use. The mesoporous adsorbents prepared were Z-4A, SMZ, BT, VC and BT.
Preparation of nano adsorbents

Nano-Al₂O₃ particles (ANP) were synthesized by sol gel method. For this purpose saturated solution of aluminium sulphate was precipitated with ammonia till a gel was obtained. The gel was then calcined in a muffle furnace. The powder ANP was stored in a dessicator till further use.

Nano ZnO particles (ZNP) were synthesized by sonicating zinc powder 0.019 g (0.3 mmol) in dust form was for 2 h with 4 mL of n-butanol at 303 K. To the above solution, 1.2 mL of triethanolamine (TEA) was added slowly. It was then calcined at 1173K in muffle furnace for 1h and stored in desiccators. The nano porous adsorbents prepared were ANP and ZNP.

Dyes used

1000 mg.L⁻¹ stock solution of dyes i.e. Basic Red-12 (BR-12), Basic violet-10 (BV-10), Acid orange-7 (AO-7) and Acid blue-1 (AB-1) were prepared by dissolving in DDW. 1000 mg.L⁻¹ solutions were prepared by dissolving appropriate amount of dye in DDW and stored in dark colored bottles and diluted by adding suitable amount of water to the stock solution as per requirement.

Chapter 3: Analysis of adsorbents

UV-Visible spectroscopy

The dye concentration before and after adsorption was carried out by using Systronics - 2201 spectrophotometer. A standard plot was drawn for known concentrations and the concentration of dyes was determined by converting the optical density to corresponding concentration. The dyes were analyzed at their respective λ_max.

FTIR Spectroscopy

The FTIR of adsorbents and surface derivatives was carried out with Perkin Elmer spectrophotometer in the range 400-4000 cm⁻¹ using perkin elmer spectrophotometer. The adsorbent was mixed with anhydrous KBr to make a pellet and 400 scans were carried out to give the average FTIR scan.
**Powder XRD analysis**
The adsorbent samples were also characterized by powder X-ray diffractometry using an X’PERT PRO PANalytical with Cu-Kα radiation. The phases of crystalline materials like mesoporous and nanoporous materials were determined.

**SEM and TEM analysis**
SEM was carried out by using ZEOL scanning electron micrograph. The micro porous structures of the adsorbents were studied. The effect of surfactant modification and carbonization on morphological changes were evaluated. TEM provided topographical, morphological, compositional and crystalline information of nano adsorbents. The images allowed us to view samples on a molecular level, making it possible to analyze structure and texture.

**Surface area measurement**
BET surface area measurement was carried out by using micromeritics surface area analyzer. This also gave monolayer volume of N₂ and pore volume of the adsorbents.

**Density measurement**
The density of the adsorbents were determined by using standard protocol. Knowing the mass and volume of adsorbent the density was calculated. The characteristics of the parameters calculated above were correlated to interpret their relative adsorption capacities.

**Determination of water extractable, alcohol extractable materials and ash in adsorbents**
Known weight of adsorbent was shaken with water or alcohol in a round bottom flask, and then it was allowed to stand for 1 h followed by boiling and refluxing. This was cooled in desiccators, filtered and weighed. The loss in weight per gram was calculated. Material was placed in a silica crucible in a muffle furnace. The heating was continued till white powder was left. This is cooled in desiccators and weighed. The amount of ash was determined in mg.g⁻¹ of the sample.
Determination of cellulose, lignin and hemicelluloses in adsorbent

The adsorbed based on plant resources were analyzed for the presence of cellulose, lignin and hemicelluloses and reducing sugars by standard protocols. The plant material based adsorbents like EB, TW and BG were analyzed for these natural components.

Determination of surface acidity and basicity

The surface acidity and basicity were determined by using Bohem titration method. Different groups are responsible for the characteristic acidity and basicity of the surface of the adsorbent which decides the adsorptive nature of the material.

Degradation study

The adsorbents prepared from the natural sources and after surface modification were evaluated for degradation by ground dumping study in environment humidity chamber.

Chapter 4: Optimization of adsorption parameters

The effect of adsorbent dose, pH and contact time on removal of ionic dyes on different adsorbents. Dye solutions of appropriate concentration were reacted with adsorbent at variable adsorbent dose, variable pH and contact time. The studies were carried out for adsorption of ionic dyes viz. BR-12, BV-10, AO-7 and AB-1 over agricultural wastes and their derivatives, carbonized agricultural wastes and their derivatives, extracted cellulose and its derivatives, mesoporous adsorbents, microporous adsorbents and nano porous adsorbents.

Chapter 5: Kinetics of adsorption processes

Adsorption kinetics depends upon the adsorbent adsorbate interface and system condition and has been investigated for their suitability for application in water pollution control. Two vital appraisal elements for adsorption process operation unit are the mechanism and the reaction rate. Dye uptake rate determines the dwelling time required for completing the adsorption process till attainment of equilibrium can be catalogued from kinetic analysis. In order to investigate potential rate controlling steps such as mass transport and chemical reaction processes four kinetic models (Lagergren’s pseudo first order, Ho and McKay’s pseudo second order, Elovich and...
intraparticle diffusion) have been used to test the experimental data following the linear regression methodology. The values of R (Regression coefficient), SEE (Standard estimated error) and RSS (Residual sum of squares) are determined. The model fit was evaluated by assuming showing highest value of R and lowest values of SEE and RSS. The tables were prepared with calculated parameters from the intercept and slope of the curves.

**Pseudo-first order kinetic model**

The first order rate expression of Lagergren based on the solid capacity is generally expressed as follows

\[
\frac{dq}{dt} = k_1(q_e - q_t)
\]

(1)

The integrated form of above equation can be expressed as

\[
\log (q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t
\]

(2)

Where \(q_e\) and \(q_t\) are the amount of dye adsorbed in mg.g\(^{-1}\) at equilibrium and time \(t\) (min) respectively, and \(k_1\), the rate constant of pseudo-first order rate constant (min\(^{-1}\)). The values of \(k_1\), \(q_e\), R, RSS and SEE for adsorption of BR-12, BV-10 and AO-7 over EB and derivatives are given in Table 1.

**Lagergren Pseudo first order kinetics data for dye interactions on EB and derivatives**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dye</th>
<th>(q_e)</th>
<th>(k_1)</th>
<th>R</th>
<th>SEE</th>
<th>RSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>EB</td>
<td>BR-12</td>
<td>3.171</td>
<td>0.0225</td>
<td>0.9684</td>
<td>0.9269</td>
<td>0.03</td>
</tr>
<tr>
<td>SDS EB</td>
<td>BR-12</td>
<td>9.261</td>
<td>0.0153</td>
<td>0.9901</td>
<td>0.0452</td>
<td>0.01</td>
</tr>
<tr>
<td>CPC EB</td>
<td>BR-12</td>
<td>4.832</td>
<td>0.0131</td>
<td>0.9613</td>
<td>0.1096</td>
<td>0.06</td>
</tr>
<tr>
<td>TX EB</td>
<td>BR-12</td>
<td>5.989</td>
<td>0.0525</td>
<td>0.9194</td>
<td>0.2581</td>
<td>0.13</td>
</tr>
<tr>
<td>EB</td>
<td>BV-10</td>
<td>18.311</td>
<td>0.0047</td>
<td>0.9294</td>
<td>0.0724</td>
<td>0.03</td>
</tr>
<tr>
<td>SDS EB</td>
<td>BV-10</td>
<td>15.223</td>
<td>0.0024</td>
<td>0.9619</td>
<td>0.0481</td>
<td>0.01</td>
</tr>
<tr>
<td>CPC EB</td>
<td>BV-10</td>
<td>15.470</td>
<td>0.0065</td>
<td>0.9792</td>
<td>0.0396</td>
<td>0.08</td>
</tr>
<tr>
<td>TX EB</td>
<td>BV-10</td>
<td>8.168</td>
<td>0.0167</td>
<td>0.8493</td>
<td>0.0621</td>
<td>0.02</td>
</tr>
<tr>
<td>SDS EB</td>
<td>AO-7</td>
<td>1.011</td>
<td>0.0081</td>
<td>0.9557</td>
<td>0.0722</td>
<td>0.03</td>
</tr>
<tr>
<td>CPC EB</td>
<td>AO-7</td>
<td>4.176</td>
<td>0.0136</td>
<td>0.9433</td>
<td>0.1397</td>
<td>0.09</td>
</tr>
<tr>
<td>TX EB</td>
<td>AO-7</td>
<td>2.396</td>
<td>0.0082</td>
<td>0.9865</td>
<td>0.3991</td>
<td>0.09</td>
</tr>
</tbody>
</table>
The pseudo first order kinetics was evaluated on the given set of data and it was found that EB and derivatives can remove BR-12. The time versus \( \log (q_e - q_t) \) plots were found to be linear suggesting that the adsorption followed the first order kinetics. The rate constant decreased with surfactant modification in first order kinetics due to double layer potential set up on the EB surface layer which reduce the probability of the diffusion film mechanism. This was observed that in many cases the Lagergren model does not fit well for the whole range of contact time and is generally applicable over initial few minutes of adsorption.

Similarly this model fitted on adsorption of BR-12, BV-10, AO-7 and AB-1 over EBC, TW, TWC, BG, and BGC and their derivatives, Micro porous materials, Meso porous and nano porous materials were carried out for Lagergren first order kinetic model.

**Pseudo second order kinetic model**

The pseudo second order kinetic model of Ho and McKay is given as

\[
\frac{dq}{dt} = k_2(q_e - q_t)^2
\]

The equation upon integration becomes

\[
\frac{t}{q_t} = \frac{t}{k_2q_e^2} + \frac{1}{q_e}t
\]

Where \( k_2 \) is rate constant of pseudo second order adsorption (g. mg\(^{-1}\).min\(^{-1}\)). This model predicts the behavior over whole range of adsorption and is in agreement with an adsorption mechanism being the rate controlling step. The applicability of this model can be verified by plotting \( t/q_t \) against time as per equation 4. The plot was straight line and the parameters \( q_e \) and \( k_2 \) can be determined from the slope and intercept of the plot.

The second order equation was also tested on the whole range of data. The pseudo second order equation (equation 4) and the values were calculated for different adsorption processes of dye adsorption over different adsorbents.

**Elovich kinetic model**

Elovich model is the most useful model to evaluate chemisorption and the Elovich model is given as
\[
\frac{dq}{dt} = \alpha e^{\beta q_t}
\]  
(5)

Where \(\alpha\) is initial rate (mg.g\(^{-1}\).min\(^{-1}\)) because \(dq/dt\) approaches \(\alpha\) when \(q_t\) approaches zero and the parameter \(\beta\) is related to the extent of surface coverage and the activation energy of for chemisorption. When \(q_t=0\) at \(t=0\), the integrated form of equation 5 is given as equation 6 as follows

\[
q_t = \frac{1}{\beta} \ln(t + t_o) - \frac{1}{\beta} \ln t_o
\]  
(6)

Where \(t_o = 1/\alpha \beta\). If \(t\) is much higher than \(t_o\), the above equation can be simplified as

\[
q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t
\]  
(7)

The parameters of Elovich equation obtained for the given set of data were evaluated for dyes adsorption over different adsorbents under study.

**Intraparticle diffusion model**

The pseudo first order and pseudo second order kinetic model could not recognize the mechanism for all adsorption processes, the dye which adsorbs from aqueous medium to the porous adsorbent surface proceeds through three steps. In the first step the film diffusion takes place moving dye from higher concentration gradient to the adsorbent surface and the second step involves particle transport, in which the dye molecules transport within the surface of adsorbent and the third step is concerned with the movement of dye to the core of the adsorbent. The third step is fast and cannot be considered as rate determining in nature. The rate determining step is either film diffusion or particle diffusion. Thus particle diffusion process is slow followed by fast steps like adsorption of dye on the surface of adsorbent. The surface of adsorbent is surrounded by immobile layer of water molecules. The dye molecules show diffusion from the bulk of dye solution in aqueous phase to the immobile layer on the surface till the equilibrium is attained between dye in the bulk and on the surface. The dye can transfer across the film on the surface and the rate of sorption depends upon the difference of concentration between the bulk of dye solution and the dye concentration on the surface of adsorbent. The intraparticle model is given in equation 8.

\[
q_t = k_{int} t^{1/2} + C
\]  
(8)
Where \( C \) is intercept; and \( k_{in} \) is intraparticle rate constant (mg.g\(^{-1}\).min\(^{-0.5}\)). The plot may represent multi-linearity indicating that all the three steps take place slowly.

The best fit model was devised for dye removal from bulk solution on different adsorbents.

**Chapter 6: Thermodynamics and isotherm studies of adsorption processes**

The adsorption isotherm gives the relationships between the amount of dye adsorbed on the adsorbent and the concentration of adsorbed dye in the solution phase at equilibrium. In this study, the adsorption mechanisms and characteristic parameters for the present processes were analyzed by three two parameter isotherms i.e. Freundlich, Langmuir and Temkin isotherm models. These models were used to explain the experimental results within wide range of concentrations and temperatures.

**Freundlich isotherm**

This is the earliest known empirical sorption isotherm which assumes that the exponential decaying adsorption site energy distribution that can be applied to non ideal sorption on heterogeneous surfaces as well as multilayer sorption and is expressed by equation 9.

\[
q_e = K_f \cdot C_e^{\frac{1}{n}} 
\]  

(9)

Where \( C_e \) is equilibrium liquid phase concentration of dye (mg.L\(^{-1}\)); \( q_e \) is equilibrium solid phase concentration (mg.g\(^{-1}\)); \( K_f \) and \( n \) are indicative adsorption isotherm parameters of adsorption capacity (L.g\(^{-1}\)) and intensity (mg.g\(^{-1}\)) respectively. This equation assumes that the strong binding sites of the adsorbent are occupied on priority and the binding strength decreases with the increase in degree of site occupation. The equation can also be represented in linear form as equation 10.

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]  

(10)

**Langmuir isotherm**

This model assumes the monolayer adsorption on definite localized sites which are identical and equivalent. This model assumes that there are no lateral interactions or
Steric hindrance between the adsorbed dye molecules even on adjacent sites. In the
derivation of this isotherm this is assumed that the adsorption is homogeneous and all
sites have equal affinity towards the dye molecules. Due to this reason each molecule
processes constant enthalpy and sorption activation energy with no transmigration of
adsorbate in the plane of the surface. Graphically it is characterized with a plateau, an
equilibrium saturation point where once a molecule occupies a site, no further
adsorption can take place. The Langmuir theory is related to rapid decrease in
intermolecular attractive forces with increase of distance between adsorbate and
adsorbent. The mathematical model of Langmuir isotherm suggests is given as follows

\[ q_e = \frac{Q_o b C_e}{1 + b C_e} \]  \hspace{1cm} (11)

The above equation can be linearized as follows

\[ \frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{b Q_0 C_e} \]  \hspace{1cm} (12)

Where \( Q_o \) and \( b \) are Langmuir constants, the constant \( Q_o \) is related to the monolayer
adsorption capacity in mol.g\(^{-1}\) and \( b \) is the binding constant in L.mol\(^{-1}\) related to
enthalpy of adsorption. The adsorption of dyes over different adsorbents were studied
and this was found that the Langmuir isotherm model fitted the data well on most of the
adsorption studies of the present work.

**Temkin adsorption isotherm**

Temkin isotherm assumes that the fall in heat of adsorption (function of temperature)
would decrease linearly for the dye and adsorbent interactions. The isotherm can be
represented by following equation

\[ q_e = \frac{RT}{b_t} \ln(a_t C_e) \]  \hspace{1cm} (13)

Where \( b_t \) is temkin constant related to the heat of sorption J mol\(^{-1}\)and \( a_t \) is temkin
isotherm constant (L.g\(^{-1}\)). This isotherm is more appropriate when adsorbate is bound
tightly with identical orientation on the surface of adsorbent.
Thermodynamics of adsorption processes

The original concepts of thermodynamics believe that in an isolated system, where energy cannot be gained or lost, and the entropy change is the driving force. In environmental engineering practice, both energy and entropy factors must be considered in order to consider various processes occurring simultaneously among adsorbent and adsorbate. The spontaneity is judged from the net negative values of free energy, \( \Delta G^0 \) at given temperature. The thermodynamics of a process can relate seemingly unrelated properties, and the thermodynamics applies to equilibrium adsorption isotherms. The equilibrium is said to be attained in sorption processes if that point is attained by raising or lowering the concentration of dye in the system. The application of Langmuir isotherm on the given set of data gives us the value of adsorption equilibrium constant ‘b’. Thermodynamic parameter \( \Delta G^0 \) is calculated by using equation 14.

\[
\Delta G^0 = -RT \ln b
\] (14)

The Langmuir equilibrium constant was calculated at three different temperatures, i.e. 303K, 313K and 323K. \( \Delta H^0 \) and \( \Delta S^0 \) were calculated by using clausius-clapeyron equation 15, the slope and intercept of the equation gave the value of these parameters respectively.

\[
\ln b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \cdot \frac{1}{T}
\] (15)

The values of thermodynamic parameters for the adsorption of dyes were calculated and this was found that the adsorption processes were spontaneous and exothermic. The entropy factor was negative for all adsorption processes.

Chapter 7: Conclusion

Different adsorption parameters are optimized, calculated and different kinetic and isotherm models were compared and the adsorption capacity of agricultural wastes, carbonized wastes, their surfactant modified derivatives, micro porous materials, meso porous materials, nano materials are compared for different kinetic models and isotherm models. The thermodynamics suggests that the processes are energetically favorable accompanied with chemical bond formation between adsorbate and adsorbents.