LIGNIN AS AN ADSORBENT FOR THE REMOVAL OF DYES FROM WASTE WATER

A THESIS

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **LIGNIN AS AN ADSORBENT FOR THE REMOVAL OF DYES FROM WASTE WATER** in fulfilment of the requirements for the award of the Degree of Doctor of Philosophy and submitted in the Department of Paper Technology of the Indian Institute of Technology Roorkee, Saharanpur Campus, Roorkee is an authentic record of my own work carried out during a period from July 2001 to December 2006 under the supervision of Dr. Satish Kumar, Professor, Department of Paper Technology, Indian Institute of Technology Roorkee, Saharanpur Campus, Roorkee.

The matter presented in the thesis has not been submitted by me for the award of any other degree in this or any other Institute.

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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

INTRODUCTION

Untreated colored effluents from textile and dyestuff industries are resistant to biochemical oxidation, highly toxic to marine and human life and carcinogenic in nature. They are stable in light, impede light penetration into receiving waters and upset the biological activity of the natural flora and fauna.

Amongst the various physico-chemical treatment processes used for removing pollutants, adsorption has been found to be an effective, economical and an easy method for the removal of color from contaminated wastewater.

Activated carbon has not found favor in view of economical considerations and regeneration difficulties. The results on other adsorbents, mainly agro residues and industrial wastes, are also not very encouraging.

Lignin is a waste material present in the black liquor of the pulp and paper industry that possesses problem of its disposal. It shows good sorption properties and has been chosen as an adsorbent for the removal of dyes from wastewater.

EXPERIMENTAL

Lignin has been obtained by acidification of spent black-liquor obtained from pulping of Sarkanda (*Saccharum munja*). The lignin particles are negatively charged which attracts more strongly the positively charged organic dyes thereby giving a higher uptake of cationic dyes. Three cationic dyes, namely, Crystal violet, Neutral red, and Toluidine blue have been chosen for

adsorption studies. The concentration of aqueous solution~~s~~ of the dyes have been estimated spectrophotometrically by drawing calibration curves at their λ_{max}.

Batch method, because of its simplicity and ease of evaluation of adsorption parameters, has been used in the study of adsorption and adsorption kinetics experiments. 0.1g of lignin is equilibrated with 10 mls of adsorbate solution. The residual dye is estimated spectrophotometrically. Adsorption isotherms at different temperatures, pH, and particle sizes have been plotted.

The specific surface area of the adsorbent has been calculated and the thermodynamic and kinetic parameters have also been evaluated.

RESULTS

Adsorption Studies

The plots of dye-removal vs. time of contact indicate that the removal of dyes occurs in two phases. In the first phase the uptake of solute is fast while in the second phase the rate of removal becomes quite slow and the subsequent removal of solute continues over longer period of time. Major part of the uptake of dye seems to be complete in six, thirty-six and two and a half hours in case of Crystal violet, Neutral red and Toluidine blue respectively. Hence, equilibrium time of eight, fifty-four and three and half hours has been taken for the three dyes respectively.

The logarithmic plots between dye removal and time of contact are linear. The result shows a positive adsorption in all adsorption isotherms. The isotherms are concave to the concentration axis. The extent of adsorption increases with increasing concentration of dyes. A rapid adsorption at low dye concentration, that markedly decreases at high dye concentrations, leads to a slow approach to saturation. At low concentration of dye, about 50 – 98% of the dye gets adsorbed showing that lignin is quite suitable for the removal of dyes.

All the three dyes show favorable adsorption but to different extents. Amongst the three dyes, at the same pH, the uptake of Neutral red is much higher than Toluidine blue and the uptake of Crystal violet is lower than both Neutral red and Toluidine blue. The difference in the extent of adsorption of the three dyes is due to the spatial geometry of their molecular structures. Toluidine blue and Neutral red are linear molecules and their positive charge at nitrogen is more accessible to the adsorbent, thereby causing a higher uptake of these compounds. On the other hand Crystal violet is a triphenyl methane dye having three benzene rings attached to a central carbon atom. It shows a planar trigonal orientation, with positively charged nitrogen at one end of the triangle with which it links to the negative sites of the adsorbent. Its geometry sterically hinders the positive site on the adsorbate molecule from coming in effective interaction with the adsorbent, resulting in a lesser uptake of Crystal violet.

Adsorption for the three dyes has been found to increase with increasing temperature. The heat of adsorption is exothermic and the values increase with the extent of adsorption and follow the order: Crystal violet > Toluidine blue > Neutral red for the same amount of adsorption.

The sorption of the cationic dyes also increases with increasing pH. This is because increasing pH results in the increased negative charge on lignin surface thereby leading to increased sorption. Adsorption is found to increase with decrease of particle size of lignin.

The adsorption data at various temperatures, pH and particle sizes of lignin has been correlated with both Langmuir and B.E.T. adsorption models. The entire data is much better represented by Langmuir model. Adsorption follows the Langmuir isotherm model for all the dyes in the concentration range studied, which is 100-2000 mg/l for both Crystal violet and Toluidine blue and 500–3500 mg/l for Neutral red. A good linearization of data is obtained for Toluidine blue when plotted for B.E.T. In the case of Neutral red linearization is obtained only at low dye concentrations. Crystal violet does not obey B.E.T.

The values of constant 'Q^0', the amount of dye adsorbed for forming a complete monolayer on adsorbent surface, as calculated from B.E.T plots are less than the ones obtained from Langmuir plots and are higher for Neutral red in comparison to Toluidine blue. The values of B.E.T. constant 'A' are negative for Neutral red (and positive for Toluidine blue) except at pH 7.0 and above 200 mesh size where the positive values follow the order : Neutral red > Toluidine blue.

Adsorption Kinetic Studies

The sorption kinetic studies indicate that for all the dyes, the sorption process is quite rapid at lower concentrations and about 70–97% of the adsorption occurs in the first hour of contact. This initial rapid adsorption subsequently leads to a slow approach to equilibrium. These curves also indicate that the amount of solute removed during the first hour of contact decreases with increase in concentration of adsorbate. The amount of adsorption is found to be dependent on the initial adsorbate concentration.

The Bt vs. t plots for all the three dyes at various temperatures, pH and particle sizes of lignin are linear and passing through the origin at and above 800 mg/l for both Crystal violet and Neutral red and at and above 750 mg/l in case of Toluidine blue. These plots are dependent on the initial concentration of the dye solutions. At higher initial concentrations the percent removal of adsorbate decreases. At lower concentrations, the Bt vs. t curves deviate from linear behaviour. This indicates that the adsorption of all the three dyes is both film and particle diffusion; controlled by particle diffusion at and above 800 mg/l for Crystal violet and Neutral red and at and above 750 mg/l for Toluidine blue; while at lower solution concentrations film diffusion also affects the adsorption. As the initial concentration increases, the film diffusion process diminishes while particle diffusion dominates.

The adsorption rate has been found to increase with increase of temperature for all the dyes. This further supports particle diffusion to be the rate controlling process. Increase in mobility of the sorbing species at higher temperature results in increased sorption rate. The adsorption rate is also markedly dependent on the particle size of the adsorbent lignin. The results of the variation of particle size show that the rate of exchange is inversely proportional to the particle size. This clearly indicates a diffusion-controlled process and not one controlled by chemical interaction because in the latter case the adsorption rate would be independent of particle size.

The shapes of McKay plots at various temperatures, particle sizes and pH for the three cationic dyes are linear. The curves do not pass through the origin, thus indicating the presence of two interdiffusion processes that comprise the overall rate of exchange: an initial very fast process, not depicted in the graphs, corresponding to film diffusion and a later comparatively slower process, corresponding to the depicted straight-line portion of the McKay plots. This behavior of McKay plots is also evidence in favor of particle diffusion mechanism as the rate-controlling step.

The values of D_i, the effective diffusion coefficient, is in the order: Toluidine blue > Neutral red > Crystal violet .The geometry and bigger size of Crystal violet as compared to the linear structure of Toluidine blue and Neutral red may be causing greater hindrance in its mobility within the pores of the sorbent.

The energy of activation (E_a) and pre-exponential constant (D_o) have been evaluated from the linear behavior of log D_i vs.1/T plots. The D_o values have been used to calculate ΔS^*, the change in entropy of adsorption. A higher value of E_a is associated with the higher value of D_o for all the dyes .The values are similar for Crystal violet and Toluidine blue and higher than that for Neutral red. The change in entropy value is negative for the sorption of Neutral red and positive for the sorption of Crystal violet and Toluidine blue indicating the disorder produced in the structure of the sorbent as a result of the uptake of Crystal violet and Toluidine blue cations.

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CHAPTER 1

GENERAL INTRODUCTION

1.1 INTRODUCTION

Rapid industrialization and many other modern day activities have led to the generation of a huge amount of materials of little value. Such materials are generally considered as wastes and their disposal is a problem. Utilization of such materials wherever possible and their safe disposal is being intensively looked into at all levels. Hazards from toxic wastes like acids, metal salts and radioactive material are quite well known. Besides this, industrial, agricultural, domestic and cooling and rinsing activities generate waste water containing many pollutants.

1.2 WASTE WATER PROBLEM

Exhaustive exploitation of natural resources has resulted in the deterioration of the environment making the healthy survival of mankind a challenge. Water, in addition to air, is the most important element of life. As a result of intense use of fresh water, the presence of toxic chemicals (inorganic and organic), biological agents and even heat and radiation in surface water are gradually increasing. The nature of these chemicals varies from place to place, industry-to-industry and level of advancement in domestic life. Thus, depending on activity, water may contain different pollutants.

The removal of toxic pollutants from water is a difficult task because of the diverse number of compounds and the extremely low concentrations normally encountered. Industry and government are becoming increasingly aware of the need to clean up industrial effluents and reduce river pollution. The standards for the quality of a waste water effluent are gradually becoming more rigid. Stringent restrictions have been imposed on the concentration of these compounds in waste waters for safe discharge and new methods of treatment are continuously being investigated and developed.

1.3 POLLUTANTS

The term pollutants, in a broad sense, refers to a substance/material that changes the natural quality of the environment by physical, chemical and biological means. Some of the most common chemicals (24) found in waste water and considered as potential pollutants are phenols, dyes, detergents, poly-nuclear hydrocarbons, poly chlorinated biphenyls (PCBs), insecticides, pesticides (74), heavy metals etc. They are toxic if present above a certain level.

1.3.1 Biological Agents

Biologically active agents (24) such as *Vibrio comma*, *Salmonella typhosa*, *Escherichia coli*, *Shigella dysenteriae* and *Yersinia entrocolitica* may be present in domestic effluent and sewage water and need to be removed. Some of the important water-borne diseases caused by biological agents are cholera, typhoid, dysentery, gastroenteritis, jaundice etc

1.3.2 Heat

Ideally the temperature of water should be constant or under minimum variation. Due to its high heat capacity, water is used as a cooling medium. Thus, many industrial plants discharge water carrying away heat (23). The high temperature of this waste water not only affects aquatic life but is also known to cause high corrosive activity and many chemical and bacteriological reactions, such as formation of tri halo methane (THM).

1.3.3 Dissolved and Non-Dissolved Chemicals

The presence of suspended solids clogs waterways, fills up dams and is harmful to aquatic life in many ways (59). These include heavy metals, dyes, phenols etc.

1.3.3.1 Heavy metals

Heavy metals are generally present as pollutants in a wide variety of industrial effluents (109). They are toxic to aquatic flora and fauna even at relatively low concentrations. The tannery industry discharges chromium in waste water. Copper, chromium, zinc and cadmium are widely generated from metal plating industry (132). Mercury from the production of electrical equipments, mining, smelting and fossil fuel combustion contribute to the pollution load of waste water. Lead is generated from a number of industrial and mining sources. Several other industries (like rubber processing, paint, chloro-alkali, oil refining, fertilizer, chemical etc.) are also well known source of heavy metal discharge. Ingestion of > 2g of zinc produces toxic symptoms in humans (55). It is important to emphasize that many of these metals are essential for human life in trace quantities but become toxic if their concentration increases above a certain minimum value. It may be added that in most waste waters the concentration of heavy metal(s) present is much larger than the safe permissible limits and therefore they need to be removed (16, 42, 47,65, 101, 125)

1.3.3.2 Phenols

Apart from metals, phenols are also considered priority pollutants (148) as they impart bad taste and carbolic odor to water and are toxic (18,113) to fish and human beings even at low concentrations. The permissible limit for phenolic concentrations in industrial effluents before discharge into municipal sewers and surface waters are 1 – 5 mg/l (82). Phenols present in waste water are generated from pulp and paper, chemical, paint, resin, pesticides, gas and coke manufacture and dyeing industries (73,75).

1.3.3.3 Dyes

Certain industries discharge waste water rich in organic content, of which dyes are one of the most frequently occurring groups of compounds. Dyestuff production units and dyeing units have always had a pressing need for techniques that allow economical pretreatment for color in the effluent. Dyes have the ability to impart color to another material and are considered important water pollutants. Colorants such as colored pigments and dyes are widely used for both domestic and industrial purposes for a variety of reasons, including color coding, brand identification, eye–appeal etc. The use of dyes dates back to the Stone Age much before the signs of first civilization. Many natural dyes are obtained from animal and vegetable sources. However, with the invention of synthetic dyes derived from petrochemical feedstocks, various forms of dyes have now become available. More than 800 dyes are being manufactured and consequently used for specific purposes. They are used in textiles, dyeing, paper and pulp, petroleum refining, pharmaceuticals, food processing, fertilizers, tannery, paint and other diverse industries. As such, the effluent of these industries as well as plants manufacturing dyes tend to contain appreciable quantity of dyes which are considered obnoxious type of pollutants because they impart undesirable color, taste and odor to water which is not acceptable due to aesthetic consideration and adversely affect human and marine life (8,147) due to toxic and carcinogenic (110) effects. In contrast to domestic waste of metabolic origin, these pollutants are resistant to bio-chemical oxidation and persist in water for longer periods and reach hazardous concentrations with multiple re-use of water. Dyes used in the textile industry are difficult to remove by conventional waste water treatment methods, since they are stable to light and oxidizing agents and are resistant to aerobic digestion. Nowadays thermally stable dyes are introduced which are difficult to degrade after use. Thus, water-containing dyes need to be treated for their removal (155).

1.3.3.4 Miscellaneous substances

Radioactive substances (24) are handled with all precautions in view of the harmful nature of radiations emitted by them. In spite of this, radioactive material are often found in effluents coming from research laboratories, hospitals, nuclear power plants and ore processing industries and need to be removed (26).

Synthetic and natural detergents are used for cleaning and emulsification purposes. Domestic waste and effluents of pharmaceutical industry may contain these surfactants (131).

1.4 TREATMENT METHODS

The type of process to be used depends on the nature of the pollutant. Some existing technologies like oxidative destruction via UV/Ozone treatment (78), dialysis (58), photo catalytic degradation (50,135), reverse osmosis (37), biological methods (143), electrochemical reduction (94) etc. may have a certain efficiency for the removal of toxic materials but their initial and operational costs are so great, that they constitute an inhibition to the dyeing and finishing industries (21,22).

Impurities in water vary in size and are largely removed by sedimentation. Gravitational separation by sedimentation is an effective technique for the removal of unstable suspended solids. Filtration is used for the removal of solids present in surface waters, precipitated hardness from lime-softened water and precipitated iron and manganese present in many well-water supplies. Many of the impurities are too small for gravitational settling alone. Chemical precipitation and biological methods are the two commonly used processes for the treatment of colored waste water. But these methods suffer from the disadvantage of sludge disposal and long-term biodegradation respectively. Conventional treatment processes, such as aerated lagoon and activated sludge processes (ASP) are frequently used to treat textile effluents (22). These methods are efficient in the removal of suspended solids and chemical oxygen demand (COD) but largely ineffective in removing color from waste water. Hence investigations have been made on physico-chemical methods of color removal from textile effluents. These studies include the use of coagulants oxidizing agents, ultra filtration, membrane filtration, chemical oxidation, coagulation, precipitation and electrochemical techniques, adsorption and ion exchange techniques (13, 15, 49, 67, 45, 114, 27, 22).

These methods have their own shortcomings e.g. coagulation requires pH control and causes further problem of sludge disposal. Ozonation, while removing color effectively, does not minimize COD. Some of these methods have been found to be quite efficient for color removal but the cost factor inhibits their large-scale use for small-scale industries. The cost of such processes, therefore, needs to be ascertained. Some workers used these methods in conjugation with each other or some other process. Graham (38) tried to remove color by filtration and coagulation. Lin and Peng (64) used coagulation in combination with electrochemical oxidation and activated sludge for treating textile waste water.

1.5 ADSORPTION

The effectiveness of adsorption for dye removal from waste waters has evolved it into an ideal alternative to other expensive treatment options (69). A survey of literature has revealed that amongst the many methods used for removing pollutants from waste water, the adsorption of impurities from solution onto solid materials is widely used because it is economic, effective, efficient, as well as versatile as it removes a broad range of assorted pollutants. The process is superior to other methods of water reuse by virtue of its low initial cost, low energy requirements, simplicity of design and possibility of reusing the spent adsorbent via regeneration. It has evolved as the frontline of defense for the removal of pollutants, which cannot be removed by other techniques. The term “adsorption” appears to have been introduced by Kayser to connote the condensation of gases on free surfaces, in contradiction to gaseous adsorption where the molecule of gas penetrate the mass of the adsorbing solid. The wider term “sorption” proposed by Mcbain embraces both types of phenomena. Adsorption process has evoked considerable interest for the removal of phenolic compounds, heavy metals, dyes and color, refractory organics and other non-biodegradable materials. A variety of solid adsorbents have been developed and used for adsorbing solutes from solutions and also from gases. The versatility and wider applicability of adsorption in pollution control has been recognized (2, 17). The process of adsorption has an edge due to its sludge-free, clean operation and complete removal of dyes from aqueous solutions having dilute or moderate concentrations. The added advantage of the adsorption method lies in the fact that the adsorbed dyes can be desorbed under specific conditions with resultant economy of operation. In brief, of all the methods, adsorption appears to offer the best prospect for overall treatment of waste water.

1.6 ADSORBENTS

The most important property that a good adsorbent (136) should possess is its porous structure resulting in higher surface area. Not only this, the time taken for adsorption equilibrium to be established should be as small as possible, so that it can be used to remove contaminants in a lesser time. Thus, for removal of pollutants, one looks to adsorbents with higher surface area and showing faster kinetics.

1.6.1 Activated Carbon

In general, activated carbon is the adsorbent of choice. In various plants that are used for treating waste water through adsorption, activated carbon in granular or powdered form is the most widely used adsorbent (3, 30, 48, 72, 86, 104, 153) for the purification of water because of its capability for efficiently adsorbing a broad range of different types of adsorbates. Adsorption on activated carbon is not usually selective as it occurs through vander Wall's forces. Its surface area range is 600 – 2000 m^2/g. It adsorbs different types of pollutants (48) like metal ions (36, 51), phenols (118), dyes (3, 102, 146), PCBs (105), detergents (68), pesticides, chlorinated hydrocarbons, humic substances, organic compounds (62) (which cause taste and odor problems) and many other chemicals and organisms (29). It has even been used for the removal of lignin and tannin colors from aqueous solutions (84). Kannan and Sundaram (53, 54) have made a comparative study on the adsorption of Acid violet, Congo red, Methylene blue and Rhodamine B dyes on commercial activated carbon. Biologically activated carbon has been used for removal of phenols (40, 150). Namasivayam et al have used $ZnCl_2$ activated carbon from coconut coir pith for the removal and recovery of nitrate from water (88). Tseng et al (46, 137) utilized pinewood-based activated carbons for adsorption of dyes and phenols.

In spite of good capacity, activated carbons that are used, suffer from several disadvantages especially if it is to be used on a regular basis for a large volume of water. They are relatively costly materials making reclamation of water an expensive proposition especially if the carbon is to be discarded after single use. Its regeneration by thermal volatilization, in which adsorbed organics are desorbed at high temperature, is uneconomical due to the high cost of energy in heating the carbon around 800 – 850^{0}C. An alternative technique is that of chemical regeneration, in which chemical reagents are applied to exhausted adsorbents. Chemical as well as thermal regeneration of spent carbon is impractical and produces additional effluent .In addition, the fragility of activated carbon particles results in considerable (10-15%) loss of the adsorbent in regeneration (14,105, 33). Therefore, the application of activated carbon in developing countries has been restricted for specialized purposes only.

1.6.2 Other Adsorbents

It would be ideal if alternative low cost adsorbents were available whose performance was comparable to that of activated carbon. This has not been possible. Thus, the search for good alternatives of activated carbon (122) is still on. Efforts continue to prepare cheaper adsorbents, generally from industrial and agricultural wastes.

The materials which have been identified as suitable low cost (71) and commercially available alternative adsorbents fall generally into two categories:

(1) Natural materials such as wood, peat, coal, lignite etc.,

(2) Industrial wastes/by-products such as slag, sludge, fly ash, bagasse, red mud – a waste from aluminum industry etc.

These materials are available generally free of cost or cost very little as compared to activated carbons.

The utilization of industrial wastes as adsorbents (12, 89, 90, 99, 115, 128, 144) meets, though to a small extent, management of waste disposal problem. Fly ash is a waste product of electrical power plants and available in large quantities during burning of coal at high temperature. It does not find favor due to its drawbacks of low sorption capacity and difficulty involved in regeneration. Disposal of used fly ash is an additional problem.

Many naturally occurring (106) as well as synthetic substances have been tried and tested for their adsorption efficacy. Alumina is a synthetic, porous, crystalline gel available in granules of different sizes, found to have a surface area (28) ranging from 200 – 300 m^2/g. The adsorption of fluoride ions on commercially available grades of activated alumina has been studied by Karthikeyan et al (56) to determine its defluoridation efficiency.

Bauxite is a naturally occurring porous, crystalline alumina contaminated with kaolinite and iron oxides in varying proportions depending on place of origin. It is widely used in place of alumina. Its surface area (76) ranges from 25 – 250 m^2/g.

Silica gel's porous, non-crystalline granules show a higher surface area (28) as compared to alumina, in the range 250–900 m^2/g. It is a good adsorbent in many industries for drying of gases and liquids and purifying hydrocarbons (9).

A number of exchange resins efficiently remove specific organic compounds (156) through cation or anion exchange mechanism.

Zeolites are double silicates capable of undergoing reversible base-exchange reactions (32, 41, 95). Their surface area (76) range is 1 – 20 m^2/g.

Literature reviewed has shown that a number of low cost adsorbents have been prepared but are not highly successful. Limitations of such studies have been : the surface area of the adsorbent has been low in many cases resulting in poor adsorptive power; comparative studies on different adsorbents have not been carried out; the adsorptive properties of the adsorbents prepared have been studied with regard to a few adsorbates only, and the performance of these alternative adsorbents has not been generally compared with activated carbon to assess their potentiality.

Different low cost by-products and waste materials like eucalyptus bark, plum kernels, red mud, slag, sawdust, bagasse pith, wood, peat, bentonite clay, chitin, agricultural residues (142, 149) have been extensively tried as adsorbents (92, 99, 120, 127-130, 145). Iron oxides were coated on to the surface of sand, and this composite media was used for adsorption studies of phenolic compounds (119). Wood saw–dust has been used as an adsorbent for the removal of heavy metals from waste water (77, 97) and the main adsorption sites for metal ions in wood were found to be on lignin. Dentel et al studied the sorption of 2,4,5-trichloro phenol and tannic acid onto montmorillonite based sorbents (25). Singh and Srivastava observed that on the basis of higher adsorption capacity, the use of activated sludge, Na-K montmorilonite, impregnated fly ash, chemically treated sawdust and activated carbon prepared from used tea leaves may be suggested for the treatment of waste water containing phenols. (118). They have also tried Iron (III) - morpholine gel for adsorption of pyro-catechol and pyrogallol (117). Alam et al have used nickel, cobalt and cadmium ferro cyanides for the removal of o-nitro phenol and o-amino phenol (1). Adsorption of chromium (VI) onto lignite was reported by

Kannan et al (52). Wu et al reported the adsorption of reactive dyes, metal ions and humic acid on chitosans (a deacetylated product of chitin) (151-152). Clays, soil, talc, ground limestone, coconut husk, sand, kaolinite, calcite, activated sludge, humus, Fullers' earth, colloidal silica, zeolites, alumina, synthetic organic resins, inorganic gels and numerous other substances (35, 63, 83, 157) find mention in literature in reference to adsorption.

1.6.3 Adsorbents for Dyes

Graebe and Liebermann first put forward the concept of color, the substance bearing it and its constituents. Later Witt propounded that a body must possess one or more groups called chromophores so that it might possess the potentiality of color. Molecules containing chromophores are termed as chromogens. The salt–forming groups that help to develop the color of a chromogen are named as auxochromes.

Research survey reveals that various adsorbents are used to remove dyestuff from waste water (10,11,19,20,34,43,61,79,83,85,91,107,108,120,154) Carbonaceous sorbents have been reported to have the capability of decolorizing dyes (123,124). McKay et al (80) studied a number of low cost materials (teak wood bark, rice husk, bentonite, clay, husk and cotton waste) as adsorbents for the removal of acidic, basic, disperse and direct dyes and reported that in general, basic dyes are adsorbed to a greater extent than the other dyes but no single characteristic of the dye or adsorbent seemed responsible for such dye–adsorbent interactions and adsorption capacities. Khattri and Singh (57) investigated the suitability of Sagaun sawdust for removing basic–dyes (Crystal violet, Methylene blue, Malachite green and Rhodamine B) from aqueous solutions and reported that the adsorption of dyes followed Langmuir equation. Further, the process was found to be exothermic in nature with intra particle diffusion as the rate-governing step. Sanghi and Bhattacharya (112) made a comparable study of activated carbon with natural adsorbents (chitin and radish leaves) for the removal of a reactive dye: Remazol brilliant violet 5 R from aqueous solutions. They found adsorption capacities of activated carbon, radish leaves and chitin to be 13.6, 40.0 and 38.2 mg.g^{-1}, respectively. Lui et al also used activated carbon for removal of basic dye (66). Ozacar and Sengil investigated calcined alunite for the removal of three reactive dyes (98): Reactive blue 114, Reactive yellow 64 and Reactive red 124, whose maximum adsorption was found to be 170.7, 236.0 and 153.0 mg.g^{-1} respectively and for the removal of two acid dyes (96): Acid blue 40 and Acid yellow 17. Adsorption of dyes on Goda sand (81) was investigated to assess the possibility of treating waste water streams from dye works for removal of toxic materials. Other workers investigated the adsorption of dyes on adsorbents as diverse as phosphorous containing carbonaceous adsorbent (126), polymer mats (133), ZnS, MnO_2 etc. In addition to the above-mentioned materials, a number of agricultural and industrial waste products have also been investigated as adsorbents for dye removal. An agricultural waste of rice mills, rice husk ash, has been studied (129) as an adsorbent for the removal of acidic dyes from aqueous solutions. The adsorption capacity was found to vary from 99.4 to 155-mg/g making rice husk ash a good adsorbent. Annadurai et al (7) used banana and orange peels as adsorbents for the removal of dyes from aqueous solutions and the adsorption of different dyes was found to be in the order: Methyl orange > Methylene blue > Rhodamine B > Congo red > Methyl violet > Amido black 10B. It was also reported by them that banana peel was more effective than orange peel. Gupta et al (39) used bagasse fly ash, a sugar industry waste, for the removal of two basic dyes: Rhodamine B and Methylene blue and reported that adsorption data fitted well with both Langmuir and Freundlich models. Bagasse fly ash has also been used for the removal of phenols (121). Netpradit et al. (93) investigated waste metal hydroxide sludge by removing azo reactive dyes from aqueous solutions. He found maximum adsorption capacity of the sludge for the reactive dyes to be in the range of 48–62 $mg.g^{-1.}$ Other low cost adsorbents studied are hematite, banana pith (73), biogas residual slurry (75) and sunflower stalks (116,130). Vasanth Kumar et al carried out experiments on the removal of Malachite green onto carbonized coconut shell (141) and carbonized paddy husk (138) and concluded that the critical mass transfer resistance is the sole rate-determining step during the adsorption process. They also carried out removal of basic dyes (139,140) onto various agro-based wastes in fixed beds and found that adsorption favors at lower initial concentration, low flow rate and at maximum bed depth. Mall and Upadhyay (70) studied the removal of Methylene blue and Malachite green using high and low carbon content fly–ash. They found that the color removal rate is more with high carbon content fly ash. N. Kanan and M. Meenakshi Sunderam (53) investigated the adsorption of acidic (Acid violet), neutral (Congo red), and basic (Methylene blue and Rhodamine B) dyes on commercial activated carbon (CAC). Adsorption studies of anionic dyes on aluminum treated corn cobs powder (44) shows that maximum adsorption of dyes was observed at low adsorbent concentration, acidic pH and 30^0C temperature. El Geundi (31) studied maize cob without any pretreatment for the removal of two basic dyes: Astrazone blue and Maxilon red, and two acid dyes, Telon blue and Erinoyl red. They found that this agricultural waste has high adsorption capacity of 160 and 94.5 mg/g. for Astrazone blue and Maxilon red and low capacity of 47.7 and 41.4 mg/g for Erinoyl red and Telon blue respectively. Saw-dust, corn cob waste, coir pith and agricultural wastes have been investigated by Ajmal et al (5), Wu et al (152) and Namasivayam et al (87) respectively as adsorbents for metals and dyes. Wool carbonizing waste obtained as a result of processing of wool was investigated by Perineau et al (103) for the adsorption of dyes. They observed that adsorption of basic dyes is 6 – 10 times than that of acid dyes. They reported that surface properties of this are such that it tends to adsorb solutes of ionic nature. Al-Qodah (6) used shale oil ash, an inorganic residue obtained after combustion of shale oil, as an adsorbent for dyes. They reported that it possesses good porosity and suggested that it can have good adsorptive behavior for both organic and inorganic pollutants. San Miguel et al used waste-tyre rubber (111) for the adsorption of organic compounds, viz. phenols, Methylene blue and textile dyes. Human hair (134) and waste paper has also been put to use for preparing alternative adsorbents. Hamabe et al used newspaper as raw material for the production of activated carbon. It possesses good surface area (100m^2/g) and the yield was 40%.

1.6.4 Lignin

It is an amorphous, hydrophobic, multifunctional phenolic network polymer. It is the non-carbohydrate component of wood, having the skeleton structure of phenyl-propane monomers containing mainly methoxy (–OCH_3) and hydroxyl (–OH) groups. Lignin is resinous binding material between cellulosic fibers that gives strength, rigidity and densities to the plant. It is the second most important renewable organic resource after petroleum. Although lignin is one of the most durable biopolymers, it is perfectly biodegradable in nature in the presence of some enzymes (100) unlike synthetic polymers that present serious environmental problems in post treatment after use.

Lignin offers unlimited scope for industrial purposes. It is an important source material for the preparation of a variety of chemicals. Lakshmana Reddy et al (60) have utilized it for the preparation of chemically activated carbon with the aim of utilizing the polluting waste from pulp mills in prevention of environmental pollution. Though it is partially consumed as a fuel by the paper industry (calorific value = 6200 cal/g), no really economically satisfying application, on a large scale, of lignin has been found. The limited use of lignin is attributed to its molecular structure, i.e. the lignin molecule lacks stereo-regularity and the repeating units of the polymer chain are heterogeneous.

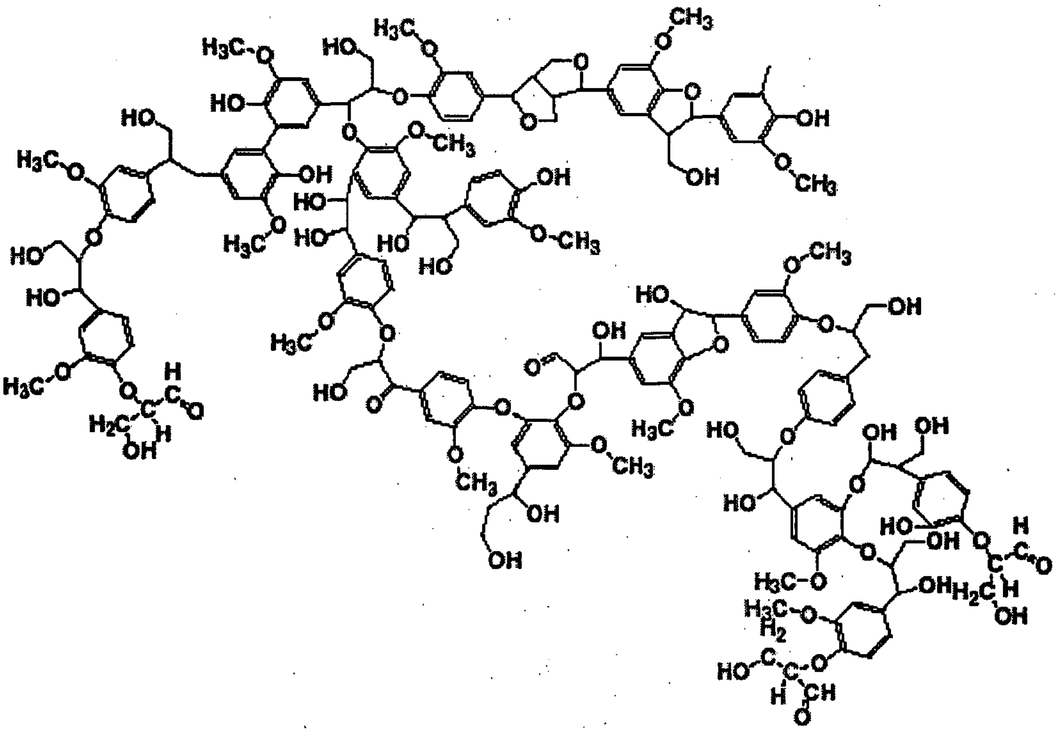

Fig. 1.1 : Representative chemical structure of lignin.

A large amount of lignin is wasting out from the pulp and paper industries as black liquor during the manufacture of paper. Black liquor is obtained during pulping of wood / agro-residues etc. with alkali. It thus contains dissolved lignin and alkali. Large paper mills burn this black liquor to generate energy as steam and recover alkali after recausticising. This alkali is reused for the pulping of wood. Thus, large paper mills with chemical recovery offer the advantage of recovery of alkali and energy, thereby drastically reducing the environmental loads from pulping section. Small paper mills in India do not have chemical recovery, face problems of its disposal and discharge weak black liquor (after dilution) having high COD, color, alkalinity and toxicity. Recovery of lignin from black liquor, to be used for other applications such as an adsorbent, can greatly reduce the environmental impact of these mills and to some extent, of the dye-using industries.

1.7 THE PROBLEM

A review of literature dealing with alternative adsorbents for the removal of dyes shows that although a number of them have been studied, but their efficiency as compared to activated carbon is considerably less. Alternative adsorbents exhibiting higher adsorption capacity, lower initial cost and potentially greater ease of regeneration are required so that they can be used to replace activated carbon.

1.8 AIM AND OBJECTIVES

Lignin is another material that is known to exhibit adsorption properties. It carries a negative charge on its' surface which attracts more strongly the positively charged dyes, thereby giving a higher uptake of cationic dyes. The greater affinity of basic dyes for the adsorbent is due to the columbic attractions between the surface anions of the adsorbent and the cations of the basic dyes. Therefore in the present work, three cationic dyes, namely Crystal violet, Neutral red and Toluidine blue have been used as adsorbates. Adsorption of these dyes on lignin has been investigated with a view to obtain information about the suitability of lignin as an adsorbent and assess the possibility of efficiently treating waste water streams from dye works with this low-cost adsorbent.

In order to make the interpretation of the results less complicated as far as possible, the experiments have been carried out with solutions of pure adsorbate. However, some measurements of adsorption in presence of salts etc. have also been made.

The work has been divided into four chapters. The first chapter deals with general introduction describing the status of the work.

The second chapter of this thesis deals with the materials and various experimental techniques (methods) used in this study for isolation of lignin, equilibrium sorption as well as kinetic studies.

The third chapter deals with the adsorption of the dyes on lignin. The studies have been performed by batch process under different conditions of dye concentration, temperature, pH, particle sizes of lignin etc.

The fourth chapter deals with the kinetics of the adsorption of dyes under different conditions. The thermodynamic parameters of the adsorption process have also been evaluated.

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CHAPTER - 2

EXPERIMENTAL MATERIALS AND METHODS

2.1 REAGENTS AND MATERIALS

2.1.1 Dyes

The three dyes-Crystal violet, Toluidine blue and Neutral red used,were of make Loba Chemie Pvt. Ltd. Bombay.

2.1.2 Other Chemicals

The reagents used in the purification of lignin were of A.R. grade. All other chemicals used (NaOH, HCl, NaCl, NaBr, NH_4Cl, $BaCl_2$, KCl, $Al(NO_3)_3 \cdot 9H_2O$, NH_4NO_3 etc.) were of L.R. grade and were used without further purifications. Solutions of all the dyes were prepared in distilled water.

2.1.3 Pulp

Unbleached Sarkanda (*saccharum munja*) pulp, for the extraction of lignin, was procured from a paper mill in north India.

2.2 INSTRUMENTATION

Measurements for pH determinations were made with Century CK 710 Water Analyzer kit. For the spectophotometric work, Shimadzu Spectro-photometer UV 2100S (Japan) (10) has been used.

2.3 PREPARATION OF ADSORBENT

2.3.1 Methods of Isolation of Lignin

Most plant tissues contain an amorphous, polymeric material called Lignin, which is an irreversible product of plant metabolism and cements cellulose fibers in plants. As early as 1939, Hess and co-workers (6) attempted to isolate lignin from plant material finely ground in a vibrational mill to a particle size 1–2 µ. Björkman (2) also used wood, ground in an oscillating mill for the isolation of Lignin. Schobinger isolated soluble native lignin from wheat straw according to Bjorkman's method. Nord and coworkers (7) isolated lignin from various coniferous and deciduous woods and from bagasse. Pew (9) treated Spruce wood and brown rot fungi, using the soil block method and obtained lignin residues. Hachinama and Jyodai modified Willstatter's method for the isolation of lignin with fuming HCl (4). All these methods have also been discussed in two reviews (3, 8).

The sulfate or Kraft cooking process is the most important of those used in the paper industry for the delignification of wood.' Kraft', in German, meaning 'strong', obtained its name from the discovery by Dhal that the addition of sodium sulfide to the soda cooking liquor increased not only the yield but also the quality of the pulp which was superior and stronger.

Nowadays most of the pulp industries obtain pulp by Kraft cooking process by using a number of raw materials softwoods, hardwoods, agricultural residues and non-woods (grasses). During pulping lignin is obtained as a by-product in the manufacture of paper, in the form of black liquor. Lignin isolated from spent black-liquor by Kraft process is called as 'thio lignin'.

2.3.2 Isolation of Lignin from Black Liquor

The cooked and unwashed Sarkanda (*Saccarum munja*) pulp was obtained from industrial source. The cooked pulp was filtered through a muslin cloth to separate black liquor. The filtrate obtained was acidified with dilute HCl till the precipitation was complete. The precipitate was then allowed to settle down and the supernatant liquid was decanted off. The precipitate was washed repeatedly with distilled water till free from chloride ions. It was dried at room temperature. The product thus obtained is crude thio lignin.

2.3.3 Purification of Crude Lignin

Purification of a fraction of the obtained crude thiolignin was carried out according to Ahlm's method (1). 10% solution of crude thio lignin was prepared in dioxane, filtered and added drop-wise from a burette into vigorously stirred anhydrous ether to precipitate lignin. The precipitate was washed with diethyl ether and then with benzene. Finally the precipitate was washed with low boiling petroleum ether and dried over anhydrous $CaCl_2$, at room temperature.

The experimental results obtained with crude thio lignin and with purified lignin were practically the same. Therefore, for all the experimental work, crude thio lignin has been used.

2.3.4 Particle Sizing of Adsorbent

The lumps of crude thio lignin obtained were broken with the help of mortar and pestle and the reduced powdered lignin was passed through sieves of different mesh sizes. The fractions corresponding to B.S.S mesh sizes 40-100 (particle radius 0.021 to 0.0075cm), 100-200 (particle radius 0.0075 to

0.0037cm) and above 200 (particle radius 0.0037 to 0.0022cm) were separated and collected. The average value of the sieve openings in cm, as mentioned in the 'Conversion table for U.S. standard screen series', (5) was taken as particle radius.

The various fractions were individually suspended in distilled water to remove the adhering fine particles, filtered and dried at room temperature. Finally, the products were stored in airtight bottles.

2.4 ESTIMATION OF DYES

The three dyes Crystal violet, Neutral red and Toluidine blue were estimated spectrophotometrically. Absorbance of the dyes was noted at various wavelengths and their λ_{max} was determined as 583 nm, 530 nm and 604 nm respectively. λ_{max} is the wavelength at which the dye solution shows the maximum absorbance of light at a fixed temperature and pH. Crystal violet and Toluidine blue were estimated at pH 7.0 while Neutral red was estimated at pH 3.7.

2.4.1 Stability of Aqueous Solutions

The aqueous solutions of the dyes were prepared in distilled water. Aqueous solutions of Crystal violet and Toluidine blue were found to be stable at room temperature and neutral pH. The solution of Neutral red dye was stable in acidic medium. The λ_{max} and absorbance of the various dyes was estimated at different pH values on the Shimadzu spectrophotometer UV 2100S. λ_{max} and absorbance remained unchanged in the pH range 3.0 -7.4 for Crystal violet and Toluidine blue and from 3.0–4.4 for Neutral red dye. Accordingly, pH of

7.0(neutral) was chosen for the estimation of Crystal violet and Toluidine blue from aqueous solutions and pH of 3.7(acidic) for Neutral red at their λ_{max} values of 583nm, 530nm and 604nm respectively.

2.4.2 Calibration Curves

Aqueous solutions of the dyes of different dilute concentrations were prepared at their respective pH. The absorbance of these solutions was measured at their respective λ_{max} values. Calibration curves, that are the linear curves between absorbance and concentration of the dye (mg/l), were constructed. These calibration curves were used for the estimation of the residual concentration of dyes upon adsorption.

Equilibration time, amount of adsorbent, as well as the concentration range of the adsorbate and the pH of the solution used in static and kinetic measurements were decided after a great deal of preliminary investigations. This equilibration time was used as contact time in the isotherm experiments.

2.5 SORPTION STUDIES

2.5.1 Batch Method

The batch technique (finite bath method) because of its relative simplicity is commonly used. Other advantages of this technique are its freedom from complex hydraulic parameters indigenous to flow–through systems, its adaptability to small volume work, ease of investigation in various conditions and general facility of operation.

A series of 50 ml Erlenmeyer flasks were used for adsorption studies. 10 ml of aqueous solutions of varying concentrations of dyes was added to each flask and maintained at the desired temperature in a constant temperature water-bath. Equal amount of lignin (0.1g) was added to each flask. The flasks were shaken for 2–3 minutes and equilibrated for eight hours in the case of Crystal violet, fifty-four hours for Neutral red and three and a half hours in the case of Toluidine blue, with intermittent shaking. The supernatant liquid was centrifuged and analyzed for the residual dye concentration. In case the pH of the residual dye is different from that of the calibration curve, the pH of the solution is adjusted. To take care of the dilution of the dye solution during the pH adjustment, the solution was diluted to known volume with distilled water of the same pH. The concentration of the residual dye in the diluted solution was estimated from the calibration curves drawn for this purpose. The amounts sorbed were determined by difference between initial and final concentrations expressed as mg of dye / g of adsorbent. Knowing the dilution made, the concentration of the residual dye in the undiluted solution was estimated. In case where the absorbance of the dye was outside the absorbance range, the solution was diluted with distilled water of the same pH. The concentration of the diluted dye was estimated from the calibration curves and the concentration of the undiluted dye was computed.

2.5.2 Effect of Temperature

To investigate the thermodynamics of the sorption process, experiments were performed at different temperatures (20^0C to 40^0C $\pm$ 1^0C).

2.5.3 Effect of pH

In order to study the effect of pH on adsorption, dye solutions of the three dyes at different pH (range 3.7–7.0) were made and adsorption studies were carried out as mentioned above.

2.5.4 Effect of Particle Size of Lignin

In order to understand the effect of particle size of lignin on the adsorption of dyes, lignin samples of different particle sizes (40-100, 100-200 and above 200 B.S.S. mesh size) were taken. Each sample was suspended in distilled water to remove the adhering fine particles and air dried at room temperature before use.

2.5.5 Effect of Salt Concentration

The effect of varying concentrations of NH_4NO_3 solution on the uptake of dyes on lignin has also been studied.

2.5.6 Effect of Quantity of Dye

This effect has been studied by varying the amount of dye added in solution, equilibrating it for 1 hour with 0.1 g of lignin and estimating it as mentioned above.

2.6 DESORPTION STUDIES

1 g of 100–200 mesh size lignin was equilibrated with 2000 mg/l solution of each dye for their respective equilibration time. The quantity of dye adsorbed was estimated spectrophotometrically. The obtained lignin–dye complex was filtered using Whatman filter paper and washed gently with distilled water to remove any unadsorbed dye and dried at room temperature. 0.1 g of this spent lignin–dye complex was equilibrated with 10 ml of each desorbing solution.1M

aqueous solutions of KCl, NaCl, NaBr, $BaCl_2$ and Al $(NO_3)_3.9H_2O$ were used as desorbing solutions. After equilibrium, the quantity of the various dyes desorbed in the supernatant desorbing solutions was estimated.

2.7 KINETIC MEASUREMENTS

2.7.1 Batch Method

Two types of experimental procedures have generally been used in studying the kinetics of adsorption. A column or a shallow bed arrangement in which the adsorbate solution is percolated through the bed of adsorbent with samples being taken periodically from the effluent is known as 'infinite bath system'. A batch operation is one in which the known amounts of adsorbent and the adsorbate solution are continuously shaken together and the aliquots are withdrawn periodically from the reaction vessel. This is also known as 'finite bath method'. The batch or finite bath technique was selected for the present study.

A weighed amount of adsorbent is placed in contact with a standard solution of the adsorbate at the preset temperature. Shaking or stirring agitates the solution. Sorption rate is determined by measuring the uptake of adsorbate in solution. Thus, a number of experiments are carried out and the uptake of the adsorbate, as a function of time, is determined. The change in the concentration of the solution is estimated by analysis of aliquots withdrawn at various intervals of time.

2.7.2 Kinetic Studies with Dyes

The details of the experimental set up are: a number of stoppered, corning glass conical flasks (100 ml capacity), containing solutions of known volume (10 ml in each case) and concentration of the dyes were placed in a thermostat-cum-shaking assembly. When the desired temperature was reached, a known amount of sorbent (0.1 g) was introduced into each flask and mechanical shaking agitated the solutions. At pre-decided intervals of time, the solution of the specified conical flasks were separated from the sorbent material by decantation and subsequent centrifugation and analyzed to determine the uptake of the dye under study. Above experiments were carried out with Sarkanda lignin as adsorbent, and the cationic dyes Crystal violet, Neutral red and Toluidine blue as adsorbate.

2.7.2.1 Effect of Concentration of Adsorbate

To observe the influence of concentration on the rate of sorption, experiments were performed for different concentrations of the dyes. The concentration range studied was 100–1000 mg/l for Crystal violet and 100–1200 mg/l in the case of both Neutral red and Toluidine blue.

2.7.2.2 Effect of Temperature

To investigate the thermodynamics of the sorption kinetics, experiments were performed at various temperatures (20^0C–40^0C ± 1^0C). Other experimental conditions like particle size and pH were kept identical for each dye.

2.7.2.3 Effect of pH

Experiments were performed at different pH (3.7 – 7.0) to investigate the effect of pH of the dye solution on the adsorption kinetics. The temperature and particle size of lignin were kept constant for each dye.

2.7.2.4 Effect of Particle Size of Adsorbent

In order to observe the effect of particle size of the adsorbent on the adsorption kinetics, experiments were performed with adsorbents of different particle sizes (40–100, 100–200 and above 200 mesh sizes), keeping the temperature and pH of each dye solution constant.

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CHAPTER - 3

ADSORPTION OF DYES ON LIGNIN

3.1 INTRODUCTION

Amongst the different pollutants of aquatic eco systems, dyes are a large and important group of industrial pollutants and include many different compounds. Most dyes and pigments are considered inert or non–toxic, though some of them are not totally innocuous. Though their environmental behavior is largely unknown, interest is prompted primarily by concern over their possible toxicity. Effluents from dyestuff manufacturing industry and other industries like textile, paper making, leather, printing etc. are generally highly colored due to discharge of large quantities of dyes along with a wide range of dissolved and suspended solids and organic contaminants such as salts, surfactants, enzymes, oil, oxidizing and reducing agents etc. Color is the first contaminant to be recognized, as the presence of very low concentrations of dyes in effluent is highly visible to the naked eye and undesirable. Growing urbanization and industrialization has resulted in increased discharge of polluted waters into receiving water bodies. Color not only deteriorates the aesthetic appearance of the stream, but also inhibits the natural process of photosynthesis due to absorbance of sunlight resulting in oxygen deficiency, thereby upsetting the aquatic growth of the natural flora and fauna.

The removal of dyes from a colored industrial effluent is a challenging problem. Nowadays thermally stable dyes have been introduced which are difficult to degrade after use. Many dyes are synthetic organic compounds and are difficult to decolorize due to their complex chemical structure and large molecular weights. These properties augment the treatment difficulties with textile dye waste water. Low bio-degradability (BOD/COD less than 0.1) of these dyes makes it difficult to remove them from waste water. There are many structural varieties of dyes that fall into either the cationic, non-ionic or anionic types. Dyes are known to cause allergic dermatitis, skin irritation, cancer and even genetic mutation. Removal of dyes from waste water is therefore of utmost importance to prevent pollution of water in the receiving watercourse.

Traditionally, biological treatment, adsorption, solvent extraction etc. are widely used methods for removing pollutants from waste water (5, 6, 29, 30, 34). Adsorption has become one of the most effective and efficient techniques for the removal of color from industrial effluent. The major advantages of an adsorption system for water pollution control are less investment in terms of initial cost and land, simple design and easy operation, no effect by toxic substances, and superior removal of organic waste constituents as compared to the conventional treatment processes. The added advantage of the adsorption method lies in the fact that the adsorbed dye can be desorbed for reuse under specific conditions, as adsorption is generally reversible. Regeneration of the adsorbent with resultant economy of operation may be possible. Also, it is a sludge-free process.

The most commonly used adsorbent of choice is activated carbon (4, 20, 23, 49). The existing commercial systems use activated carbon exclusively. The cost of activated carbon and relatively high cost involved in regenerating it for reuse are some of the major problems that render the operation of adsorption system a costly affair. Due to the expense of carbon for waste water treatment, a search for substitutes is underway. Waste water treatment requires vast quantities of activated carbon, so improved and tailor-made adsorbents are needed for these demanding applications. Such adsorbents should be easily available, economically feasible and readily and quantitatively regenerated chemically. The final choice of the adsorbent is a matter of economics. The choice is not a matter of sorption capacity only but also of regeneration, waste management and total cost of treatment. Taking these into account, it may turn out that a cheap sorbent with low sorption capacity is more appropriate than the expensive activated carbon under some water-specific circumstances. Use of low cost and affordably disposable adsorbent can bring down the cost of decolorisation to a significant extent.

The use of non-conventional adsorbents in waste water treatment has become the target of research interest in recent years. With a view to find some other suitable adsorbents, investigators have studied a number of less expensive adsorbents. Notable amongst these are bauxite, fly ash, soils, clays, ion-exchangers etc. Many natural adsorbents like cellulose, peat, wood, lignin, agro-residues etc. have also been used to study the adsorption of dyes from aqueous solutions. Considerable amount of works (7, 13-15, 19, 25, 26, 35, 39-42) have been reported in literature on color removal from waste water.

Lignin (10), a waste product of the pulp and paper industry, has been shown to adsorb a number of acid–base dyes (28, 43, 44) and many other organic compounds viz. amines (37), phenols, dyes (9), alcohols (50), acids

(16), etc. The use of lignin as an adsorbent for the removal of cationic and anionic dyes from their aqueous solutions has been explored. Lignin particles are negatively charged which attracts more strongly the positively charged dyes, thereby giving a higher uptake of cationic dyes. The greater affinity of basic dyes for the adsorbent is due to the columbic attractions between the surface anions of the adsorbent and the cations of the basic dyes. Though its capacity is lower than that of commercial grade activated carbon, the low material cost makes it an attractive option for the treatment of domestic waste water. Lignin is a potential material for the removal of dyes from waste water and can be used to treat the effluents from textile and other industries discharging colored waste water. The results of laboratory investigations show that lignin holds promise for effluent treatment for the removal of dyes.

This chapter describes the investigations on the sorption of three cationic dyes: Crystal violet, Neutral red and Toluidine blue on lignin as an adsorbent. It includes the sorption equilibria, various adsorption models, factors affecting adsorption, some preliminary investigations undertaken to fix up necessary parameters for studying the sorption equilibrium by batch process and the results on the sorption of the three dyes under different conditions of temperature, pH, particle size of lignin etc.

3.2 EQUILIBRIA AND KINETICS

The suitability of the process of adsorption, as a unit operation, for the treatment of wastes can be determined in terms of two aspects viz., the equilibria and the kinetics of adsorption. The rate of adsorption mostly depends on the method by which the adsorbate comes in contact with the adsorbent material. The essential requirements for the unit process are rapid separation of pollutants and a longer life of the adsorbing material.

Adsorption from solution on to a solid occurs as a result of the driving forces of lyophobic character of the solute, relative to the particular solvent, or of a high affinity of the solute for the solid. The mechanism of the adsorption process involves three steps:

1. The first is the transport of the adsorbate through a surface film to the exterior of the adsorbent (film diffusion).
2. In the second step the diffusion of adsorbate takes place within the pores of the adsorbent (pore diffusion).
3. The third and final step is adsorption of solute at the interior surfaces bounding the pore and capillary spaces of the adsorbent (intraparticle diffusion).

The overall rate of the process of adsorption depends on the slowest step. For a batch process "pore diffusion" and for a continuous flow system "film diffusion" are the most likely rate controlling factors.

The phenomenon of adsorption, in general, includes ion–exchange, physical adsorption and chemical adsorption. Ion exchange or exchange adsorption is the reversible interchange of ions between two phases. It is a process in which ions of one substance concentrate at the surface of the absorbent as a result of electrostatic attraction to charged sites at the adsorbent surface. Exchange adsorption depends on the charge and hydrated size of ions involved. Both natural and synthetic products are used as ion - exchange substances. Physical adsorption is adsorption occurring as a result of vander Waal's forces (dispersion forces). Mostly it is reversible and non-specific in nature. Chemical adsorption is a result of specific interactions between the sorbing species and sorbent material. In most cases it is irreversible in nature and is effective at high temperature e.g., sorption of phenols on silica or activated carbon involves hydrogen-bond formation.

When adsorption is irreversible, solute molecules cannot be eluted from the sorbent material. In reversible adsorption the solute is adsorbed at the surface and then moves towards the interior of the adsorbent. This process continues till the equilibrium distribution of the solute between solid and solution phase occurs. In this type of adsorption recovery of solute is possible.

3.3 FACTORS AFFECTING SORPTION

Many factors influence the rate of adsorption and extent to which a particular adsorbate can be adsorbed. The parameters that have been investigated for optimizing the use of lignin in waste water treatment are:

3.3.1 Nature of Adsorbate

Adsorption increases with decrease in solubility of solute in solvent. The solute-solvent bond is to be broken up before adsorption takes place. Normally, solubility of organic compounds decreases with increase in length of carbon-chain and consequently adsorption increases with ascending homologous series. Other factors of importance, which have profound influence on the extent of adsorption, are molecular size, structure and polarity of adsorbate molecules present in waste water and their concentration.

3.3.2 Nature of Adsorbent

Though every solid is an adsorbent, the physico-chemical nature of adsorbent can have profound effect on both, the rate and the capacity for adsorption. As adsorption is a surface phenomenon, portion of the total surface available for adsorption depends on the particle size and shape of the adsorbent material. The adsorption capacity for a non-porous or a porous adsorbent varies as the inverse of the particle diameter but for highly porous adsorbents the adsorption rate is independent of particle diameter. Apart from this, the chemical nature of the adsorbent material is also of interest that determines the rate of adsorption.

3.3.3 Method of Contact

The uptake of adsorbate material also depends on the type and rate of contact i.e., the rate of adsorption may be different in "Batch mixing" or "Continuous flow system."

3.3.4 Adsorbate Concentration

The increase in concentration of the adsorbate in solution results in increase in the magnitude of adsorption at a given temperature and pH. Several investigators have studied this parameter and the results are generally expressed by a linear form of Freundlich and Langmuir adsorption isotherms (32, 36, 46)

3.3.5 Adsorbent Dose

It is important to determine the dose of adsorbent required to achieve a desired level of treatment. Swamy et al (36) observed that the percent removal of O-Cresol increases with increase in adsorbent dose, while removal per unit weight of adsorbent increases with decrease in adsorbent dose.

3.3.6 Contact Time

Contact time is also an important factor from the design point of view. Adsorption of adsorbate species is faster in the initial stages of contact period and becomes slow near equilibrium (31-33, 46). Contact time required to attain equilibrium is a function of particle size, pH, rate of agitation, temperature etc. Pretreatment of adsorbent also influences the equilibrium time. It was found that if contact time is less, efficiency decreases.

3.3.7 pH

The removal of dyes from waste water with conventional and non-conventional adsorbents is highly sensitive to its pH, as it may affect the surface charge of the adsorbents, degree of ionization and the rate of adsorption. Change in pH affects the adsorption process through dissociation of functional groups on the adsorbate and adsorbent (24, 33).

3.3.8 Particle Size

Adsorption is a surface phenomenon such that the extent of adsorption is proportional to specific surface area (micropores). Thus, the adsorption is greater for small particle size (21). Although particles of smaller size provide large surface area for higher adsorption but are unsuitable for continuous column application.

3.4 ADSORPTION MODELS

During adsorption the solute goes to the interface till equilibrium is attained between that in bulk phase and that at the surface, at a constant temperature. At the position of equilibrium, there is a defined distribution of solute between the two phases. It is conventional to depict the distribution by plotting the amount of solute adsorbed per unit weight of adsorbent vs. the concentration of solute remaining in the solution at equilibrium i.e. equilibrium concentration, at constant temperature. An expression of this type is termed as "adsorption isotherm".

For decades the Langmuir and the Freundlich theories have been used to model the adsorption behavior of dyes at equilibrium (3, 43). The sorption process is then discussed in terms of constants that are characteristic for the individual systems (27, 47). The type of isotherms followed by a system can be any, or a combination of the following models:

3.4.1 Langmuir Adsorption Model

It is valid for monolayer adsorption. It is based on the assumptions that:

a) Maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface.

b) That the energy of adsorption is constant and is distributed uniformly at the surface.

c) That there is no transmigration of adsorbate in the plane of the surface.

The Langmuir isotherm is represented as:

$$q_e = \frac{Q^0 \, b \, C_e}{(1 + b \, C_e)} \qquad \ldots\ldots\ldots\ldots(1)$$

where:

C_e = remaining concentration of solute in solution at equilibrium.

q_e = amount of solute adsorbed per unit weight of adsorbent.

Q^o = Langmuir constant related to the number of moles of solute adsorbed per unit weight of adsorbent, for forming a monolayer on the surface.

b = Langmuir constant related to the free energy or net enthalpy of adsorption ($b \propto e^{-\Delta H/RT}$)

The expression can also be written as:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \qquad \ldots\ldots\ldots\ldots(2)$$

Thus, a plot of C_e / q_e vs. C_e results in a straight line of slope $1/Q^o$ and intercept $1/Q^ob$, indicating the applicability of the Langmuir model for the formation of monolayer coverage of dye on the outer surface of the adsorbent.

The assumptions of Langmuir model are not true for most systems of waste water treatment, yet this equation is very useful for the treatment of adsorption data. For example, the value of Q^o for organic wastes on activated carbon does not represent monolayer formation but a fractional limiting capacity for adsorption, which is also a factor of practical utility.

3.4.2 Freundlich Adsorption Model

It is an empirical relationship describing the sorption of solutes from a liquid to a solid surface. It is a special case for heterogeneous surface energies in which the energy term varies as a function of surface coverage due to variation in heat of adsorption. Freundlich equation can be represented as:

$$q_e = K_f \cdot C_e^{1/n} \qquad \text{............(3)}$$

Data are usually fitted to the logarithmic form of the equation:

$$\log q_e = \log K_f + \frac{1}{n} (\log C_e) \qquad \text{............(4)}$$

where 'K_f' is the Freundlich constant related to the relative sorption capacity of the adsorbent and 'n' is a constant related to energy or intensity of adsorption. The plot of log q_e vs. log C_e is linear with slope of 1/n and an intercept equal to log K_f.

This gives an expression encompassing the heterogeneous surface energies and the exponential distribution of active sites and their energies. This isotherm does not predict any saturation of the adsorbent surface and can only be applied in the low to intermediate concentration range.

3.4.3 B.E.T. Adsorption Model

Derived by Brunauer, Emmert and Teller is indicative of sequential multilayer adsorption and is represented by the equation:

$$q_e = \frac{A \cdot C_e \cdot Q^0}{C_s - C_e \left[1 + (A-1) \frac{C_e}{C_s} \right]} \qquad \text{............(5)}$$

where,

q_e and C_e are the same as above,

C_s = saturation concentration of solute.

Q^o = number of moles of solute adsorbed in forming a complete monolayer on adsorbent surface.

A = a constant, expressive of the energy of interaction with the surface.

The B.E.T. model has been linearised to yield the following equation:

$$\frac{C_e}{(C_s - C_e)\,q_e} = \frac{1}{A\,Q^0} + \frac{A-1}{AQ^0} \cdot \frac{C_e}{C_s} \qquad \text{...........(6)}$$

The constants A and Q^o can be evaluated by plotting $\frac{C_e}{(C_s - C_e)q_e}$ vs. $\frac{C_e}{C_s}$.

3.5 HEAT OF ADSORPTION

The process may be exothermic or endothermic. The exact nature of the process can only be determined by the values of the heat of adsorption.

The isosteric heat of adsorption is calculated by the equation:

$$Q = R\,\frac{T_1 T_2}{T_1 - T_2}\,\log\frac{C_1}{C_2} \qquad \text{...........(7)}$$

where, for the same amount of adsorption:

C_1 = equilibrium concentration of the solute at temperature T_1,

C_2 = equilibrium concentration of the solute at temperature T_2,

R = Universal gas constant.

3.6 EQUILIBRIUM PARAMETER

The essential characteristics of Langmuir's isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter R_L (22) that is defined by the equation:

$$R_L = \frac{1}{1 + bC_0} \qquad \text{...........(8)}$$

where,

C_o = the initial concentration in ppm,

b = the Langmuir constant for energy of adsorption.

R_L predicts the efficiency of the process. It indicates the nature of the isotherm and its shape. R_L values between zero and one indicate favorable adsorption.

R_L Values	Type of Isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L < 0$	Irreversible

3.7 SURFACE AREA

The specific surface area plays an important role in determining the physical and chemical properties of a substance. In this study the adsorption from solution technique has been used for the determination of surface area of the lignin sample. Toluidine blue has been taken as the solute.

If X_m (in $mol.g^{-1}$) is the amount of solute adsorbed at monolayer per gram of adsorbent,

A_m (in m^2) is the cross-sectional area occupied by the adsorbate unit on the surface and

L (in mol^{-1}) is Avagadro's number ($= 6.023 * 10^{23}$),

S the specific surface area of lignin (in $m^2. g^{-1}$) (8) is given by the expression :

$$S = \frac{X_m \cdot A_m \cdot L}{N} \qquad \text{...........(9)}$$

where N is the coverage factor (here taken as 1 for Toluidine blue). In this study A_m value for Toluidine blue has been taken as 0.3 nm^2 (38) as estimated from its chemical structure.

3.8 RESULTS AND DISCUSSION

3.8.1 Evaluation of Sorption Parameters

The parameters to be fixed up for investigating the equilibrium by batch process are:

a) Equilibrium time of adsorbate and adsorbent.

b) Concentration of adsorbate in solution.

c) Particle size of adsorbent material.

d) Quantity of adsorbent.

e) pH and temperature.

f) Volume of the adsorbate solution.

g) Presence of salts in adsorbate solution.

A moderately wide range of adsorbate concentration has been chosen for running of adsorption isotherms. 100 to 2000 mg/l in case of both Crystal violet and Toluidine blue and 500 to 3500 mg/l in case of Neutral red. This has been decided, keeping in view the concentration ranges at which noticeable changes in concentration of dyes have been observed.

After trying a variety of fractions of particle sizes of lignin it was found that the removal of dyes is most convenient when 100 to 200 mesh size of particles are taken. Thus, 100 to 200-mesh size of lignin particles have been used through out these investigations.

The equilibration time for optimum adsorption of the three dyes has been determined experimentally by observing the effect of the time of contact (Table 3.1; Figs. 3.1 – 3.3) at a fixed adsorbate concentration (2000 mg/l for Crystal violet, 1000 mg/l for Toluidine blue and 4500 mg/l for Neutral red). The quantity of adsorbent has been decided after making a few trial runs. 100 mg (0.1 g) of absorbent per 10 ml of solution has been maintained for all the adsorption experiments.

The results of these experiments, depicted in Fig. 3.4, are the plots of percent dye removal vs. time of contact for Crystal violet, Neutral red and Toluidine blue. The nature of the plots indicate that the removal of dyes occur in two phases. In the first phase the uptake of solute is fast while in the second phase the rate of removal becomes quite slow and subsequent removal of solute continues over a long period of time.

The major part of the uptake of Crystal violet seems to be complete in six hours, Toluidine blue in two and a half hours and Neutral red in thirty-six hours. As such, in case of Crystal violet all sorption determinations have been made after equilibrating the solution with adsorbent for eight hours and three and a half hours in the case of Toluidine blue. In the case of Neutral red the sorption rate is comparatively slow because determinations are carried out at pH 3.7(as the color of the dye is found to be stable in the pH range 3.0–4.4) while other dyes are estimated at pH 7.0. At pH 8.0 Neutral red gets precipitated during estimation and any further determination is not possible. Thus, all observations for Neutral red have been made after equilibrating the solution with adsorbent for fifty-four hours.

The logarithmic plots between percent dye removal and the time of contact are shown in Fig. 3.5 for the three dyes. All the plots are linear. Mathematically it may be represented as:

$$P_S = K_t \cdot t^m$$

or $$\log P_s = m \log t + \log K_t \qquad ....(10)$$

where,

P_s = percent solute removal,

t = time of contact (minutes),

$\text{Log} K_t$ = the intercept of the linear plot (indicative of rate factor),

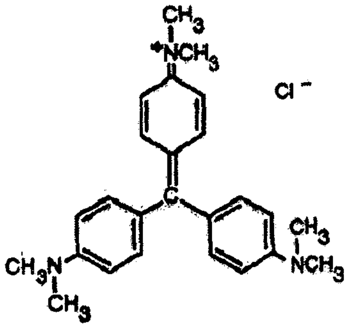
m = the slope (reflects the mechanism of adsorption).

3.8.2 Adsorption of Dyes

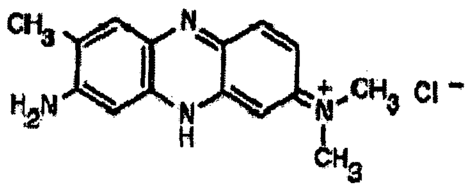
In order to determine the sorption potential of lignin as an adsorbent for the removal of dyes, the study of sorption isotherms is essential.

The adsorption data for Crystal violet, Neutral red and Toluidine blue are given in Tables 3.2-3.4, Tables 3.5-3.7 and Tables 3.8-3.10 respectively. The adsorption isotherms for Crystal violet are shown in Figs. 3.6-3.8, for Neutral red in Figs. 3.9-3.11 and for Toluidine blue the adsorption isotherms are shown in Figs. 3.12-3.14. The isotherms indicate positive adsorptions in all the adsorptions isotherms. These are concave to the concentration axis. Although the extent of adsorption increases with increasing concentration of adsorbate and the adsorption mechanism appears to be more efficient, the percentage removal of dye is quite high at low adsorbate concentration i.e. the process of adsorption is not uniform and the percentage removal of dyes decreases with the increase in initial concentration of dye. Annadurai and Krishnan (1,2) have also been reported similar results for the removal of dyes. The exponential decrease in the percentage removal of dyes with increase in initial dye concentration may be due to the reduction in immediate solute adsorption arising due to the decrease in the availability of active sites on the lignin surface as against the high number of active sites required at relatively high concentration of dye. Thus, the nature of the isotherms reveal a relatively rapid initial rate of adsorption at low adsorbate concentration which decreases markedly at high adsorbate concentration with a slow approach to saturation. At low concentration of dyes about 50% to 98% of the dyes get adsorbed showing that lignin is quite suitable for the removal of dyes. Amongst the three dyes, at the same pH, the uptake of Neutral red is higher than that of Toluidine blue and the uptake of Crystal violet is lower than both Toluidine blue and Neutral red. Thus, the decreasing order of the extent of adsorption of dyes by lignin is: NR > TB > CV, but at the pH chosen for the adsorption studies (pH 7.0 for Crystal violet and Toluidine blue, pH 3.7 for Neutral red) the order is TB > NR > CV.

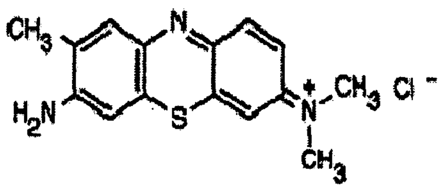
The difference in the extent of adsorptions of Crystal violet, Neutral red and Toluidine blue may be due to the spatial geometry of their molecular structures. All the three dyes possess positively charged nitrogen that provides a positive site for the adsorbate molecules to interact effectively with the adsorbent, the lignin particles, having the negatively charged sites. All the three dyes thus show favorable adsorption but to different extents. The structure of three dyes, Crystal violet, Neutral red and Toluidine blue, used in these investigations is given below:



Crystal violet



Neutral red



Toluidine blue

Both Neutral red and Toluidine blue are linear molecules. On the other hand Crystal violet is a triphenyl methane dye having three benzene rings attached to a central carbon atom. It shows a planar triangular orientation. It has a positive charge at one corner of the triangle, with which it links with the negative sites of the adsorbent. Due to its trigonal spatial geometry its adsorption is less than that of the other two linear dyes.

The adsorption isotherms of the three cationic dyes, Crystal violet, Neutral red and Toluidine blue at different temperatures are shown in Figs. 3.6, 3.9 and 3.12 respectively. It is observed that adsorption increases with increase in temperature in all the three cases. The heat of adsorption as calculated (from equation 7) for the same amount of adsorption for the three dyes are given in Table 3.11. It is observed that the values are negative indicating the process to be exothermic. The values are higher for Crystal violet in comparison to Toluidine blue and Neutral red. Figs. 3.15–3.17 shows the isosteric heats of adsorptions for lignin-dye system plotted against the amount of dye adsorbed. The curve is linear in all the cases.

The attraction between the dye molecules tends to increase the heat of adsorption as surface coverage approaches unity and the average separation of the adsorbate molecule becomes small. However, the multilayer may begin to form on some parts of the surface before the monolayer is complete. The complications in the actual systems and the heterogeneity of the surface cause a progressive diminution in the heat of adsorption as the surface coverage increases long before the monolayer is complete. The increase in the heat of adsorption due to intermolecular attractions may be marked by the reductions in the same due to adsorption in higher layers.

The effect of pH on adsorption process has been studied at different pH values for the three dyes. The variation of solution pH is reported to significantly affect the dye adsorbed (1,2) i.e. the system is strongly pH dependant. The experimental results indicate that the adsorption of the three dyes on lignin increases with increase in pH, for the pH range studied, as is evident from Table 3.3 for Crystal violet, Table 3.6 for Neutral red and Table 3.9 for Toluidine blue. The number of active sites on the surface of the adsorbent may increase with varying pH. The rate of adsorption is maximum at pH 7.0. Lower pH is unfavorable for adsorption. This is due to excess of H^+ ions in solution causing a decrease in the availability of sorption sites on lignin for the dye molecules.

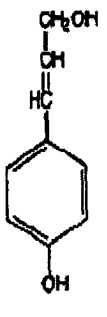
Kannan and Sunderam (11) have also reported the increase in adsorption with increase in pH values in the case of basic dyes Methylene blue and Rhodamine B. Karthikeyan et al also observed the rate of adsorption to be maximum at pH 7.0 for the adsorption of Zn (II) onto chitosans (12) The isotherms at different pH for the three dyes are given in Figs. 3.7, 3.10 and 3.13 respectively, showing the adsorption of the dyes to be highly pH sensitive. Mahesh et al (18) have reported the favorable adsorption of phenol at low pH on activated carbon. The decrease in adsorption with increase in pH has been explained on the basis of aqua-complex formation and its subsequent acid–base dissociation at the solid–liquid interface.

Lignin is an aromatic, complex, polymeric product of p–hydroxy phenyl propane units present in most plant tissues (18% to 38% by weight), arising from the enzyme initiated dehydrogenative polymerization of its three primary precursors:

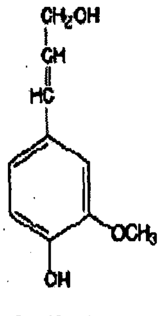
(a) Trans – p – coumaryl alcohol.

(b) Trans – coniferyl alcohol.

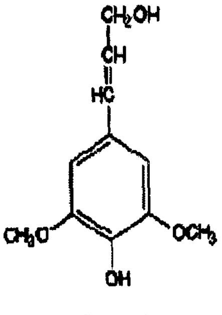
(c) Trans – sinapyl alcohol.



p-Coumaryl alcohol



Coniferyl alcohol



Sinapyl alcohol

The negative charge on the surface of lignin arises from the dissociation of phenolic -OH groups. At low pH the dissociation of -OH groups is suppressed and this results in a negative surface charge density of smaller magnitude, in comparison to dissociation of -OH groups at higher pH, which provides an increased negative charge on the lignin surface. The negatively charged points, balanced by counter ions of opposite charge on lignin surface, provide the adsorption sites. As the number of sites increase with increasing pH of the dye solution, the uptake of the solute also increases. The adsorption of the three dyes increases with increase in pH from 3.7 to 7.0. Wieber et al (48) also observed an increase in adsorption of Cu^{++} and Zn^{++} ions from solution by lignin due to dissociation of phenolic -OH and carboxylic groups.

Namasivayam et al (24) observed maximum removal of nitrate in the pH range 3.0 to 10.0 followed by a decrease on further increasing the pH to 11.0 and attributed it to electrostatic repulsion. The percent adsorption of phenol on activated carbon has been reported (33) to increases up to pH 6 and then decreases with further increase in pH.

The effect of particle size of adsorbent is given in Tables 3.4, 3.7 and 3.10 for Crystal violet, Neutral red and Toluidine blue respectively. As adsorption is a surface phenomenon, portions of the total surface available for adsorption depends on the particle size of the adsorbent material. As particle size is reduced the surface area of lignin particles increases which results in increased chance of contact between lignin particle and the dye molecules. This can be attributed to the breaking of larger particles that tends to open tiny cracks and channels on the particle surface, providing added surface area that can be employed in the adsorption process. Thus, the higher rate of adsorption by lignin with smaller particle sizes may be due to the availability of more specific surface area on the adsorbent. Figs. 3.8, 3.11 and 3.14 show that the adsorption capacity of lignin for the three dyes increases as the particle size of the adsorbent decreases. This indicates that the surface area associated with the pores inside the particle is being freed, at least partially, and that the effective adsorption regime is confined to the external surface and a narrow layer just below the surface.

The increase in adsorption with increase in temperature may be attributed to the increased dissociation of the -OH groups on lignin thereby enhancing the negative charge on lignin with increase in temperature. Thus, the number of adsorption sites also increases with increase in temperature, leading to increased uptake of dye at higher temperatures.

The adsorption data reveals that the Langmuir isotherm model is applicable. The Langmuir plots for all the three dyes are obtained at different temperatures (Figs.3.18–3.20), at different pH (Figs. 3.21–3.23) and at different particle sizes of lignin (Figs. 3.24–3.26), for Crystal violet, Neutral red and Toluidine blue respectively. The resultant linear graphical relationship of the Langmuir plots indicates that the data fits the Langmuir model in the entire adsorbate concentration range. The values of Langmuir constants 'Q^o' and 'b' are listed in Table 3.12. The observed values of 'Q^o', the amount of dye adsorbed for forming a complete monolayer on the lignin surface, for the three dyes increases with increase in temperature and pH of the dyes solutions and with the decrease in the particle size of lignin; thus indicating that a greater quantity of dye is required for the formation of a monolayer at the surface of lignin with increase in the temperature and pH and with decrease in particle size of lignin. This is in accordance with the concept discussed above. The values of 'Q^{o}' at various temperatures, pH and particle sizes of lignin for Neutral red are higher than those for Toluidine blue, which in turn are higher than those obtained for Crystal violet. A similar trend is observed with the adsorption results of these dyes on lignin at different temperatures, pH and particle sizes of lignin i.e. Neutral red > Toluidine blue > Crystal violet.

The values of Langmuir constant 'b' reflect the steepness of the approach to saturation. The value of 'b' is the reciprocal of the concentration at which half saturation of the adsorbent is obtained. From the given table it is evident that 'b' values increase with an increase in temperature for Crystal violet and Toluidine blue and with decrease in particle size of lignin for all the three dyes. However, in case of 'b' values of Crystal violet and Toluidine blue, no regular trend is observed with an increase in pH. In the case of Neutral red, 'b' values decrease with an increase in pH from 3.7 to 6.0.

A good linearisation of data is obtained for Toluidine blue at various temperatures, pH and particles sizes of lignin when plotted for B.E.T. as shown in Figs. 3.27–3.35. In the case of Neutral red linearisation is obtained only at low dye concentration at various temperatures, pH and particle sizes of lignin (Figs. 3.36–3.44). Crystal violet does not obey B.E.T. model. Plots for the same at different temperatures, pH, and particle sizes of lignin are shown in Figs. 3.45–3.52, indicating only monolayer adsorption.

The values of B.E.T. constants, 'Q^{o}' and 'A', as calculated from B.E.T.

plots for Toluidine blue and Neutral red at various temperatures, pH and particle sizes of lignin are given in Table 3.13. The value of 'Q^{o}' are much lower than those obtained from Langmuir plots. The values of B.E.T. constant 'A' reflects the energy of interaction with the surface and are lower for Neutral red in comparison to Toluidine blue.

R_L values predict the efficiency of the process. The R_L values calculated for Crystal violet, Neutral red and Toluidine blue at different temperatures, pH and particle sizes of lignin for different concentration ranges of each dye are given in Table 3.14. All the values are much lower than one, thus indicating favorable adsorption in each case except for Crystal violet at pH 4.0 where the negative values indicate irreversible adsorption. Khattri (17) reported adsorption of dyes on Sone sand with R_L value of 0.07–0.12 for Methylene blue and 0.08–0.13 for Malachite green. Karthikeyan (12) reported R_L values between 0.219-0.746 for 2-14 mg/l of Zn ions in solution.

The effect on adsorption of increasing quantity of dye in solution has been studied for all the three dyes. Results are given in Table 3.15 for Crystal violet, Neutral red and Toluidine blue. All dyes indicate an increase in adsorption with increase in the amount of dye added as shown in Fig. 3.53–3.55, but the corresponding residual concentration also increases with an increase in the quantity of dye added (Figs. 3.56–3.58) and the % removal of the dye shows a marked decline with an increase of quantity of dye (Figs. 3.59–3.61).

Many times salts are also present in waste waters. Hence the effect of salt concentration on the sorption of a fixed concentration of these three dyes has also been studied. The plots of log K_d vs. log $[NH^+]$ of Crystal violet, Neutral red and Toluidine blue are linear (Figs. 3.62 – 3.64), with slopes 0.9232, -0.336 and -0.3814 respectively. A slope value of 0.9232 in case of Crystal violet is closer to 1.0 needed for ion exchange mechanism, suggesting that most of the uptake of the Crystal violet dye takes place via ion exchange mechanism route. The values for Neutral red and Toluidine blue indicate that the uptake of the adsorbate does not take place via ion–exchange mechanism. The linear plots also indicate that the adsorption correlates with Freundlich adsorption isotherm.

3.8.3 Surface Area

The specific surface area of the lignin has been calculated at various pH values and particle sizes. The value of A_m for Toluidine blue was taken as 0.3 nm^2 (38). The values so obtained are given in Table 3.16. Values of specific surface area increase with decrease in particle size, which is the normal behavior observed with many other adsorbents. The values of surface area calculated are dependent on the pH of the solution and increase with increase in pH. These values are far less than reported by Jodl (10) (180 m^2/g) from the adsorption data of water vapor on cuoxam spruce lignin and more than reported by Jindal (9) for the adsorption of Methylene blue on eucalyptus wood lignin. The specific surface area values of the samples of Bentonite, Sepiolite, Zeolite and Kaolin obtained by Methylene blue solution adsorption are 136, 118, 44 and 14.3 (m^2/g) respectively (8). Surface area of Kraft lignin used for adsorption of Cu and Cd from aqueous solutions (22) was characterized to be 1260 m^2/g.

3.8.4 Desorption Studies

The desorption of Crystal violet, Neutral red, and Toluidine blue dyes from the lignin surface has been studied using a number of mono, bi and tri-valent cations. The data for the three dyes, given in Table 3.17 indicates the following order:

$$NH_4^+ > K^+ > Na^+$$

$$Al^{3+} > Ba^{2+} > Na^+$$

This indicates that the desorption process follows the lyotropic series of ions. The desorption studies with different desorbing solutions also indicates that only 0.3% to 1.4% of the total dyes adsorbed could be desorbed. Thus, we may conclude that desorption of lignin does not take place with the various desorbing solutions used. Hence no further desorption experiments were performed.

3.9 REGENERATION

Since thermal regeneration of adsorbent is likely to cause air pollution problems and chemical regeneration will lead to increased water pollution, it is not desirable to regenerate lignin in view of its low-cost and ease of availability, provided its disposal after use is easy and safe. The spent carbonaceous adsorbent can be disposed of simply by burning: one option can be firing in a steam boiler.

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Table 3.1 : Adsorption of Crystal violet, Neutral red and Toluidine blue on lignin of 100 - 200 mesh size at 30^{0}C.

Crystal violet			Neutral red			Toluidine blue		
Initial conc. of dye = 2000 mg.l $^{-1}$			Initial conc. of dye = 4500 mg.l $^{-1}$			Initial conc. of dye = 1000 mg.l $^{-1}$.		
Time (h)	Equilibrium conc. (mg.l^{-1})	Adsorption (g.g^{-1})	Time (h)	Equilibrium conc. (mg.l^{-1})	Adsorption (g.g^{-1})	Time (h)	Equilibrium conc. (mg.l^{-1})	Adsorption (g.g^{-1})
4.00	1575.60	0.04	4.00	3279.15	0.12	0.50	482.40	0.05
7.50	1525.00	0.05	5.50	3087.00	0.14	1.00	344.90	0.07
8.00	1508.00	0.05	8.00	2820.51	0.17	2.25	83.99	0.09
9.50	1507.20	0.05	10.00	2794.05	0.17	3.25	30.45	0.10
12.00	1506.00	0.05	12.00	2733.36	0.18	4.25	18.03	0.10
27.50	1475.98	0.05	26.75	2611.98	0.19	5.25	12.26	0.10
34.00	1434.26	0.06	36.00	2426.13	0.21	6.25	8.83	0.10
---	---	---	51.25	2288.58	0.22	7.25	6.12	0.10
---	---	---	75.50	2236.33	0.23	8.25	4.63	0.10
---	---	---	98.75	2231.88	0.23	---	---	---

Table 3.2 : Adsorption of Crystal violet on lignin of 100 - 200 mesh size at pH 7.0, at various temperatures.

Initial conc. (mg.l^{-1})	Temperature							
	20^{0}C		25^{0} C		30^{0} C		40^{0} C	
	Equilibrium conc. (mg.l^{-1})	Adsorption (mg.g^{-1})	Equilibrium conc. (mg.l^{-1})	Adsorption (mg.g^{-1})	Equilibrium conc. (mg.l^{-1})	Adsorption (mg.g^{-1})	Equilibrium conc. (mg.l^{-1})	Adsorption (mg.g^{-1})
100	2.70	9.73	5.22	9.48	5.55	9.45	0.80	9.92
200	3.96	19.60	5.75	19.43	10.00	19.00	3.63	19.64
400	81.28	31.87	75.74	32.43	36.60	36.34	5.56	39.44
600	179.33	32.07	167.21	43.28	71.75	52.82	7.53	59.24
800	460.59	33.94	304.05	49.59	165.90	63.41	59.91	74.00
1000	645.20	35.48	474.69	52.53	311.10	68.89	204.80	79.52
1200	807.77	37.23	663.23	53.68	497.28	70.27	401.90	79.81
1400	1002.00	39.80	847.12	55.28	688.00	71.20	601.00	79.90
1600	1193.30	40.67	1023.15	57.68	884.10	71.60	800.08	79.99
1800	1387.70	41.23	1219.48	58.55	1080.80	72.00	974.40	82.56
2000	1573.80	42.62	1395.69	60.43	1278.40	72.16	1150.93	84.90

Table 3.3 : Adsorption of Crystal violet on lignin of 100 - 200 mesh size at 30^{0}C, at various pH.

Initial conc. (mg.l^{-1})	pH					
	4		6		7	
	Equilibrium conc. (mg.l^{-1})	Adsorption (mg.g^{-1})	Equilibrium conc. (mg.l^{-1})	Adsorption (mg.g^{-1})	Equilibrium conc. (mg.l^{-1})	Adsorption (mg.g^{-1})
100	2.00	9.80	3.20	9.68	5.55	9.45
200	6.54	19.35	5.95	19.40	10.00	19.00
400	15.36	38.46	7.38	39.27	36.60	36.34
600	215.05	38.49	36.21	56.38	71.75	52.82
800	411.80	38.82	164.99	63.50	165.90	63.41
1000	611.11	38.89	360.95	63.90	311.10	68.89
1200	810.00	39.00	551.67	64.83	497.28	70.27
1400	1007.50	39.25	750.20	64.98	688.00	71.20
1600	1205.20	39.48	948.00	65.20	884.10	71.60
1800	1403.40	39.66	1144.50	65.55	1080.80	72.00
2000	1601.50	39.85	1343.30	65.67	1278.40	72.16

Table 3.4 : Adsorption of Crystal violet on lignin of various particle sizes at 30^{0}C ,at pH 7.0.

Initial conc. (mg.l^{-1})	Mesh size					
	40 - 100		100 – 200		Above 200	
	Equilibrium conc. (mg.l^{-1})	Adsorption (mg.g^{-1})	Equilibrium conc. (mg.l^{-1})	Adsorption (mg.g^{-1})	Equilibrium conc. (mg.l^{-1})	Adsorption (mg.g^{-1})
100	9.00	9.10	5.55	9.45	5.55	9.45
200	16.31	18.37	10.00	19.00	10.00	19.00
400	47.50	35.25	36.60	36.34	12.16	38.78
600	84.28	51.57	71.75	52.82	17.91	58.21
800	189.24	61.08	165.90	63.41	129.36	67.06
1000	330.65	66.93	311.10	68.89	266.11	73.30
1200	504.99	69.50	497.28	70.27	461.83	73.80
1400	704.50	69.55	688.00	71.20	660.30	73.97
1600	904.22	69.58	884.10	71.60	857.50	74.20
1800	1102.90	69.71	1080.80	72.00	1052.60	74.74
2000	1301.76	69.82	1278.40	72.16	1244.55	75.50

Table 3.5 : Adsorption of Neutral red on lignin of 100 - 200 mesh size at pH 3.7, at various temperatures.

Initial conc. ($mg.l^{-1}$)	Temperature							
	25^0C		30^0 C		35^0 C		40^0 C	
	Equilibrium conc. ($mg.l^{-1}$)	Adsorption ($mg.g^{-1}$)	Equilibrium conc. ($mg.l^{-1}$)	Adsorption ($mg.g^{-1}$)	Equilibrium conc. ($mg.l^{-1}$)	Adsorption ($mg.g^{-1}$)	Equilibrium conc. ($mg.l^{-1}$)	Adsorption ($mg.g^{-1}$)
500	2.51	49.75	2.35	49.76	2.51	49.75	2.46	49.75
1000	3.91	99.61	3.66	99.63	4.01	99.60	4.06	99.59
1250	8.14	124.19	9.61	124.04	6.40	124.36	10.33	123.97
1500	56.63	144.34	43.23	145.67	39.52	146.05	32.79	146.72
1750	183.20	156.68	170.98	157.90	139.01	161.10	118.69	163.13
2000	312.93	168.71	314.28	168.57	285.00	171.50	262.78	173.72
2250	548.71	170.13	550.72	169.93	519.22	173.08	489.92	176.01
2500	779.79	172.02	751.41	174.86	727.70	177.23	717.90	178.21
2750	997.24	173.28	1080.96	183.40	900.91	184.91	888.80	186.12
3000	1259.76	174.02	1139.76	186.02	1120.43	187.96	1101.12	189.88
3250	1499.60	175.09	1550.20	186.43	1353.84	189.62	1327.79	192.22
3500	1740.72	175.93	1630.75	186.92	1589.70	191.03	1533.73	196.63

Table 3.6 : Adsorption of Neutral red on lignin of 100 - 200 mesh size at 30^0C, at various pH.

Initial conc.	pH							
	3.7		5		6		7	
$(mg.l^{-1})$	Equilibrium conc. $(mg.l^{-1})$	Adsorption $(mg.g^{-1})$	Equilibrium conc. $(mg.l^{-1})$	Adsorption $(mg.g^{-1})$	Equilibrium conc. $(mg.l^{-1})$	Adsorption $(mg.g^{-1})$	Equilibrium conc. $(mg.l^{-1})$	Adsorption $(mg.g^{-1})$
500	2.35	49.76	1.89	49.81	1.69	49.83	1.95	49.81
1000	3.66	99.63	3.70	99.63	5.33	99.47	5.38	99.46
1250	9.61	124.04	12.68	123.73	7.10	124.29	8.36	124.16
1500	43.23	145.67	42.22	145.78	41.10	145.89	30.75	146.93
1750	170.98	157.90	157.82	159.22	128.65	162.14	61.09	168.89
2000	314.28	168.57	306.44	169.36	275.48	172.45	245.79	175.42
2250	550.72	169.93	490.34	175.97	462.32	178.77	439.83	181.02
2500	751.41	174.86	690.31	180.97	564.86	193.51	511.27	198.87
2750	1080.96	183.40	892.70	185.73	775.59	197.44	685.23	206.48
3000	1139.76	186.02	1049.82	195.02	885.69	211.43	788.63	221.14
3250	1550.20	186.43	1289.20	196.08	1065.33	218.47	961.78	228.82
3500	1630.75	186.92	1429.20	207.08	1214.99	228.50	1096.45	240.35

Table 3.7 : Adsorption of Neutral red on lignin of various particle sizes at 30^{0}C and pH 3.7.

Initial conc. (mg.l^{-1})	Mesh size					
	40 – 100		100 – 200		Above 200	
	Equilibrium conc. (mg.l^{-1})	Adsorption (mg.g^{-1})	Equilibrium conc. (mg.l^{-1})	Adsorption (mg.g^{-1})	Equilibrium conc. (mg.l^{-1})	Adsorption (mg.g^{-1})
500	5.65	49.43	2.35	49.76	7.08	49.29
1000	50.22	94.98	3.66	99.63	7.11	99.29
1250	106.99	114.3	9.61	124.04	7.89	124.21
1500	257.84	124.22	43.23	145.67	9.96	149.00
1750	417.33	133.27	170.98	157.90	33.02	171.70
2000	623.95	137.61	314.28	168.57	135.03	186.5
2250	868.76	138.12	550.72	169.93	309.22	194.08
2500	1099.63	140.04	751.41	174.86	460.29	203.97
2750	1323.78	142.62	1080.96	183.40	674.94	207.51
3000	1555.94	144.41	1139.76	186.02	887.81	211.22
3250	1791.27	145.87	1550.20	186.43	1130.01	212.00
3500	1963.69	153.63	1630.75	186.92	1348.72	215.13

Table 3.8 : Adsorption of Toluidine blue on lignin of 100 - 200 mesh size at pH 7.0, at various temperatures.

Initial conc. ($mg.l^{-1}$)	Temperature							
	20^0C		25^0 C		30^0 C		40^0 C	
	Equilibrium conc. ($mg.l^{-1}$)	Adsorption ($mg.g^{-1}$)	Equilibrium conc. ($mg.l^{-1}$)	Adsorption ($mg.g^{-1}$)	Equilibrium conc. ($mg.l^{-1}$)	Adsorption ($mg.g^{-1}$)	Equilibrium conc. ($mg.l^{-1}$)	Adsorption ($mg.g^{-1}$)
100	1.37	9.86	1.54	9.85	1.53	9.85	1.06	9.89
200	4.76	19.52	4.14	19.58	3.48	19.65	1.12	19.88
300	13.31	28.67	7.10	29.29	3.88	29.61	2.31	29.76
400	18.10	38.19	11.27	38.87	7.32	39.27	3.72	39.63
500	27.62	47.24	14.19	48.58	9.93	49.01	4.89	49.51
600	35.66	56.43	16.99	58.30	11.85	58.82	6.91	59.31
700	93.96	60.60	35.06	66.49	22.76	67.72	11.94	68.81
800	119.80	68.02	47.47	75.25	40.46	75.95	14.96	78.50
900	142.65	75.73	110.28	78.97	46.98	85.3	41.36	85.86
1000	216.82	78.32	173.57	82.64	66.12	93.39	48.08	95.19
1500	511.55	98.84	385.54	111.45	137.80	136.22	111.25	138.87
2000	965.79	103.42	737.35	126.25	458.81	154.12	259.10	174.09

Table 3.9 : Adsorption of Toluidine blue on lignin of 100 - 200 mesh size at 30^0C, at various pH .

Initial conc. ($mg.l^{-1}$)	pH							
	4		5		6		7	
	Equilibrium conc. ($mg.l^{-1}$)	Adsorption ($mg.g^{-1}$)	Equilibrium conc. ($mg.l^{-1}$)	Adsorption ($mg.g^{-1}$)	Equilibrium conc. ($mg.l^{-1}$)	Adsorption ($mg.g^{-1}$)	Equilibrium conc. ($mg.l^{-1}$)	Adsorption ($mg.g^{-1}$)
100	2.14	9.79	1.08	9.89	1.85	9.81	1.53	9.85
200	4.20	19.58	2.89	19.71	4.11	19.59	3.48	19.65
300	7.35	29.26	5.50	29.45	7.35	29.26	3.88	29.61
400	17.05	38.29	8.52	39.15	10.80	38.99	7.32	39.27
500	18.87	48.11	22.80	47.72	13.69	48.63	9.93	49.01
600	45.64	55.43	31.11	56.81	28.28	57.17	11.85	58.82
700	79.49	62.05	50.12	64.99	45.74	65.43	22.76	67.72
800	104.91	69.51	88.72	71.13	79.83	72.02	40.46	75.95
900	132.14	76.78	138.21	76.18	122.83	77.72	46.98	85.3
1000	212.63	78.74	181.15	81.88	147.57	85.24	66.12	93.39
1500	510.19	98.98	498.49	100.15	315.03	118.50	137.80	136.22
2000	912.63	108.74	880.21	111.98	692.97	130.70	458.81	154.12

Table 3.10 : Adsorption of Toluidine blue on lignin of various particle sizes at 30^{0}C and pH 7.0.

	Mesh size					
	40 – 100		100 – 200		Above 200	
Initial conc. (mg.l^{-1})	Equilibrium conc. (mg.l^{-1})	Adsorption (mg.g^{-1})	Equilibrium conc. (mg.l^{-1})	Adsorption (mg.g^{-1})	Equilibrium conc. (mg.l^{-1})	Adsorption (mg.g^{-1})
100	7.71	9.23	1.53	9.85	1.12	9.89
200	31.47	16.85	3.48	19.65	2.31	19.77
300	47.47	25.25	3.88	29.61	3.60	29.64
400	63.36	33.66	7.32	39.27	5.43	39.46
500	80.41	41.96	9.93	49.01	7.11	49.29
600	169.77	43.02	11.85	58.82	9.20	59.08
700	212.63	48.74	22.76	67.72	11.14	68.89
800	260.98	53.9	40.46	75.95	16.50	78.35
900	306.87	59.31	46.98	85.3	18.72	88.13
1000	339.02	66.10	66.12	93.39	30.85	96.92
1500	549.56	86.14	137.80	136.22	56.31	144.37
2000	1033.48	96.65	458.81	154.12	125.62	187.44

Table 3.11 : Heat of adsorption of Crystal violet, Neutral red and Toluidine blue at different adsorption levels.

Crystal violet pH 7.0		Neutral red pH 3.7		Toluidine blue pH 7.0	
Adsorption (mg.g^{-1} lignin)	Heat of adsorption (Kcal mole^{-1})	Adsorption (mg.g^{-1} lignin)	Heat of adsorption (Kcal mole^{-1})	Adsorption (mg.g^{-1} lignin)	Heat of adsorption (Kcal mole^{-1})
25.00	-7.96	130.00	-2.83	80.00	-17.48
30.00	-14.28	137.50	-3.58	90.00	-20.25
35.00	-16.11	140.00	-3.72	95.00	-20.41
40.00	-18.13	142.50	-3.99	100.00	-21.01
45.00	-23.58	145.00	-4.05	105.00	-22.20
50.00	-29.17	147.50	-4.25	110.00	-23.67
55.00	-33.37	150.00	-4.47	115.00	-25.76
---	---	152.50	-4.90	120.00	-28.15
---	---	---	---	125.00	-30.64

Table 3.12 : Langmuir constants of Crystal violet, Neutral red and Toluidine blue at various temperatures, pH and particle sizes of lignin.

	b (mg^{-1})			Q^0 ($mg.g^{-1}$)		
	Crystal violet	Neutral red	Toluidine blue	Crystal violet	Neutral red	Toluidine blue
Temp. (^0C)						
20	0.02	---	0.02	42.4	---	106.4
25	0.02	0.08	0.03	61.0	175.4	128.2
30	0.03	0.05	0.03	74.1	188.7	161.3
35	---	0.05	---	---	192.3	---
40	0.08	0.05	0.05	83.3	196.1	178.6
pH						
3.7	---	0.05	---	---	188.7	---
4	-0.20	---	0.02	37.9	---	111.1
5	---	0.03	0.03	---	200.0	112.4
6	0.08	0.02	0.02	66.2	222.2	135.1
7	0.03	0.03	0.03	74.1	232.6	161.3
Particle size (mesh)						
40 –100	0.03	0.02	0.01	72.5	151.5	109.9
100 –200	0.03	0.05	0.03	74.1	188.7	161.3
Above 200	0.05	0.06	0.04	76.3	217.4	217.4

Table 3.13 : B.E.T. constants of Neutral red and Toluidine blue at various temperatures, pH and particle sizes of lignin.

	A (mg^{-1})		Q^0 (mg.g^{-1})	
	Neutral red	Toluidine blue	Neutral red	Toluidine blue
Temp. (^{0}C)				
20	---	61.3	---	54.4
25	-315.7	149.0	105.6	67.1
30	-899.0	99.0	123.6	101.0
35	-1924.0	---	129.9	---
40	-36999.0	62.0	135.1	80.6
pH				
3.7	-899.0	---	123.6	---
4	---	77.5	---	64.5
5	-409.0	149.0	122.2	67.1
6	-1099.0	150.0	130.0	66.7
7	127.7	99.0	130.6	101.0
Particle size (mesh)				
40 –100	-564.0	26.7	88.7	37.5
100 –200	-899.0	99.0	123.6	101.0
Above 200	1151.0	32.5	144.8	153.8

Table 3.14 : R_L values for the adsorption of Crystal violet, Neutral red and Toluidine blue at various temperatures, pH and particle sizes of lignin.

	Crystal violet	Neutral red	Toluidine blue
Temp. (^{0}C)			
20	0.358 to 0.027	---	0.299 to 0.021
25	0.036 to 0.028	0.023 to 0.003	0.263 to 0.017
30	0.249 to 0.016	0.042 to 0.006	0.227 to 0.014
35	---	0.040 to 0.006	---
40	0.108 to 0.006	0.042 to 0.006	0.169 to 0.010
pH			
3.7	---	0.042 to 0.006	---
4	-0.052 to -0. 003	---	0.310 to 0.002
5	---	0.060 to 0 .001	0.250 to 0.017
6	0.108 to 0.006	0.075 to 0.011	0.310 to 0.022
7	0.249 to 0.016	0.070 to 0.011	0.227 to 0.014
8	0.131 to 0.008	----	---
Particle size (mesh)			
40 –100	0.267 to 0.018	0.088 to 0.013	0.654 to 0.086
100 –200	0.249 to 0.016	0.042 to 0.006	0.227 to 0.014
Above 200	0.165 to 0.010	0.032 to 0.005	0.206 to 0.013

Table 3.15 : Adsorption of various amounts of Crystal violet, Neutral red and Toluidine blue on lignin of 100 - 200 mesh size at 30^{0}C.

Crystal violet pH 7.0		Neutral red pH 3.7		Toluidine blue pH 7.0	
Amount of dye added (mg)	Conc. adsorbed (mg.g^{-1})	Amount of dye added (mg)	Conc. adsorbed (mg.g^{-1})	Amount of dye added (mg)	Conc. adsorbed (mg.g^{-1})
1.00	7.09	1.00	8.08	1.00	9.32
1.50	8.47	1.50	8.37	1.50	12.81
2.00	10.15	2.00	8.74	2.00	15.28
2.50	11.12	2.50	8.79	2.50	18.68
3.00	11.87	3.00	8.86	3.00	20.67
3.50	12.61	3.50	8.88	3.50	23.05
4.00	12.60	4.00	8.93	4.00	25.01
5.00	12.62	---	---	5.00	30.08
---	---	---	---	7.50	38.97

Concentration of dye = 100 mg.l^{-1}; Time of contact = 1 h.

Table 3.16 : Values of Specific Surface area of lignin.

Particle size (mesh size)	pH	Surface area (m^2/g)
40-100	7.0	64.9
100-200	7.0	95.2
Above 200	7.0	128.5
100-200	6.0	79.9
100-200	5.0	66.3
100-200	4.0	65.6

Table 3.17 : Desorption of Crystal violet, Neutral red and Toluidine blue from the surface of lignin of 100 – 200 mesh size with various 1M electrolytes.

Dye adsorbed	10.25 mg/g		168.57 mg/g		172.46 mg/g	
	Crystal violet		Neutral red		Toluidine blue	
Electrolyte (10 ml)	Dye removed (mg.g^{-1})	Removal (%)	Dye removed (mg.g^{-1})	Removal (%)	Dye removed (mg.g^{-1})	Removal (%)
KCl	0.07	0.72	1.65	0.98	1.29	0.75
NH_4Cl	0.10	0.95	1.77	1.05	1.66	0.96
NaCl	0.03	0.33	1.23	0.73	0.60	0.35
NaBr	0.04	0.36	1.28	0.76	0.65	0.38
$BaCl_2$	0.08	0.74	1.92	1.14	1.34	0.78
$Al(NO_3)_3.9H_2O$	0.11	1.04	2.45	1.45	1.90	1.10

Weight of lignin - dye complex taken = 0.1 g.

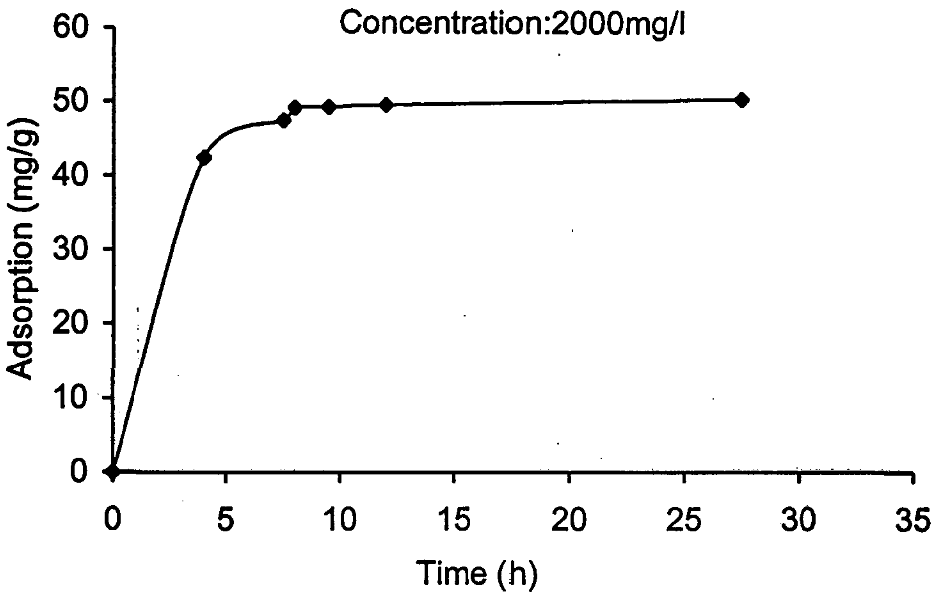

Fig. 3.1: Adsorption of Crystal violet dye as a function of time.

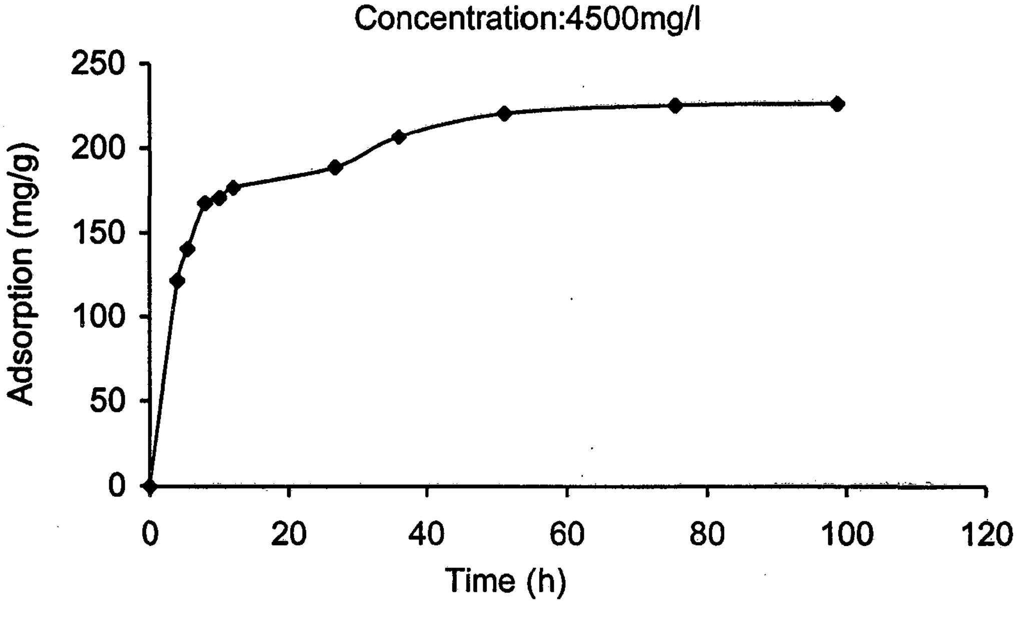

Fig. 3.2: Adsorption of Neutral red dye as a function of time.

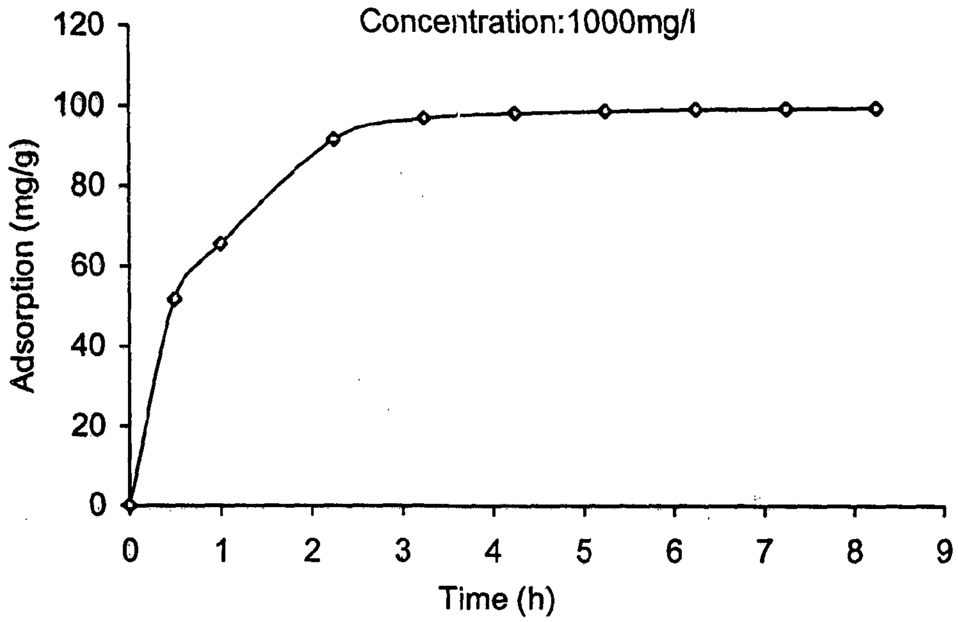

Fig. 3.3: Adsorption of Toluidine blue dye as a function of time.

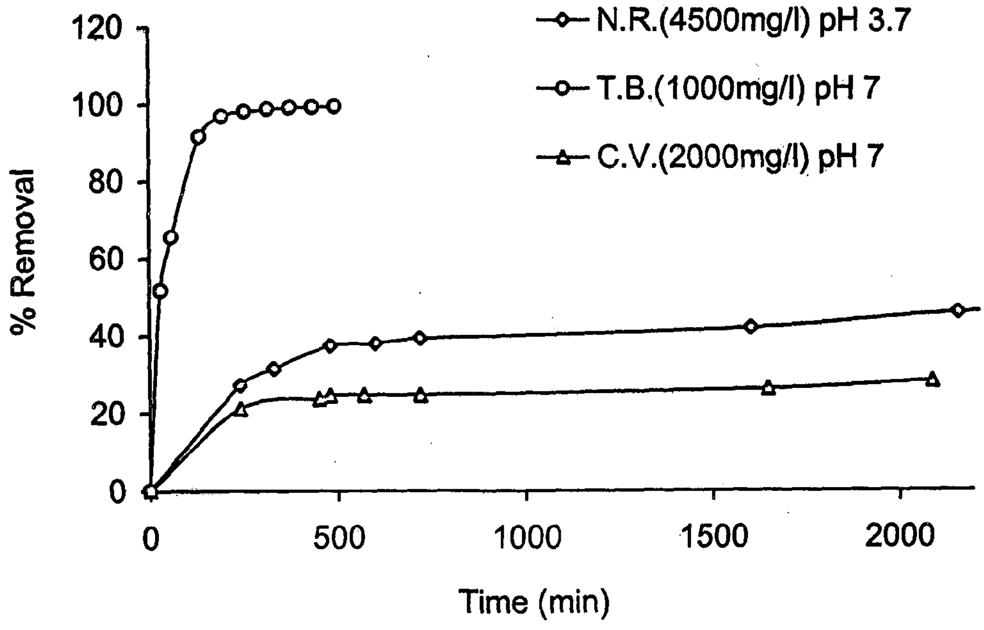

Fig. 3.4: Percent removal of Crystal violet, Neutral red and Toluidine blue dyes as a function of time.

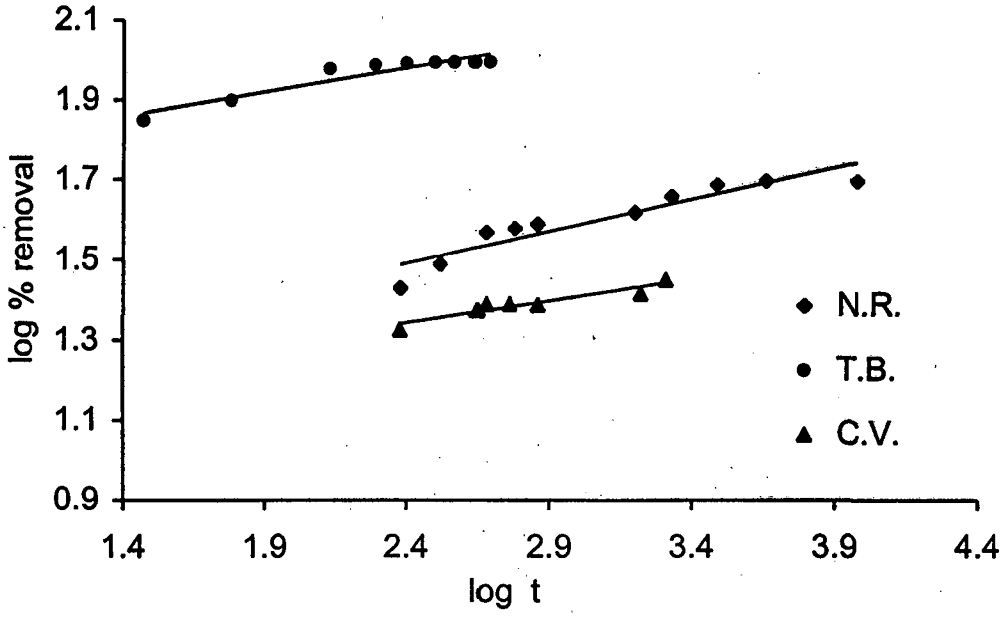

Fig. 3.5: Log percent removal of Crystal violet, Neutral red and Toluidine blue dyes as a function of log time.

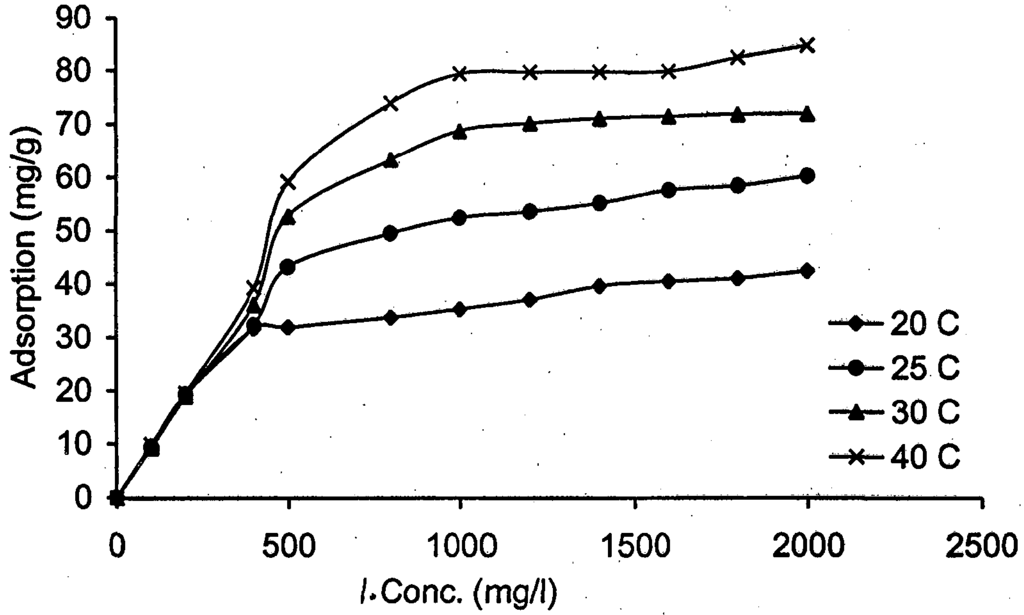

Fig. 3.6: Adsorption isotherms of Crystal violet dye at various temperatures.

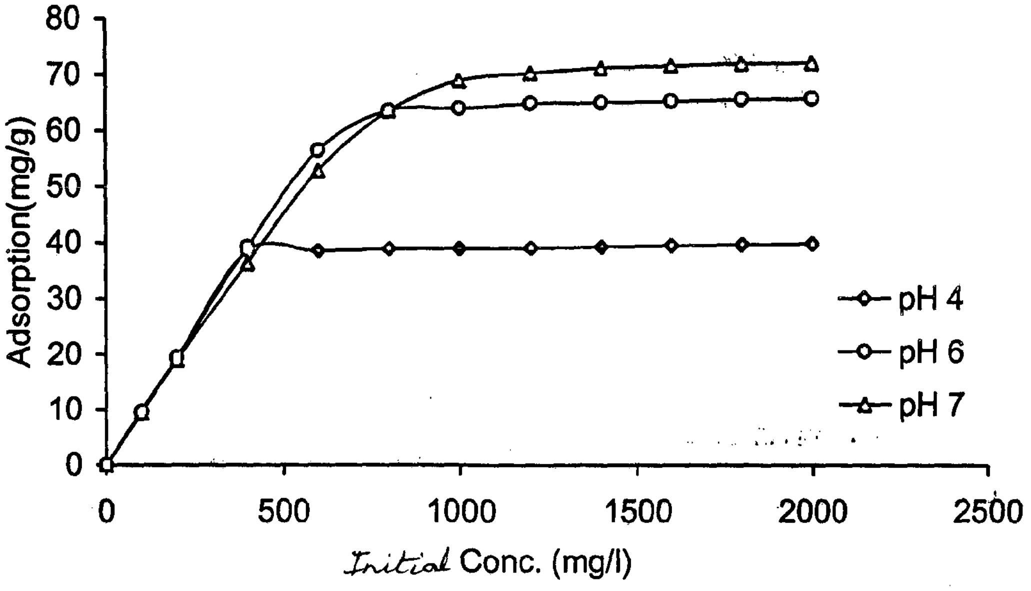

Fig. 3.7: Adsorption isotherms of Crystal violet dye at various pH.

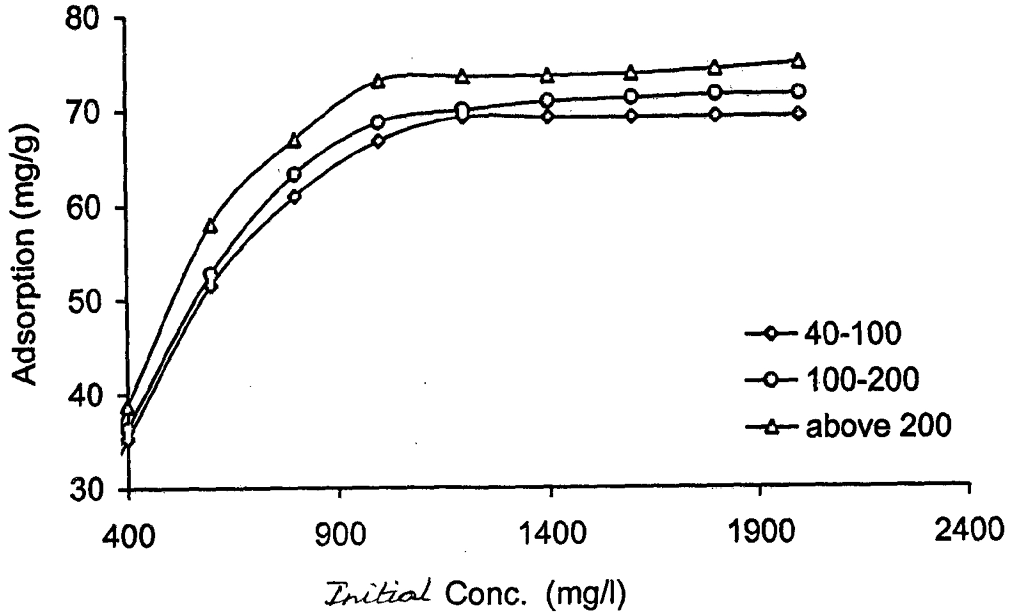

Fig. 3.8: Adsorption isotherms of Crystal violet dye at various particle sizes of lignin.

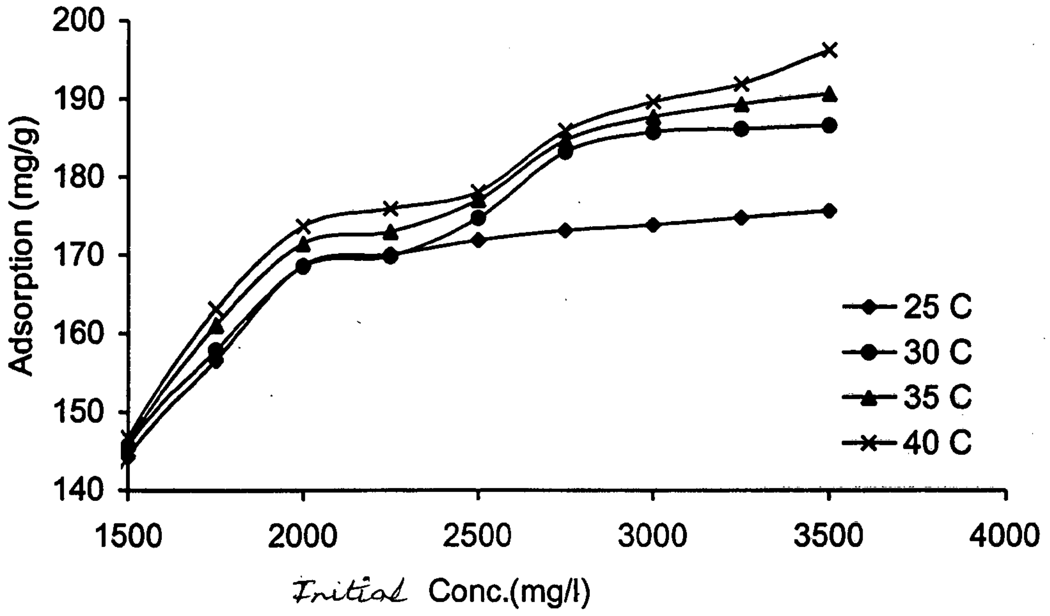

Fig. 3.9: Adsorption isotherms of Neutral red dye at various temperatures.

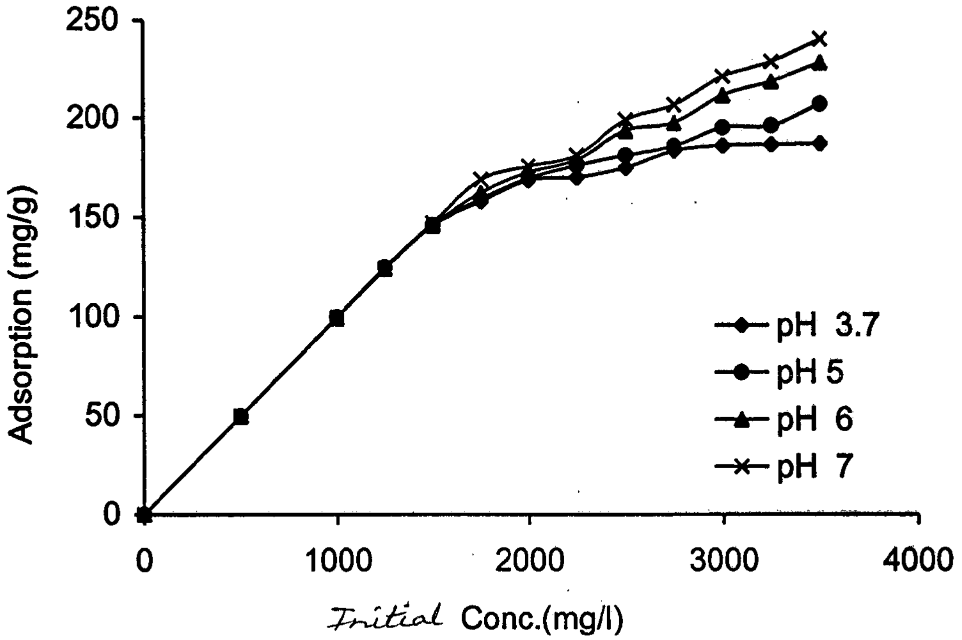

Fig. 3.10: Adsorption isotherms of Neutral red dye at various pH.

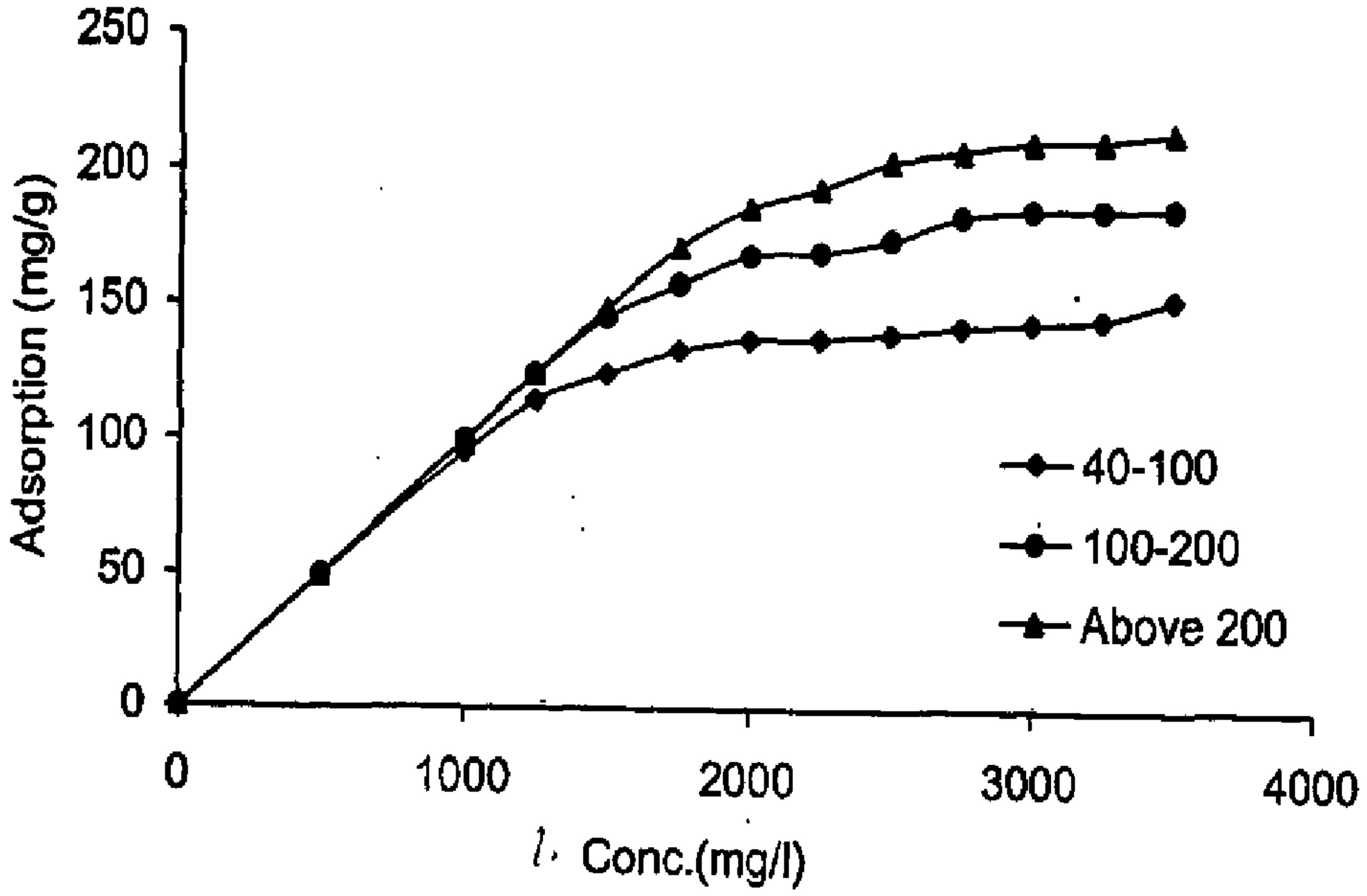

Fig. 3.11: Adsorption isotherms of Neutral red dye at various particle sizes of lignin.

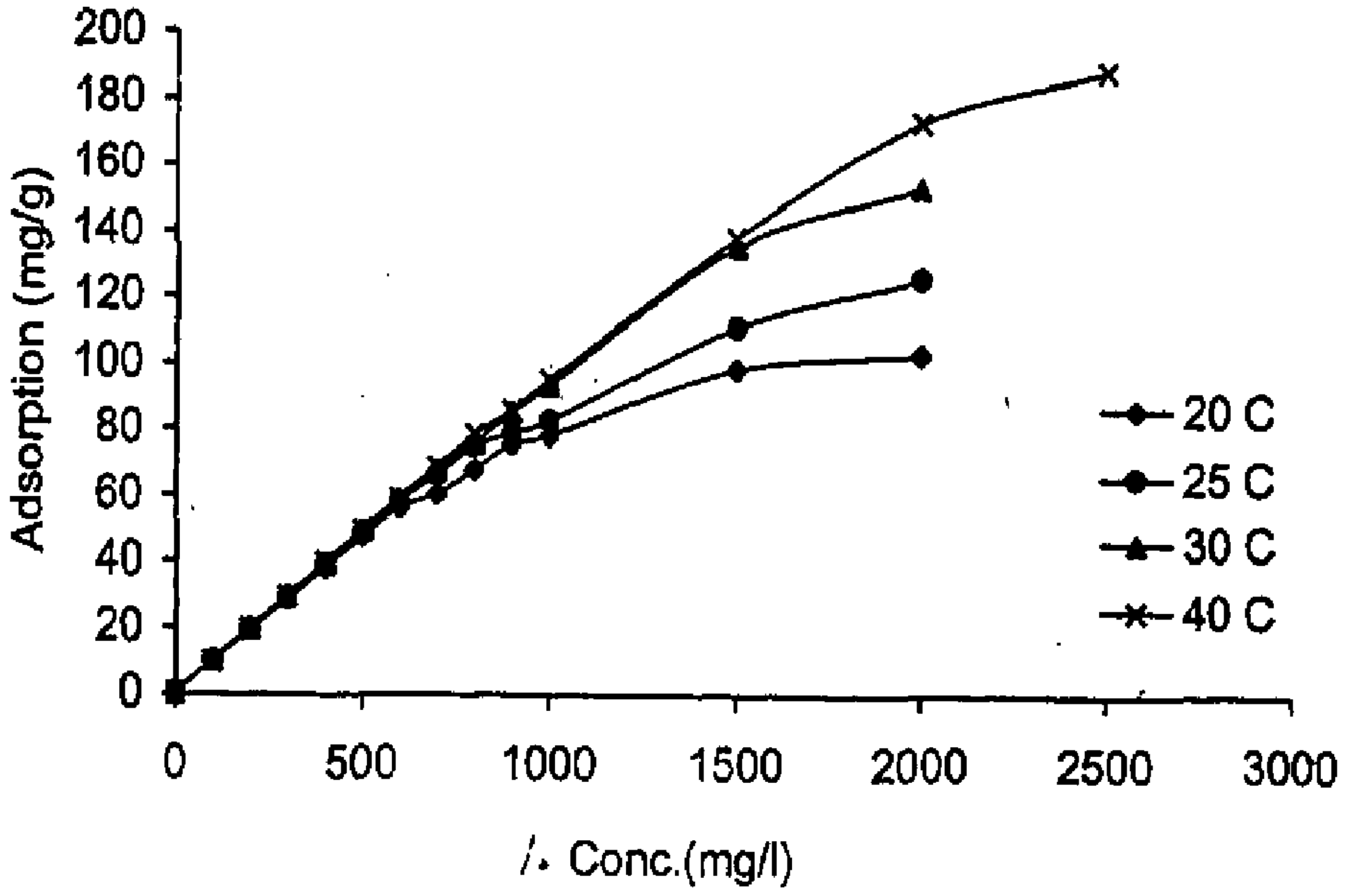

Fig. 3.12: Adsorption isotherms of Toluidine blue dye at various temperatures.

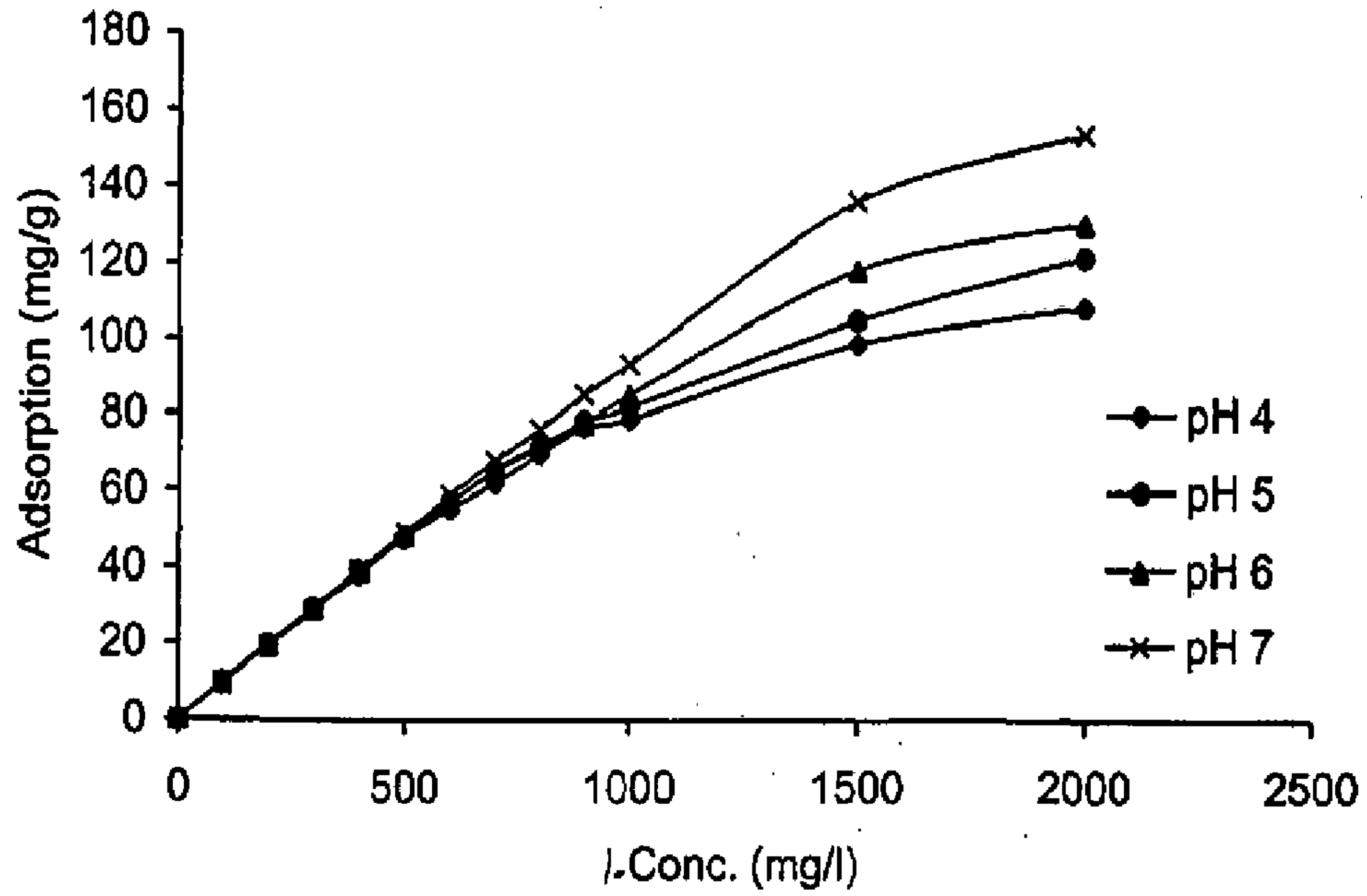

Fig. 3.13: Adsorption isotherms of Toluidine blue dye at various pH.

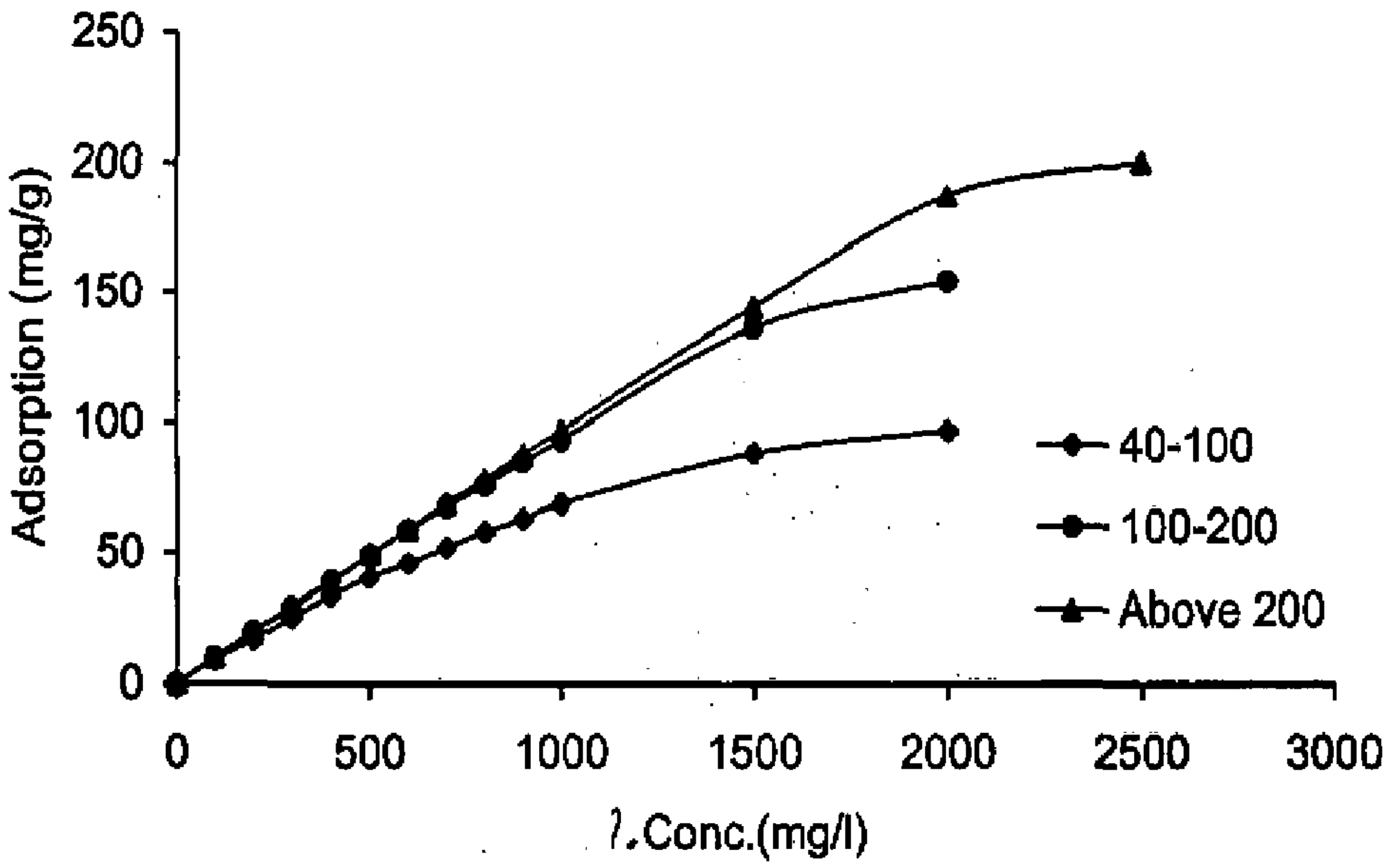

Fig. 3.14: Adsorption isotherms of Toluidine blue dye at various particle sizes of lignin.

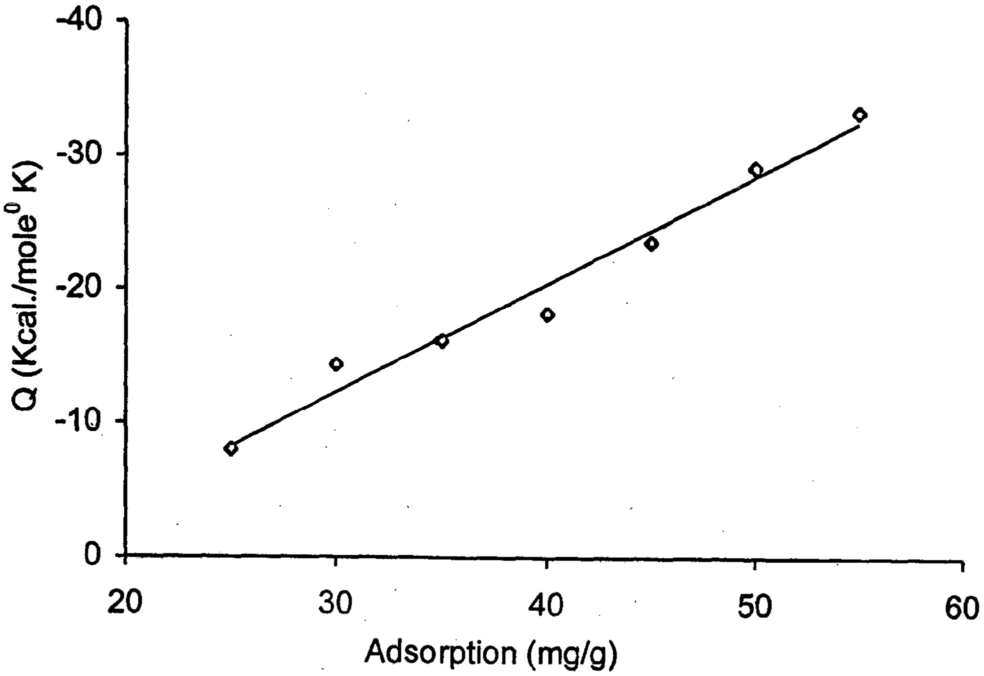

Fig. 3.15: Heat of adsorption of Crystal violet dye as a function of adsorption.

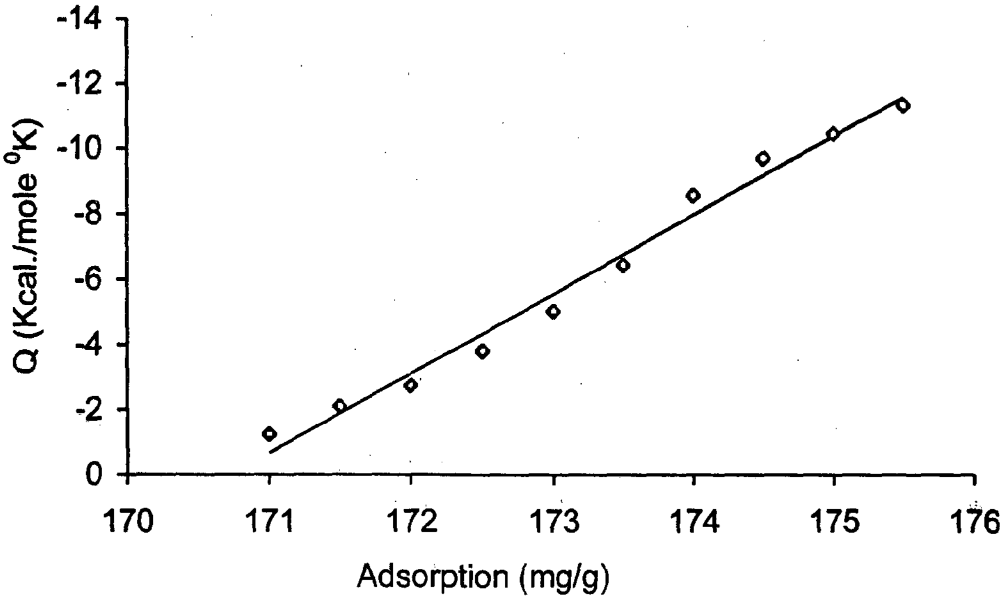

Fig. 3.16: Heat of adsorption of Neutral red dye as a function of adsorption.

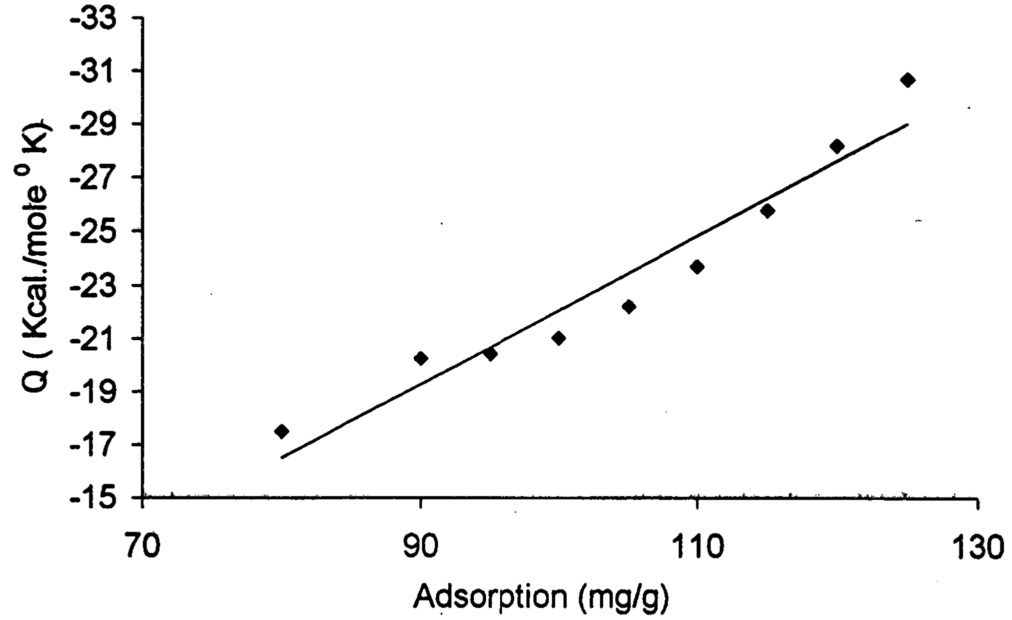

Fig. 3.17: Heat of adsorption of Toluidine blue dye as a function of adsorption.

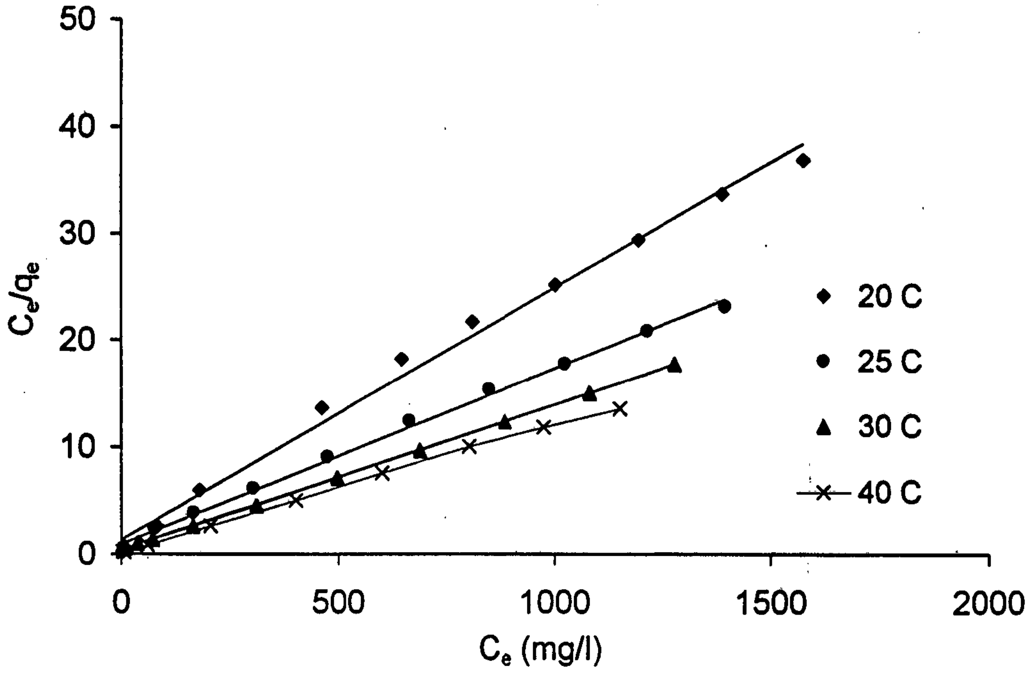

Fig. 3.18: Langmuir plots of Crystal violet dye at various temperatures.

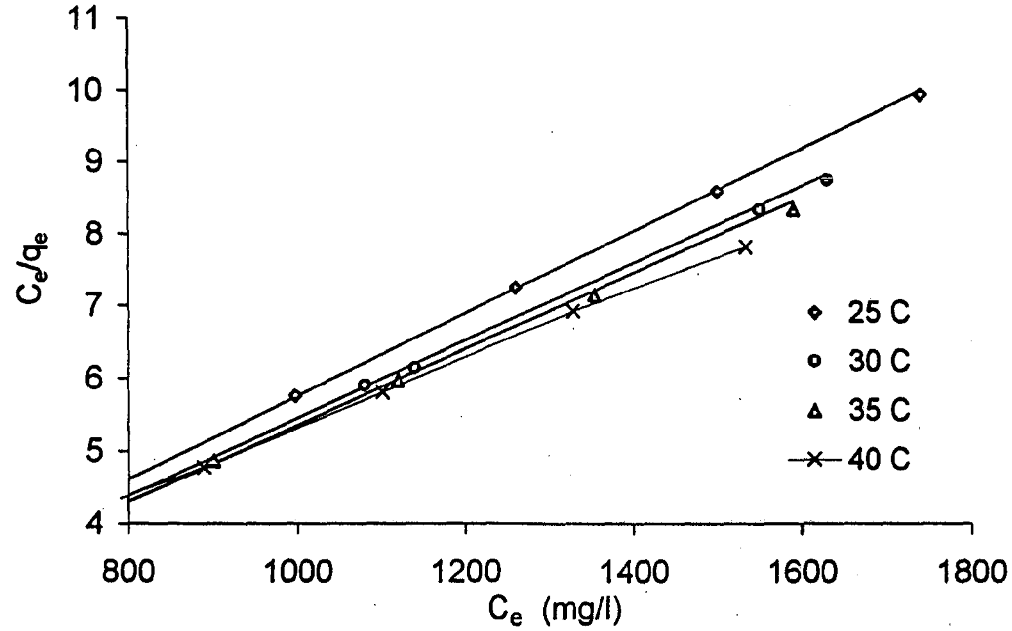

Fig. 3.19: Langmuir plots of Neutral red dye at various temperatures.

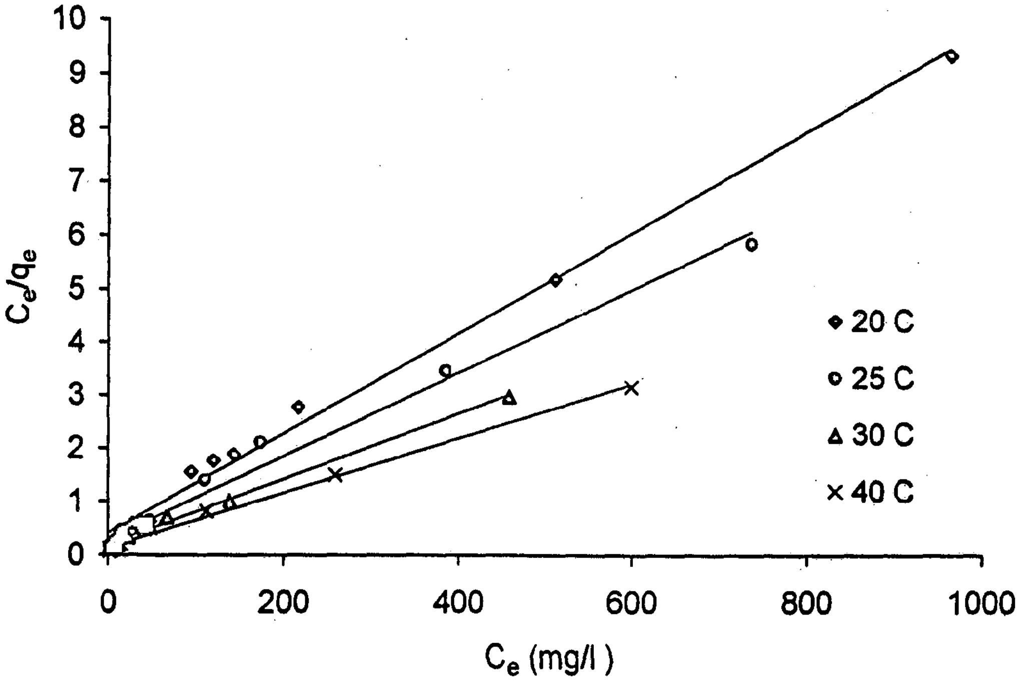

Fig. 3.20: Langmuir plots of Toluidine blue dye at various temperatures.

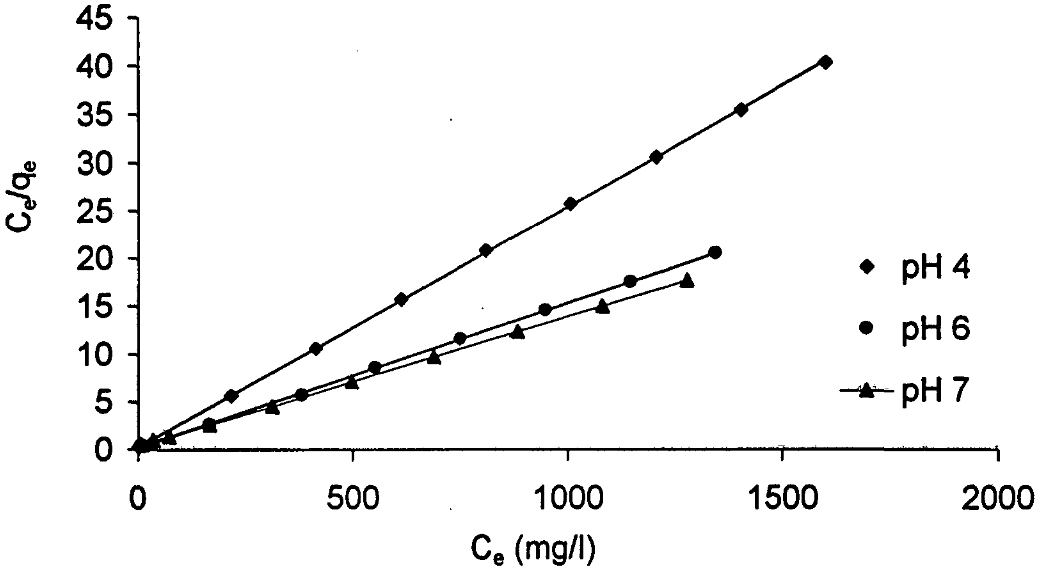

Fig. 3.21: Langmuir plots of Crystal violet dye at various pH.

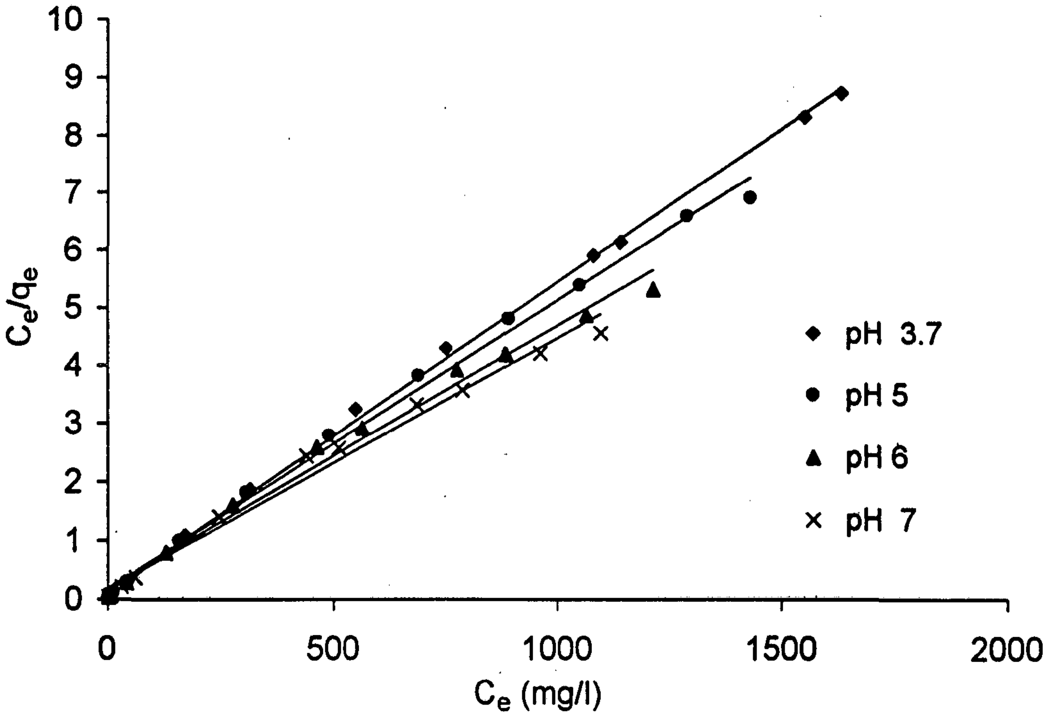

Fig. 3. 22: Langmuir plots of Neutral red dye at various pH.

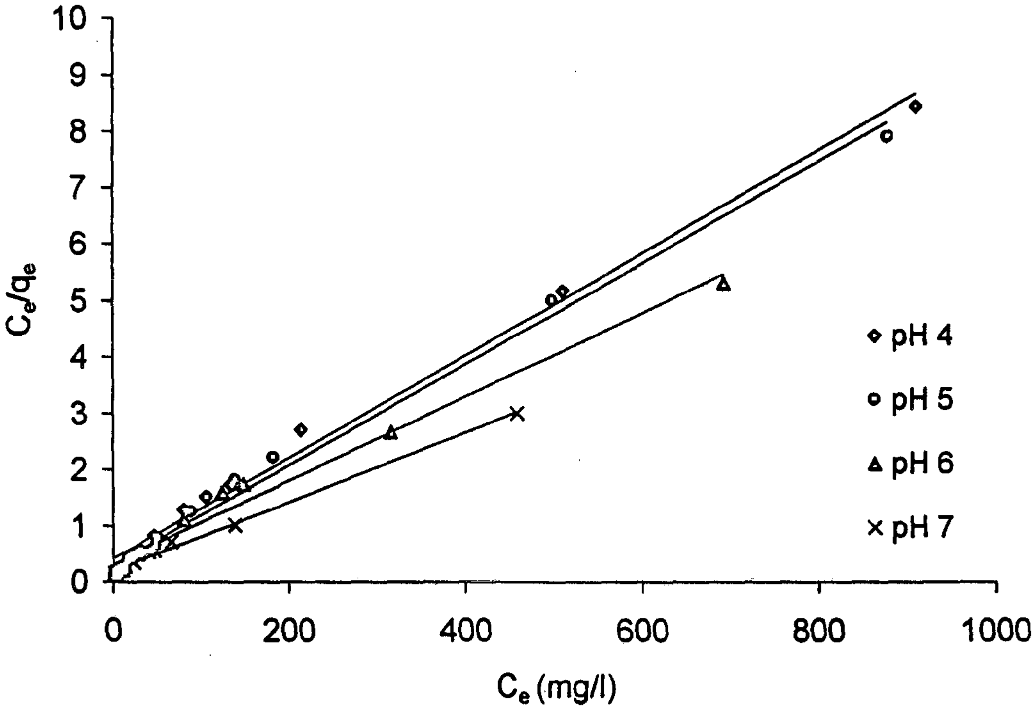

Fig. 3.23: Langmuir plots of Toluidine blue dye at various pH.

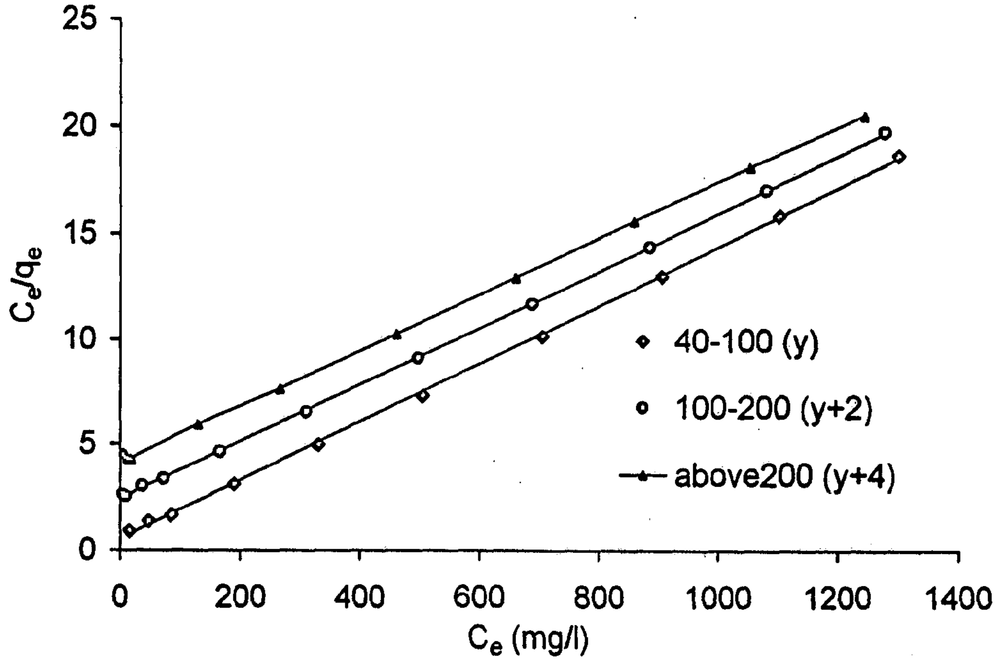

Fig. 3.24: Langmuir plots of Crystal violet dye at various particle sizes of lignin.

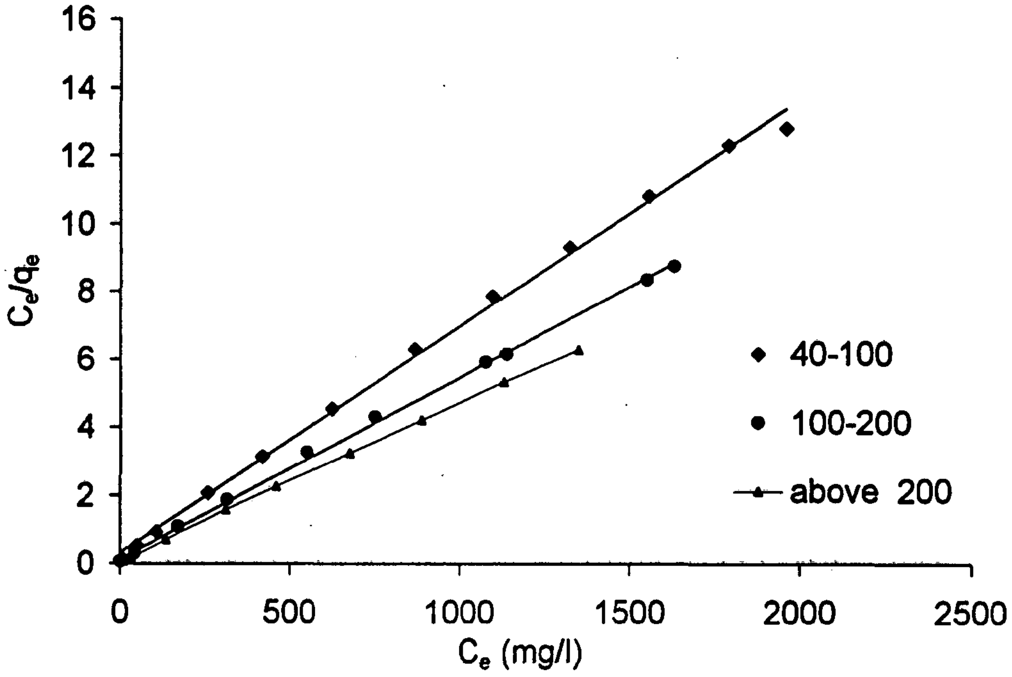

Fig. 3.25: Langmuir plots of Neutral red dye at various particle sizes of lignin.

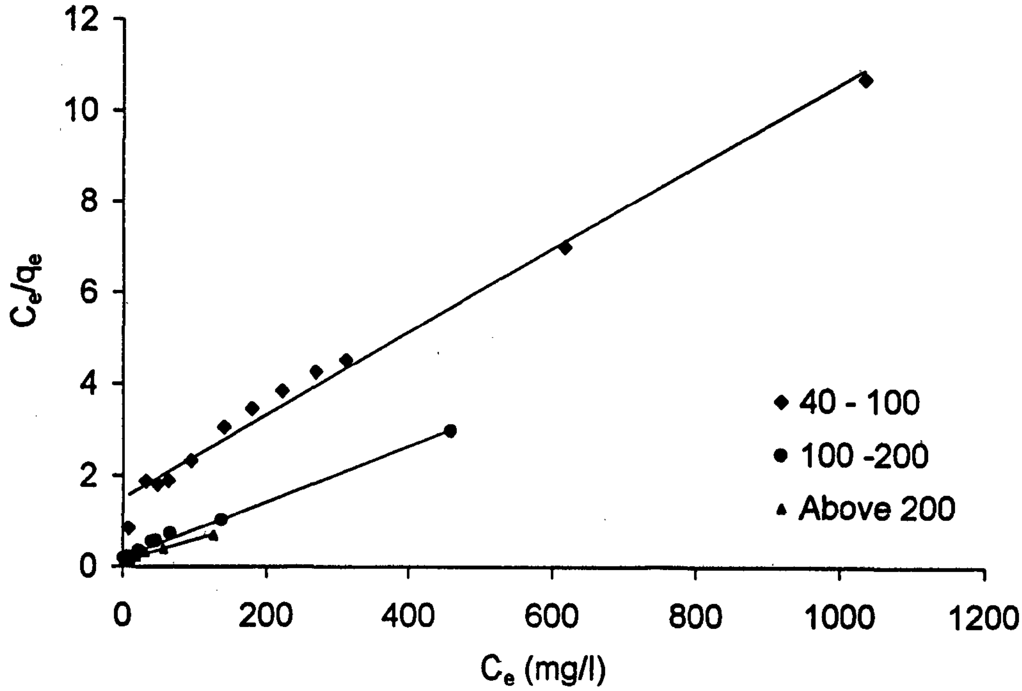

Fig. 3.26: Langmuir plots of Toluidine blue dye at various particle sizes of lignin.

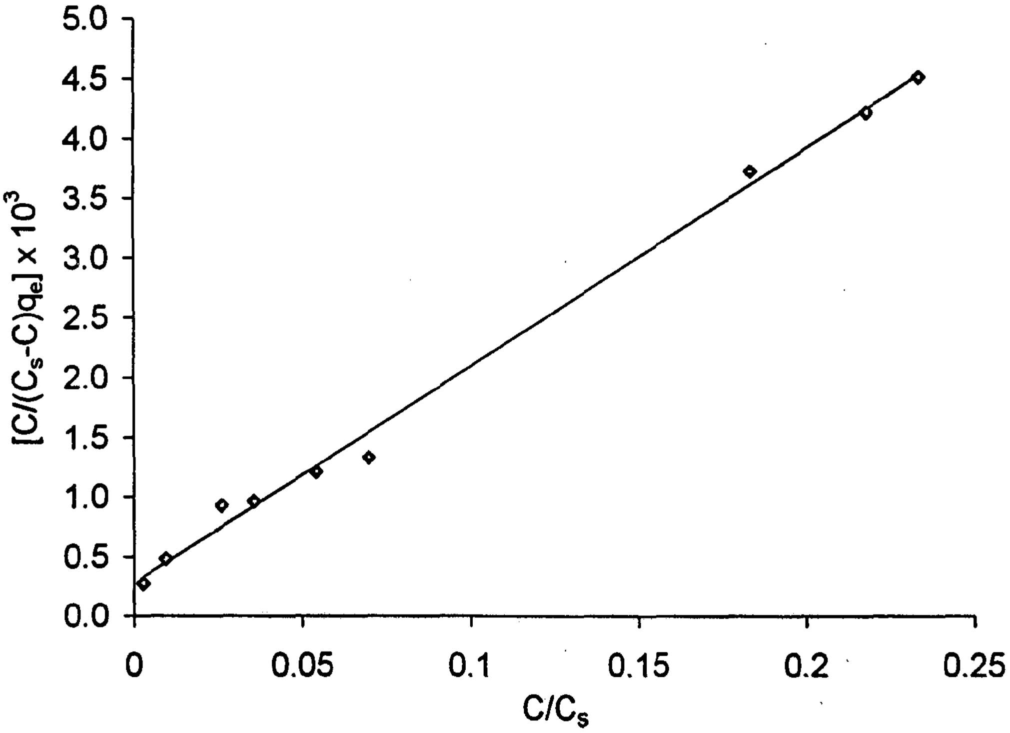

Fig. 3.27: B.E.T. plot of Toluidine blue dye at 20°C.

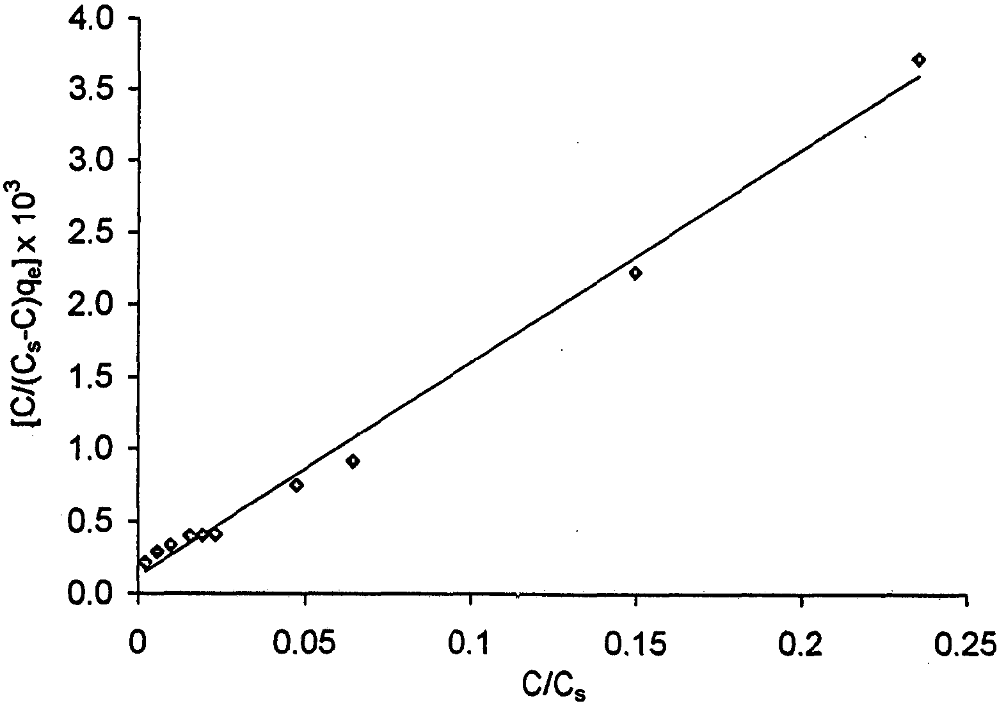

Fig. 3.28: B.E .T. plot of Toluidine blue dye at 25°C.

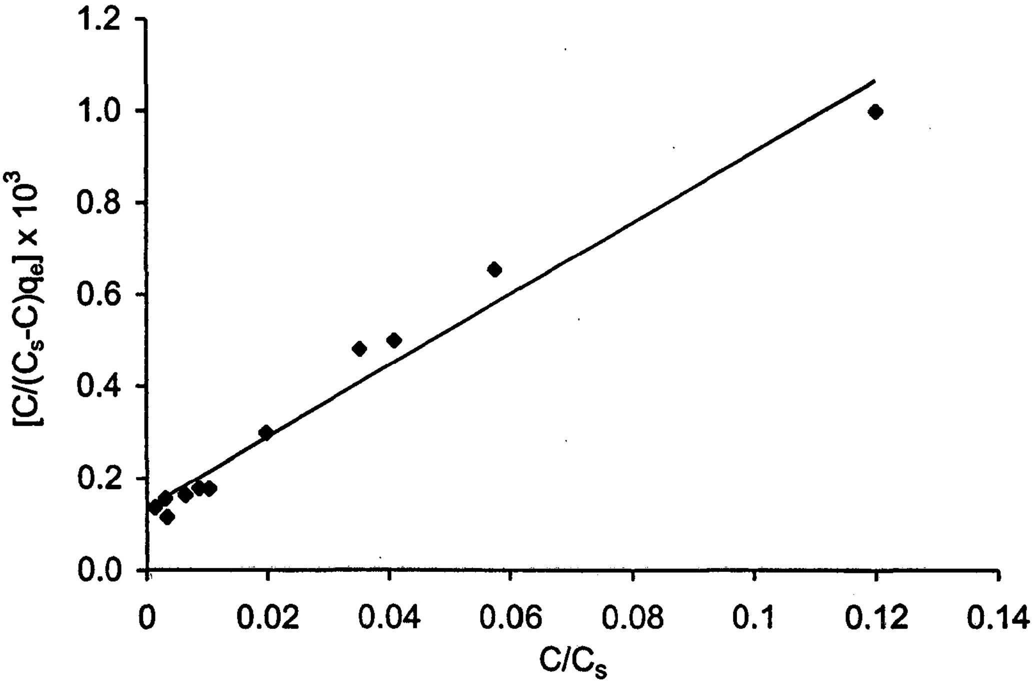

Fig. 3.29: B.E.T. plot of Toluidine blue dye at 30^{0}C, pH 7.0 and 100-200 mesh size of lignin.

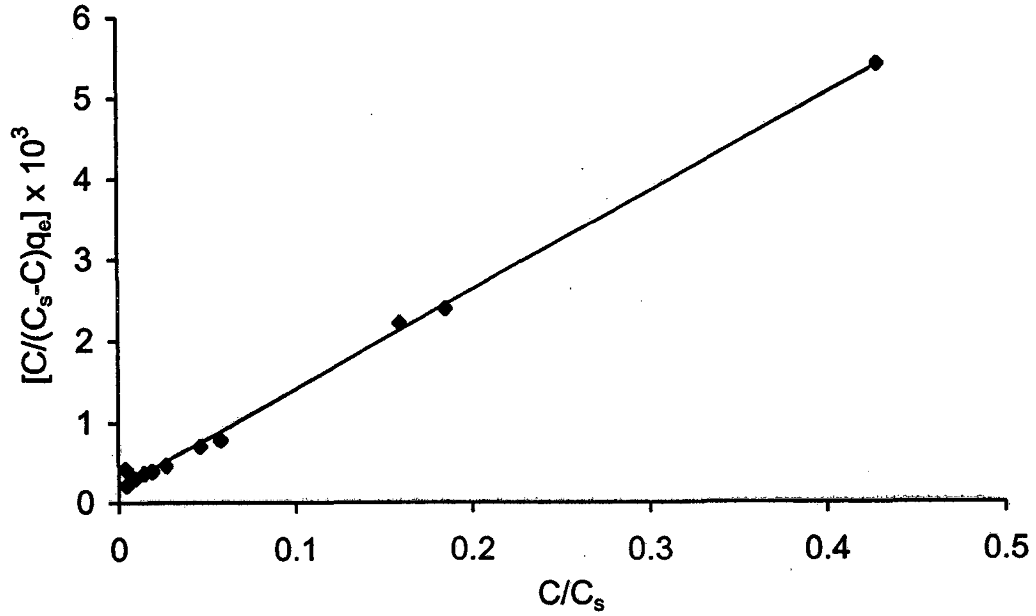

Fig. 3.30: B.E.T. plot of Toluidine blue dye at 40^{0}C.

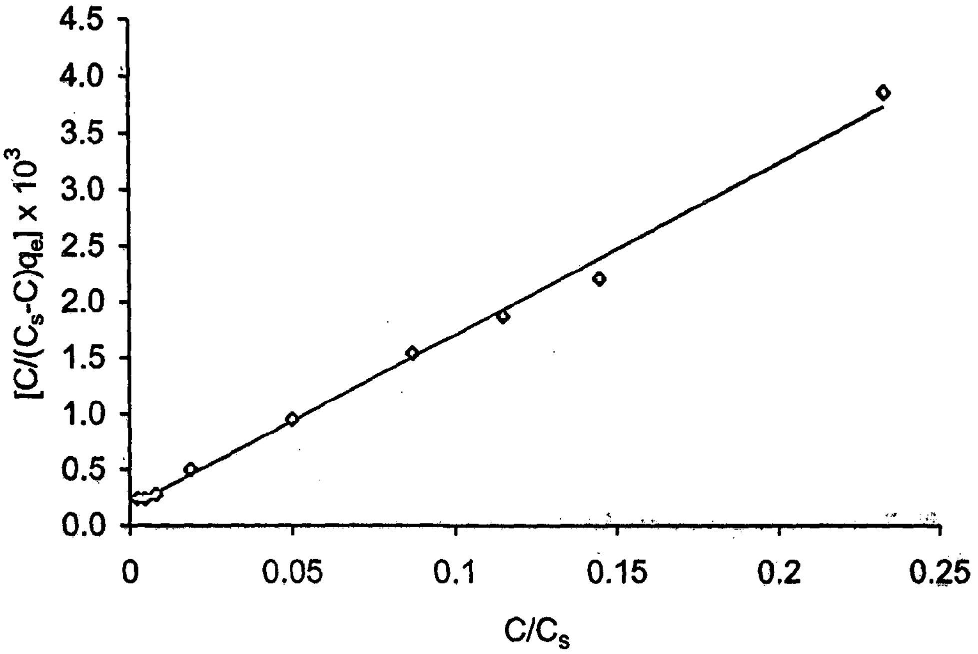

Fig. 3.31: B.E.T. plot of Toluidine blue dye at pH 4.0.

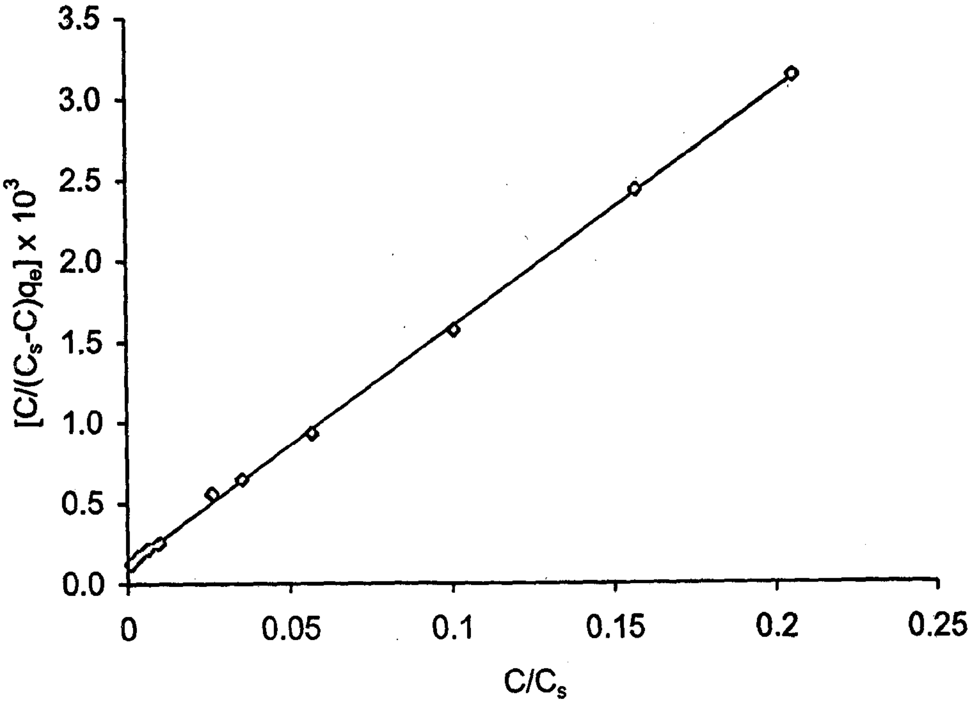

Fig. 3.32: B.E.T. plot of Toluidine blue dye at pH 5.0.

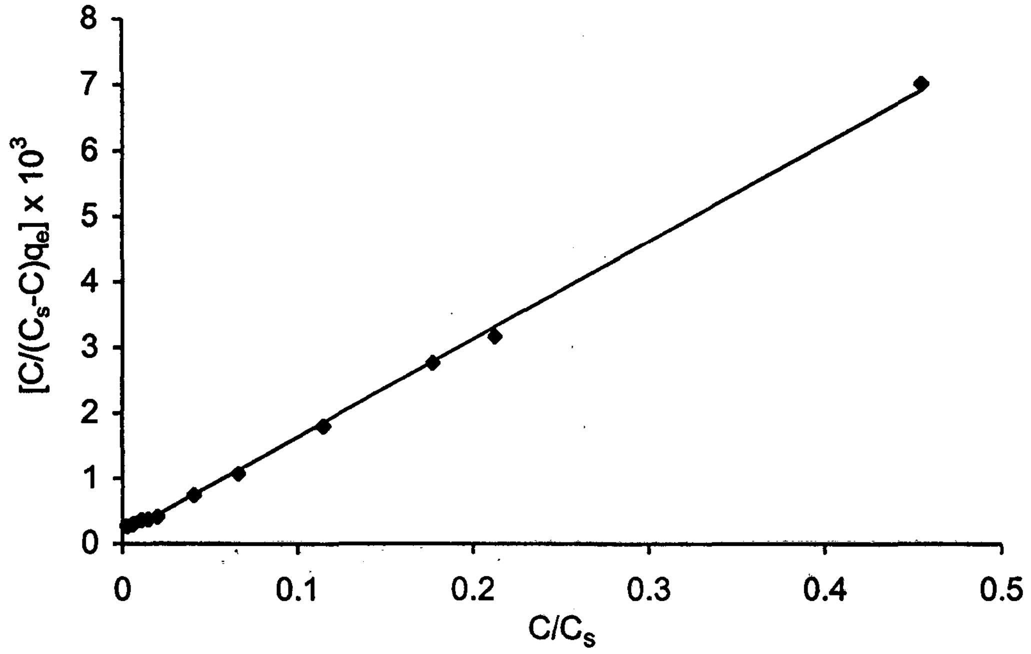

Fig. 3.33: **B.E.T. plot of Toluidine blue dye at pH 6.0.**

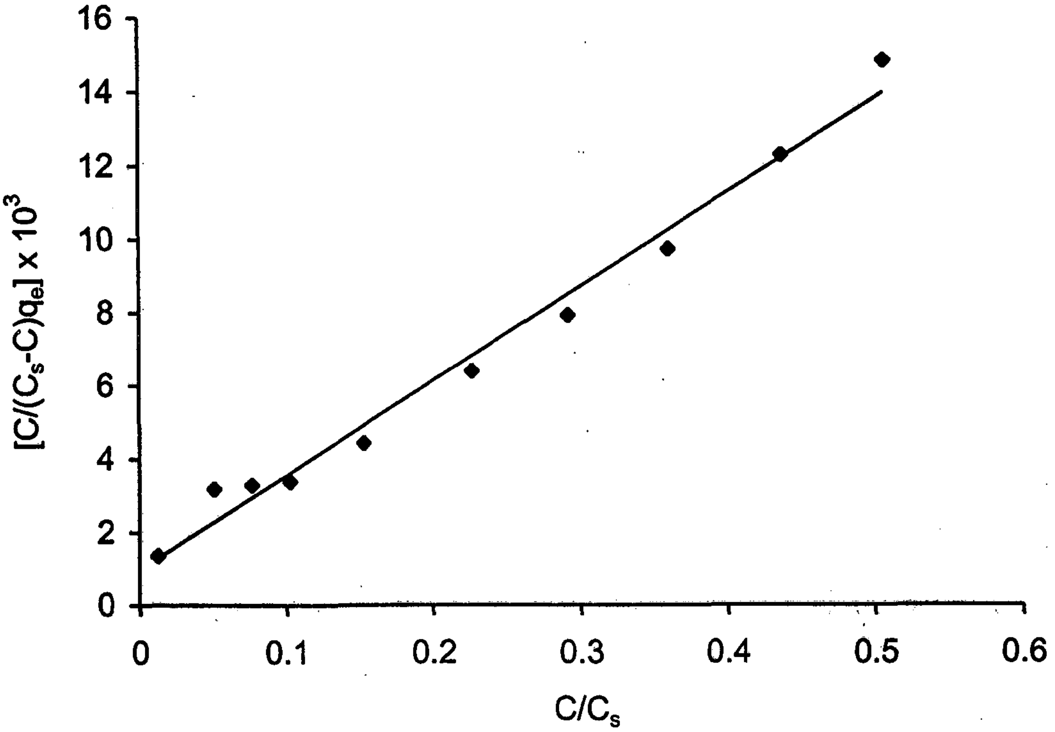

Fig. 3.34: **B.E.T. plot of Toluidine blue dye at 40-100 mesh size of lignin.**

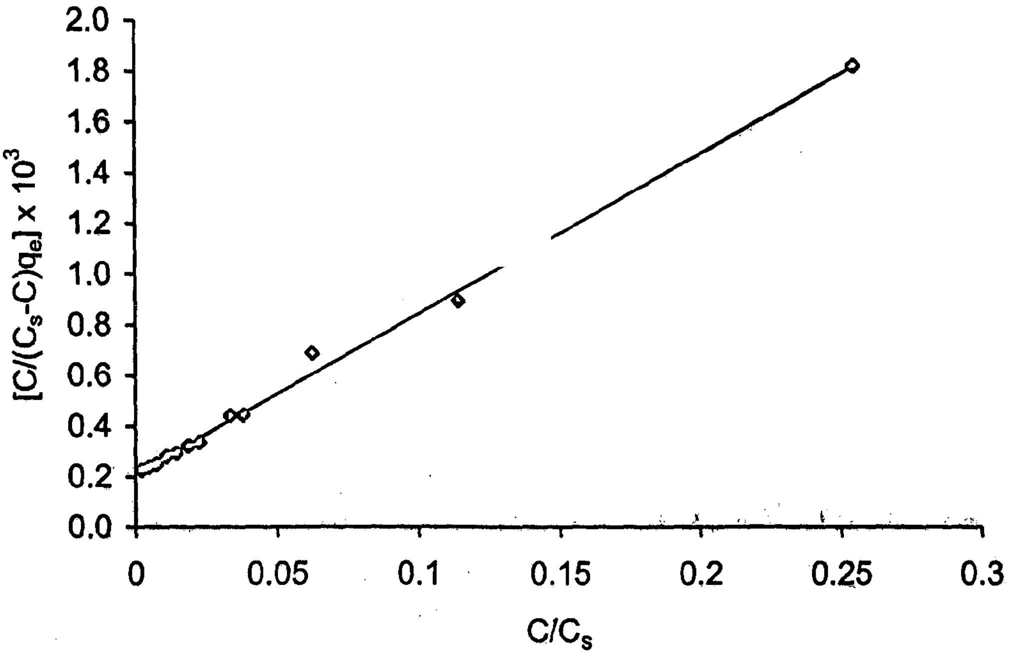

Fig. 3.35: B.E.T. plot of Toluidine blue dye at above 200 mesh size of lignin.

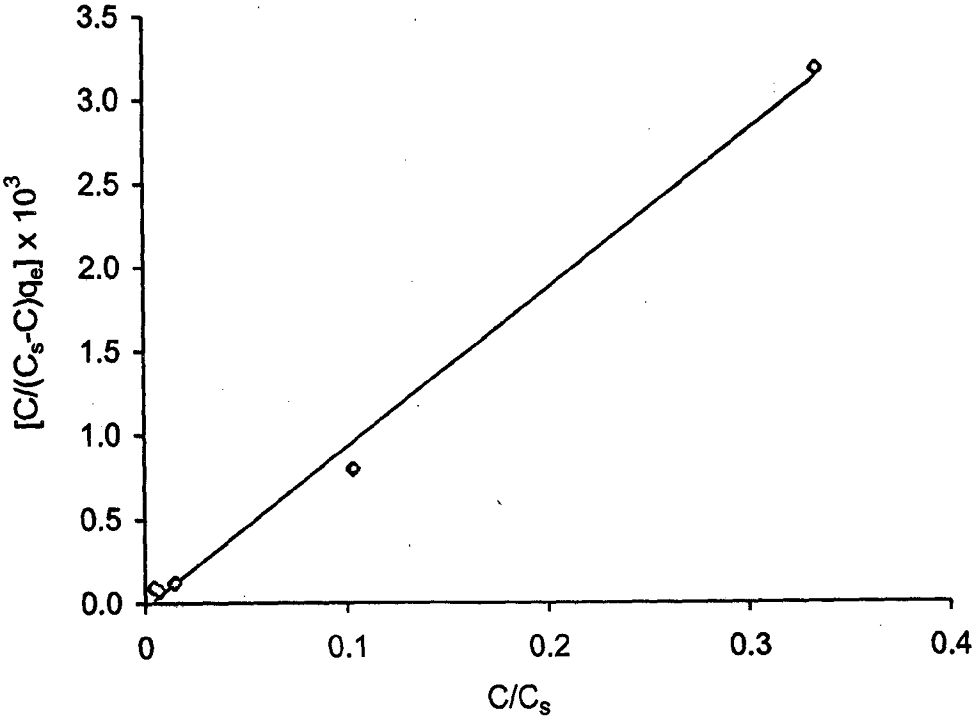

Fig. 3.36: B.E.T. plot of Neutral red dye at 25^0C.

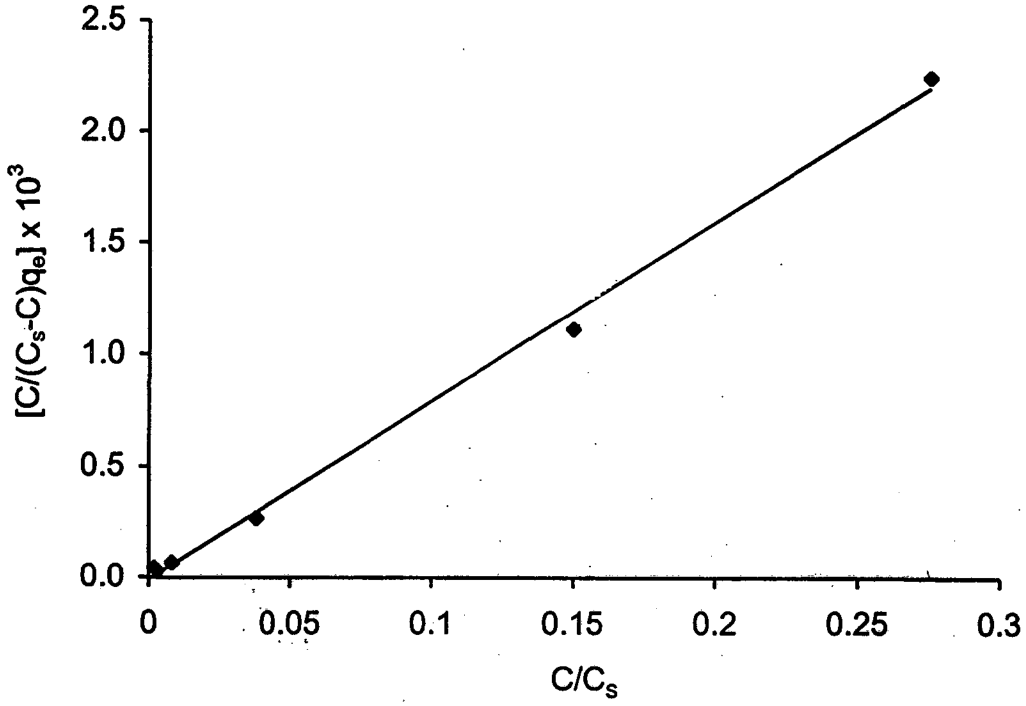

Fig. 3.37: **B.E.T. plot of Neutral red dye at 30^{0}C, pH 3.7 and 100-200 mesh size of lignin.**

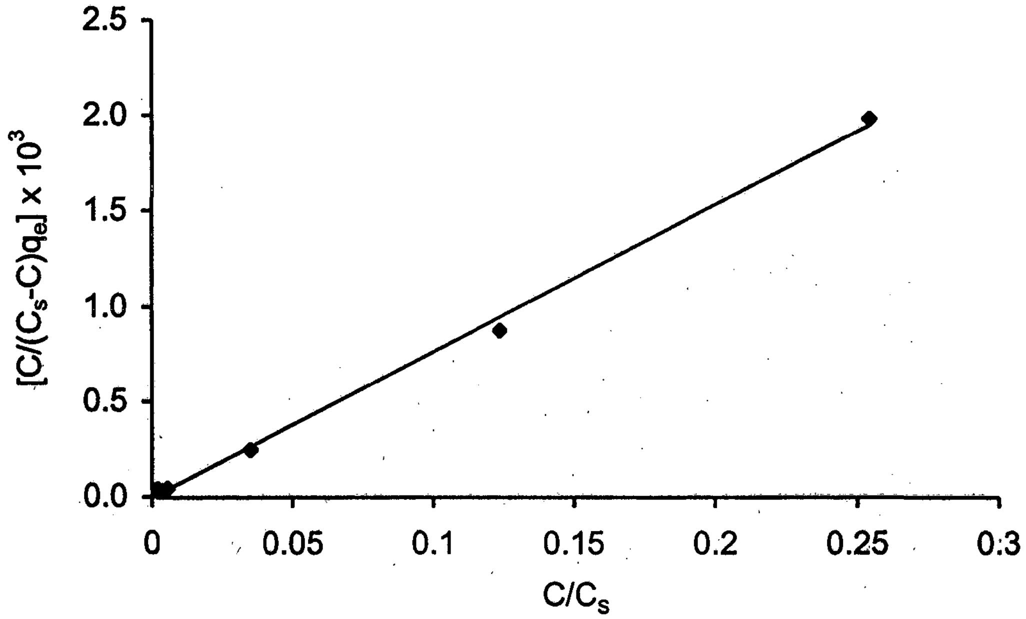

Fig. 3.38: **B.E.T. plot of Neutral red dye at 35^{0}C.**

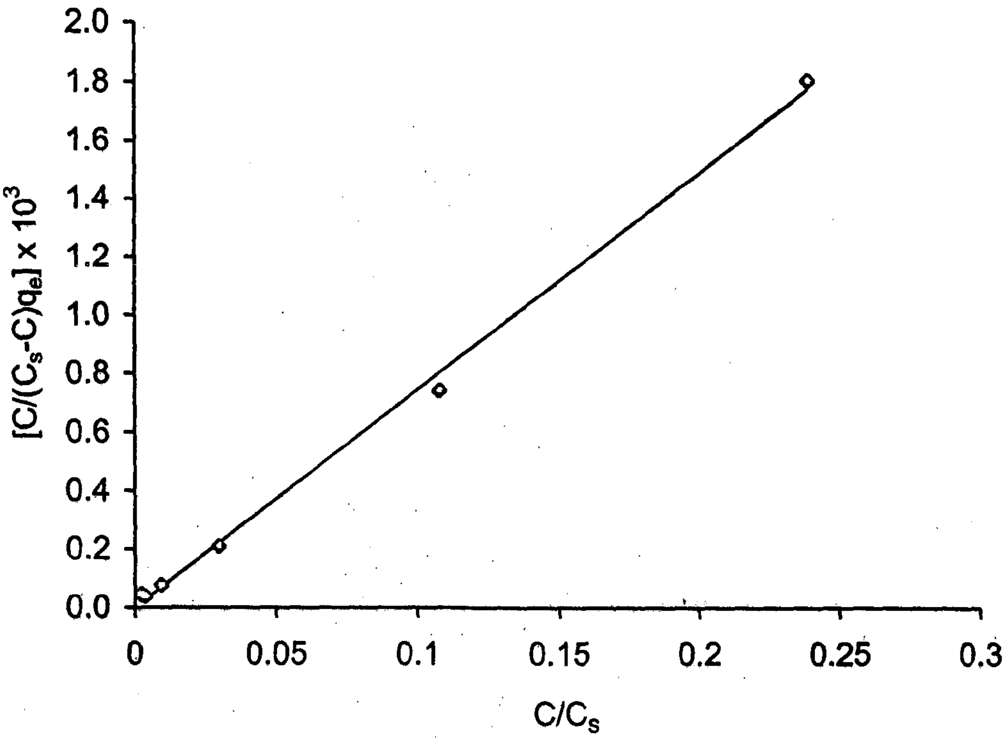

Fig. 3.39: B.E.T. plot of Neutral red dye at 40^0C.

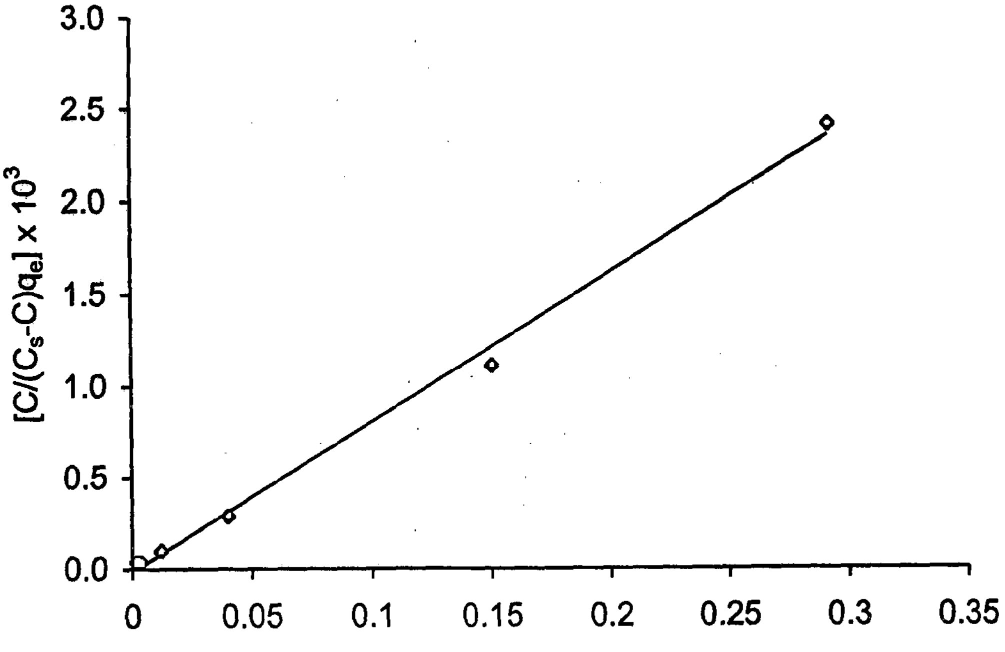

Fig. 3.40: B.E.T. plot of Neutral red dye at pH 5.0.

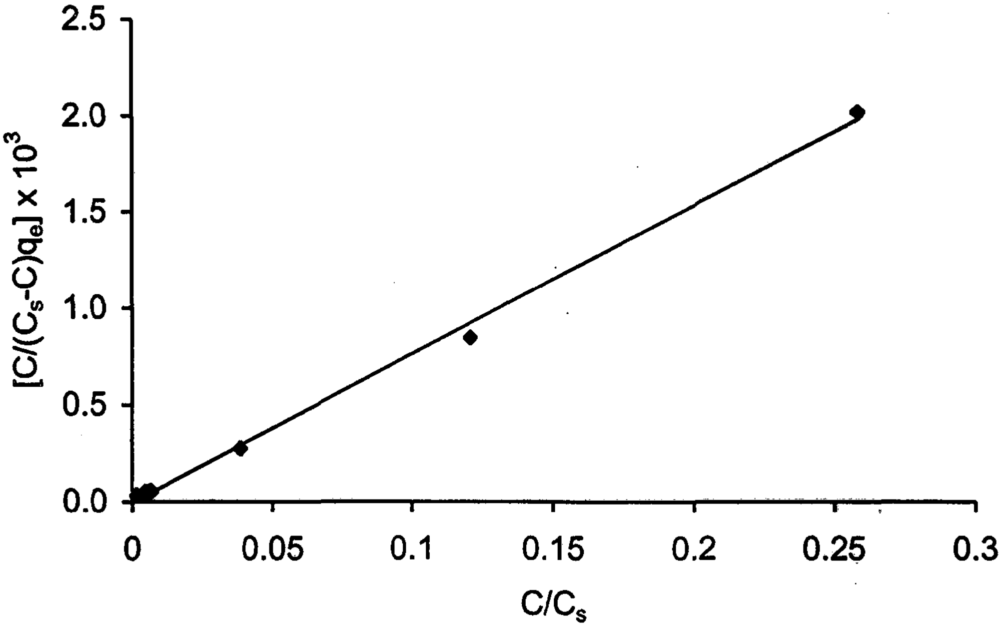

Fig. 3.41: B.E.T. plot of Neutral red dye at pH 6.0.

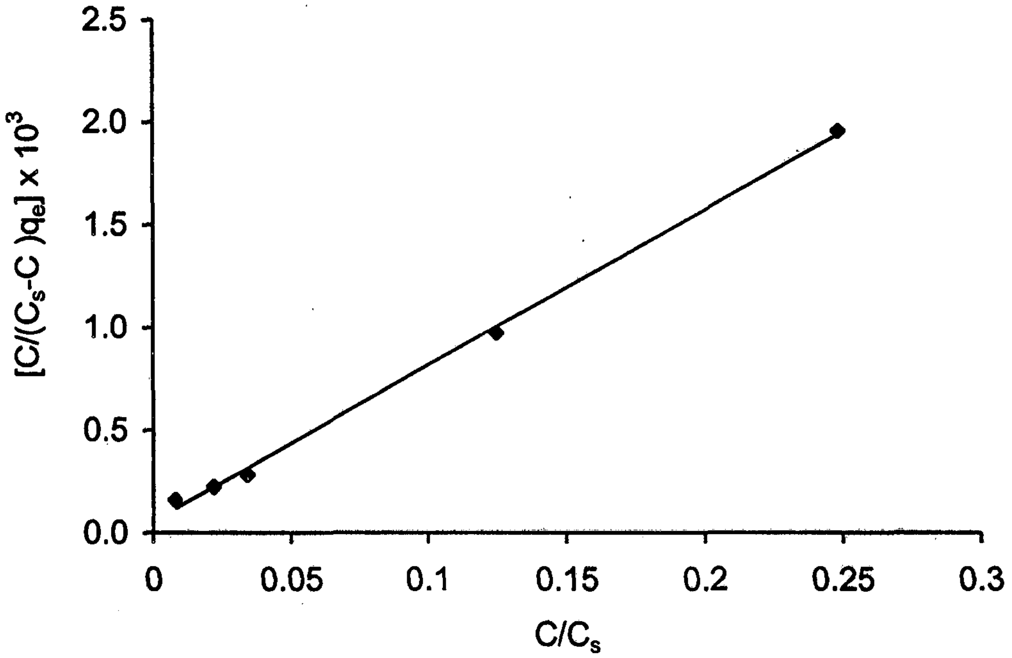

Fig. 3.42: B.E.T. plot of Neutral red dye at pH 7.0.

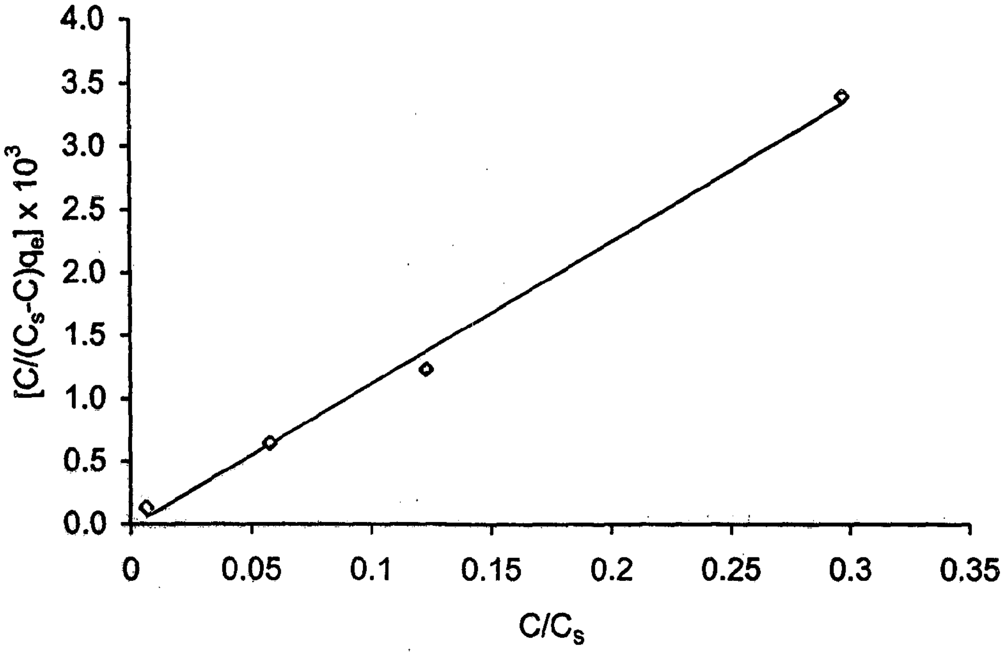

Fig. 3.43: B.E.T. plot of Neutral red dye at 40-100 mesh size of lignin.

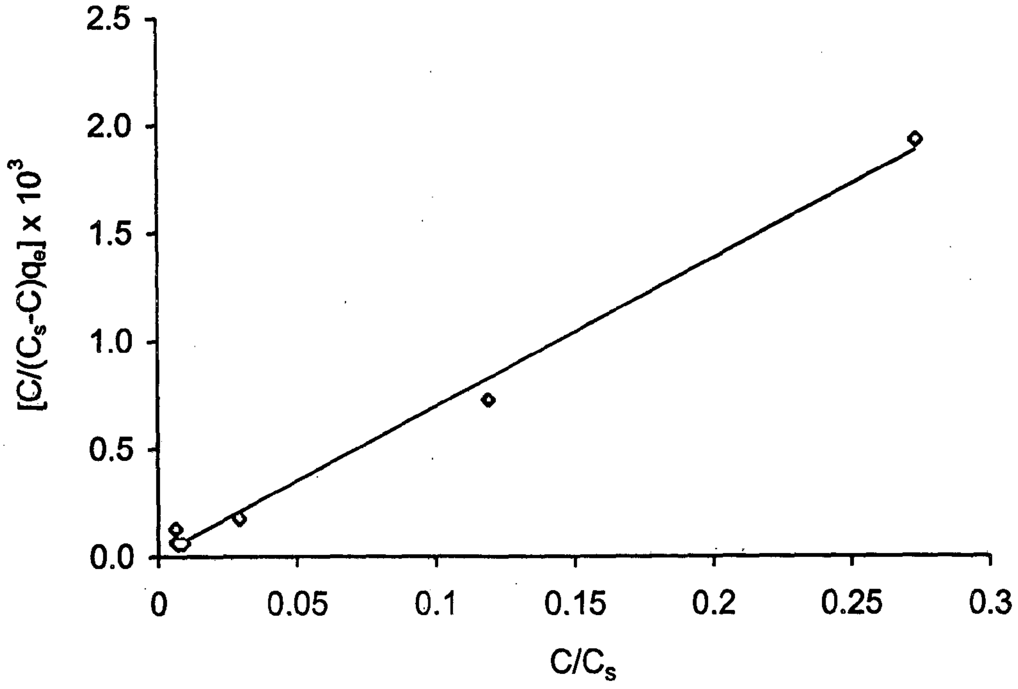

Fig. 3.44: B.E.T. plot of Neutral red dye at above 200 mesh size of lignin.

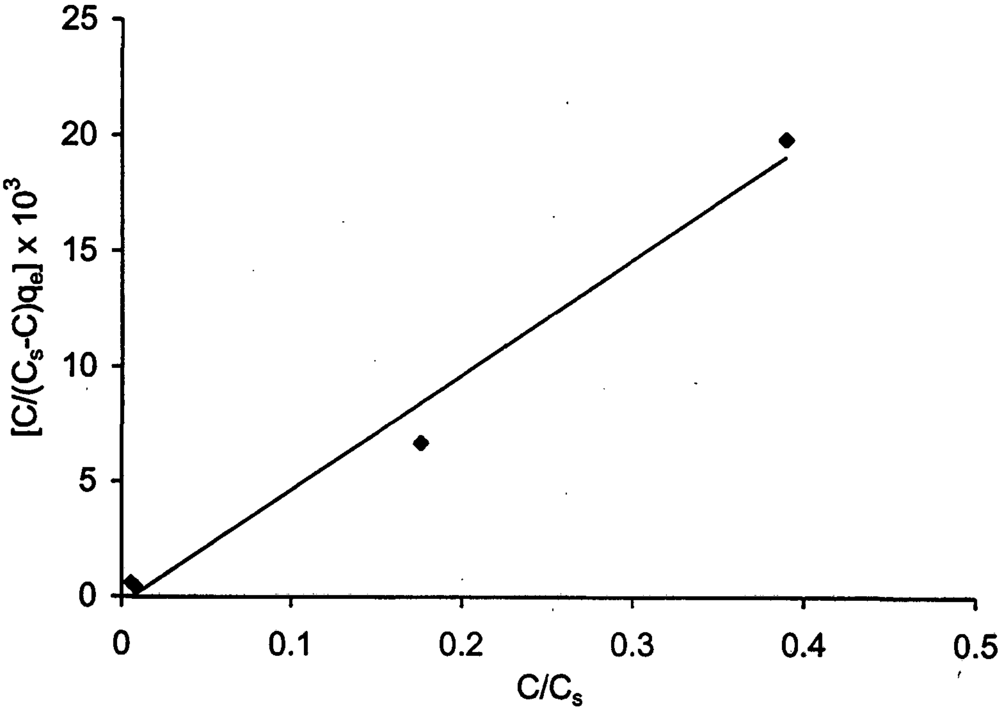

Fig. 3.45: B.E.T. plot of Crystal violet dye at 20^{0}C.

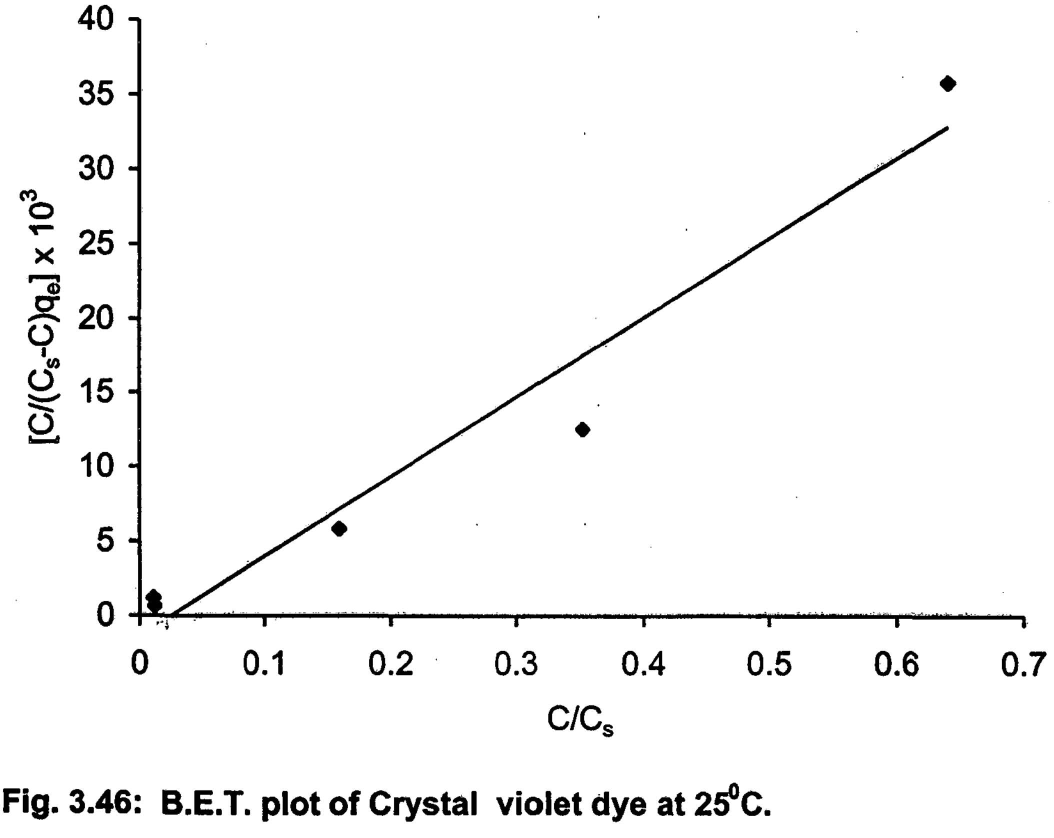

Fig. 3.46: B.E.T. plot of Crystal violet dye at 25^{0}C.

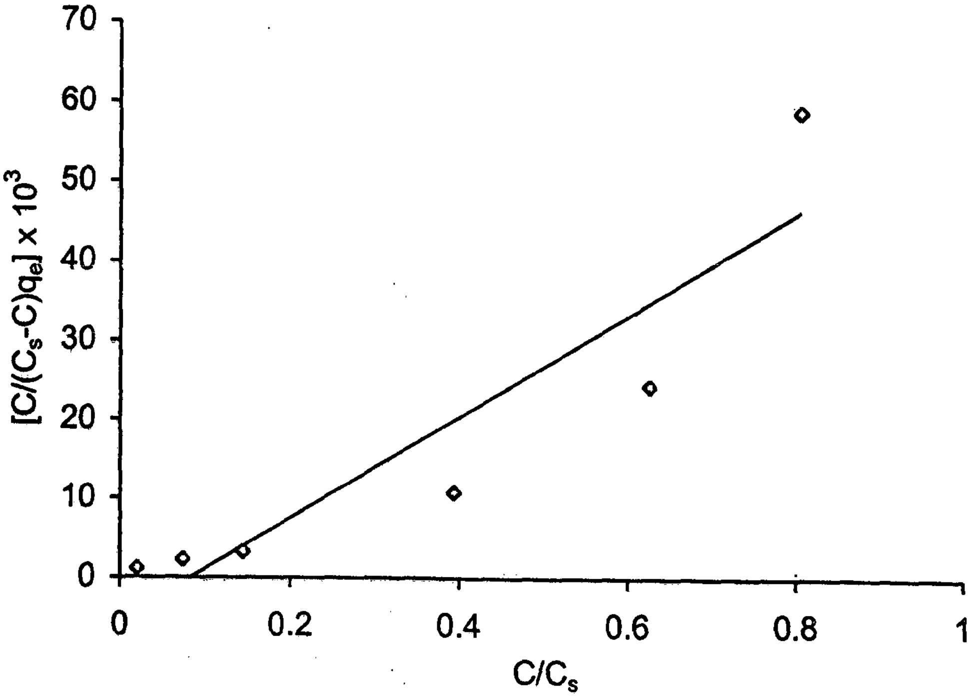

Fig. 3.47: **B.E.T. plot of Crystal violet dye at 30^{0}C, pH 7.0 and 100-200 mesh size of lignin.**

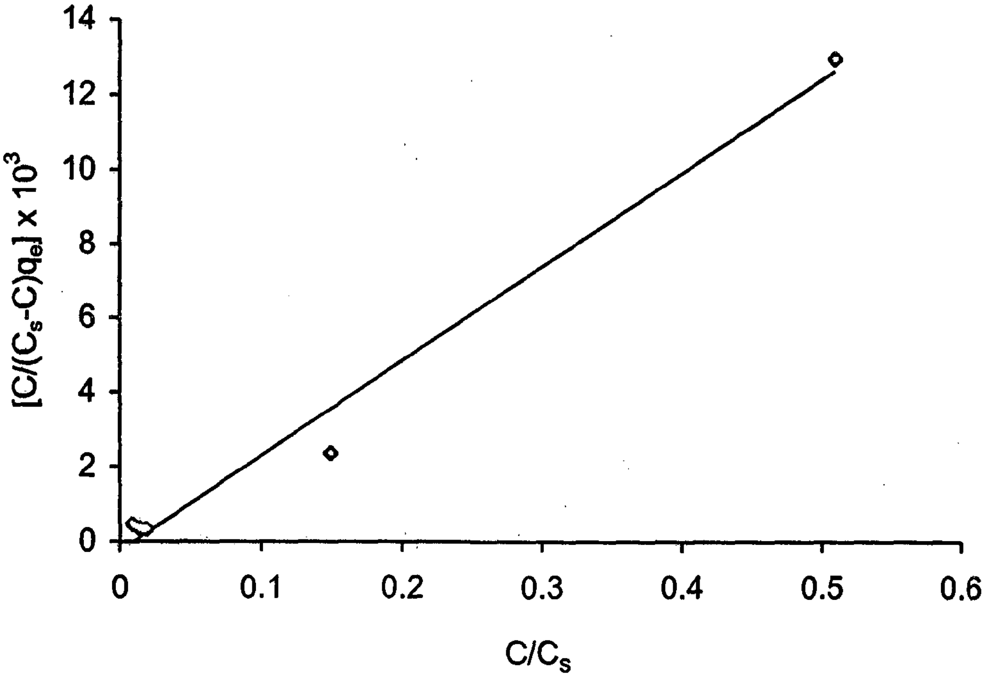

Fig. 3.48: **B.E.T. plot of Crystal violet dye at 40^{0}C.**

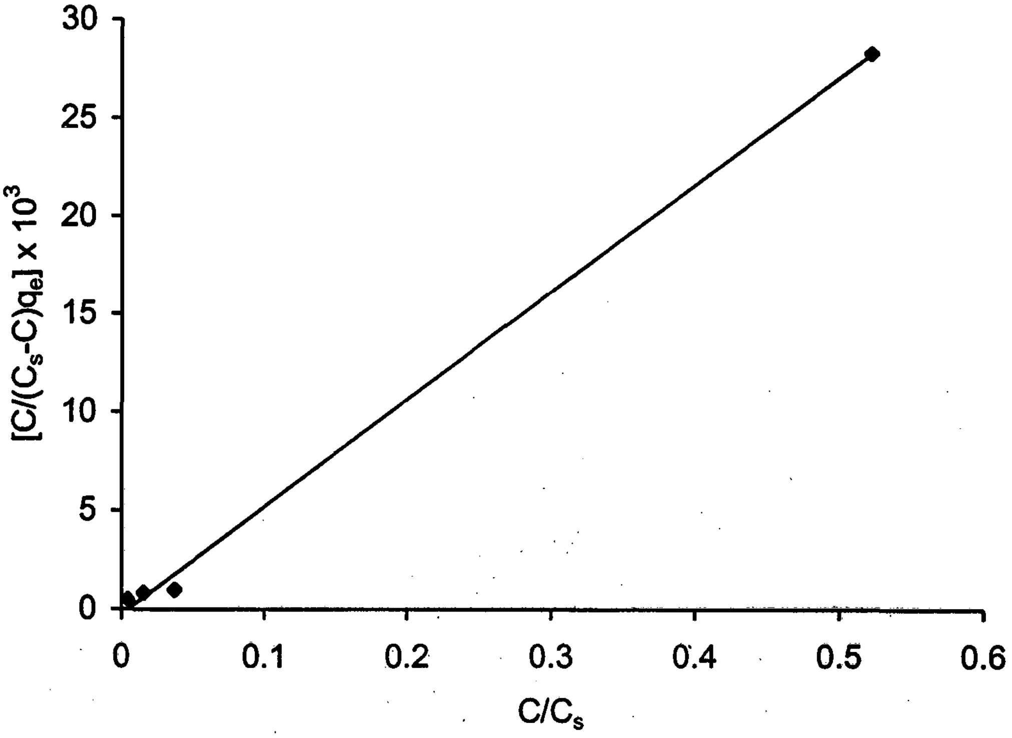

Fig. 3.49: B.E.T. plot of Crystal violet dye at pH 4.0.

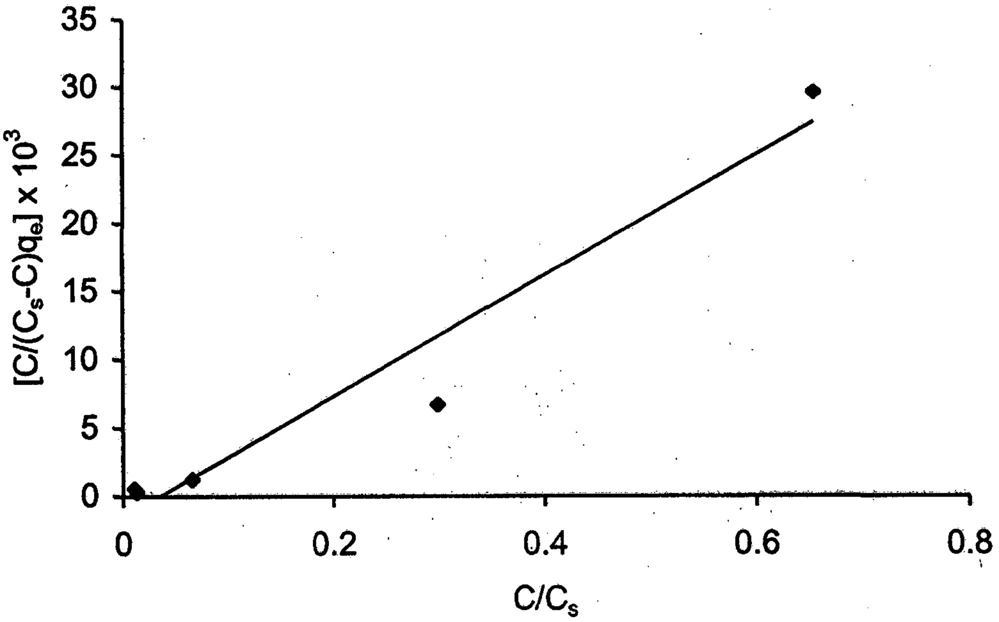

Fig. 3.50: B.E.T. plot of Crystal violet dye at pH 6.0.

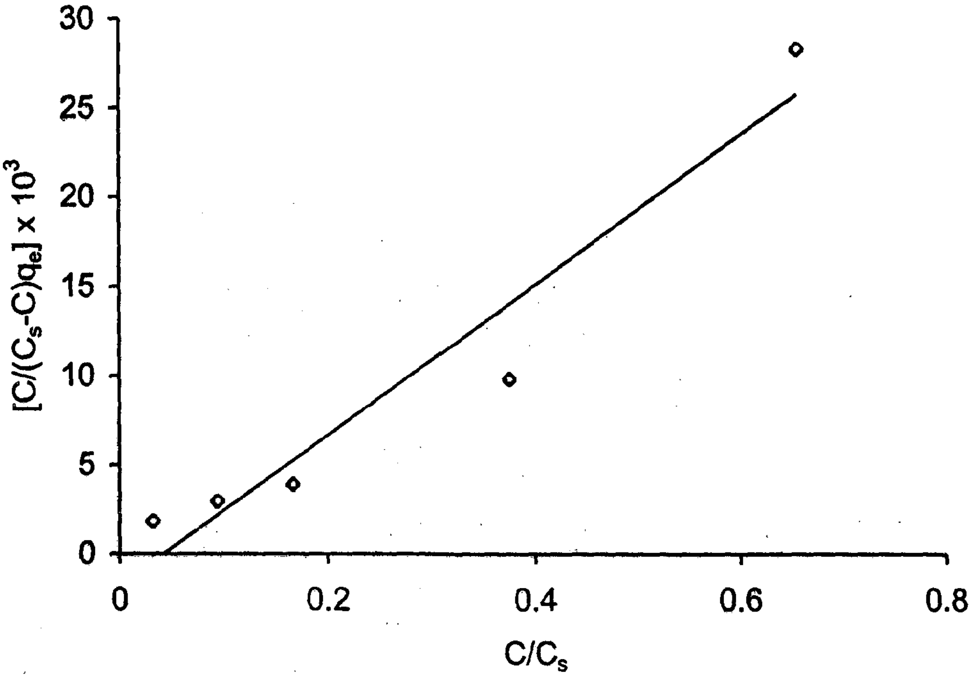

Fig. 3.51: B.E.T. plot of Crystal violet at 40-100 mesh size of lignin.

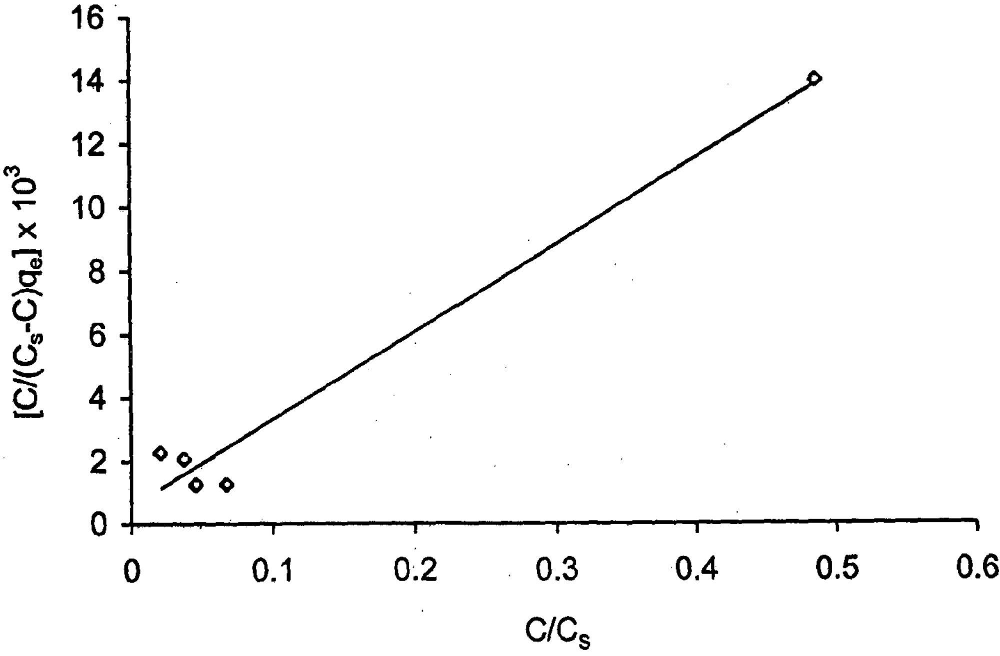

Fig. 3.52: B.E.T. plot of Crystal violet dye at above 200 mesh size of lignin.

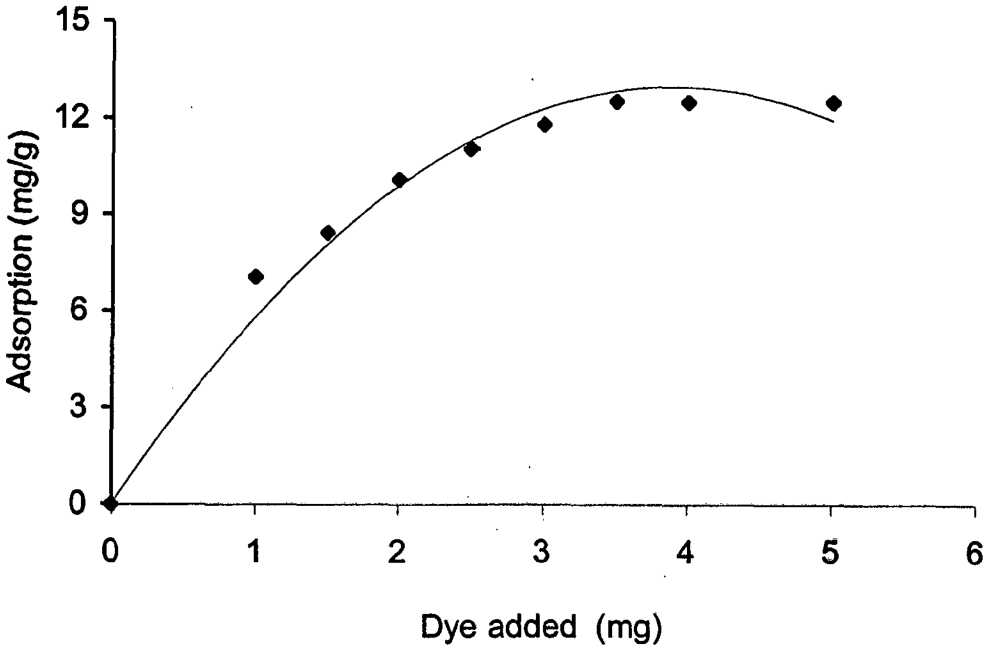

Fig. 3. 53: Effect of Crystal violet added on adsorption of dye.

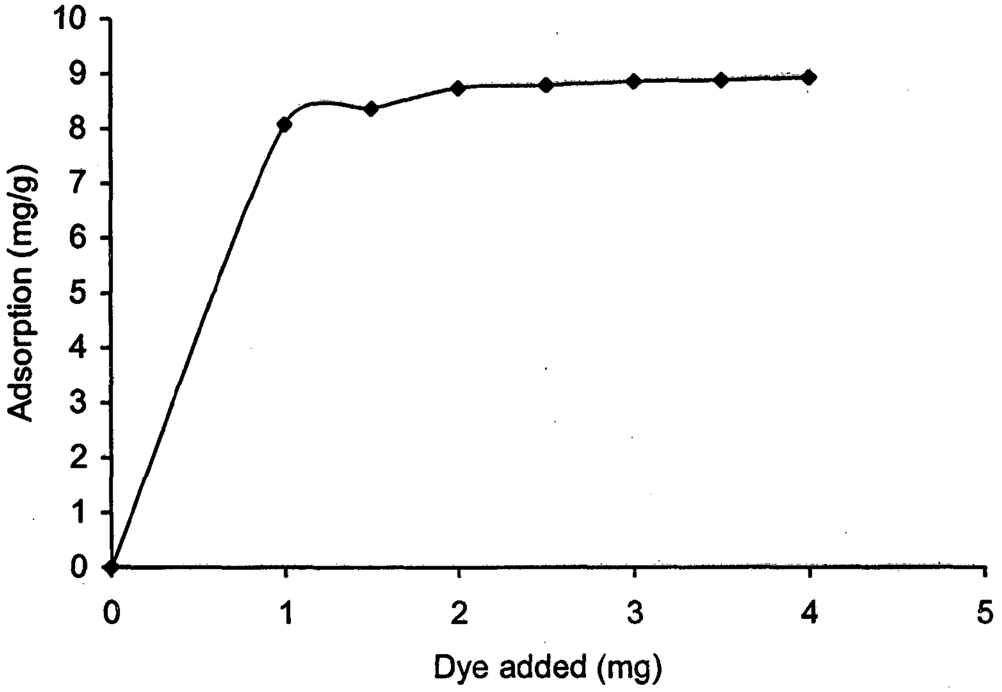

Fig. 3.54: Effect of Neutral red added on adsorption of dye.

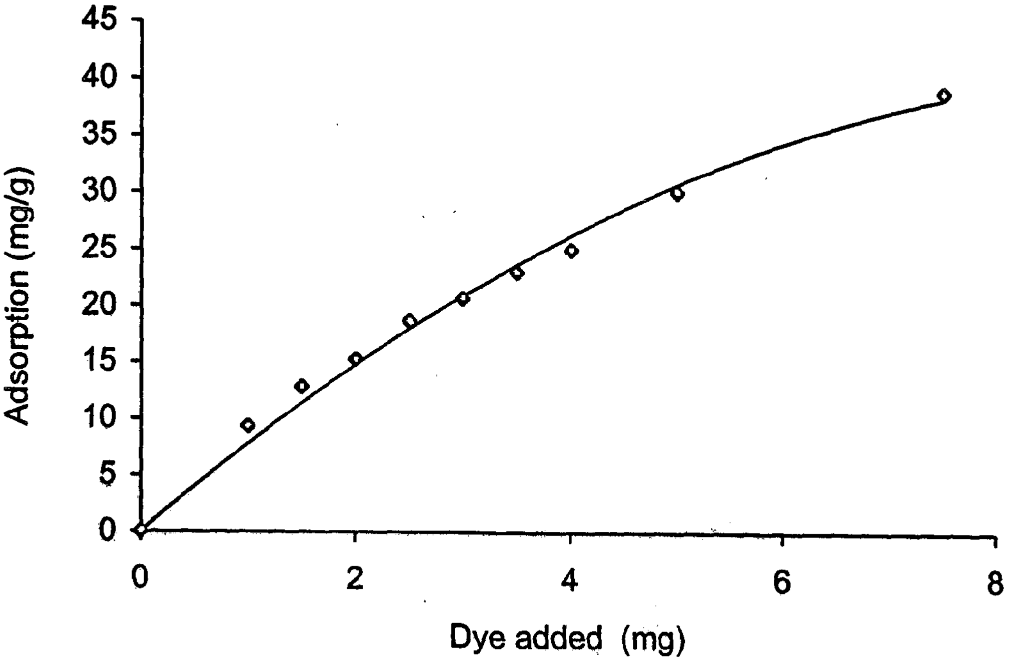

Fig. 3. 55: Effect of Toluidine blue added on adsorption of dye .

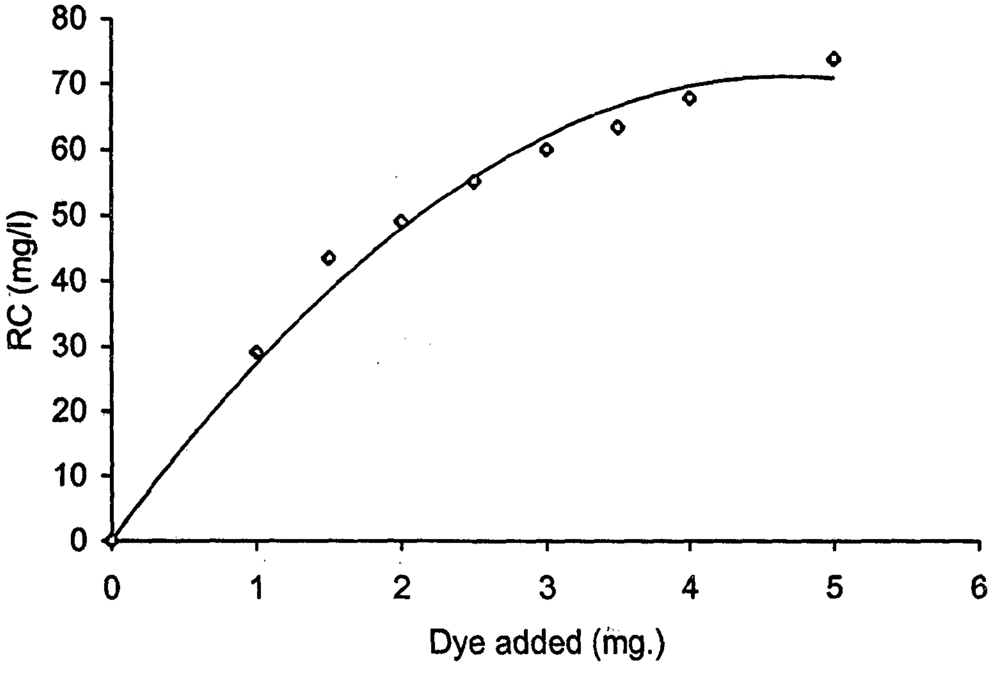

Fig. 3.56: Effect of Crystal violet added on residual concentration of dye.

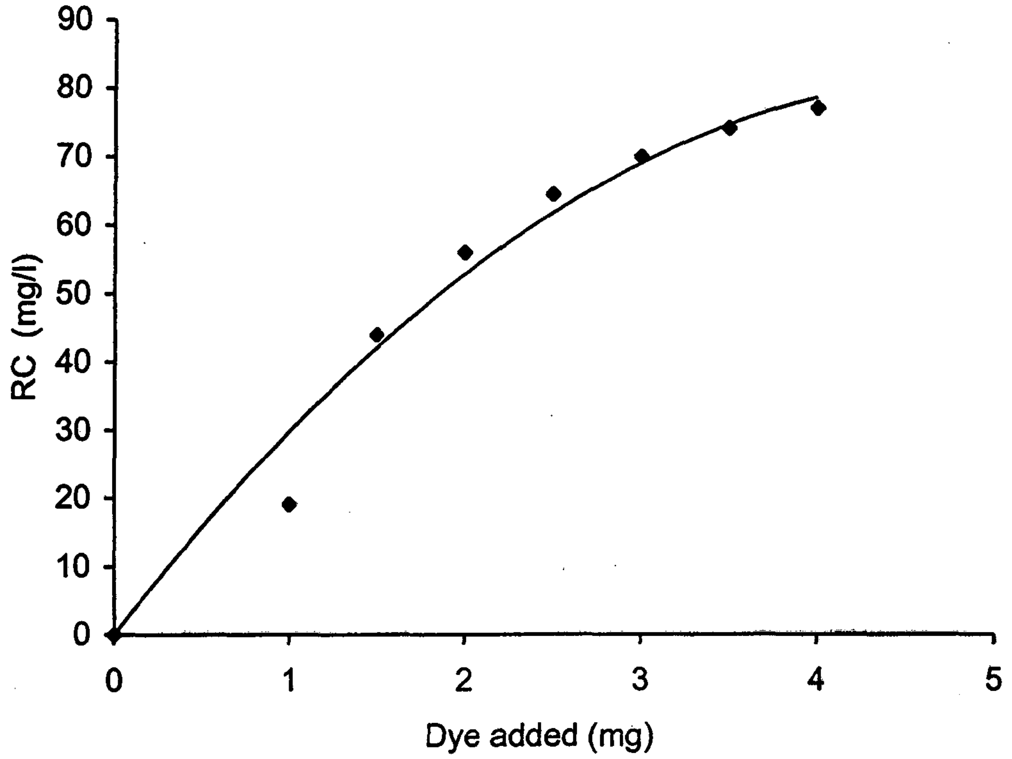

Fig. 3.57: Effect of Neutral red added on the residual concentration of dye.

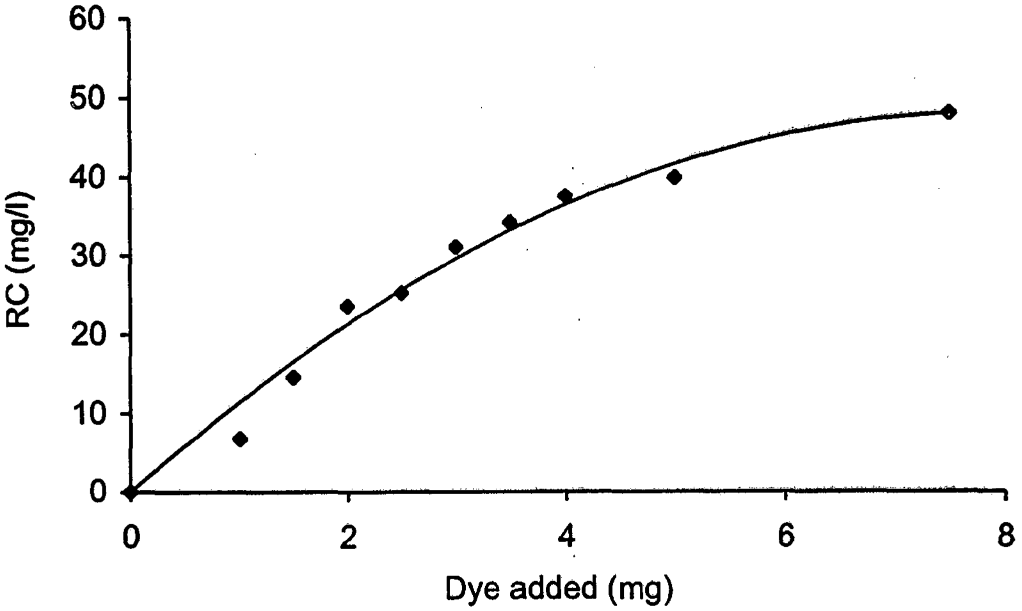

Fig. 3.58: Effect of Toluidine blue added on residual concentration of dye .

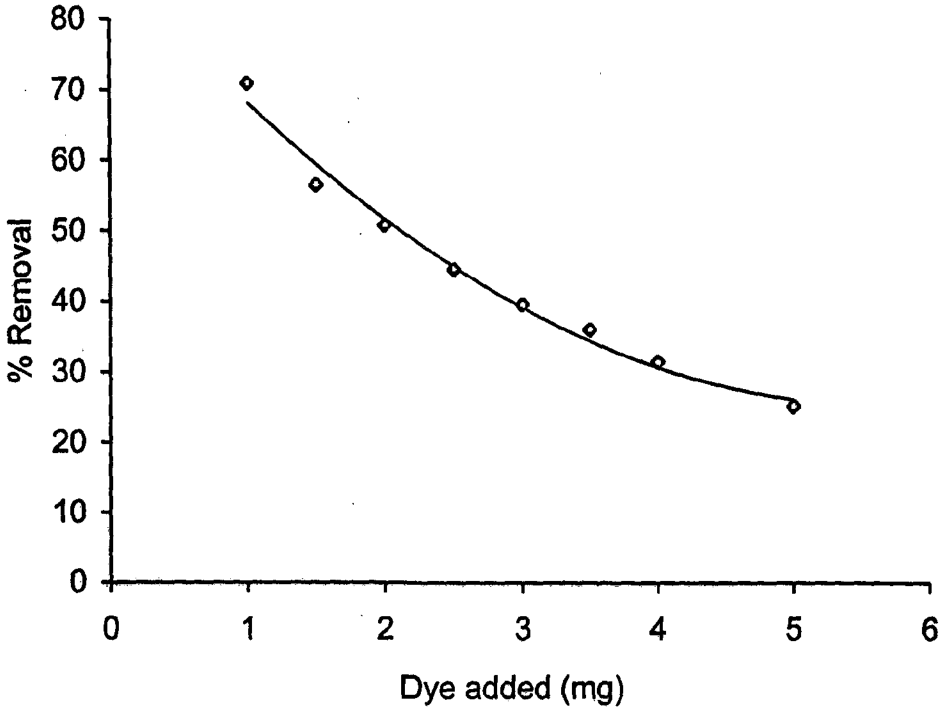

Fig. 3.59: Effect of Crystal violet added on % removal of dye.

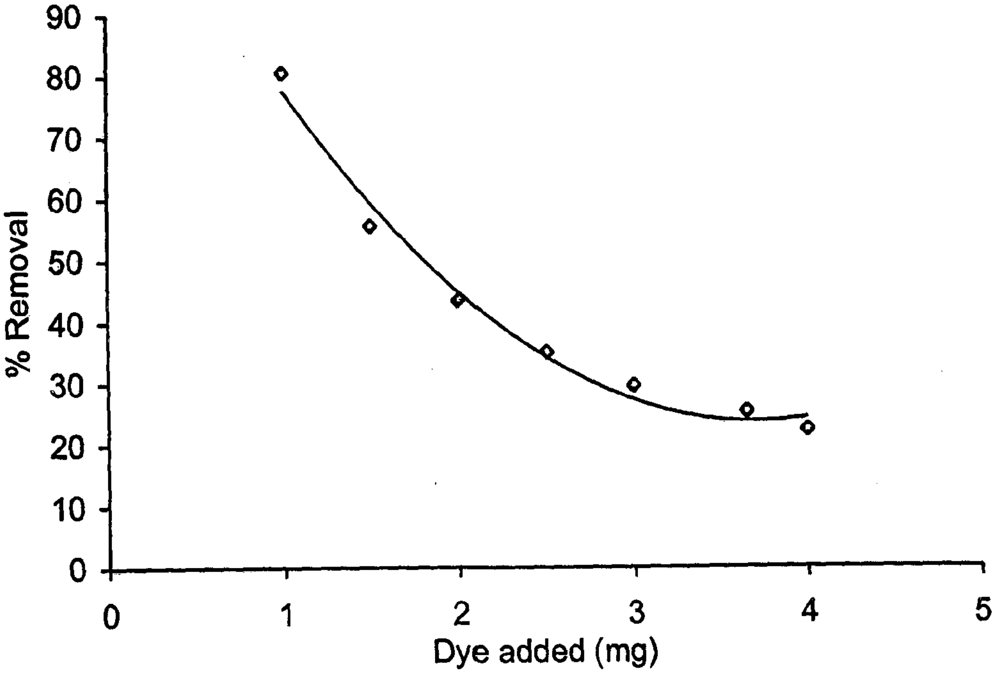

Fig. 3.60: Effect of Neutral red added on % removal of dye.

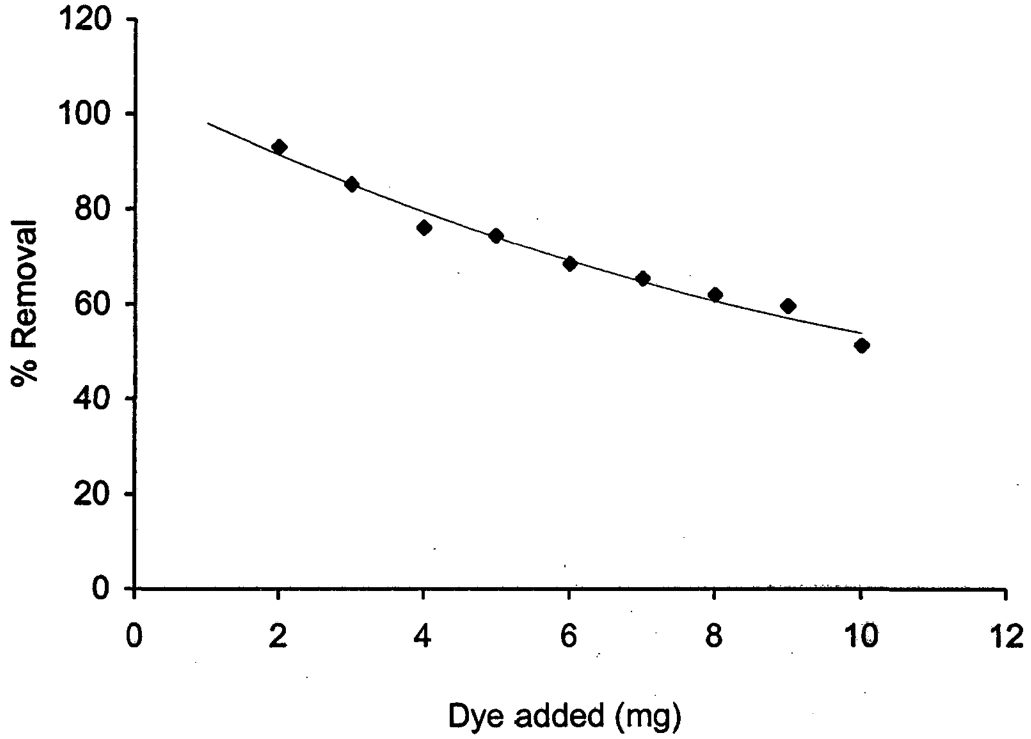

Fig. 3.61: Effect of Toluidine blue added on % removal of dye.

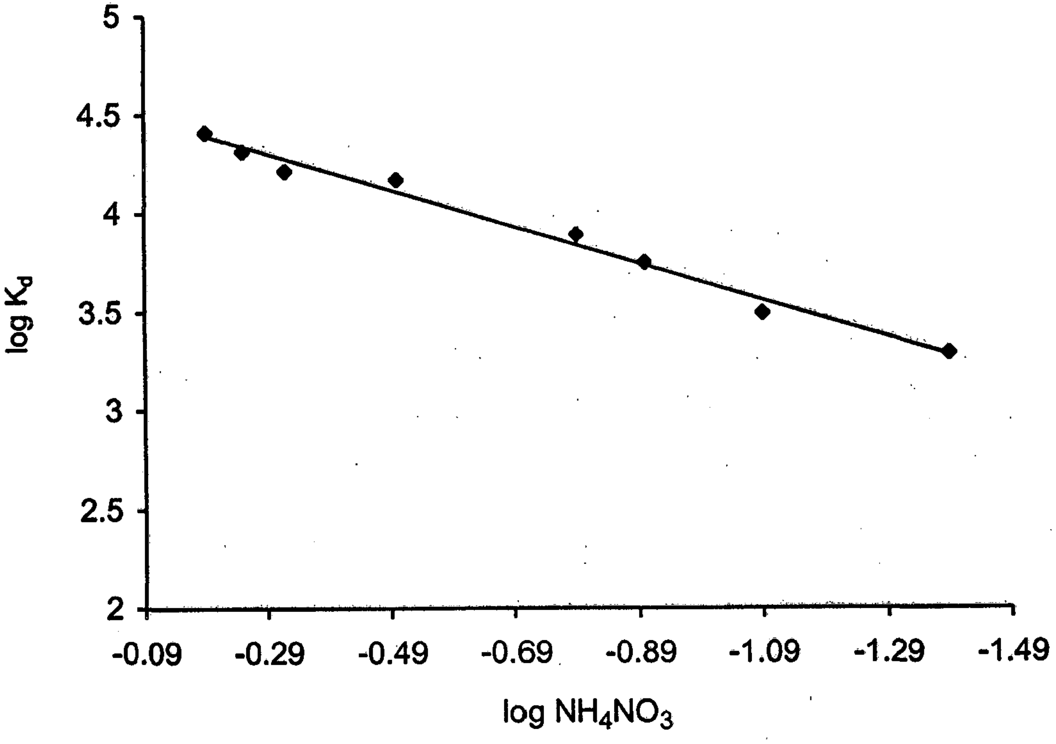

Fig. 3.62: Adsorption of Crystal violet dye as a function of NH_4NO_3 concentration.

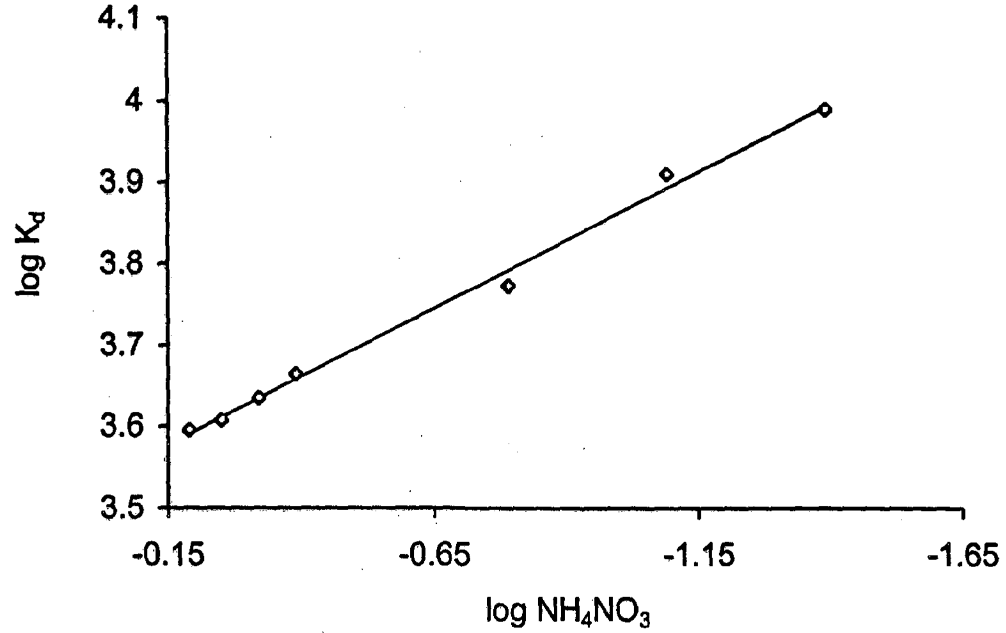

Fig. 3.63: Adsorption of Neutral red dye as a function of NH_4NO_3 concentration.

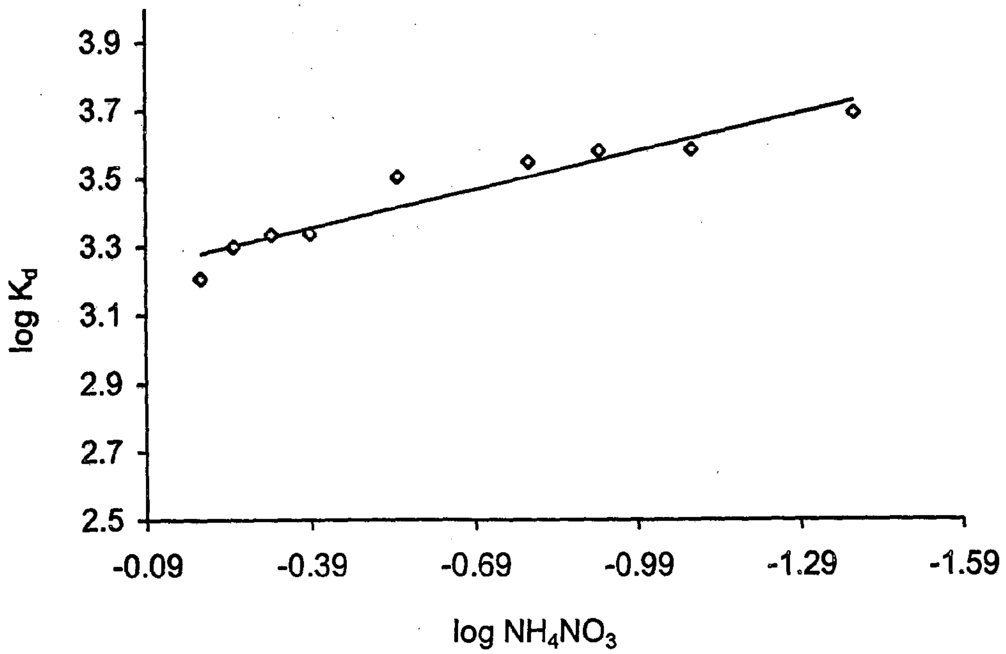

Fig. 3.64: Adsorption of Toluidine blue dye as a function of NH_4NO_3 concentration.

CHAPTER - 4

ADSORPTION KINETICS OF DYES ON LIGNIN

4.1 INTRODUCTION

Adsorption finds extensive applications in industry, laboratories and various technical processes. It is an effective process for the removal of dissolved organic substances from water and wastewaters. Successful application of this technique demands adsorbents of known kinetic parameters and sorption characteristics. A prehand knowledge of optimal conditions would herald a better design and modeling of the process. A thorough study of the sorption kinetics reveals the mechanism of rate controlling step and in some cases, sheds significant light on the internal physical structure of the adsorbent material.

Although there had been previous experimental studies of the rates of ion-exchange reactions, Nachod and Wood made the first attempt to start systematic investigations on ion exchange kinetics and elucidated the rate controlling mechanism. G.Schulze first introduced the concept of diffusion and also pointed out that the rate-determining step in the exchange kinetics is the inter- diffusion of counter ions.

It is desirable to have a quantitative understanding of the process to evaluate the internal physical structure of the adsorbent material. In determining the nature of the rate-limiting step, several characteristics of adsorbent, adsorbate and solution phase are of importance. These characteristics were derived from ion-exchange theory and have been described by Helfferich (3) and Weber and Morris (27). These factors include the particle size, amount of adsorbent, initial concentration of adsorbate, degree of mixing, affinity of adsorbate for adsorbent and diffusion coefficient of the solute molecule in bulk solution as well as within the pores of the adsorbent material.

The ion exchange kinetics of simple metal cations has been studied by a number of workers and it is now well established that the rate-determining step in the exchange sorption is the inter-diffusion of counter ions. The rates of exchange adsorption is controlled by diffusion either through a hydrostatic boundary layer called "film diffusion control" or through the pores of the resin matrix called "particle diffusion control" (3,16).

The rate of ion exchange adsorption is mainly controlled by film diffusion under conditions of (a) small adsorbent particle size, (b) dilute adsorbate solution, (c) mild/poor stirring and (d) high affinity for adsorbent. In contrast, it is controlled by particle diffusion under conditions of (a) large adsorbent particle size, (b) high adsorbate concentration, (c) vigorous/good stirring and (d) low adsorbate/adsorbent affinity. Otherwise both processes control it. Many workers treat more of the cases as those involving both the film as well as the particle diffusion mechanism.

Lignin is now being used for wastewater treatment. A survey of literature reveals that lignin exhibits sorption properties. Since we have studied the sorption characteristics of lignin for the removal of the three cationic dyes (Chapter 3), it becomes imperative to study the sorption rates of these dyes on lignin as a function of adsorbate concentration, temperature, pH and particle size of the adsorbent lignin.

The present work is an attempt to study the kinetics and mechanism of the adsorption process with an aim to obtain information about the rate-determining step of the process. The study has been performed at different temperatures, pH and particle sizes of the adsorbent using batch technique.

This chapter describes the results of kinetic studies and value of diffusion coefficients as well as some thermodynamic parameters which have been evaluated to determine the mechanistic aspects of the process. The effective diffusion coefficients have been evaluated at three different temperatures. The energy barriers against the diffusion of exchanging ions have been estimated from the Arrhenius equation. Entropies of activation for the sorption process have also been calculated.

4.2 MECHANISM OF SORPTION

It is necessary to determine the step which controls the overall mechanism of adsorption in order to determine the rate at which dissolved organic substances are removed from dilute aqueous solutions by solid adsorbents. There are essentially three consecutive steps in the adsorption of organic material on porous adsorbent (3, 16). These are :

a) Transport of the adsorbate to the external surface of the adsorbent,

b) Transport of the adsorbate within the pores of the adsorbent (except for a small amount of adsorption that occurs on the surface of the adsorbent),

c) Adsorption of the adsorbate on the interior surface of the adsorbent.

It is generally accepted that the process (c) is very rapid and does not represent the rate-determining step in the uptake of organic compounds (2, 26). For the remaining two steps, if external transport is rapid as compared to the internal transport, the rate of adsorption is governed by the step (b) i.e. particle diffusion; while if the internal transport is more rapid than the external one, the rate is governed by the step (a). In the latter case, the transport of adsorbate to the boundary may not be possible at a significant rate, thereby leading to the formation of a liquid film with a concentration gradient surrounding the sorbent particle and the overall rate is governed by the diffusion of adsorbate through this film i.e. film diffusion.

The kinetics of adsorption is important from the point of view of controlling the process efficiency (23, 24). Different workers have used various kinetic models. A number of methods have been devised to find out the nature of the rate-limiting step that depends on the characteristics of adsorbent particle size, adsorbate concentration and the rate of mixing. Helfferich (3) and others (1, 17, 26) have described these characteristics in detail.

The theories developed on the basis of ion exchange phenomenon have conveniently been used for the sorption of dyes for determining the kinetic and thermodynamic parameters of the sorption processes.

4.3 RATE EXPRESSIONS AND EVALUATION OF KINETIC AND THERMODYNAMIC PARAMETERS

As the batch technique has been used, kinetic adsorption data obtained in this work were analyzed by applying the Reichenberg (20) and Helfferich mathematical models using equations (1) - (4) to distinguish between the film diffusion and particle diffusion controlled rate processes.

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[\frac{-D_i\, t\, \pi^2\, n^2}{r^2}\right] \qquad \text{...........(1)}$$

or

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[-n^2\, Bt\right] \qquad \text{...........(2)}$$

where,

n = the number of exchanger particles, an integer that defines the infinite series solution,

F = the fractional equilibrium that is reached at time 't', obtained by the expression:

$$F = \frac{Q_t}{Q_\infty} \qquad \text{...........(3)}$$

where,

Q_t = the amount of adsorbate taken up at time t,

Q_∞ = the maximum uptake at equilibrium.

B = the time constant, given by the expression:

$$B = \frac{\pi^2 D_i}{r^2} \qquad \text{...........(4)}$$

where,

D_i = effective diffusion coefficient of the ingoing ions,

r = the radius of the spherical adsorbent particles.

The rate factor in the adsorption process is of recognized importance for the economic and industrial employment of adsorbents. Thus knowing the value of 'B' and mean particle radius 'r', the value of D_i can be evaluated.

It can be seen from equation (2) that 'F' is a calculable mathematical function of Bt and vice versa, and depends only upon D_i / r^2. In the proposed work, Bt values (the product of multiplying B by time t) at different temperatures, pH and particle sizes have been obtained for each observed value of 'F', from Reichenberg's table (20). The linearity test of Bt vs. t plots has been employed to distinguish between adsorption controlled by the particle and film diffusion mechanisms. If a Bt vs. time plot is linear (slope = B) and passing through the origin, then the adsorption rate is governed by diffusion in the particle, otherwise it is governed by film diffusion. The experimental conditions were set for particle diffusion as the sole rate-determining step to study the thermodynamics of the sorption process.

The energy of activation 'E_a' has been determined by applying the Arrhenius type expression (16):

$$D_i = D_0 \exp\left[-\frac{E_a}{RT}\right] \qquad \text{...........(5)}$$

The pre-exponential constant 'D_o' (analogous to Arrhenius frequency factor) gives the entropy of activation ΔS^* as (16):

$$D_0 = 2.72\, d^2 \frac{kT}{h} \exp\left[\frac{\Delta S^*}{R}\right] \qquad \text{...........(6)}$$

where,

k = Boltzman constant.

h = Planck constant.

R = gas constant.

d = average distance between successive exchange sites (conventionally taken as 5 Å i.e. 5 X 10^{-8} cm in lignin).

T = temperature (= 273 ^{0}K).

4.4 RESULTS AND DISCUSSION

4.4.1 Adsorption Kinetics of Cationic Dyes

The adsorption kinetics data for Crystal violet, Neutral red and Toluidine blue at various concentrations of dyes, temperatures, particle sizes of lignin and pH are given in Tables 4.1–4.7. The plots of F vs. t and Bt vs. t at various concentrations of dyes, temperatures, particle sizes of lignin and pH of the three cationic dyes, are shown in Figs. 4.1–4.24. Figs. 4.1–4.3 and 4.7–4.15 represent F vs. t and Figs. 4.4–4.6 and 4.16-4.24 represent Bt vs. t along with the respective B values for the three dyes. McKay plots [log (1 – F) vs. t] for sorption process of Crystal violet at various temperatures, particle sizes of lignin and pH are depicted in Figs. 4.25–4.27 and those for Neutral red and Toluidine blue are depicted in Figs. 4.28–4.30 and Figs. 4.31–4.33 respectively. Fig. 4.34 indicates a linear relationship between B and $1/r^2$ for the three dyes. The linear plots of logarithm of effective diffusion coefficient (D_i) and the reciprocal of temperature ($^0K^{-1}$) for the sorption of Crystal violet, Neutral red and Toluidine blue are shown in Fig. 4.35. Kinetics and thermodynamic parameters of the diffusion process of the three dyes are listed in Tables 4.8 and 4.9.

Figs. 4.1-4.3 are the plots of F vs. t for Crystal violet, Neutral red and Toluidine blue respectively at various concentrations of the dye solutions. These curves indicate that the adsorption is quite fast at lower concentrations

(100-500 mg/l) of the dye solutions and about 70–97% of the adsorption occurs within the first sixty minutes of contact. This initial rapid adsorption subsequently leads to a slow approach to equilibrium. These curves further indicate that the percent amount of dye adsorbed / removed during the first one hour of contact decreases with increase in concentration of dye. The amount of adsorption is found to be dependant on the initial adsorbate concentration.

In all the three cases the corresponding Bt vs. t plots (Figs. 4.4-4.6) are linear and passing through the origin at dye concentrations equal or above 800 mg/l for Crystal violet and Neutral red and 750 mg/l for Toluidine blue. But these plots indicate that the sorption rate is dependant on the initial concentration of the dye. Non-linear behavior curves are observed in dye concentrations between 100 – 500 mg/l for Crystal violet and Neutral red and between 100 – 600 mg/l for Toluidine blue. This shows that sorption process is film diffusion controlled at lower concentrations and is both, partially particle-diffusion and partially film-diffusion controlled, at higher dye concentration i.e. at and above 800 mg/l for Crystal violet and Neutral red and for Toluidine blue at and above 750 mg/l. With the increase in initial dye concentration, the film diffusion mechanism changes to the more dominant particle diffusion.

The increase in sorption rate with increase in temperature of the three dyes (Figs. 4.7–4.9) further supports particle diffusion mechanism as the dominant rate-controlling step (14, 20). Increase in mobility of Crystal violet, Neutral red and Toluidine blue ions at higher temperatures results in the increased sorption rate. Similar behavior has also been reported by Karthikeyan et al (8)and Mohan et al (16).

The sorption rate is markedly dependent on particle size of the adsorbent (Figs. 4.10–4.12). The rate of exchange is inversely proportional to the particle size.

In the case of Crystal violet the sorption rate shows a marked dependence on pH (Fig. 4.13). It increases significantly with increase in pH. The sorption rate increases marginally with increase in pH for Neutral red (Fig. 4.14) but has been observed to be independent of pH of the adsorbate for Toluidine blue (Fig. 4.15).

The plots of Bt vs. t (Figs. 4.16–4.24) for Crystal violet, Neutral red and Toluidine blue dyes are obtained by replacing F values by the corresponding values of Bt. The plots of Bt vs. t at different temperatures, particle sizes and pH for the three dyes are straight lines passing through the origin, indicating that the rate-determining step is diffusion through the particle. The 'B' values are calculated from these plots. The plots of Bt vs. t (Figs. 4.19–4.21) show that the rate of exchange is inversely proportional to the particle size. This clearly indicates a diffusion controlled process and not one controlled by chemical interactions because in the latter case the exchange would be independent of particle size. Similar results were observed by Swelam and Salem (22) during the study of kinetics of ion exchange reactions of calcium / hydrogen ions in mixed solvent (water-glycerol) media on KU_2 -20 (cation exchanger).

The linear McKay plots [log (1 – F) vs. time] at various temperatures, particle sizes and pH (Figs. 4.25 – 4.33) for the three cationic dyes do not pass through the origin. These deviations from origin indicate that pore diffusion is not the only rate-controlling step. There may be some other process also controlling the rate, both of which maybe operating simultaneously. It indicates that the predominant adsorption of dye contributing component is pore-diffusion that may be being preceded by rapid external mass transfer. These McKay plots do not depict the initial portion of the dye uptake (the instantaneous adsorption stage) attributed to film diffusion because due to the rapidity of this interdiffusion process, film diffusion could not be followed experimentally .The depicted linear portion of the Mckay plot is the adsorption stage attributed to pore diffusion. Hence the overall rate of exchange process comprises of two components, one corresponding to the rapid film diffusion and a relatively slower one corresponding to the linear portion of the McKay plots i.e. pore diffusion. This observation further confirms the observations of the 'F vs. time' curves that indicate the rapid initial uptake is followed by a slower uptake of the adsorbate with increasing time. This is in conformity with the earlier observations of temperature effect on exchange diffusion coefficient (1). Several workers (6, 10-13, 15, 21) have reported intra-particle diffusion as one of the (and not the sole) rate limiting steps in their study of kinetics of adsorption of dyes on various adsorbents. Vasanth Kumar et al (25), in their decolorization study onto carbonized agro-based waste found that the predominant adsorption-contributing component was external mass transfer followed by intra-particle diffusion. Kannan et al (7) have observed similar results for the removal of mercury (II) ions by adsorption onto different activated carbons.

The plots of diffusion rate constant 'B' against $1/r^2$ (Fig. 4.34) are linear for all the three dyes. The linearity of the dependence also confirms that diffusion within the particle is the step that controls the sorption rate.

As the system tends towards equilibrium the film diffusion becomes less significant and the particle diffusion process dominates rapidly. It may be argued that the effective diffusion coefficient, D_i, here is mainly comprised of two components, which is due to the simultaneous diffusion of the ingoing dye ions through the pores of different mesh widths and different electric fields along the diffusion path. The diffusion within the pores of wider mesh-sizes and weaker retarding forces of electrostatic interaction (particularly at the surface of the sorbent) accounts for the faster component of D_i and that within the pores of narrower mesh sizes and stronger retarding forces accounts for the slower one. As the temperature increases, the contribution of the faster component of D_i increases (Fig. 4.35). It is because of the increasing mobility of ingoing species at higher temperature that overcomes to some extent, the influence of retarding forces acting on the diffusing adsorbate ions causing D_i to increase with the temperature. Although D_i values are low, they are high enough to cause adsorbate transport from bulk to solid phase. Mohan et al (16) reported D_i values of 2.35×10^{-14} m^2/s to 5.98×10^{-14} m^2/s for adsorption of Cu(II) and 2.30×10^{-14} m^2/s to 4.56×10^{-14} m^2/s for adsorption of Cd(II) on lignin at various temperatures. A perusal of data in Table 4.8 indicates that the values of effective diffusion coefficient increase with increase in temperature in all the cases. Diffusion coefficient values of all the three cationic dyes follow the same trend in which these get adsorbed on lignin: D_i value is higher for Toluidine blue in comparison to Neutral red and that of Crystal violet is less than that of both. This difference may be due to the spatial geometry of their molecular structure. The planar triangular orientation of Crystal violet, in comparison to the linear structure of Toluidine blue and Neutral red may be causing greater hindrance in its mobility within the pores of the adsorbent. Swelam et al (22) reported that the value of D_i increases with the increase in temperature and are higher for exchange in medium with higher dielectric constant.

The log D_i vs. 1/ T plots drawn for the sorption of these dyes (Fig. 4.35) is linear in nature. This permits use of the Arrhenius equation (Equation 5) for the determination of D_o and E_a from the intercepts and slopes respectively of the linear plots. D_o values are further used to evaluate the entropy of activation ΔS^* (Equation 6) for the sorption of cations of Crystal violet, Neutral red and Toluidine blue on lignin.

The values of D_o, E_a and ΔS^* for the three dyes are listed in Table 4.9. It can be seen from this table that the higher activation energy value is associated with the higher value of pre-exponential constant D_o for all the dyes. Similar behavior was observed by Mohan et al (16) who reported D_o values of 3.77×10^{-10} and 4.35×10^{-4} m^2/s for Cu(II) and Cd(II) respectively and E_a values of 9.84 [Cu (II)] and 24.33 [Cd (II)] kJ/mole.

A comparison for the sorption of cations may be worthwhile in determining the efficiency of the sorbent under study, for the removal of dyes. The values of effective diffusion coefficient observed in the present case are comparable to those observed for the exchange or sorption of surfactants Cetyl pyridinium chloride (CPC) and Cetyl trimethyl ammonium tribromide (CTAB) on lignin (2) (of the order of 10^{-9} $cm^2.sec^{-1}$) and to those observed for the exchange of sorption of Rb^+ and Cs^+ on chromium ferroyanide gel (as cited in (2): of the order of $10^{-8}cm^2.\ sec^{-1}$). However, obtained values are higher as compared to those observed for the self-diffusion for alkali metal ions in analcite and for the exchange sorption of complex cations of Co(III) on chromium ferrocyanide gel (as cited in (2): of the order of 10^{-14} to 10^{-20} and 10^{-12} cm^2 sec^{-1}. respectively). The observed values are also comparable to those observed for the exchange of Rb^+ and Cs^+ on the H^+ form of tin and zirconium antimonate (as cited in (2): of the order of 10^{-9} to 10^{-10} cm^2/ sec.).

It can be concluded from Table 4.9 that the values of activation energy (E_a) for Crystal violet and Toluidine blue are similar and much higher in comparison to that of Neutral red. For Crystal violet, this may be attributed to its trigonal spatial geometry that causes more steric hindrance to its mobility through the pores of sorbent material and thus needs more energy to undergo diffusion. Swelam et al (22) reported that the E_a of the exchanging cations in pure aqueous solutions is usually low as compared with the values obtained in presence of increasing proportions of glycerol and attributed it to the low swelling of the resin particles in presence of organic solvents.

The entropy of activation ΔS^* value has been calculated to be negative for the sorption of Neutral red and positive for the sorption of Toluidine blue and Crystal violet. The negative value of ΔS^* has been taken as indicative of a comparatively higher degree of mobility and the lack of an orientational effect which the ingoing ion exerts upon the water environment. Further the negative value of ΔS^* also indicates that as a result of sorption of Neutral red no significant change occurs in the internal structure of the sorbent material. Several workers have observed a negative value of ΔS^* for various sorption systems. Swelam et al observed ΔS^* values in the range of –72.28 to

-91.43 J.$^0K^{-1}mol^{-1}$. Gupta (2) has observed ΔS* value as negative for the sorption of CP^+ ion and positive for the sorption of relatively bigger CTA^+ ion. Positive values of ΔS* have also been observed by several workers (2, 5, 9) and also by Patel and Sudhakar (4) for the adsorption of anionic dyes on aluminum treated corn cobs powder, by Karthikeyan et al (8) for the adsorption of fluoride on activated alumina and Zn (II) onto chitosans, by Namasivayam et al (18) for the adsorption of nitrate on activated carbon from coir pith and by Mohan et al (16) for the adsorption of Cu (II) and Cd (II) on kraft lignin.

Positive value of ΔS* shows increased randomness at the solid–solution interface during the adsorption of dye and indicate an increase in degree of freedom during adsorption. As such a positive ΔS* value observed for Crystal violet and Toluidine blue sorption indicates a greater disorder produced in the structure of the adsorbent as a result of the uptake of the dye cation .The adsorbed water molecules, which are displaced by the adsorbate species, gain more translation entropy than is lost by adsorbate molecules, thus allowing the prevalence of randomness in the system (19). The positive value associated with Crystal violet and Toluidine blue would thus be a reflection of their respective restricted diffusion path and large orientation effect upon the water environment.

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Table 4.1 : Adsorption kinetics data for the residual concentration of Crystal violet at 800 mg/l and pH 7.0 at various temperatures.

Temperature					
25^0C		30^0C		35^0C	
Time (min)	RC (mg/l)	Time (min)	RC (mg/l)	Time (min)	RC (mg/l)
20	710	20	666	35	768
60	675	40	616	60	399
90	647.5	60	579	80	364
120	633.5	80	546	100	318
150	620	110	495	130	296
170	600	140	450	160	252
220	584.5	200	396	190	222
250	570	260	348.5	225	142

Table 4.2 : Adsorption kinetics data for the residual concentration of Crystal violet at 800 mg/l and pH 7.0 at various particle sizes of lignin.

Particle size (mesh size)					
40-100		100-200		Above 200	
Time (min)	RC (mg/l)	Time (min)	RC (mg/l)	Time (min)	RC (mg/l)
30	682	20	666	10	550
60	610.5	40	616	20	450
90	605	60	579	30	369
120	594	80	546	60	244
150	561	110	495	90	180
180	514.5	140	450	120	112
210	468	200	396	180	58
270	456	260	348.5	270	31.5

Table 4.3 : Adsorption kinetics data for the residual concentration of Neutral red at 800 mg/l and pH 3.7 at various temperatures.

Temperature					
30^{0}C		35^{0}C		40^{0}C	
Time (min)	RC (mg/l)	Time (min)	RC (mg/l)	Time (min)	RC (mg/l)
20	630	20	554	30	476
40	564	40	462	45	420
60	488	65	393	60	364
90	430	85	355	75	318
120	384	105	308	105	257
150	336	140	247	130	204
180	296	170	211	160	162
220	260	200	180.6	190	131
260	236	280	127.4	250	81

Table 4.4 : Adsorption kinetics data for the residual concentration of Neutral red at 800 mg/l and pH 3.7 at various particle sizes of lignin.

Particle size (mesh size)					
40-100		100-200		Above 200	
Time (min)	RC (mg/l)	Time (min)	RC (mg/l)	Time (min)	RC (mg/l)
30	618	20	630	30	477
40	588	40	564	45	417
60	552	60	488	60	375
80	516	90	430	90	315
100	486	120	384	120	264
130	456	150	336	150	226
190	408	180	296	180	189
230	369	220	260	220	153
260	354	260	236	260	135

Table 4.5 : Adsorption kinetics data for the residual concentration of Toluidine blue at 750 mg/l and pH 7.0 at various temperatures.

Temperature					
30^0C		35^0C		40^0C	
Time (min)	RC (mg/l)	Time (min)	RC (mg/l)	Time (min)	RC (mg/l)
30	470	20	502.5	20	274
45	440	40	286.2	40	150
60	368	65	180.3	60	107.5
75	342	85	148.8	80	65
90	315	105	99	105	37.5
105	290	140	56.5	125	24
150	225	200	23.9	160	18.2
250	144	280	14	250	11

Table 4.6 : Adsorption kinetics data for the residual concentration of Toluidine blue at 750 mg/l and pH 7.0 at various particle sizes of lignin.

Particle size (mesh size)					
40-100		100-200		Above 200	
Time (min)	RC (mg/l)	Time (min)	RC (mg/l)	Time (min)	RC (mg/l)
30	580	30	470	30	288
50	516	45	440	45	217.5
70	472	60	368	60	147
90	448	75	342	90	104
110	412	90	315	120	66
130	384	105	290	150	39.6
150	376	150	225	180	28
180	332	250	144	210	22
230	303	---	---	---	---

Table 4.7 : Adsorption kinetics data for the residual concentration of Crystal violet, Neutral red and Toluidine blue at pH 5.0.

Crystal violet (800 mg/l)		Neutral red (800 mg/l)		Toluidine blue (750 mg/l)	
Time (min)	RC (mg/l)	Time (min)	RC (mg/l)	Time (min)	RC (mg/l)
30	765	20	592.8	30	510
60	748	40	496.6	45	468
95	715	60	450.6	60	405
140	672	90	370	75	378
170	666	120	318	90	350
200	660	150	267	105	325
245	642	180	237	120	300
275	630	220	222	150	275
---	---	240	208	180	240

Table 4.8 : Values of Effective diffusion coefficient (D_i).

Temp. (^0C)	$D_i * 10^9$ ($cm^2.sec^{-1}$)		
	Crystal violet	Neutral red	Toluidine blue
25	3.0	---	---
30	8.4	11.1	15.6
35	16.5	17.4	44.4
40	---	21.9	62.7

Table 4.9 : Values of D_0 and thermodynamic parameters.

Dye	D_0 ($cm^2.sec^{-1}$)	E_a (Kcal.mole^{-1})	ΔS^* (cal.deg^{-1}mole^{-1})
Crystal violet	$1.3*10^{14}$	30.8	39.0
Neutral red	22.9	12.9	-19.3
Toluidine blue	$2.8 * 10^{14}$	30.8	40.6

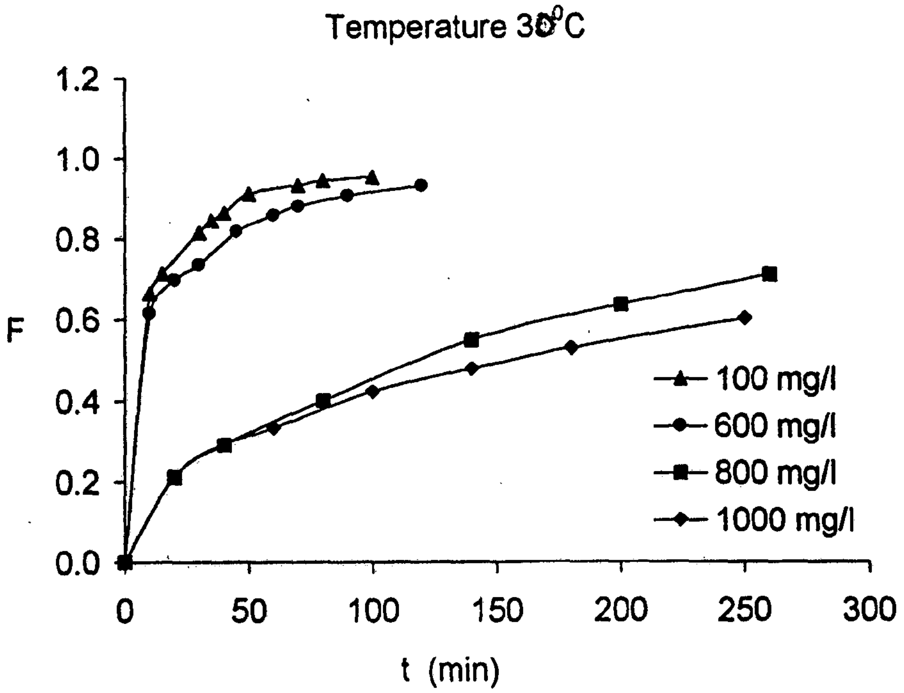

Fig. 4.1 : Plots of F vs.t at various concentrations of Crystal violet.

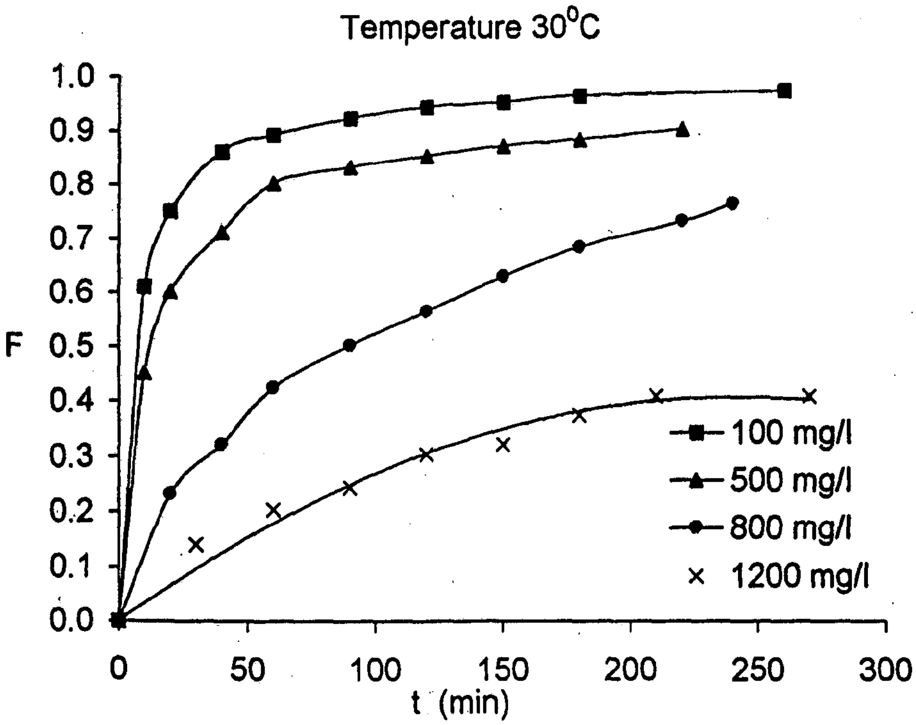

Fig. 4. 2 : Plots of F vs.t at various concentrations of Neutral red.

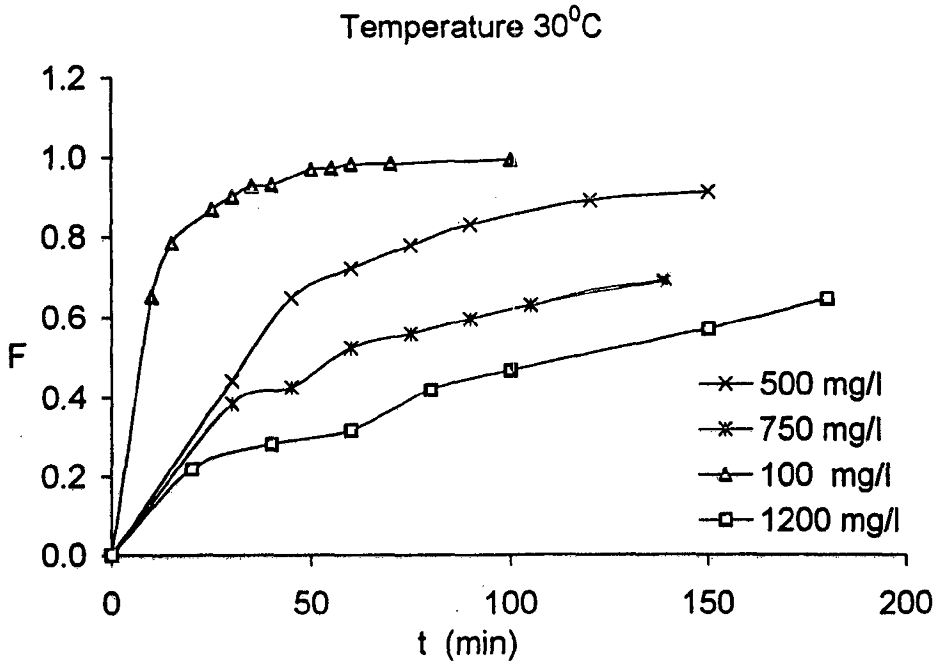

Fig. 4.3 : Plots of F vs. t a various concentrations of Toluidine blue .

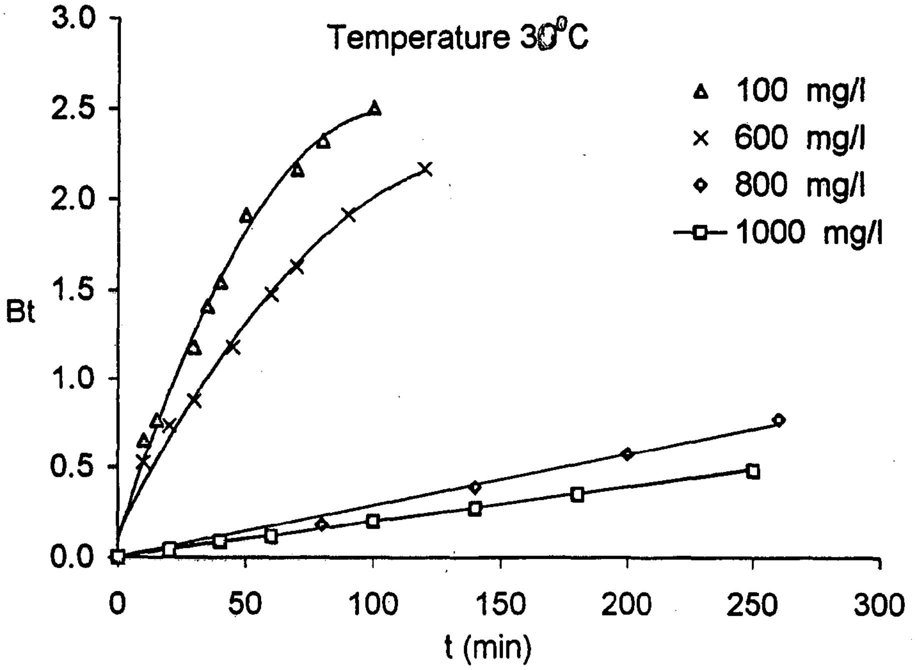

Fig. 4.4 : Plots of Bt vs. t at various concentrations of Crystal violet .

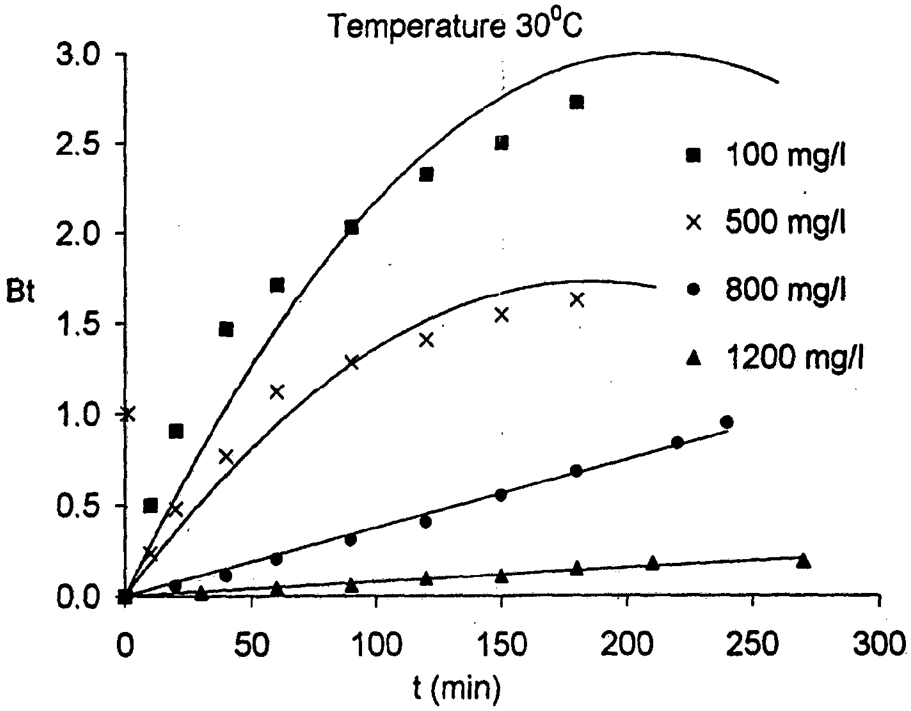

Fig. 4.5 : Plots of Bt vs. t at various concentrations of Neutral red .

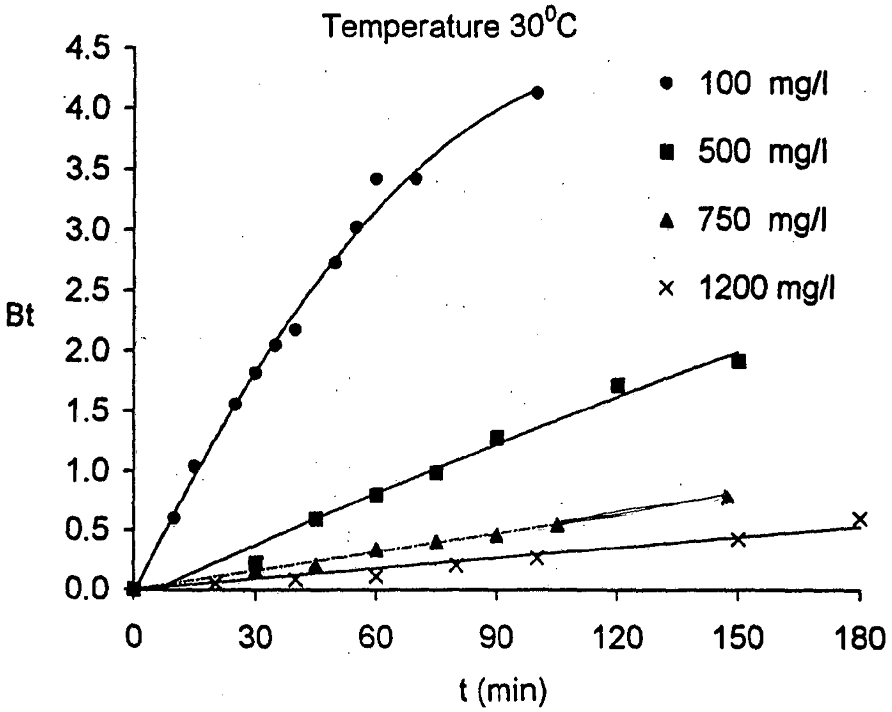

Fig. 4.6 : Plots of Bt vs. t at various concentrations of Toluidine blue.

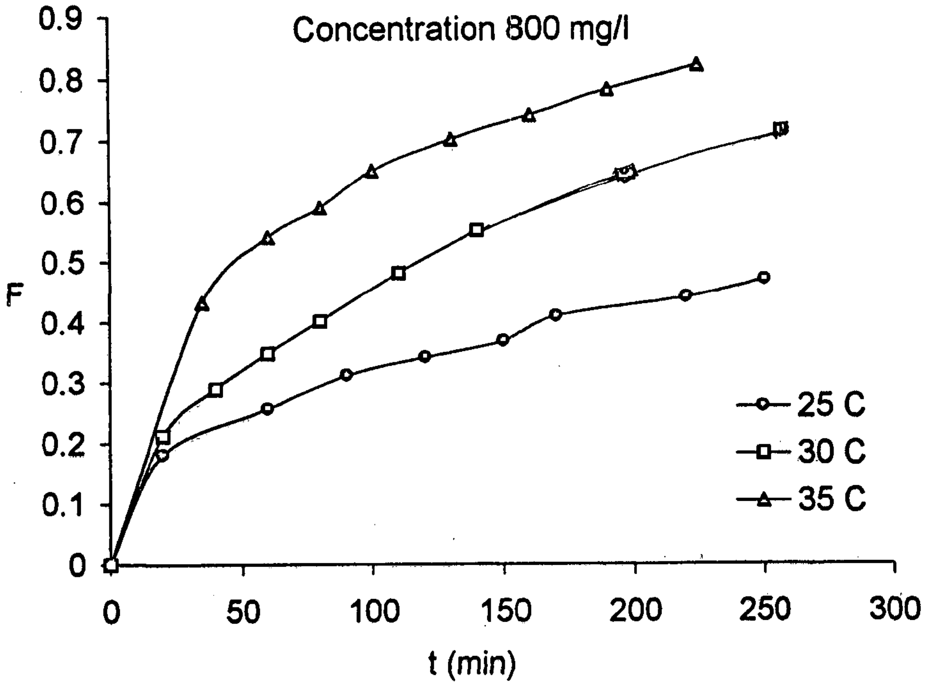

Fig. 4.7 : Plots of F vs. t at various temperatures of Crystal violet.

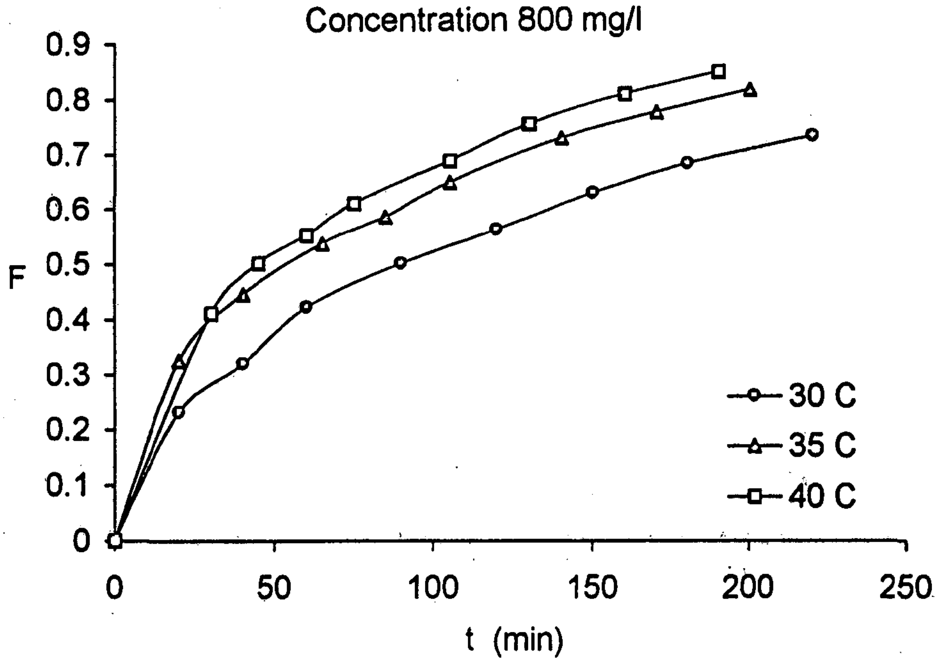

Fig. 4.8 : Plots of F vs. t at various temperatures of Neutral red.

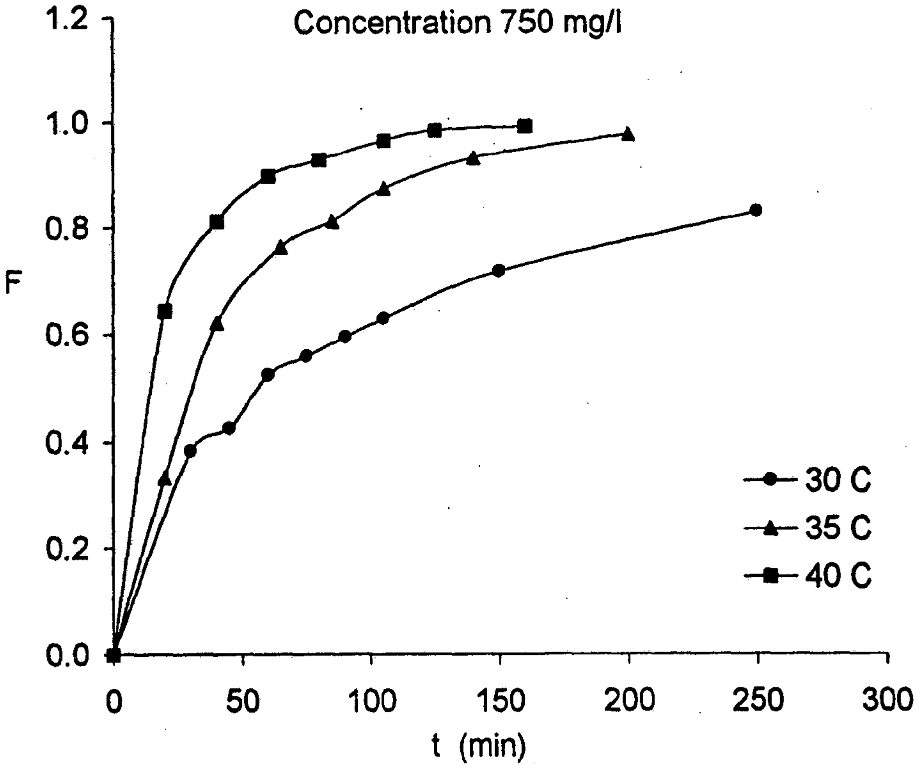

Fig. 4.9 : Plots of F vs. t at various temperatures of Toluidine blue.

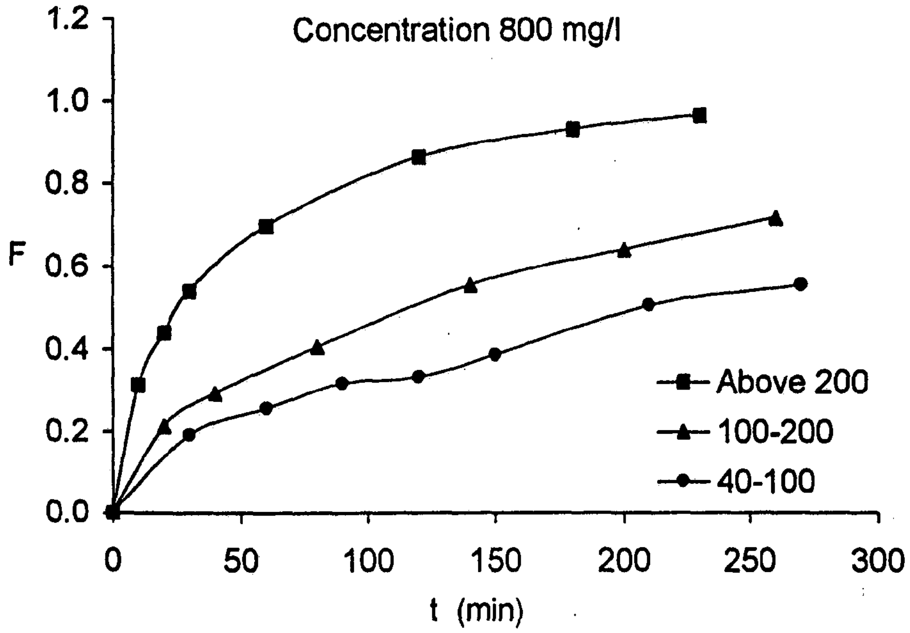

Fig. 4.10 : Plots of F vs. t at various particle sizes of lignin for Crystal violet .

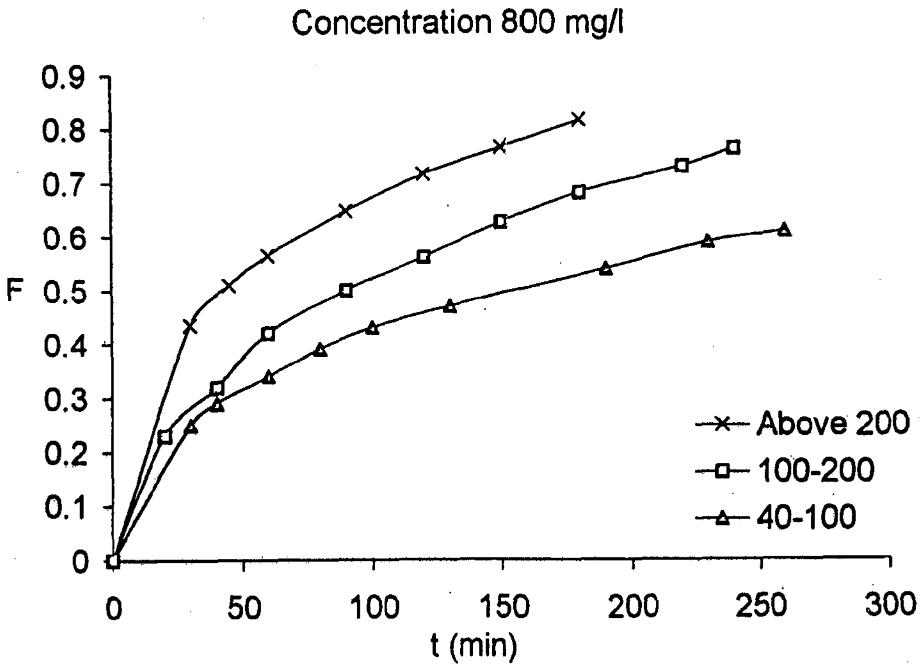

Fig. 4.11 : Plots of F vs. t at various particle sizes of lignin for Neutral red.

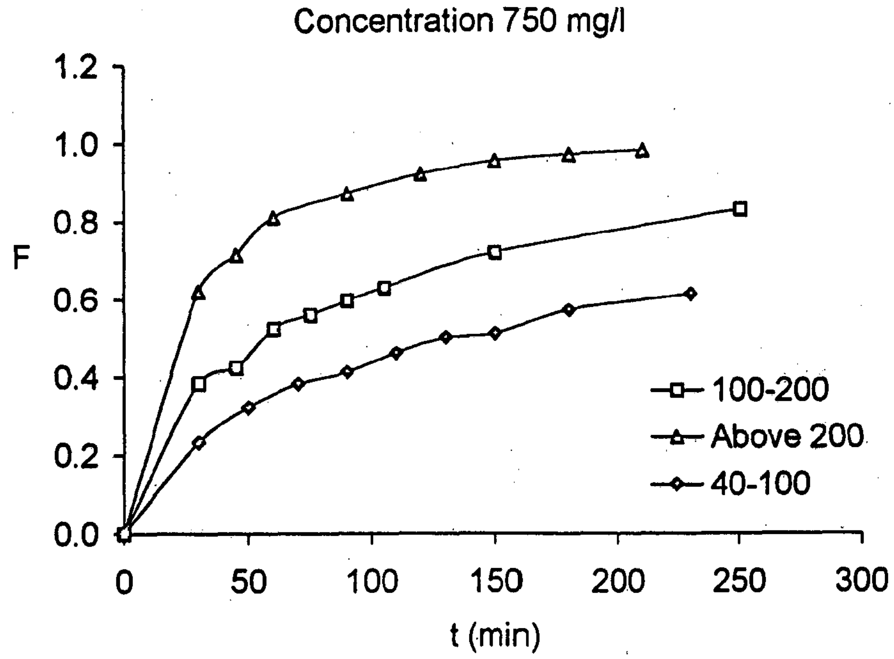

Fig. 4.12 : Plots of F vs. t at various particle sizes of lignin for Toluidine blue.

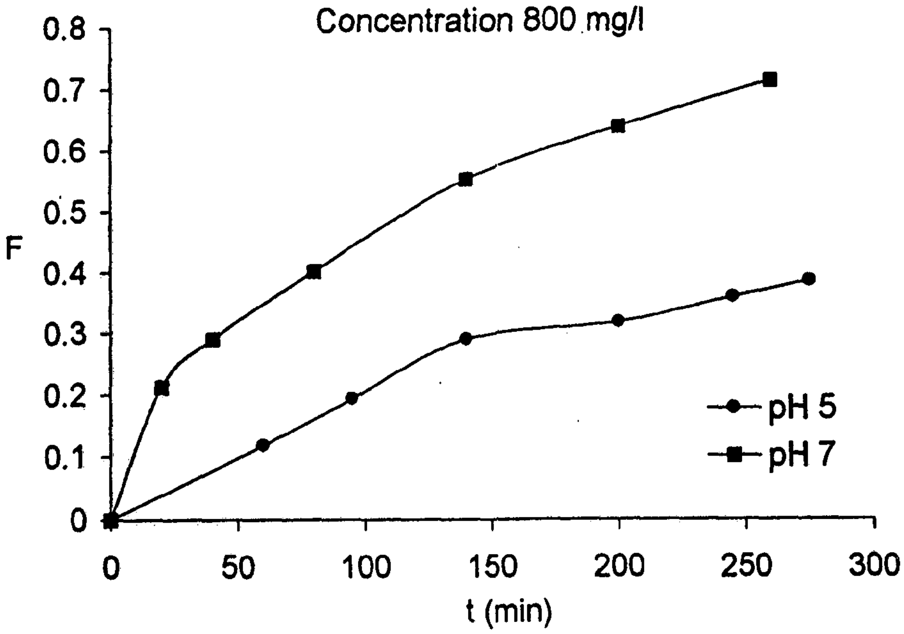

Fig. 4.13 : Plots of F vs. t at various pH of Crystal violet.

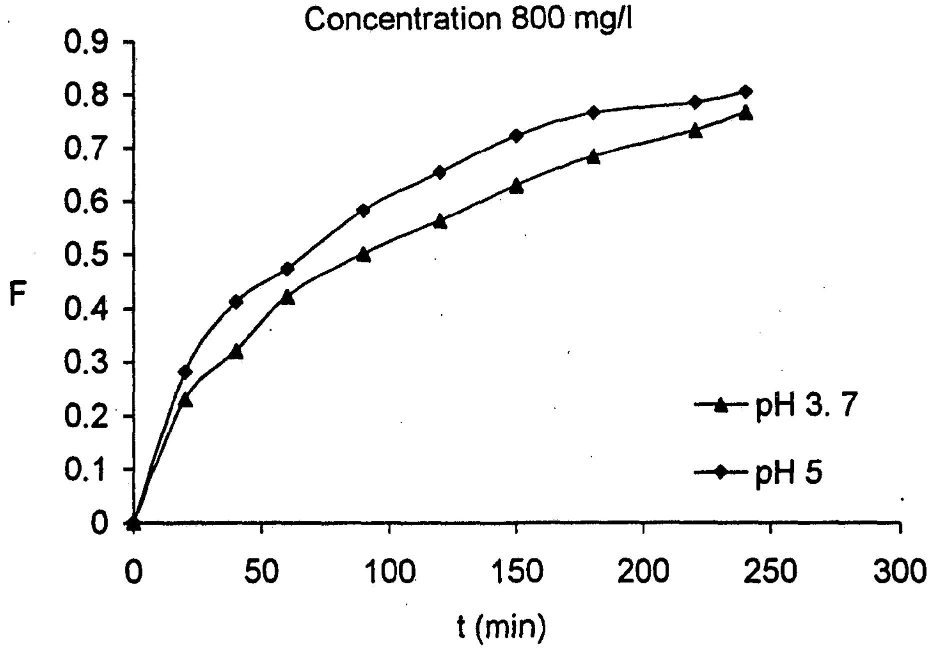

Fig. 4.14 : Plots of F vs. t at various pH of Neutral red.

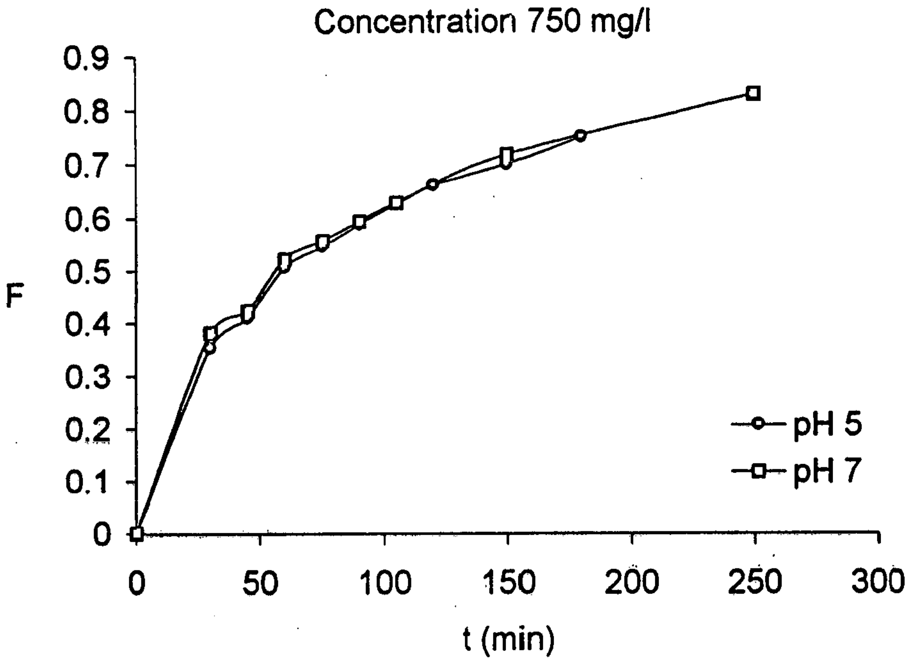

Fig. 4.15 : Plots of F vs.t at various pH of Toluidine blue.

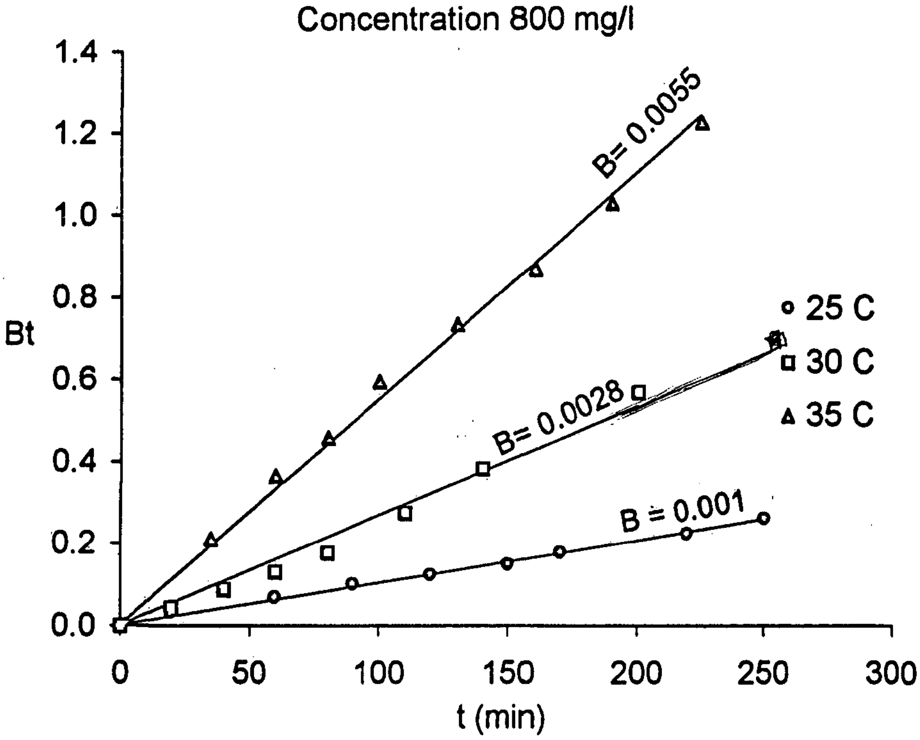

Fig. 4.16 : Plots of Bt vs. t at various temperatures of Crystal violet.

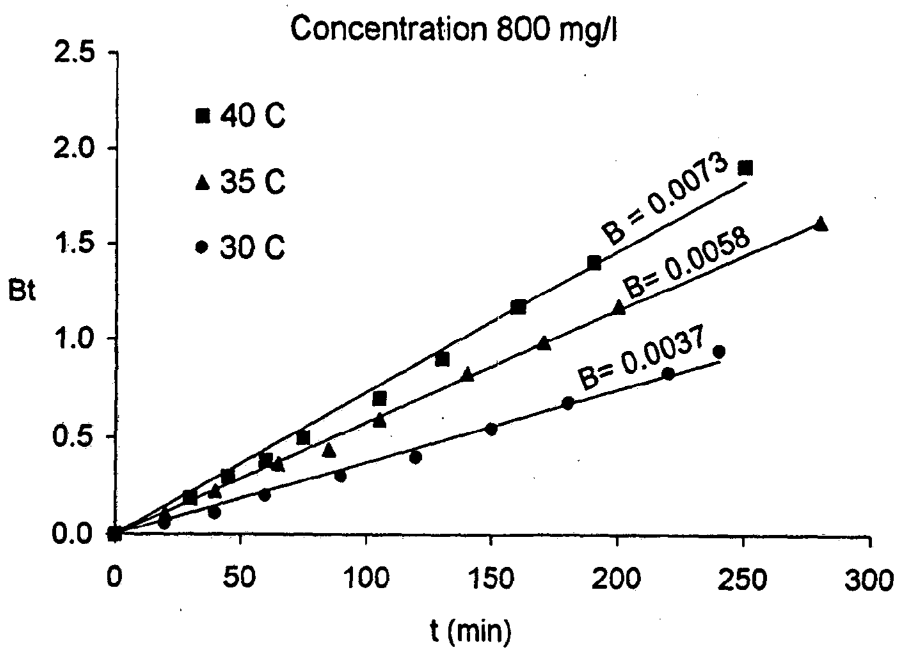

Fig. 4.17 : Plots of Bt vs.t at various temperatures of Neutral red.

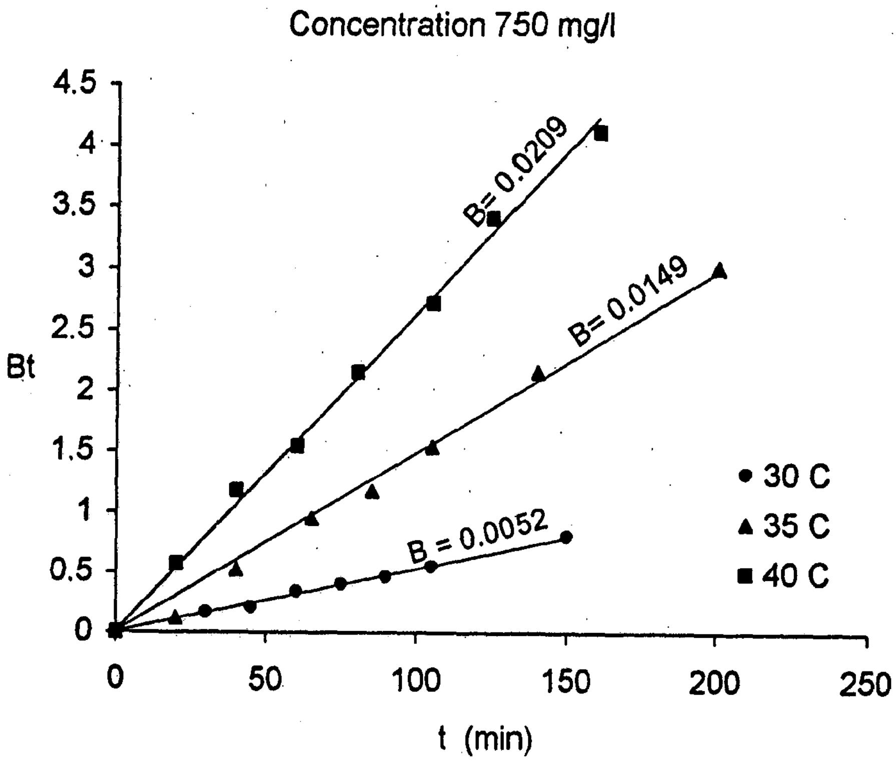

Fig. 4.18 : Plots of Bt vs.t at various temperatures of Toluidine blue.

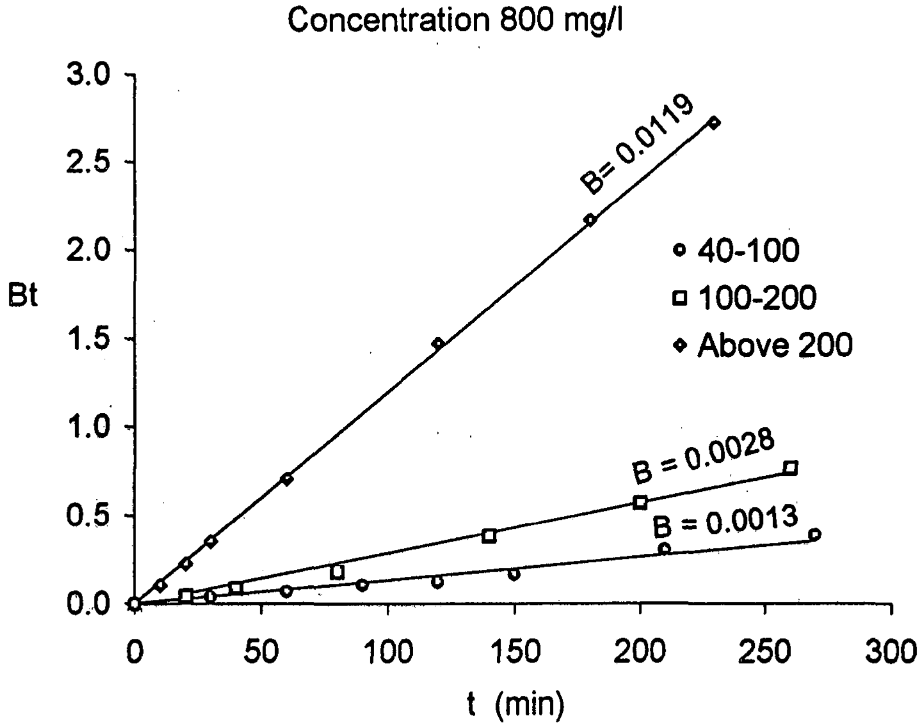

Fig. 4.19 : Plots of Bt vs. t at various particle sizes of lignin for Crystal violet.

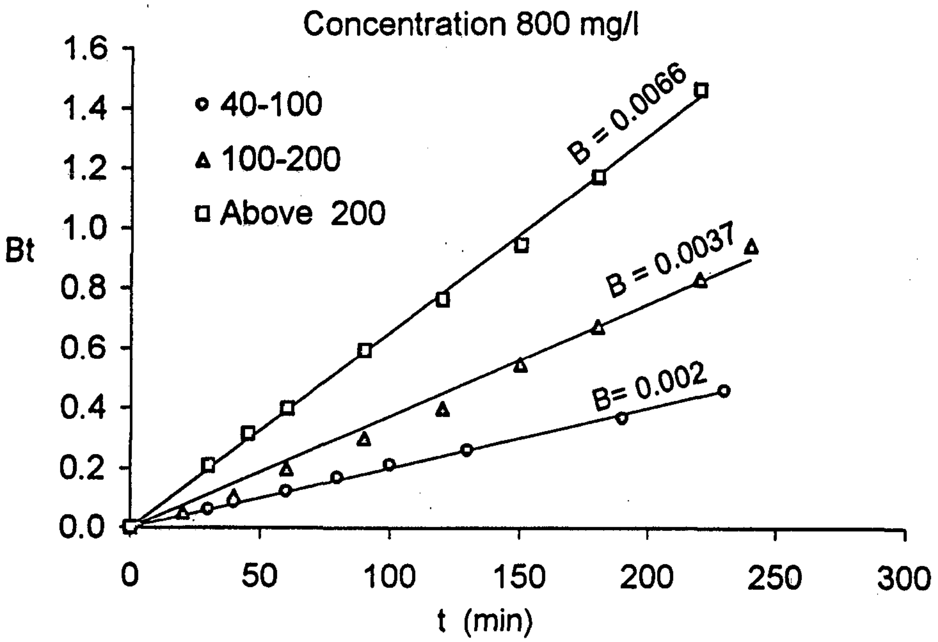

Fig. 4.20 : Plots of Bt vs. t at various particle sizes of lignin for Neutral red.

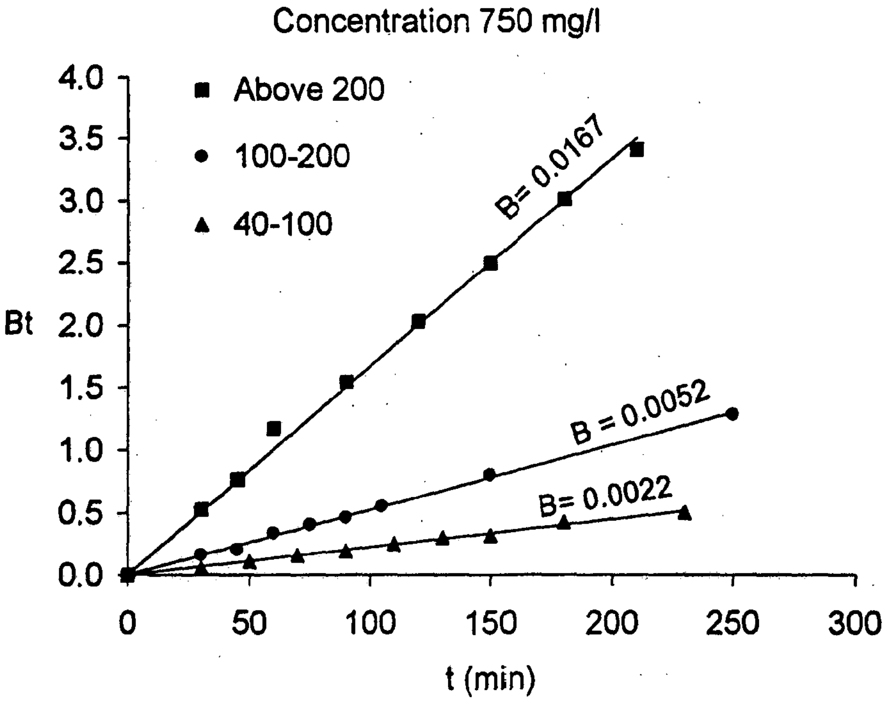

Fig. 4.21 : Plots of Bt vs. t at different particle sizes of lignin for Toluidine blue.

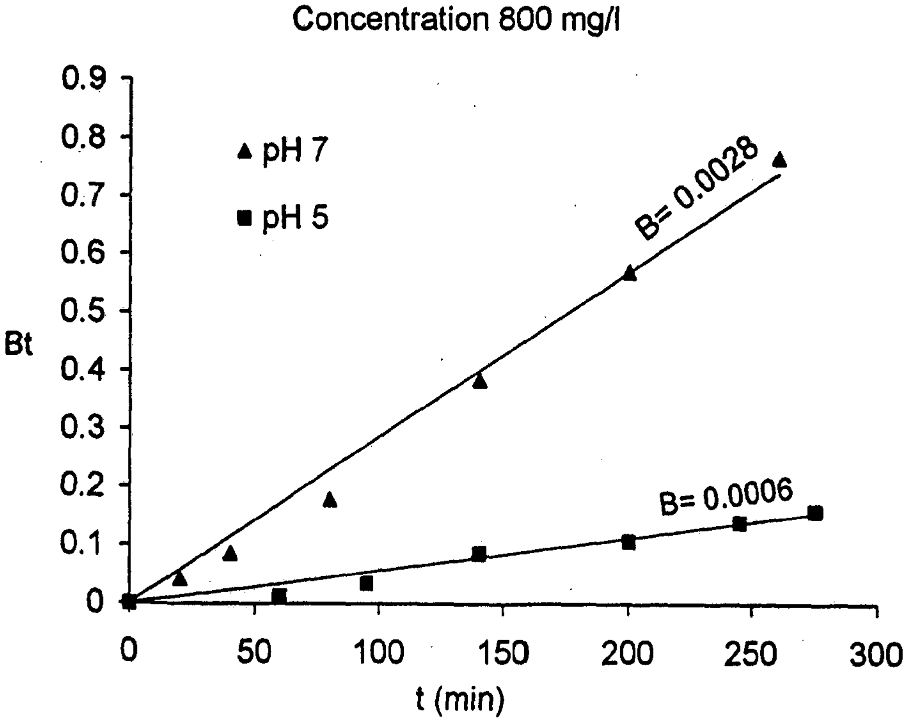

Fig. 4.22 : Plots of Bt vs. t at various pH of Crystal violet.

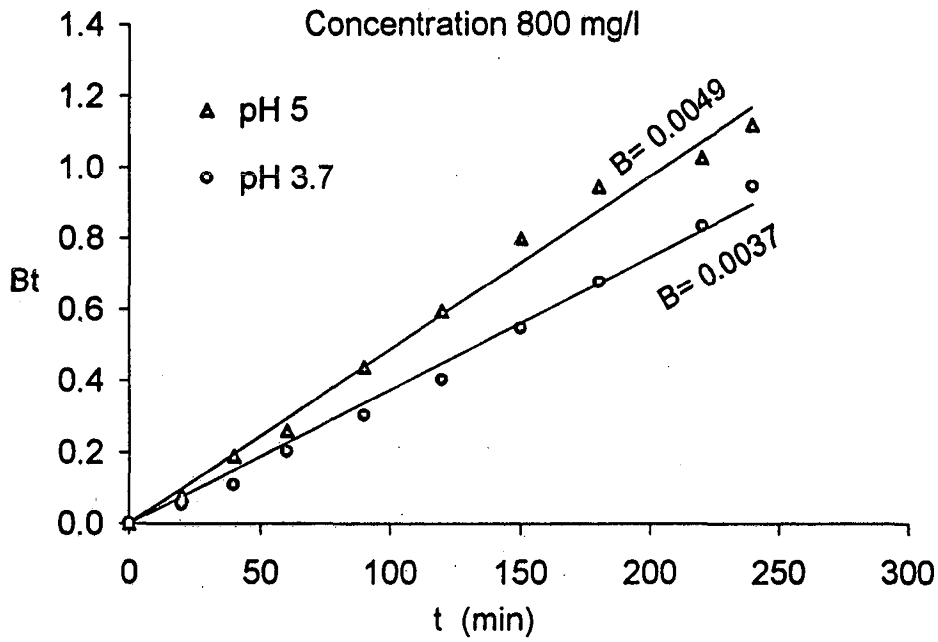

Fig. 4.23 : Plots of Bt vs. t at various pH of Neutral red.

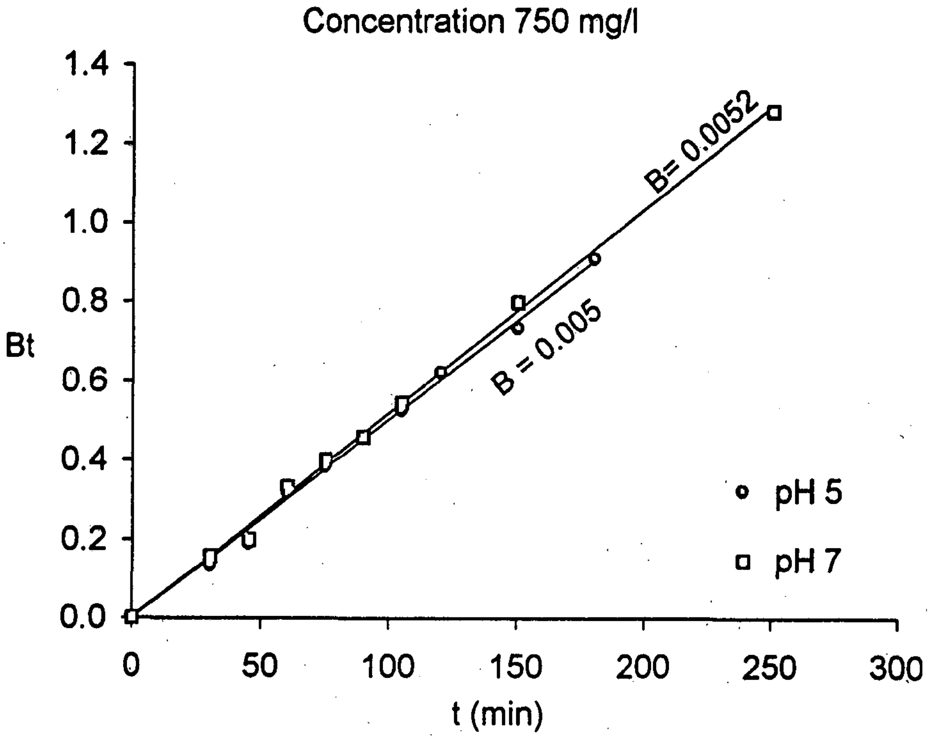

Fig. 4.24 : Plots of Bt vs. t at various pH of Toluidine blue.

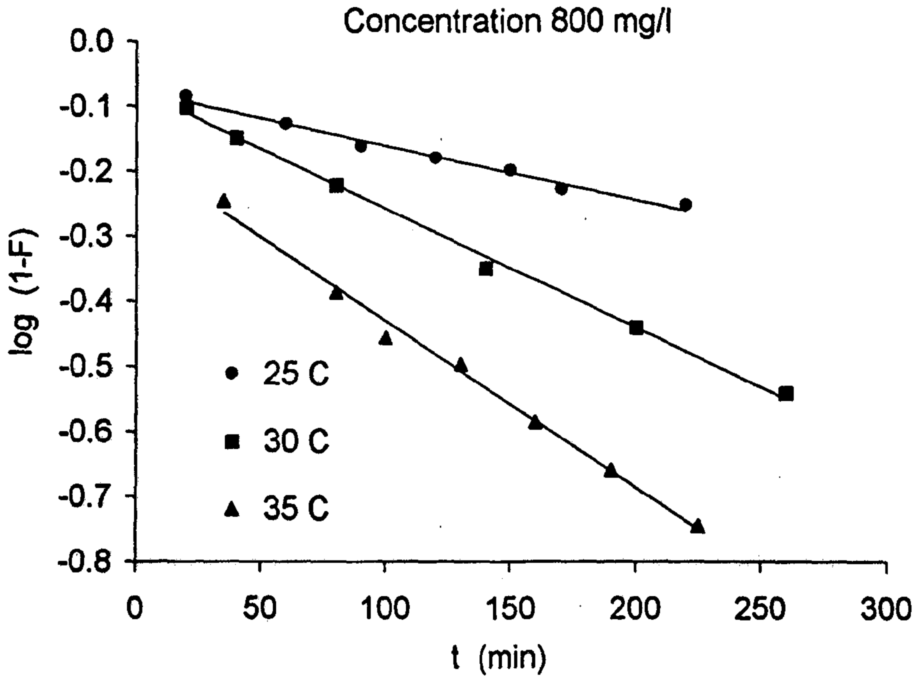

Fig. 4.25 : Mckay plot at various temperatures of Crystal violet.

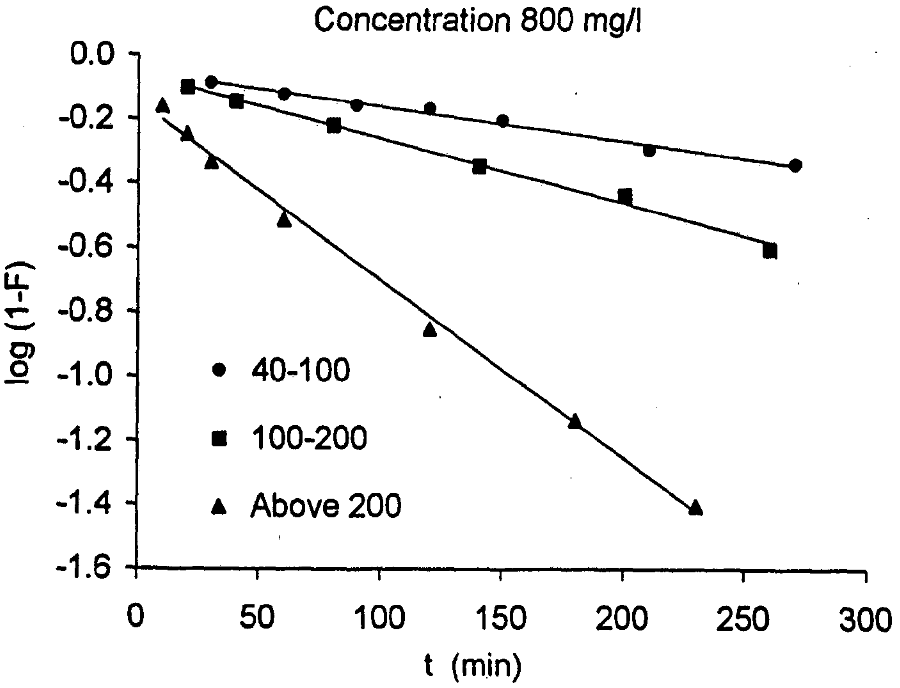

Fig. 4.26 : Mckay plots at various particle sizes of lignin for Crystal violet.

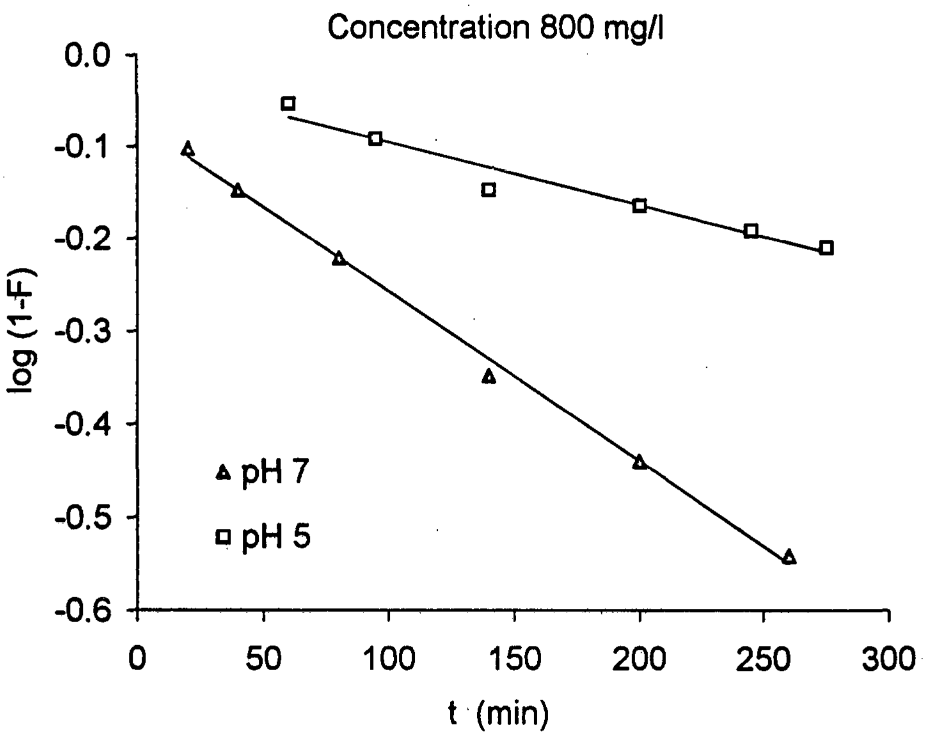

Fig. 4.27 : Mckay plots at various pH of Crystal violet.

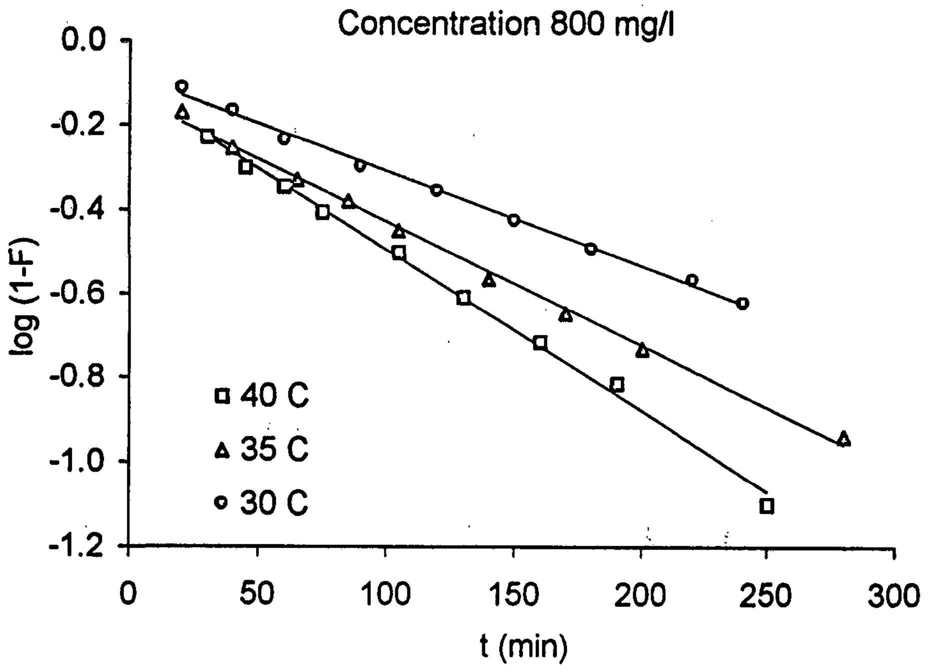

Fig. 4.28 : Mckay plots at various temperatures of Neutral red.

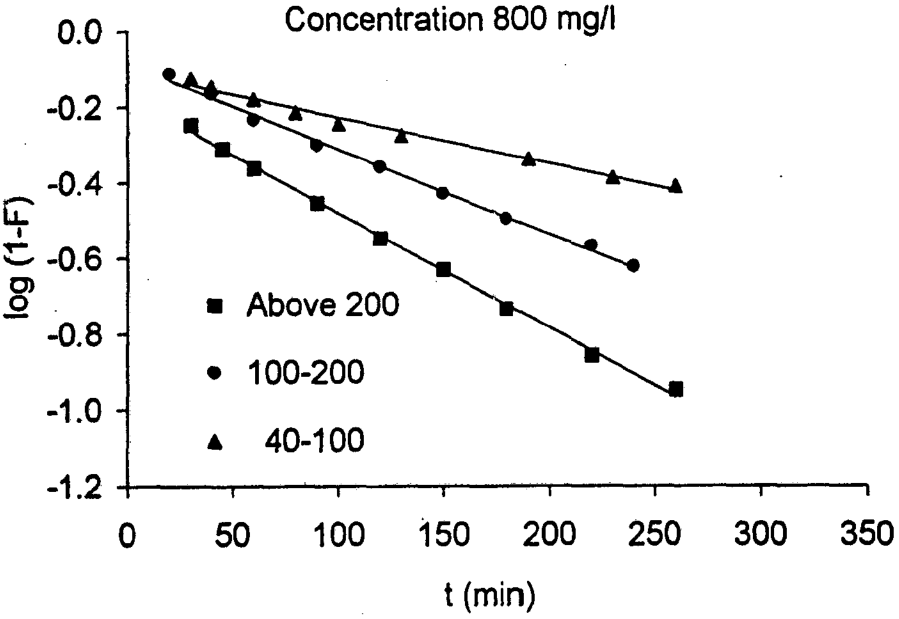

Fig. 4.29 : Mckay plots at various particle sizes of lignin for Neutral red.

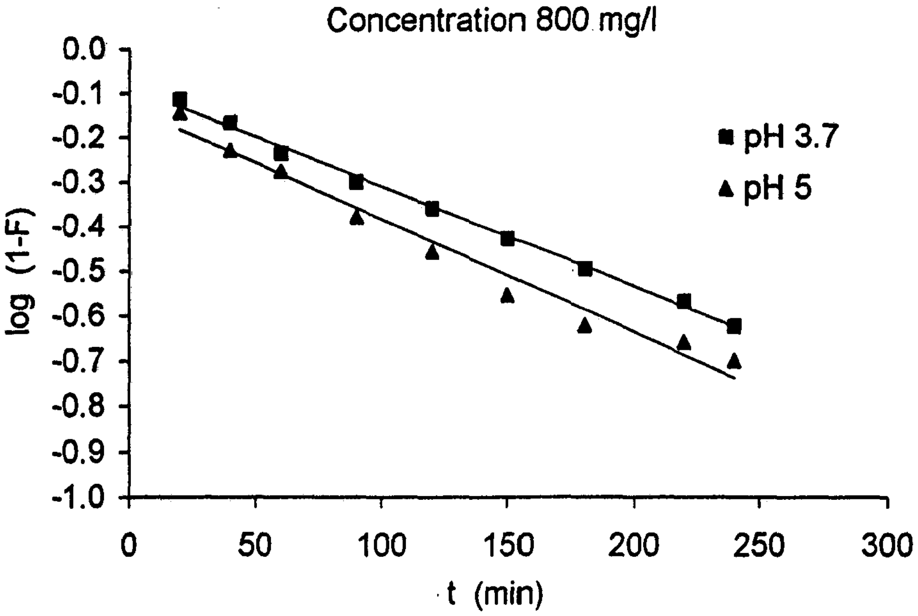

Fig. 4.30 : Mckay plots at various pH of Neutral red.

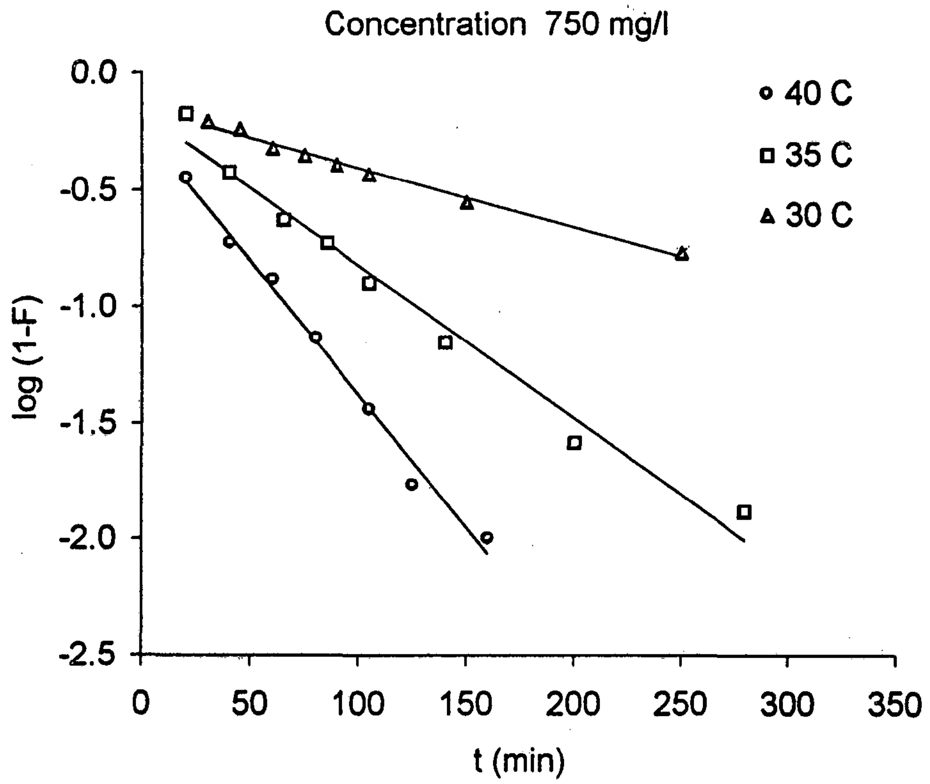

Fig. 4.31 : Mckay plots at various temperatures of Toluidine blue.

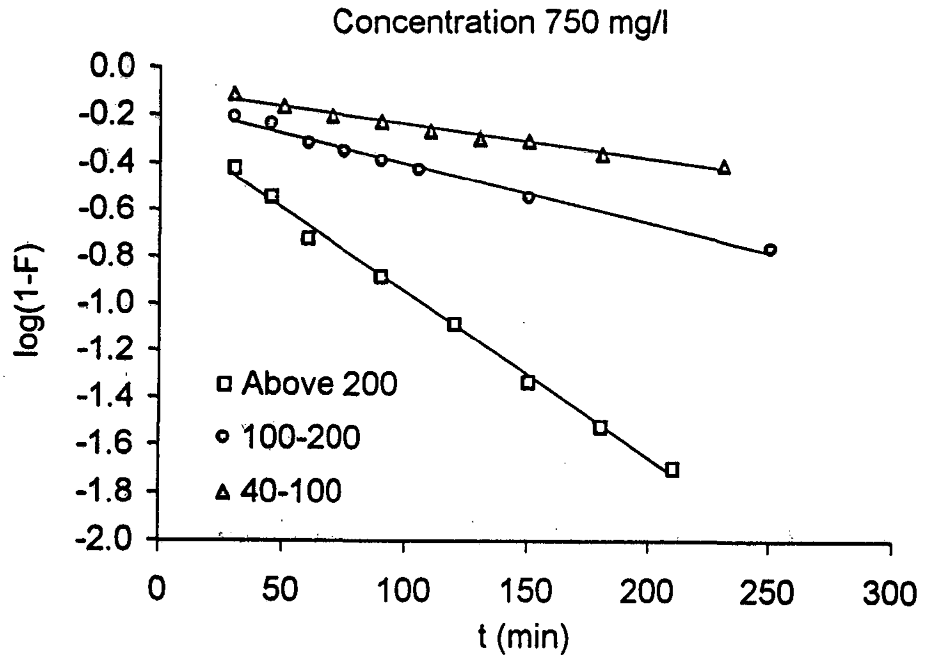

Fig. 4.32 : Mckay plots at various particle-sizes of lignin for Toluidine blue.

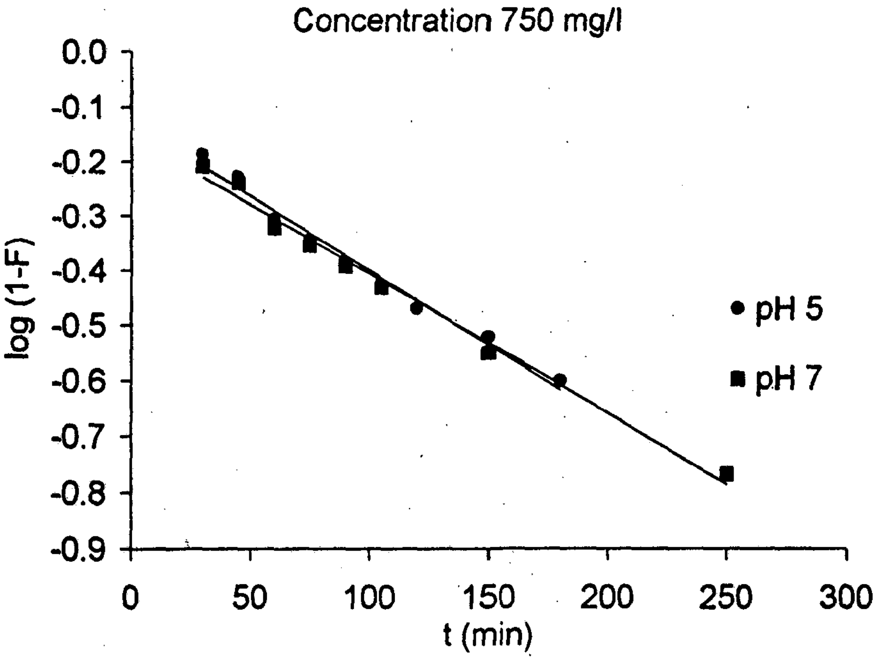

Fig. 4.33 : Mckay plots at various pH of Toluidine blue.

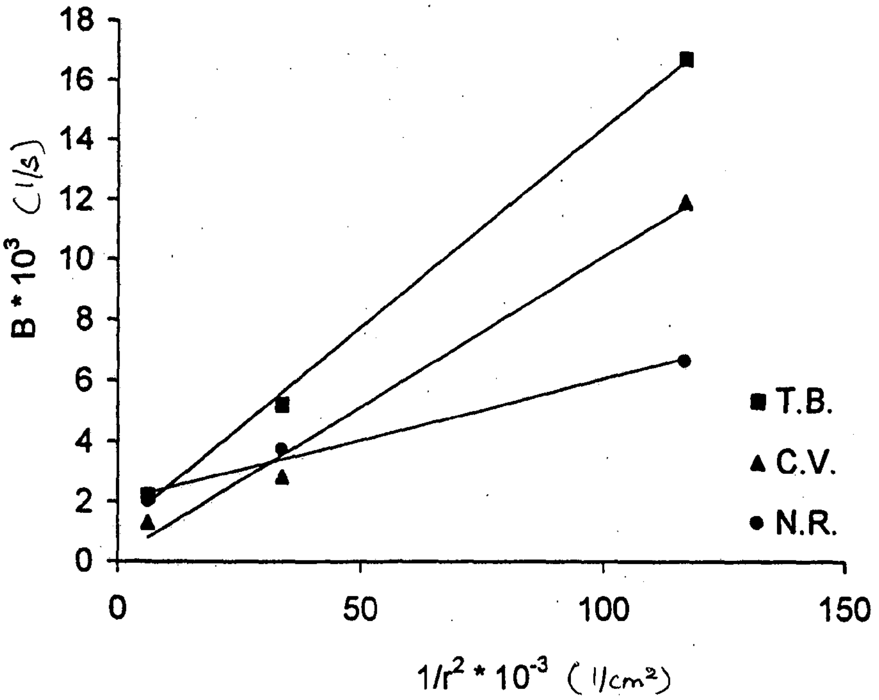

Fig. 4.34 : Plots of B vs.1/r^2 for Crystal violet, Neutral red and Toluidine blue.

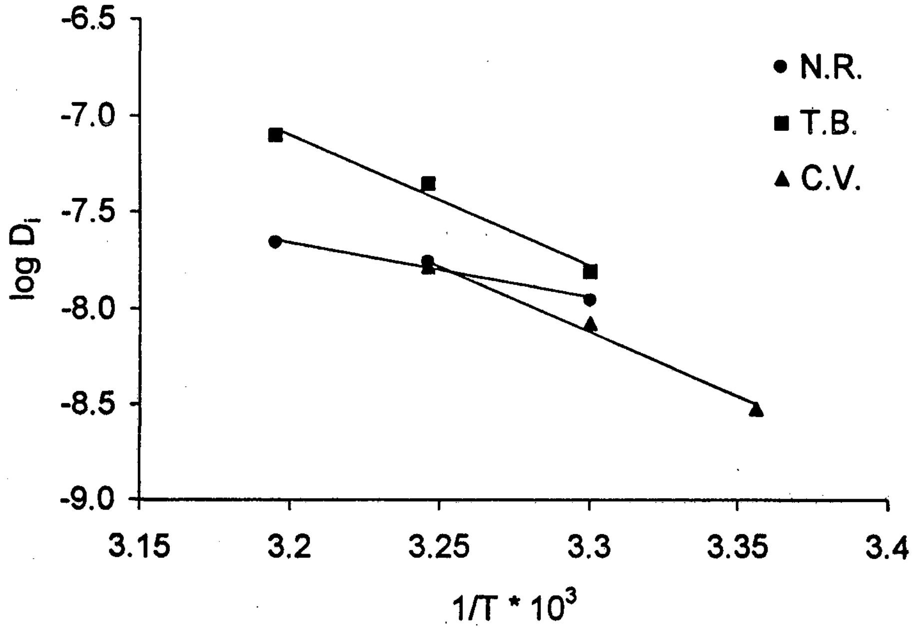

Fig. 4.35 : Plot of log D_i vs. 1/T for Crystal violet, Neutral red and Toluidine blue.

CHAPTER - 5

CONCLUSIONS

Large quantities of low cost adsorbents will increasingly be needed for water treatment. Lignins are inexpensive; most are non-toxic and available in large quantities as a waste. The present study demonstrates that lignin obtained from Sarkanda black liquor serves as a value-added adsorbent (over its fuel value) for the removal of dyes from water and waste water. The raw material employed for the preparation of substrate is widely available and inexpensive. The method of its preparation is very simple and the production cost is low. Its cationic-dye binding capacity is appreciably high under suitable experimental conditions, with comparable efficiency.

Following conclusions are drawn from the study:

5.1 ADSORPTION STUDIES

1. Results show that lignin can act as a good sorbent for the removal of Crystal violet, Neutral red and Toluidine blue dyes. It is possible to remove 22% of a 2 g/l solution of Crystal violet in 4 hours, 35% of a 4.5 g/l solution of Neutral red in 8 hours and 95% of a 1 g/l solution of Toluidine blue in 2 hours from their respective 1 litre solutions using 10 g of crude lignin in each case.
2. Adsorption of the dyes increases with increase in temperature, pH and decrease in particle size of lignin.

3. Adsorption data of Crystal violet, Neutral red and Toluidine blue dyes fits into the Langmuir model at various temperatures, pH, and particle sizes of lignin.
4. The adsorption data also fits into B.E.T. equation for Toluidine blue and Neutral red (only at low concentration).
5. Desorption of the dyes with different electrolytes is very low (0.3–1.4%). Thus, regeneration of the adsorbent is not feasible.

5.2 KINETIC STUDIES

1. Adsorption kinetics data suggests that the rate-determining step is diffusion through the particle. Sorption process is film diffusion controlled at lower concentrations and is both, partially particle-diffusion and partially film-diffusion controlled, at higher dye concentration i.e. at and above 800 mg/l for Crystal violet and Neutral red and at and above 750 mg/l for Toluidine blue.
2. Diffusion coefficient values of all the three cationic dyes follow the order in which these are adsorbed on lignin: D_i value is higher for Toluidine blue in comparison to Neutral red and that of Crystal violet is less than that of both.
3. The values of activation energy (E_a) for Crystal violet and Toluidine blue are similar and much higher in comparison to that of Neutral red.
4. The entropy of activation ΔS^* value is negative for Neutral red and positive for Toluidine blue and Crystal violet.

From the above laboratory investigations it can be concluded that the biosorbent, Sarkanda lignin has good potential as an adsorbent for the removal of Crystal violet, Neutral red and Toluidine blue from water / waste water. It acts as a good scavenger of basic dyestuff and the capacity of this compound is quite significant for all the dyes.