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THE ADSORPTION OF DISPERSE DYES ON POWDERED ACTIVATED CARBON

by

Seymour G. Hall

A Dissertation Submitted to
the Faculty of the Graduate School at
The University of North Carolina at Greensboro
in Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

Greensboro
1975

Approved by

Victor S. Salvin
Dissertation Adviser

APPROVAL PAGE

This dissertation has been approved by the following committee of the Faculty of the Graduate School at the University of North Carolina at Greensboro.

Dissertation Adviser Victor S. Salvin

Committee Members Eunice M. Deemer

Pauline E. Keeney

Mildred B. Johnson

Bert A. Goldman

Arthur L. [illegible]

March 3, 1975
Date of Acceptance by Committee

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The experiments undertaken in order to understand the variables which affect the adsorption characteristics of the dye-carbon system represented the major experimental part of the investigation. The disperse dyes and activated carbon were studied with and without the auxiliary chemicals normally present in a dye effluent such as surfactants, alkaline salts, acids, and bases. To gain some understanding of the dye-carbon adsorption system, six experimental areas were investigated. These were: The effects of concentration, the effects of pH, the effects of nonionic surfactants, the effects of anionic surfactants, the effects of alkaline salts, and the effects of an alkaline salt in the presence of a nonionic surfactant.

Three different classes of disperse dye were chosen for these experiments: Disperse Yellow 54, a quinonapthalone type used for batch dyeing polyester and polyester blends, Disperse Red 73, a monazo type commonly used in thermosol dyeing of polyester fabrics, and Disperse Blue 7, an anthraquinone type widely accepted by the carpet industry for dyeing nylon carpets. The powdered activated carbon used in this study was Hydrodarco C, a lignite type developed specifically for water treatment by ICI Incorporated, Wilmington, Delaware.

Linear Langmuir adsorption isotherms were obtained for Disperse Blue 7, Disperse Red 73 and Disperse Yellow 54 at concentration levels of 200 ppm, 100 ppm and 50 ppm. Hydrodarco C additions of 0 ppm, 100 ppm, 300 ppm, 500 ppm, 1,000 ppm and 5,000 ppm were made at each dye

concentration level. The dye-carbon mixtures were stirred for 24 hours at 22°C ± 2°C to assure equilibrium and filtered through a Gelman Type A glass fiber filter. The samples were then scanned from 700 mu to 400 mu on a Coleman-Hitachi Model 124 Spectrophotometer to determine the maximum absorbance values. The adsorption isotherms were calculated from the absorbance data.

The adsorption characteristics of the dye-carbon system were sensitive to changes in pH. As the pH of the system was increased a greater amount of dyestuff was removed from solution. This was contrary to what normally happened in adsorption reactions and was due to the tendency of the dyestuffs to agglomerate as the pH of the system increased.

The addition of Triton X-100, a nonionic surfactant greatly reduced the adsorptive capacity of the activated carbon. The surfactant solubilized the dyestuff and altered the equilibrium of the dye-carbon system by competing with the disperse dyestuff for the available surface sites on the activated carbon. Low concentrations of Tergitol Anionic 4, an anionic surfactant had little or no effect on the capacity of the activated carbon to remove disperse dyestuffs from solution.

The effects of an alkaline salt such as tetrasodium pyrophosphate (TSPP) on the dye-carbon system was explained by the fact that the disperse dyestuffs tended to agglomerate with increasing pH and were more easily removed by filtration. The data from the TSPP experiments were similar to the data concerning the effects of increased pH on the dye-carbon system. However, the combined effects of TSPP and Tergitol Anionic 4 produced entirely different results and very little dye was adsorbed from solution.

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Chapter I

INTRODUCTION

The textile industry discharges hundreds of millions of gallons of water each year and a sizeable portion of this water has been termed "ecologically unacceptable" largely due to the coloring matter in the discharged effluent. During the past few decades the textile industry has attempted to combat its water pollution problems by directing its efforts toward developing highly sophisticated biological waste treatment plants. Little, if any, attention has been given to the non or partially biodegradable refractory compounds which pass through a biological treatment system relatively unchanged.

The advent of manmade fibers such as the polyolfins, polyamides, polyesters, cellulose acetate, and acrylics created a need for a new class of dyestuffs. Besides being hydrophobic these synthetic fibers, except for some polyamides and acrylics, were practically void of chemical reaction sites. Therefore, the previously known dyestuffs which were used for natural fibers were of little practical value and a new class of dyestuffs had to be developed. This led to the introduction of disperse dyestuffs which brought forth a range of colors which could satisfactorily dye the synthetics and opened up a new era in textile manufacturing. Although the disperse dyes had satisfactory fastness properties they were only slightly soluble in water and non-responsive to biological waste treatment processes.

The problem is compounded by the fact that the amount of disperse dyestuff is increasing rapidly. This is largely due to the consumer acceptance of polyester fabrics. In a recent report from the U. S. Tariff Commission the amount of disperse dyestuff produced domestically in 1973 was over 50 million pounds, which represented a 25.4% increase over the 1972 production (1).

One potential method for treating textile wastes which contain large amounts of disperse dyes is with powdered activated carbon. The decolorization properties of activated carbon are well known and have been utilized for years by many industries to remove colored organic compounds from solution. The physical characteristics of the carbon such as its large surface area and broad range of physical and chemical properties make it an excellent absorbent for colored organic compounds and, theoretically, capable of removing disperse dyes from solution. The literature contains numerous examples of activated carbon being utilized by the textile industry for color removal. However, the majority of uses are concerned with the removal of water soluble dyes, such as the direct colors. The few references dealing with the removal of disperse dyes have been negative. As recently as 1974 in a technical article dealing with the decolorization of textile mill waste, Woldman stated, "Personal communication with suppliers of activated carbon indicated, based on their experience, that disperse dyes cannot be removed by activated carbon" (2).

The fact that the literature reports disperse dyes cannot be removed by activated carbon is a point of serious concern. It cannot be explained based on what is already known about the chemical/ physical characteristics of the dyestuff or what has been reported concerning the chemical/physical properties of activated carbon. A dye/carbon adsorption system is extraordinarily complex involving a multitude of interactions affected by such things as: pH, concentration, temperature, time, nature of solute, nature of solvent, activation conditions of the carbon and other variables. In order to gain some understanding as to why dispersed dyes are or are not removed from solution by activated carbon the dye/carbon system requires analysis and study, component by component. Research of this nature has the capability of providing valuable information to the textile manufacturer, dyestuff producer, environmental technologist, and carbon producer. The objectives of the study were:

1. To determine the adsorption characteristics of disperse dyes on powdered activated carbon

2. To determine the effects of auxiliary substances which are normally present in a dye effluent such as surfactants, alkaline salt and pH on the adsorption equilibrium of the dye/carbon system

3. To determine the effects of dye concentration on the adsorption equilibrium of the dye/carbon system

4. To compare the principles of disperse dye sorption on hydrophobic fibers with the adsorption of the dye on powdered activated carbon

The following hypotheses appeared logical and were investigated in this study:

1. The adsorption of disperse dyes on powdered activated carbon follows physical adsorption laws and can be characterized by adsorption isotherms.

2. Deviations from the physical adsorption laws occur as the dye/carbon system becomes more complex by the addition of surfactants, alkaline salt, acids, and bases.

3. Disperse dyes exist in equilibrium with the powdered activated carbon.

4. The presence of surfactants change the equilibrium characteristics of the dye/carbon system in relation to the solubilization effect of the surfactant with the dye.

5. The structural characteristics of the dye influence the adsorption equilibrium of the dye on the carbon.

Chapter II

LITERATURE SURVEY

Pollution Legislation

Although pollution laws were in existence prior to 1900, it was not until 1972 when the Water Quality Act was passed that Congress began giving some serious attention to the increasing evidence of water pollution. The Water Quality Act of 1972 is the most comprehensive and restrictive federal legislation that has been passed on water pollution control. As stated in Declaration of Goals and Policy, "the objective of this Act is to restore and maintain the chemical, physical and biological integrity of the Nation's waters." Three major policies which directly affect industrial discharges are set forth in Title I of the Act:

> 1. It is the national goal to eliminate the discharge of pollutants into navigable waters by 1985.
> 2. It is the national goal to achieve interim water quality goals by July 1, 1983, to protect and promulgate fish, shellfish and wildlife.
> 3. It is the national policy to prohibit the discharge of toxic pollutants in toxic amounts.

It is mandatory that industry comply with the intent of these policies and implement them in accordance with the best technology which is currently available. Lund and Koski constantly underscore this point (3, 4).

Textile Industry Profile

There are approximately 800 textile mills in the United States and nearly 80% are operated by small, independent, and frequently, family controlled companies. The industry can be divided into three broad categories which typify the products produced. These are Cotton Goods, Wool Goods, and Synthetics (5).

Textile manufacturing utilizes approximately 1% of all water consumed for manufacturing in the United States. This represents 12 trillion gallons of water per year. Although this is not a large amount of water when compared with other industries, it is significant for the following reasons:

1. The industry remains concentrated in the Southeastern United States dependent on inland water supplies which are variable due to climatic and seasonal changes.

2. The industry is located predominantly in small cities and towns and represents a major source of industrial pollution to these areas.

3. The industry is characterized as consisting of numerous dyeing and finishing operations handling a diverse range of textile products.

Color Contamination

The significant advances made toward improving the fastness properties of textile dyestuffs has not been without some limitations. Many of the physical and chemical properties of the dyes which made the dyes resistant to fading and wash-down also made the dyes resistant to common waste treatment systems. The technology which created a better dye, created a dye which was difficult to remove from a textile waste stream.

As pointed out by Nemerow (6), the removal of dyestuff from textile waste streams is important because the dye contamination is visible. Although the coloration of a water supply may not be harmful it is objectionable to anyone using the water or to viewers of a stream receiving textile dye effluent. The approximate quantity of dye waste produced per year may be estimated based on the fact that approximately two-thirds of the dyes consumed annually in the United States are used by the textile industry to dye fibers, yarns and fabrics. In 1973 the total domestic production of dyes amounted to 284 million pounds, an increase of 21 million pounds from 1972 (7), therefore, the textile industry utilized approximately 190 million pounds of dye in 1973. Since approximately 10% of the dye ends up ultimately in the waste stream, 19 million pounds of dye must be treated prior to being discharged. This estimate clearly indicates that dye removal is an industry-wide problem.

In the textile industry the most widely used method for treating dye waste is in most instances biological (8, 9). Whether or not this method is the most effective for color removal is debatable and the basis for much needed research. The most optimistic color removal efficiencies to date range from 20 to 80% for carefully controlled biological treatment systems. Alspaugh (10) has stated that the more sophisticated the biological treatment system, the more color removed.

However, it has recently been pointed out by Flege (11) that although biological treatment methods can degrade selected dyestuffs the degradation products may be more toxic than the dye themselves. Other physical and chemical methods reported in the literature for color removal include such processes as: wet air oxidation (12), foam fractionation (13), chemical coagulation (14, 15, 16, 17, 18), high energy irradiation (19), activated carbon columns (20, 21, 22, 23, 24), activated silica (25), and the use of hyperfiltration (26).

Uses of Carbon for Color Removal

Activated carbons are currently used in the chemical and pharmaceutical industries as a purification procedure. Carbons are also utilized to clean contaminated liquids so that the reuse of electroplating solutions, dry cleaning solvents and cooking oils has been made possible. The ability of activated carbon to remove odor and taste from potable water has created new markets for carbon by many water treatment plants throughout the United States. Undoubtedly there are hundreds of uses for activated carbon, many of which are propriatary steps in a manufacturing process and are difficult to ascertain. It is known that uses for activated carbon extend all the way from the selective adsorption of penicillin in the pharmaceuticals industry to the purification of distilled liquors in the beverage industry (27).

An exceptional characteristic of activated carbon is its ability to decolorize solutions containing colored organic compounds. For this reason the textile industry has been experimenting with activated carbon for dye removal. One of the first industrial installations for removing color from textile dye waste with activated carbon was at Hollytex Mills, a carpet producer in Southhampton, Pennsylvania (28). At the 1974 American Association of Textile Chemists and Colorists Technical Conference in New Orleans, the Hanes Corporation announced plans for the installation of a carbon adsorption system for removing textile waste at their Winston-Salem plant (29). Recently, J. M. MacCrum (30) and E. L. Shunney (31) have considered the use of activated carbon for textile dye waste. However, some published work has indicated possible limitations with activated carbon. Alspaugh (32) reported erratic removal rates with activated carbon blaming colloidal solids as a possible cause. Rodman (33) could only remove 10% or less of disperse dye with activated carbon while high removal efficiencies were obtained for such water soluble dyes as Reactive Red 3, Direct Blue 106 and Acid Black 26A. In a recent article, Woldman (34) further substantiated the belief that disperse dyestuffs cannot be removed by activated carbon. Woldman arrived at this conclusion not through analytical experimentation but through personal contacts with several carbon producers.

Carbon Characterization

Activated carbons are characterized as having a large surface area which may be as large as 2,500 m^2/g (35). The large surface area is the result of thermal oxidation in an atmosphere of air, carbon dioxide, or steam at temperatures approaching 1,000^{o}C. As combustion proceeds, a preferential oxidation occurs causing a highly irregular surface which is responsible for the unusually large surface area of the carbon. This irregular surface can be classified into two systems, depending upon the size of the resulting irregularity (pore). The large pores are termed macropores and completely permeate each particle acting as large access ways for diffusion. Although the existence of these macropores is a well known characteristic of activated carbon, the macropores contribute very little to the adsorptive properties of the carbon. It is the macropores which have diameters in the order of 10-100 angstrom units that are extremely important for color removal (36). In an article on the steriochemistry of disperse dyes, Merian (37) stated that a typical disperse dye of molecular weight 300 is similar in size to a disk with a 12 angstrom average diameter which is within the range necessary for adsorption on activated carbon to take place. The type of adsorption which takes place due to the relative size of the adsorbed molecules and the pore size of the activated carbon is termed physical adsorption and usually results in the formation of relatively weak dispersion forces or of van der Waals forces between the carbon and the adsorbed molecules. However, according to Snoeyink and Weber (38), any interpretation of the adsorptive behavior of activated carbon based solely on the pore characteristics and distribution obviously is incomplete. This is substantiated by Wolf (39) who has shown the existence of inorganic salts on the activated carbon surface and has indicated that interactions could result between the inorganic salt and the molecules being adsorbed. Possible interactions between the inorganic salts on the activated carbon and the dye or other solution constituents include complex formation, ion-pair formation, precipitation reactions and oxidation-reduction reactions.

Oxygen constitutes 2 to 25% by weight of the activated carbon depending upon the temperature and method of activation. Studies by Harker (40) showed that the oxygen interacts with unpaired electrons to form oxygen complexes on the surface of the activated carbon. An interpretation of this phenomenon was proposed by Barrer (41), who found that the oxygen complexes alter the adsorption characteristics of the carbon which tends to increase the polarity of the surface. It is therefore reasonable to assume that compounds which have a natural tendency to form free energy bonds with oxygen, such as disperse dyes, probably adsorb more easily on oxygenated surfaces than on non-oxygenated surfaces. The surface of activated carbon is extremely complex and difficult to characterize, and both physical and chemical forces are responsible for the adsorption of organic molecules on the activated carbon surface.

Similarities Between Activated Carbon and Synthetic Fibers

It should be noted that there are certain morphological similarities between the structure of activated carbon and synthetic fibers. Carbon has the ability to remove color molecules from solution in much the same way as a fiber removes dye molecules from solution during the dyeing process. The adsorption of dyes onto fibers has been studied by Turner and Chanin (42) and can be explained by using adsorption isotherms and studying reaction rates. Hassler (43) has shown that the adsorption characteristics of activated carbon with organic dye molecules can also be explained in terms of adsorption isotherms and rates of reaction.

The porosity or pore structure of activated carbon is a unique property of this material. As mentioned previously, at least two systems of pores of distinctly different sizes exist in every activated carbon particle. Textile fibers can also be considered to have a porous type of surface somewhat dependent upon the crystalline and non-crystalline regions of the fiber. Since the micropores of activated carbon are similar in size to some of the molecules which are responsible for color in various materials, the pore dimensions assume considerable importance. A carbon with very fine pores will adsorb small molecules while leaving the larger ones behind in solution. Or, on the other hand, a carbon with large pores will preferentially remove large molecules while the smaller ones are displaced by the more adsorbable larger species (44). This phenomenon has also been observed in textile fibers. Permeability measurements by Morton (45) indicated that dry viscose is impermeable to molecules of ethanol, benzene, and picric acid, although these substances readily passed through wet viscose. The pores in the dry state must, therefore, be less than five angstroms while in the water-swollen state the average diameter was calculated to be approximately 20 to 30 angstroms.

Much of the adsorptive action of activated carbon can be explained in terms of attractive forces exerted by the enormous surface area within each particle (46). These forces are similar to the short range dispersion forces found in textile fibers known as van der Waals forces. Van der Waals forces, although relatively weak when compared to chemical bond energies, are responsible for many properties of textile fibers and activated carbon. In textile fibers and activated carbon both chemical and physical adsorption can occur simultaneously. Furthermore, a classification of physical or chemical may be arbitrary depending upon which properties are measured. Active carbons and textile fibers are not pure substances and contain measurable quantities of chemically bound oxygen, hydrogen and other elements. The presence of chemical groups such as carboxyl, carbonyl, methyl, methoxy or hydroxyl attached to the surface accounts for the small amount of ion exchange effect and hydrogen bonding which has been observed in activated carbon and is greatly responsible for the dyeability of textile fibers. No simple description can explain all the observed experimental data for either the adsorption of organic molecules on activated carbon or the dyeing of a textile fiber -- both are complex systems with a multitude of possible interactions (47, 48).

Dyeing Theory

The theory of dyeing synthetic fibers with disperse dyes can be considered as a reaction occurring between a hydrated dye molecule in solution and a fiber substrate. The dye molecules are attracted to the fiber by polar forces and become attached to the fiber surface through water molecules which link dipoles in the dye to dipoles in the fiber. Wegmann (49) proposed that once the dye molecule reached the fiber surface the hydrophobic non-polar part of the dye molecule can interact further with the polar surface of the fiber.

The mechanism of dyeing involves the adsorption of the dye from its water solution. Disperse dyes are characterized by their limited water solubility. According to Salvin (50) the water solubility of disperse dyes vary from 5-100 mg/l and are largely present in the dyebath as a water dispersion with a particle size of 1-2 microns. The relationship between aqueous solubility and dyeing properties was studied by Bird (51), who postulated that very low aqueous solubility resulted in slow dyeing, but a low rate of dyeing did not necessarily indicate low aqueous solubility. Koshti (52) explained the earlier work by Bird. He determined that the build-up of dye within the fiber was dependent upon the solubility of the dye and the rate of diffusion of the dye into the fiber. Dyes with very low solubilities had only a small portion of dye available for adsorption while dyes with very high aqueous solubilities tended to remain in the dyebath. Both extremes altered the partition coefficient of the dye/fiber system and greatly reduced the percentage of dye exhausted on the fiber.

The theory and mechanism of dyeing synthetic fibers with disperse dyes cannot be complete without some discussion of surfactants. A disperse dyebath always contains dispersing agents which are surfactants or closely related compounds. These substances according to Bird (53) have a solubilizing effect on the disperse dyes. The disperse dye can be considered to dissolve in the surfactant, hence a competition develops between the detergent and the fiber for the dye. This competition increases the amount of dye in solution which decreases the partition coefficient and the percentage of dyebath exhaustion. Usually the surfactant exerts a retarding action on the dyeing system but the surfactant can also increase the rate of dyeing for dyes which do not readily dissolve in water by facilitating dissolution of the solid dye particles.

Adsorption Isotherms

The adsorption of a dye from solution onto activated carbon can be considered to be a distribution of dyestuff between a liquid (water) phase and a solid (carbon) phase. The ratio of the distribution between these two phases then becomes a measure of the position of equilibrium during adsorption and is affected by such variables as time, temperature, concentration, pH, etc. The preferred means for depicting this distribution is the adsorption isotherm (54).

Langmuir (55, 56) considered the surface of activated carbon to be composed of simple spaces each capable of adsorbing one dye molecule. He further postulated that all the spaces were equal in their affinity for a dye molecule, that one space did not affect the forces of the surrounding spaces, and at equilibrium the rate of adsorption was equal to the rate of desorption. The Langmuir theory requires three basic assumptions:

1. That maximum adsorption corresponds to a saturated monolayer of adsorbed molecules on the surface of the carbon
2. The energy of adsorption is constant for any given system

3. There is no movement from one site to another site on the surface of the carbon by the adsorbed molecules. The Langmuir adsorption isotherm is derived from the equation:

$$X = \frac{kXmC}{1+kC}$$

X = grams of dye on carbon per kilogram of carbon

k = constant related to the energy of adsorption

C = concentration of dye in solution in grams per liter

Xm = grams of dye on carbon per kilogram of carbon in forming a complete monolayer on the carbon surface

Inverting the equation it can be expressed linearly as:

$$\frac{1}{X} = \frac{1}{kXmC} + \frac{1}{Xm}$$

An equation which is sometimes more useful than the Langmuir equation from an empirical standpoint is the Freundlich (57) or van Bemmelen equation which, because of its simplicity, has been utilized for many years to define the adsorption parameters of activated carbon. The equation is:

$$\frac{x}{m} = kC^n$$

x = the amount of dye adsorbed on the carbon

m = mass in grams of carbon

C = concentration of dye in solution in grams per liter

k & n = constants which can be determined by extrapolation when plotting a log-log graph of the data

A linear log-log relationship can be expressed by the equation:

$$\log \frac{x}{m} = \log k + n \log C$$

so that n is the slope of the line and k is the antilogarithm of the intercept. According to Freundlich, the amount of dye adsorbed increases indefinitely with increasing concentration.

Other theories have been developed to explain the more complete adsorption process that leads to multilayer formation. The most important of these theories was presented by Brunauer, Emmett, and Teller, known as the BET theory (58). Both the Langmuir and the BET theory make the assumption of uniform energies of adsorption on the surface. For adsorption from solution the BET theory makes an additional assumption that layers of sorbate beyond the first have equal energies of adsorption. The BET equation is expressed as:

$$\frac{X}{Xm} = \frac{AC}{(C_S-C)\ 1+(A-1)\ \frac{C}{C_S}}$$

X = grams of dye on carbon per kilogram of carbon

C_S = saturation content of the dye

C = measured concentration of dye in solution at equilibrium

Xm = grams of dye on carbon per kilogram of carbon in forming a complete monolayer on the carbon surface

A = constant expressive of the energy of interaction with the surface

Chapter III

EXPERIMENTAL PROCEDURE

Carbon Selection

Different grades of powdered activated carbons are capable of producing pronounced variations in their removal properties. Therefore, it was necessary to screen out the least effective carbons in order to determine which was most suitable for further experimentation. The powdered activated carbons evaluated in this study were Hydrodarco 3000, Hydrodarco 4000, Hydrodarco H and Hydrodarco C which were obtained from ICI America Incorporated, Wilmington, Delaware. The carbons were developed specifically for water treatment and were produced in the United States from virgin lignite, a variety of coal similar to peat and bituminous.

A five gallon composite sample of effluent was obtained from a textile dye waste disposal plant located in Greensboro, North Carolina. This particular plant treats approximately three million gallons of waste water per day from a commission dyeing and finishing plant, a denim manufacturing plant and from a vertical flannel mill. The effluent was considered to be typical of biologically treated textile waste and likely contained a mixture of dyes including indigoids, vats, disperse, sulfurs, pigments and directs. Additionally durable press resins, salts, dispersing agents, scouring agents and organophosphorus materials were also present. The effluent was used for this entire series of experiments.

Three concentration levels of powdered carbon were evaluated: 1,000 ppm, 3,000 ppm, and 5,000 ppm. The four adsorption parameters which were investigated included nitrogen removal, phosphorus removal, color removal and chemical oxygen demand removal. Although the major thrust of the experiment was concerned with dye adsorption or color removal, it was decided in this preliminary study to investigate these other parameters in order to obtain a clearer picture of the adsorption process. Furthermore, it was hoped that this additional experimental data might stimulate future researchers in this area.

A weighed amount of carbon was slowly transferred to a 300 ml beaker containing 250 ml of waste water. The solution was constantly stirred during carbon addition to assure that the carbon was completely wetted out and homogeneously dispersed. The beakers were then placed on a gang stirrer at a low speed setting for 24, 48 and 72 hours at a temperature of 22°C ± 2°C. The long stirring times were chosen in order to obtain equilibrium conditions and to determine the maximum adsorption efficiencies of the carbons. The contents of the beakers were filtered through a 47 mm Gelman Type A glass fiber filter and analyzed according to the following test procedures.

1. Nitrogen. The classical Kjeldhal method determines organically bound nitrogen in the trinegative state (59). Two hundred milliter samples were poured into 500 ml Kjeldhal flasks containing 10 ml of concentrated sulfuric acid, 6.7 gm of potassium sulfate, 1.5 ml of mercuric oxide and three or four boiling beads to prevent excessive bumping during digestion. The samples were carefully mixed,

placed under an exhaust hood and heated until the solutions cleared. Digestion was allowed to proceed for an additional 30 minutes before removing and cooling in an ice bath. The samples were then diluted to 300 ml with distilled water to which 0.5 ml of phenolphthalein indicator and 50 ml of a previously prepared solution of sodium hydroxide-sodium thiosulfate were added. The samples were distilled into boric acid indicating solution and titrated with 0.02 N sulfuric acid to a pale lavender color.

2. Phosphorus. The analysis for phosphorus involved two separate procedures: Conversion of the organic phosphorus compound to the soluble orthophosphate form, and a colorimetric determination. Fifty milliliter samples were pipetted into digestion flasks containing 1 ml of concentrated sulfuric acid and 5 ml of concentrated nitric acid. The samples were placed under an exhaust hood and allowed to digest until colorless and fumes of sulfur dioxide were evolved. After digestion the samples were cooled and the pH was adjusted to a range of 4-10 with 50% sodium hydroxide. Thirty-five milliliter samples were pipetted into 50 ml volumetric flasks and 10 ml of a previously prepared vandate-molybate reagent was added. The samples were brought to the 50 ml mark on the flask with the addition of distilled water and allowed to set for approximately 10 minutes to assure proper color development. After color development the samples were analyzed on a Coleman-Hitachi Model 124 Spectrophotometer at a wavelength setting of 440 mu.

3. Color. Since the samples contained a mixture of textile dyes and chemicals it was decided to obtain complete spectra curves for each sample and add the absorbances at 450 mu, 550 mu, and 650 mu as an indication of the total color in the samples. A Coleman-Hitachi Model 124 Spectrophotometer was used to scan the samples from 700 mu to 400 mu at a slit width of 0.5 mu. Absorbance was read directly from the spectra curves.

4. Chemical oxygen demand. The chemical oxygen demand (COD) is a measure of the oxygen equivalent of that portion of the organic matter in a sample which can be oxidized by a strong chemical oxidant (60). Five milliliter samples were pipetted into 250 ml flasks containing 25 ml of dichromate oxidizing solution (potassium dichromate, concentrated sulfuric acid, concentrated phosphoric acid). A small amount of silver sulfate and mercurous sulfate was added to each sample. The samples were then placed on a hot plate and slowly heated to 165°C. After cooling, the samples were titrated with a previously prepared ferrous solution of 0.05 N ammonium sulfate in the presence of ferrion indicator.

Carbon Characterization

A common practice of activated carbon suppliers is to provide some chemical and physical data to differentiate between various types and grades of carbon. The data is extremely helpful as it allows the researcher to narrow down the carbon selections to the few which appear promising instead of randomly choosing carbons and wasting much time and effort. In this study the data led to the selection of Hydrodarco 3000, Hydrodarco 4000, Hydrodarco C and Hydrodarco H for the initial screening experiments. However, after the best carbon had been selected experimentally it was necessary to further characterize the carbon with the following tests:

1. Apparent density. The apparent density is defined as the weight of carbon per unit volume expressed in grams per liter or pounds per cubic foot. Ten grams of carbon were carefully poured into a dry 100 ml graduated cylinder. The bottom of the cylinder was gently tapped until the carbon stopped settling and this was recorded in milliliters of packed carbon volume (61). The density was calculated from:

$$\text{Apparent density (pounds per cubic foot)} = \frac{624}{\text{packed volume}}$$

or

$$\text{Apparent density (grams per liter)} = \frac{10 \times 100}{\text{packed volume}}$$

2. pH. The pH of the carbon is defined as the pH of a suspension of a carbon in distilled water. A 2 gm sample of carbon was stirred at low speed for 24 hours in 50 ml of distilled water. After allowing sufficient time for the carbon to settle, the pH was determined with a Model 701 Orlon pH meter.

3. Iodine number. The iodine number of activated carbon is defined as the amount of iodine adsorbed by 1 gm of carbon at an equilibrium filtrate concentration of 0.02 N iodine. The iodine

number provides some insight into the surface characteristics of the carbon. The principle of the method is that iodine in aqueous solution is adsorbed by activated carbon (62). After filtration the iodine remaining in the filtrate is back titrated with standard sodium thiosulfate. The reaction is:

$$I_2 + 2\ Na_2S_2O_3 \longrightarrow 2\ NaI + Na_2S_4O_6$$

A 0.4 gm sample of oven dried carbon was placed in a 150 ml beaker. The carbon was completely wetted with 10 ml of 5% hydrochloric acid. One hundred and fifty milliliters of previously prepared stock iodine solution (2.70-2.75 gm of iodine and 4.05 gm of potassium iodide per liter of distilled water) was added to the beaker and the solution was homogeneously mixed. The solution was then filtered and titrated with 0.01 N solution thiosulfate.

4. Specific surface area. A quantity of nitrogen from a known mixture of nitrogen and an inert nonabsorbable carrier gas was adsorbed on the surface of the activated carbon. The thermal conductivity of the gas mixture was measured to indicate the adsorption and desorption process. The adsorption of nitrogen was carried out at low temperature and the desorption of nitrogen was carried out at high temperature. Different mixtures of the nitrogen and inert carrier were used in order to develop adsorption isotherms of the adsorption and desorption process. This test was carried out by the carbon producer.

5. Phenol number. This test was originally developed to evaluate carbons for the removal of tastes and odors from drinking water supplies (63). The amount of carbon required to reduce the phenol concentration in 1,000 ml of water from 0.10 to 0.01 ppm is known as the phenol number. This test was carried out by the carbon producer.

6. Molasses number. This test measured the removal of color from a standard solution of molasses. The test provided some information concerning the properties of powdered activated carbon for removing high molecular weight organic molecules from solution. This test was carried out by the carbon producer.

7. Moisture and ash content. The amount of moisture in the activated carbon and the ash content after combustion was determined by Thermal Gravimetric Analysis. By utilizing this technique, the changes in the weight of the carbon as a function of both time and temperature can be continuously recorded. With the aid of an automatic programmer, the temperature was controlled to increase at a rate of 80°C per minute from room temperature to 800°C. Prior to testing the carbon sample, a temperature deviation curve was determined with magnetic standards to calibrate the instrument for the temperature range of the activated carbon. The instrument used for this series of experiments was a TGS-1 manufactured by the Perkin-Elmer Corporation.

8. Average particle diameter. This is a weighed average diameter of a carbon particle and was determined by screen analysis. To obtain a value, the average particle diameter was calculated by multiplying the weight of each fraction by its average diameter, adding the products and dividing by the total weight of the sample. The average diameter of each fraction is the size midway between the sieve opening through which the fraction had passed and the sieve opening on which the fraction was retained (64).

9. Carbon, hydrogen, nitrogen analysis. To further characterize the chemical properties of the activated carbon the amount of carbon, hydrogen and nitrogen was determined. A Hewlett Packard Model 185 CHN Analyzer was used for this work. The principle of operation involved the conversion of the activated carbon to nitrogen, carbon dioxide and water in the presence of an oxidation catalyst at elevated temperatures. The nitrogen and carbon dioxide peaks were used to determine the amount of nitrogen and carbon in the sample. The water peak was used to calculate the amount of hydrogen. By limiting the size of the carbon sample and carefully controlling the burning time, temperature and carrier at gas flow rates, the peak height was directly proportional to the amount of reaction product and could, therefore, be used to calculate the composition of the activated carbon (65). A cyclohexand-2,4-dinitrophenylhydrazone standard containing 51.79% carbon, 5.07% hydrogen and 20.14% nitrogen was used to calibrate the instrument. The calibration constants were computed thusly:

$$\text{Carbon } K_C = \frac{51.79}{\text{Measured C Peak Height from Standard} - \text{Measured C Peak Height from Blank}}$$

$$\text{Hydrogen } K_H = \frac{5.07}{\text{Measured H Peak Height from Standard} - \text{Measured H Peak Height from Blank}}$$

$$\text{Nitrogen } K_N = \frac{20.14}{\text{Measured N Peak Height from Standard} - \text{Measured N Peak Height from Blank}}$$

These constants were used to calculate the percentage of carbon, hydrogen and nitrogen in the activated carbon:

$\% \text{ C} = \text{peak height of activated carbon} \times K_C$

$\% \text{ H} = \text{peak height of activated carbon} \times K_H$

$\% \text{ N} = \text{peak height of activated carbon} \times K_N$

Dye Characterization

Three different classes of disperse dyes were chosen for these experiments: Disperse Yellow 54, a quinonapthalone type used for batch dyeing polyester and polyester blends, Disperse Red 73, a monoazo type commonly used in thermosol dyeing of polyester fabrics, and Disperse Blue 7, an anthraquinone type widely accepted by the carpet industry for dyeing nylon carpets. According to Muller (66), disperse dyes with quinonapthalone, monoazo and anthraquinone structures accounted for approximately 78% of all disperse dyes used commercially. In 1968 approximately 679,000 pounds of Disperse Yellow 54 and approximately 360,000 pounds of Disperse Blue 7 were produced for dyeing synthetic fibers. No production figures were available for Disperse Red 73. Typical disperse dyes are sold as 30-35% pure dye with 65-70% additives such as lignin sulfonate, salts, and related compounds. The aqueous solubility of disperse dyes is less than 100 mg/l and the dyes tend to agglomerate under certain conditions of time, temperature, pH and dyebath makeup. The criteria used for the selection of the disperse dyes in this study included chemical and physical structure, production volume and area of interest. The following parameters were investigated in order to characterize the dyes:

1. Equilibrium time. The time required for a dye-carbon system to reach equilibrium had to be determined before any experimental work on adsorption could begin. This was necessary because all theories of adsorption and dyeing were predicated upon the fact that an equilibrium exists between the dye molecule and the substrate. The equilibrium time was determined by preparing 100 ppm solutions of Disperse Blue 7, Disperse Red 73, and Disperse Yellow 54 and stirring with 300 ppm Hydrodarco C at a temperature of 22^{o}C ± 2^{o}C. Samples of dye were weighed to 0.15 gm and dispersed in 1,500 ml of distilled water. Using a graduated cylinder, 250 ml portions of dye were poured into six 300 ml beakers to which 300 ppm of Hydrodarco C was added. The beakers were placed on a six position stirrer at low speed for the required amount of time. Samples were taken for analysis at time intervals of 30 minutes, 1 hour, 4 hours, 8 hours, 16 hours, and 24 hours. The samples were filtered through a Gelman Type A glass fiber filter and scanned on a Coleman-Hitachi Model 124 UV-Visible Spectrophotometer from 700 mu to 400 mu. The maximum absorbance values were measured and recorded.

2. Dye concentration curves. Dye concentration curves were determined in order to show the linear relationship between the absorbance value obtained spectrophotometrically and the amount of dyestuff in solution. Curves were determined for dyestuff concentrations of 200 ppm, 100 ppm and 50 ppm. Standard solutions of Disperse Blue 7, Disperse Red 73, and Disperse Yellow 54 were prepared by dispersing 0.20 gm, 0.10 gm, and 0.05 gm of each dye in 1.0 l of distilled water. The dyes were scanned from 700 mu to 400 mu on a Coleman-Hitachi Model 124 Spectrophotometer. The maximum absorbance values were then plotted against the known concentrations of the dye standards.

3. Dye solubility. The dyeing characteristics of disperse dyes are strongly influenced by their solubilities in water (67). Since no study concerning disperse dyes would be complete without solubility data tne aqueous solubilities of Disperse Yellow 54, Disperse Red 73 and Disperse Blue 7 were determined. Solutions of each dye were prepared by dispersing 0.05 gm of dye in 500 ml of distilled water and stirring to homogeneously mix the solutions. The dyes were transferred to 500 ml glass stoppered flasks and placed in a darkened area at $22^{o}C \pm 2^{o}C$ for 60 days. The flasks were isolated to prevent jarring so that the insoluble portion of the dye would settle to the bottom of the flask. After 60 days a glass pipette was used to carefully remove a 5 ml sample of each dye solution. The amount of dye in solution was determined spectrophotometrically by converting the absorbance values to ppm dye.

4. Filtration effect. Filtration was necessary to physically separate the solid carbon particles from the remaining solution prior to spectrophotometric determination. Therefore, the amount of dye which was physically removed along with the carbon had to be determined. Standard solutions of 100 ppm Disperse Blue 7, Disperse Red 73, and Disperse Yellow 54 were made by dispersing 0.10 gm of each dyestuff into 1.0 l of distilled water. Triplicate samples of each dye were prepared for analysis by transferring three 250 ml portions of each dye to 300 ml beakers and stirring for 24 hours. The dyes were then scanned from 700 mu to 400 mu on a Coleman-Hitachi UV-Visible Spectrophotometer both before and after filtration through a Gelman Type A glass fiber filter. The maximum absorbance values were converted to ppm dye.

Adsorption Experiments

The experiments undertaken in order to understand the adsorption characteristics of the dye-carbon system represented the major experimental part of the investigation. The disperse dyes and activated carbon were studied with and without the auxiliary chemicals normally present in a dye effluent such as surfactants, alkaline salts, acids, and bases. To gain some understanding of the dye-carbon adsorption system, six experimental areas were investigated. These were: The effects of concentration, the effects of pH, the effects of nonionic surfactants, the effects of anionic surfactants, the effects of alkaline salts, and the effects of an alkaline salt in the presence of a nonionic surfactant.

1. Concentration effects. Concentration levels of 200 ppm, 100 ppm and 50 ppm were chosen for Disperse Blue 7, Disperse Red 73, and Disperse Yellow 54. Hydrodarco C additions of 0 ppm, 100 ppm, 300 ppm, 500 ppm, 1,000 ppm and 5,000 ppm were made at each dye concentration level. The dye-carbon mixtures were stirred for 24 hours at 22°C ± 2°C to assure equilibrium and filtered through a Gelman Type A glass fiber filter. The samples were then scanned from 700 mu to 400 mu on a Coleman-Hitachi Model 124 Spectrophotometer to determine the maximum absorbance values. The adsorption isotherms were calculated from the absorbance data.

2. pH effects. A concentration level of 100 ppm dyestuff and 300 ppm Hydrodarco C was chosen. Standard solutions of Disperse Blue 7, Disperse Red 73, and Disperse Yellow 54 were prepared by dispersing 0.1 gm of dye in 1.0 l of distilled water. A graduated cylinder was used to split each dye into 250 ml portions which were transferred to 300 ml beakers to which 0.075 gm of Hydrodarco C was added. The pH was varied by small additions of 50% sodium hydroxide and 1 N hydrochloric acid. The pH was determined on a Model 701 pH meter manufactured by Orion Research. Two standard buffer solutions were used to calibrate the instrument prior to analyzing the dye samples. The pH of the solution was checked before and after stirring for 24 hours at 22°C ± 2°C. In order to correlate color removal with pH effects the samples were filtered through a Gelman Type A glass fiber filter and scanned from 700 mu to 400 mu on a Coleman-Hitachi Model 124 Spectrophotometer. The maximum absorbance values were converted to ppm dye.

3. Nonionic surfactant effects. A concentration of 100 ppm dyestuff and 300 ppm Hydrodarco C was chosen. Standard solutions of Disperse Blue 7, Disperse Red 73 and Disperse Yellow 54 were prepared by dispersing 0.150 gm of dye in 1,500 ml of distilled water. The nonionic surfactant used in these experiments was Triton S-100, a 100% active product manufactured by the Rohm and Haas Company. The surfactant is an alkylaryl polyether with the following general formula (68):

$$R\text{-}R_1\text{-}(OCH_2CH_2)_xOH \qquad X = 8\text{-}10\ (OCH_2CH_2)$$

A graduated cylinder was used to measure each dye into 250 ml portions which were transferred to 300 ml beakers to which 0.075 gm of Hydrodarco C was added. To each beaker either 0 ppm, 50 ppm, 100 ppm, 500 ppm or 1,000 ppm of Triton X-100 was added. The mixtures were stirred for 24 hours at $22^oC \pm 2^oC$ to assure equilibrium and filtered through a Gelman Type A glass fiber filter. The samples were then scanned from 700 mu to 400 mu on a Coleman-Hitachi Model 124 Spectrophotometer. The maximum absorbance values were converted to ppm dye.

4. Anionic surfactant effects. A concentration of 100 ppm dyestuff and 300 ppm Hydrodarco C was chosen. Standard solutions of Disperse Blue 7, Disperse Red 73, and Disperse Yellow 54 were prepared by dispersing 0.150 gm of dye in 1,500 ml of distilled water. The anionic surfactant was Tergitol Anionic 4, a 28% active product manufactured by the Union Carbide Corporation. The compound is a sodium sulfate derivative of 7-ethyl-2-methyl, 4-undecanol (69). A graduated cylinder was used to measure each dye into 250 ml portions which were

transferred to 300 ml beakers to which 0.075 gm of Hydrodarco C was added. To each beaker either 0 ppm, 50 ppm, 100 ppm, 500 ppm or 1,000 ppm of Tergitol Anionic 4 was added. The mixtures were stirred for 24 hours at 22°C ± 2°C to assure equilibrium and filtered through a Gelman Type A glass fiber filter. The samples were then scanned from 700 mu to 400 mu on a Coleman-Hitachi Model 124 Spectrophotometer. The maximum absorbance values were converted to ppm dye.

5. Alkaline salt effects. A concentration of 100 ppm dyestuff and 300 ppm Hydrodarco C was chosen. Standard solutions of Disperse Blue 7, Disperse Red 73 and Disperse Yellow 54 were prepared by dispersing 0.150 gm of dye in 1,500 ml of distilled water. The alkaline salt used in these experiments was TSPP, a 100% product of tetrasodium pyrophosphate commonly used as a buffer in dyeing and finishing processes. A graduated cylinder was used to measure each dye into 250 ml portions which were transferred to 300 ml beakers to which 0.075 gm of Hydrodarco C was added. To each beaker either 0 ppm, 50 ppm, 100 ppm, 500 ppm or 1,000 ppm TSPP was added. The mixtures were stirred for 24 hours at 22°C ± 2°C to assure equilibrium and filtered through a Gelman Type A glass fiber filter. The samples were then scanned from 700 mu to 400 mu on a Coleman-Hitachi Model 124 Spectrophotometer. The maximum absorbance values were converted to ppm dye.

6. Alkaline salt/anionic surfactant combined effects. The combination of alkaline salt, anionic surfactant and disperse dyestuff closely approximates a "real" dyehouse effluent. A concentration of

100 ppm dyestuff and 300 ppm Hydrodarco C was chosen. Standard solutions of Disperse Blue 7, Disperse Red 73, and Disperse Yellow 54 were prepared by mixing 0.150 gm of dye in 1,500 ml of distilled water. A graduated cylinder was used to measure each dye into 250 ml portions which were transferred to 300 ml beakers to which 0.075 gm of Hydrodarco C was added. To each beaker either 0 ppm, 50 ppm, 100 ppm or 500 ppm of Tergitol Anionic 4 and tetrasodium pyrophosphate was added. The mixtures were stirred for 24 hours at $22^oC \pm 2^oC$ to assure equilibrium and filtered through a Gelman Type A glass fiber filter. The samples were then scanned from 700 mu to 400 mu on a Coleman-Hitachi Model 124 Spectrophotometer. The maximum absorbance values were converted to ppm dye.

Effect of Surfactant on Dyeing Polyester Fabric

The experiment was undertaken to relate the effects of a nonionic and anionic surfactant on the adsorption properties of activated carbon, with the dyeing behavior of polyester fabric. A Gaston County Model 101 high temperature pressurized beaker bath machine was used to dye the fabric. All dyeings were carried out with a 2.0 gm sample of 100% polyester fabric and 1.0% (owb) Disperse Yellow 54. The experimental variables were 0.1% Triton X-100, 0.5% Triton X-100, 1.0% Triton X-100, 0.1% Tergitol Anionic 4, 0.5% Tergitol Anionic 4, and 1.0% Tergitol Anionic 4. The fabric was dyed at 250^oF for two hours, cooled, rinsed and dried at 220^oF. A Bauch and Lomb Model 505 Spectrophotometer with a reflectance attachment was used to evaluate the samples. Reflectance curves were obtained for each sample from 400 mu to 700 mu.

Chapter IV

RESULTS AND DISCUSSION

Carbon Selection

The removal properties of Hydrodarco 3000, Hydrodarco 4000, Hydrodarco C and Hydrodarco H are presented in Table 1. The color was determined spectrophotometrically from the maximum absorbance value of the solution at 450 mu, 550 mu and 650 mu. The high color value of the control was due to the composition of the sample which contained such a diverse range of dyestuffs as indigoids, vats, disperse, sulfurs, pigments and direct colors. All carbons except Hydrodarco 3000, appeared to reach equilibrium during the first 24 hours of stirring. This is based on the fact that most of the pollutant was removed in the first 24 hours and very little was removed from 24 hours to 72 hours. Hydrodarco 3000 and Hydrodarco 4000 removed far less color from solution than Hydrodarco C or Hydrodarco H which reduced the total color value of the solution by 86.21% and 75.86% respectively after 24 hours of stirring. Visually, the Hydrodarco C and Hydrodarco H changed the color of the solution from a dark blue to a very pale blue which would probably be suitable for discharging to a receiving stream without causing aesthetic problems.

The phosphorus content of the control was largely from the flame retardant finishing of cotton and polyester fabrics. These were nonbiodegradable organic compounds, some of which were halogenated.

Table 1

The Removal Properties of Various Types of Powdered Activated Carbons

Type of Carbon	% Color Removed	% Phosphorus Removed	% Nitrogen Removed	% COD Removed
		Stirred 24 Hours		
Hydrodarco 3000	27.59	42.19	23.08	36.36
Hydrodarco 4000	51.24	43.75	28.85	63.64
Hydrodarco H	75.86	70.30	59.62	78.79
Hydrodarco C	86.21	84.38	62.91	84.85
Control	0	0	0	0
		Stirred 48 Hours		
Hydrodarco 3000	58.62	62.50	0	63.64
Hydrodarco 4000	37.93	48.44	0	50.76
Hydrodarco H	72.41	73.44	51.51	84.85
Hydrodarco C	82.76	79.69	63.46	84.85
Control	6.90	20.31	0	33.33
		Stirred 72 Hours		
Hydrodarco 3000	58.62	54.69	25.00	66.67
Hydrodarco 4000	31.03	31.25	3.85	60.61
Hydrodarco H	79.31	81.25	38.46	69.70
Hydrodarco C	79.31	85.94	63.46	72.73
Control	24.14	31.25	0	48.49

Other phosphorus compounds making up the control included phosphated alcohols, phosphoric acid and various phosphorus containing alkaline salts. Since the phosphorus content of the samples were determined after chemical digestion it represented both the organic and inorganic phosphorus compounds which were present in the textile waste. Hydrodarco 3000 and Hydrodarco 4000 removed limited amounts of phosphorus while Hydrodarco C and Hydrodarco H reduced the levels of phosphorus in the waste water by 84.38% and 70.31% respectively after 24 hours of stirring.

The Kjeldahl nitrogen content of the control was derived largely from textile resins such as melamines and glyoxals and other organic nitrogen compounds from preparation, dyeing and finishing operations. Although all four grades of activated carbon reduced the nitrogen content of the samples to some degree, the best was Hydrodarco C, which removed 62.91% after 24 hours of stirring.

The removal values for the chemical oxygen demand (COD) followed wnat would be expected from the previous data. Since COD is the amount of oxygen needed to chemically oxidize the organic compounds it followed that any material which removed organic substances such as color, phosphorus and Kjeldahl nitrogen would also reduce the COD of the sample. After 24 hours of stirring, Hydrodarco C removed 84.85% of the COD.

This initial series of experiments indicated that Hydrodarco C had superior removal properties. From Figures 1-4 it can be seen that not only did Hydrodarco C remove more color, phosphorus, nitrogen and

Figure 1

Color Removal Properties of Powdered Activated Carbons

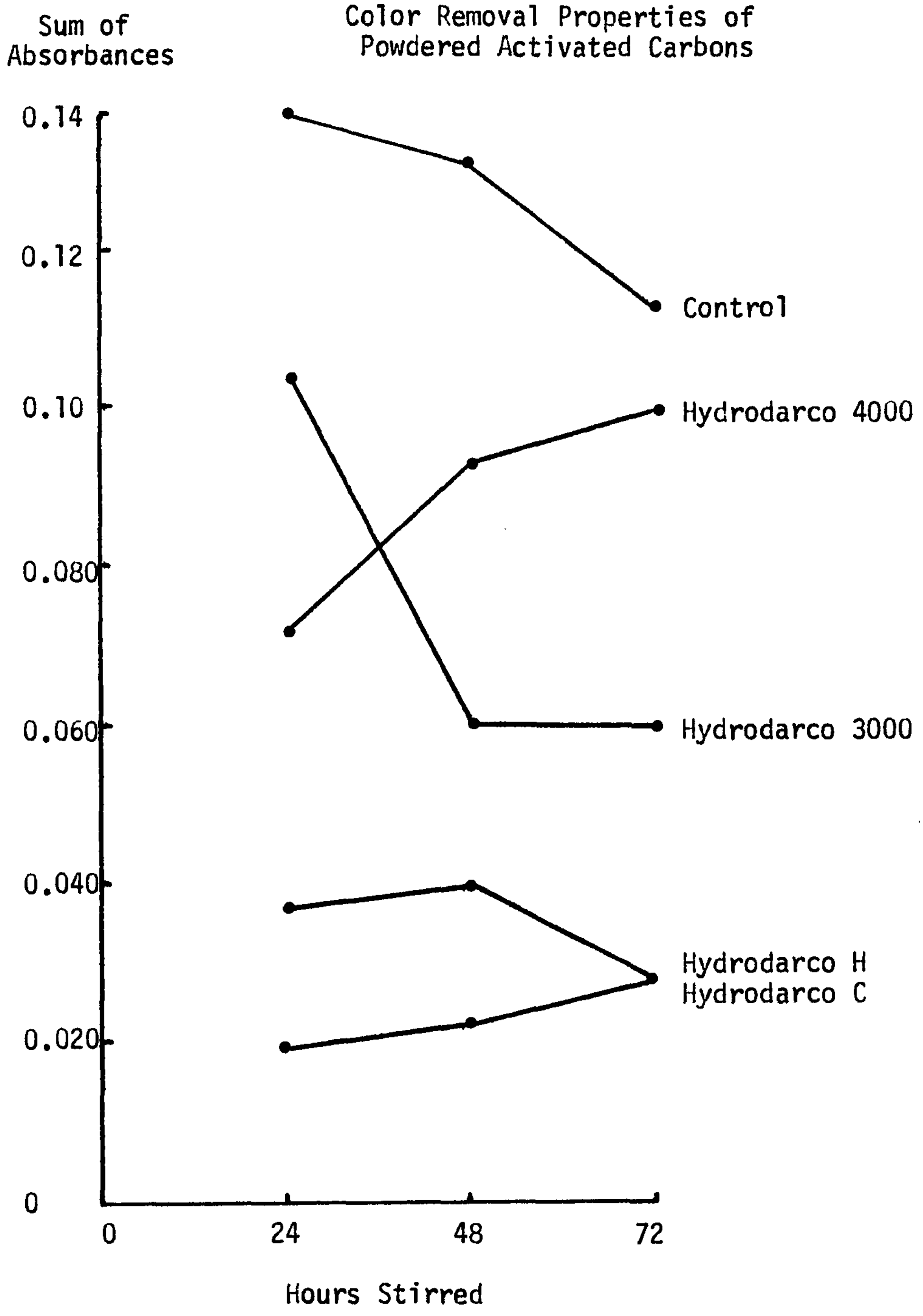


Figure 2

Phosphorus Removal Properties of Powdered Activated Carbons

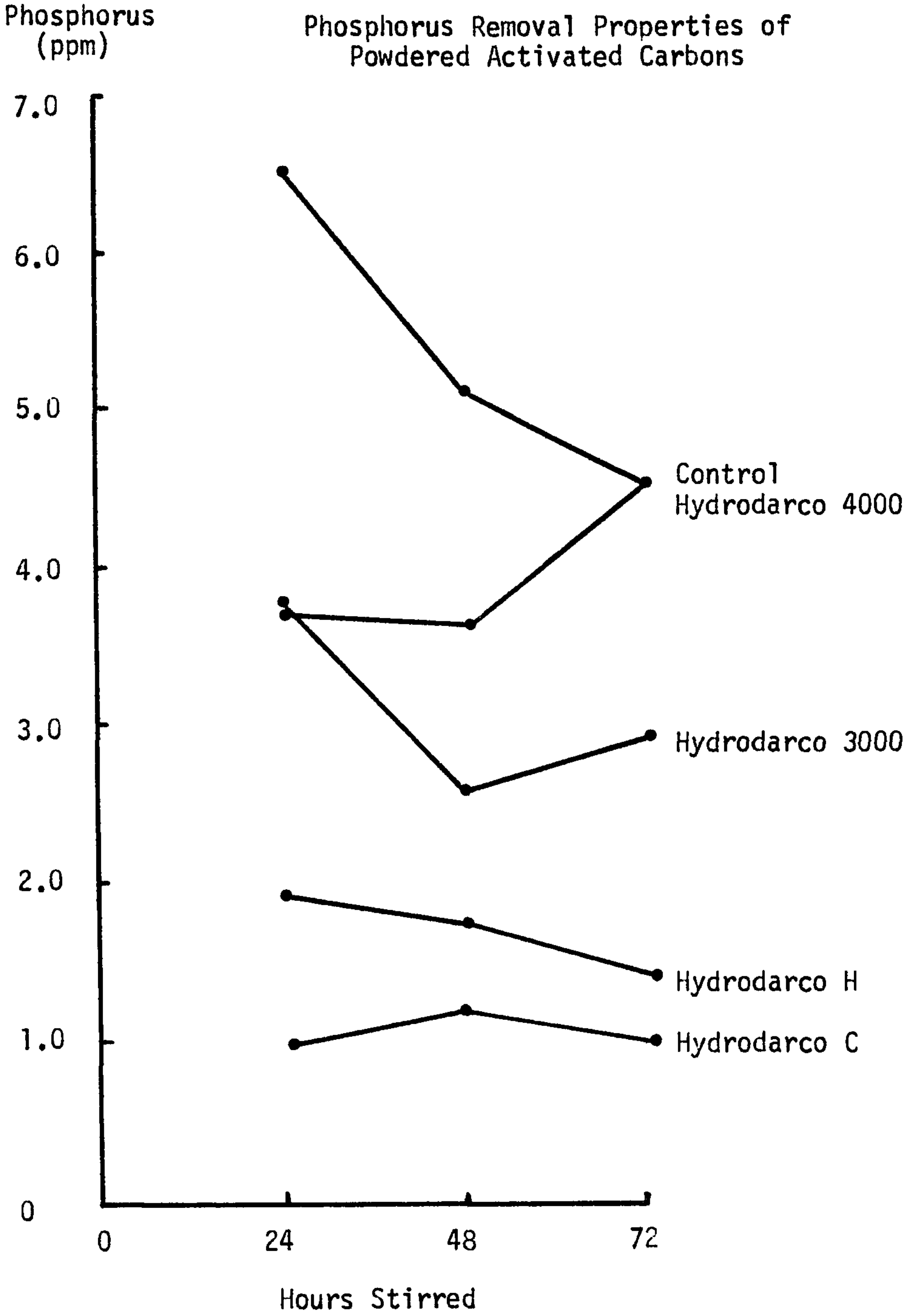


Figure 3

Nitrogen Removal Properties of Powdered Activated Carbons

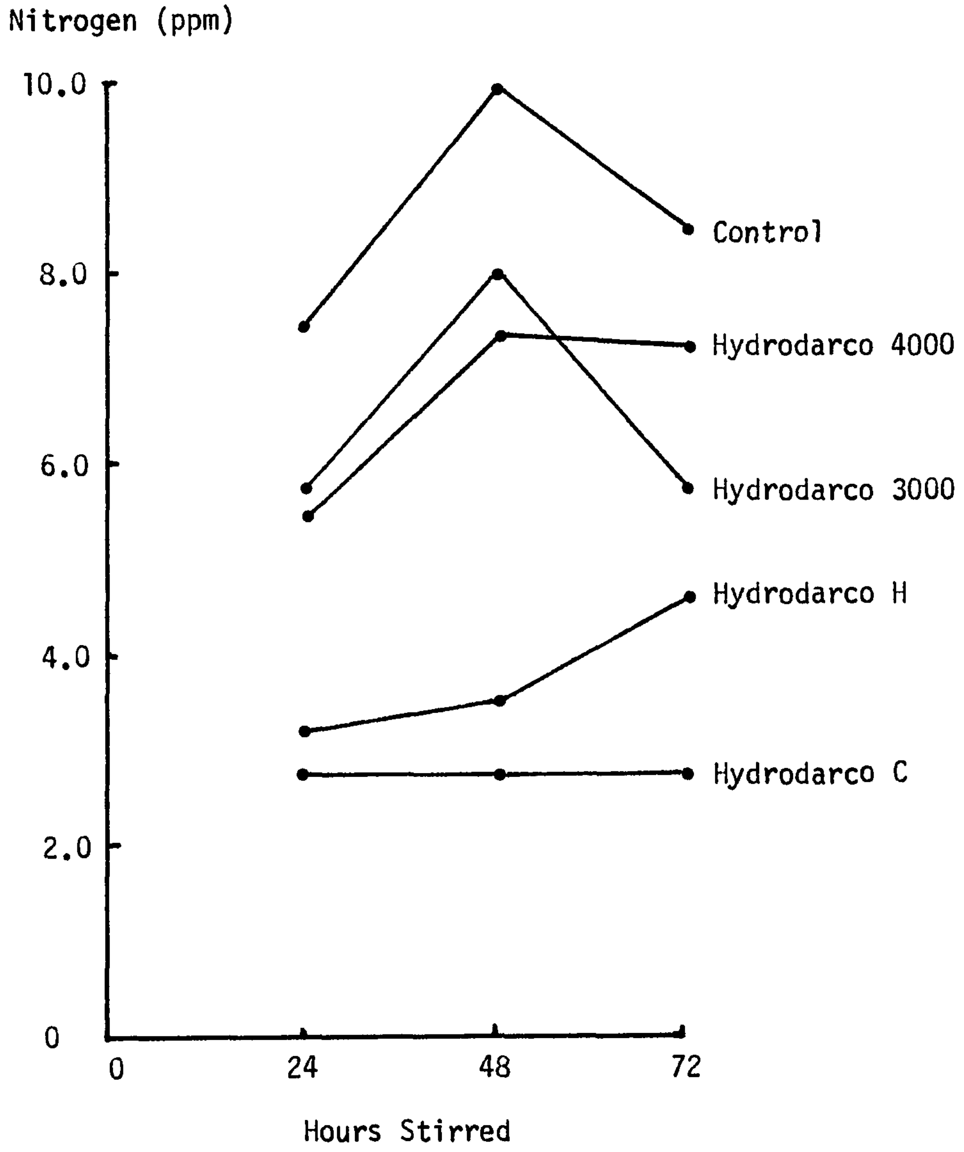
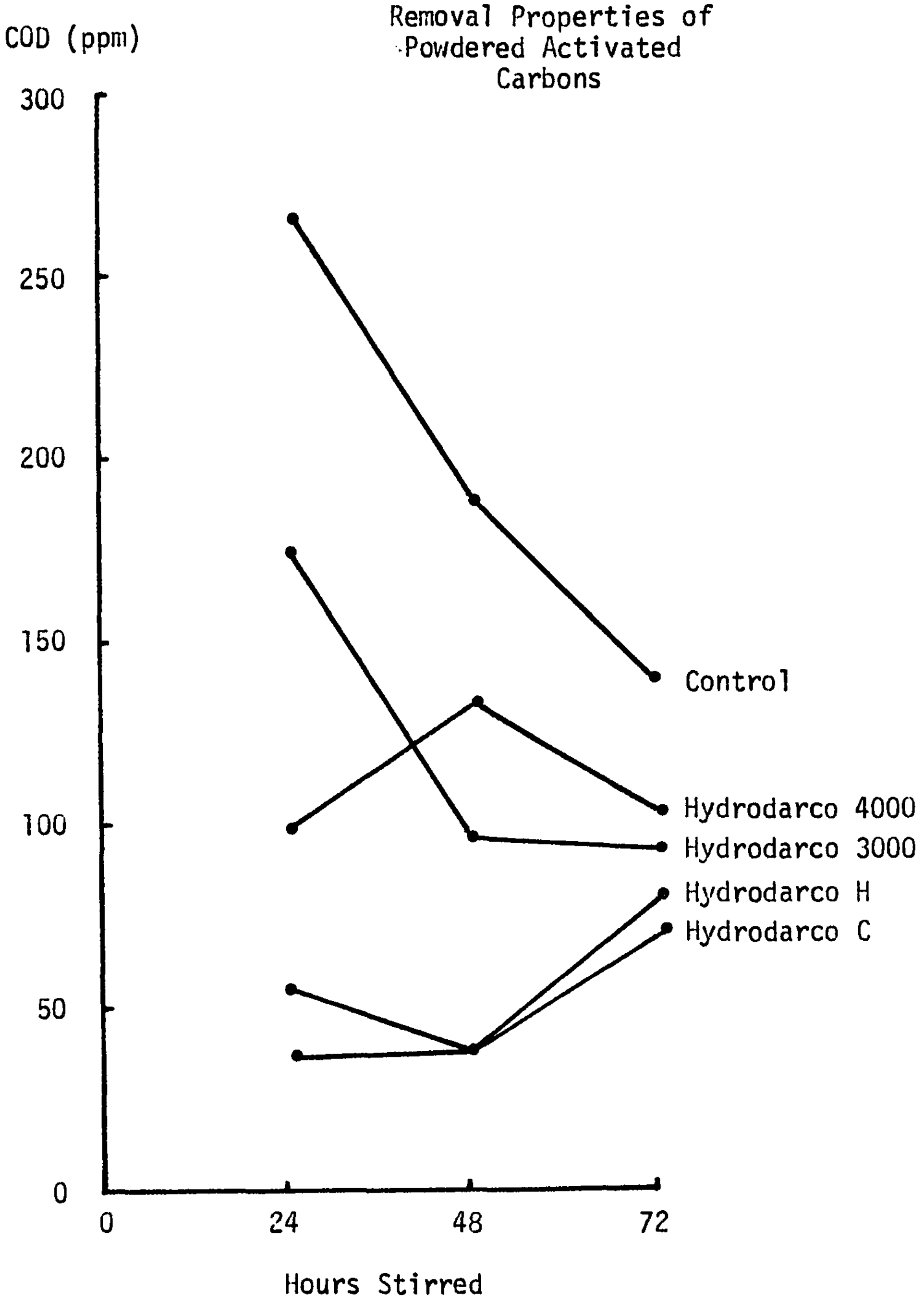


Figure 4

Chemical Oxidation Demand Removal Properties of Powdered Activated Carbons



COD than did the other carbons, but Hydrodarco C appeared to attain equilibrium more rapidly as evidenced by its small change in slope after 24 hours of stirring. For these reasons, Hydrodarco C was chosen as the adsorption medium for the remainder of the experimental work.

To further demonstrate the versatility of Hydrodarco C at lower carbon concentrations, the experiment was repeated with 3,000 ppm Hydrodarco C and with 1,000 ppm Hydrodarco C. The results for 3,000 ppm Hydrodarco C stirred for 24, 48 and 72 hours are tabulated in Table 2. Again it showed that after 24 hours of stirring Hydrodarco C effectively removed 83.56% of the color, 83.52% of the phosphorus, 50.59% of the Kjeldahl nitrogen and 82.14% of the COD. The results for 1,000 ppm Hydrodarco C stirred for 24, 48 and 72 hours are tabulated in Table 3. Except for the amount of color removed from solution there was a sharp decrease in the removal efficiency of the Hydrodarco C at the 1,000 ppm level. Although 85.14% of the color was removed from solution after 24 hours only 18.18% of the phosphorus, 48.15% of the Kjeldahl nitrogen and 34.62% of the COD was removed. This indicates that the organic color molecules tend to be more readily adsorbed than some other organic substances and that a competitive or preferential adsorption reaction could result when treating a combined textile waste with low doses of activated carbon.

Carbon Characterization

The chemical and physical properties of the Hydrodarco C used in this study are tabulated in Table 4.

Table 2

The Removal Properties of 3,000 ppm Hydrodarco C

Sample	% Color Removed	% Phosphorus Removed	% Nitrogen Removed	% COD Removed
		Stirred 24 Hours		
Hydrodarco C	83.56	83.52	50.59	82.14
Control	0	0	0	0
		Stirred 48 Hours		
Hydrodarco C	84.93	83.52	50.59	81.43
Control	27.40	27.84	25.88	20.00
		Stirred 72 Hours		
Hydrodarco C	86.30	82.39	56.47	72.86
Control	24.65	39.40	38.24	50.00

Table 3

The Removal Properties of 1,000 ppm Hydrodarco C

Sample	% Color Removed	% Phosphorus Removed	% Nitrogen Removed	% COD Removed
		Stirred 24 Hours		
Hydrodarco C	85.14	18.18	48.15	34.62
Control	0	0	0	0
		Stirred 48 Hours		
Hydrodarco C	83.78	18.18	50.00	65.69
Control	0	11.69	12.35	25.00
		Stirred 72 Hours		
Hydrodarco C	83.78	7.79	24.07	76.92
Control	0	0	0	1.92

Table 4

The Physical and Chemical Properties of Hydrodarco C

Analysis	Result
Tamped Density, grams/milliliter	0.50 - 0.70
Surface Area, meter^2/gram	523 - 550
pH	10.0 - 10.5
Molasses RE, dry basis	95
Water Solubles, percentage	5.5
Moisture, percentage	5.62
Phenol Value, dry basis	49
Ash, percentage	28.4
Iodine Number, average	583
Average Particle Size, microns	30
Particle Count billion/gram	125
Screen Analysis, percentage	
+ 100 mesh	0.3
100 x 200 mesh	9.7
200 x 325 mesh	23.0
- 325 mesh	67.0
Carbon, percentage	68.98
Nitrogen, percentage	0.83
Hydrogen, percentage	0.96

The moisture and ash content of the Hydrodarco C was determined by Thermal Gravimetric Analysis as shown in Figure 5. The y-axis represents the weight in milligrams of Hydrodarco C lost during combustion and the x-axis represents the increase in temperature from ambient to 700°C. The first break in the curve which occurred at approximately 100°C was the moisture content of the Hydrodarco C and the second break beginning around 550°C indicated the amount of volatile organic compounds being evolved during combustion. The remainder of the sample represented the ash content which consisted mostly of inorganic metallic compounds.

Determination of Equilibrium Time

The data in Table 5 indicates that an 8-16 hour stirring time was satisfactory for attaining equilibrium. To assure that equilibrium conditions were reached, all adsorption experiments were stirred for 24 hours. It was observed that although the three disperse dyes were subjected to the same identical experimental conditions and although equilibrium times were approximately the same, the amount of color removed from solution was quite different for each dye. The Disperse Yellow 54 was reduced 0.004 gm, the Disperse Red 73 was reduced 0.010 gm and the Disperse Blue 7 was reduced 0.013 gm after 24 hours of stirring. This observation will be discussed in detail during the interpretation of the adsorption isotherms for the dyes.

Figure 5

Thermogravimetric Curve of Hydrodarco C

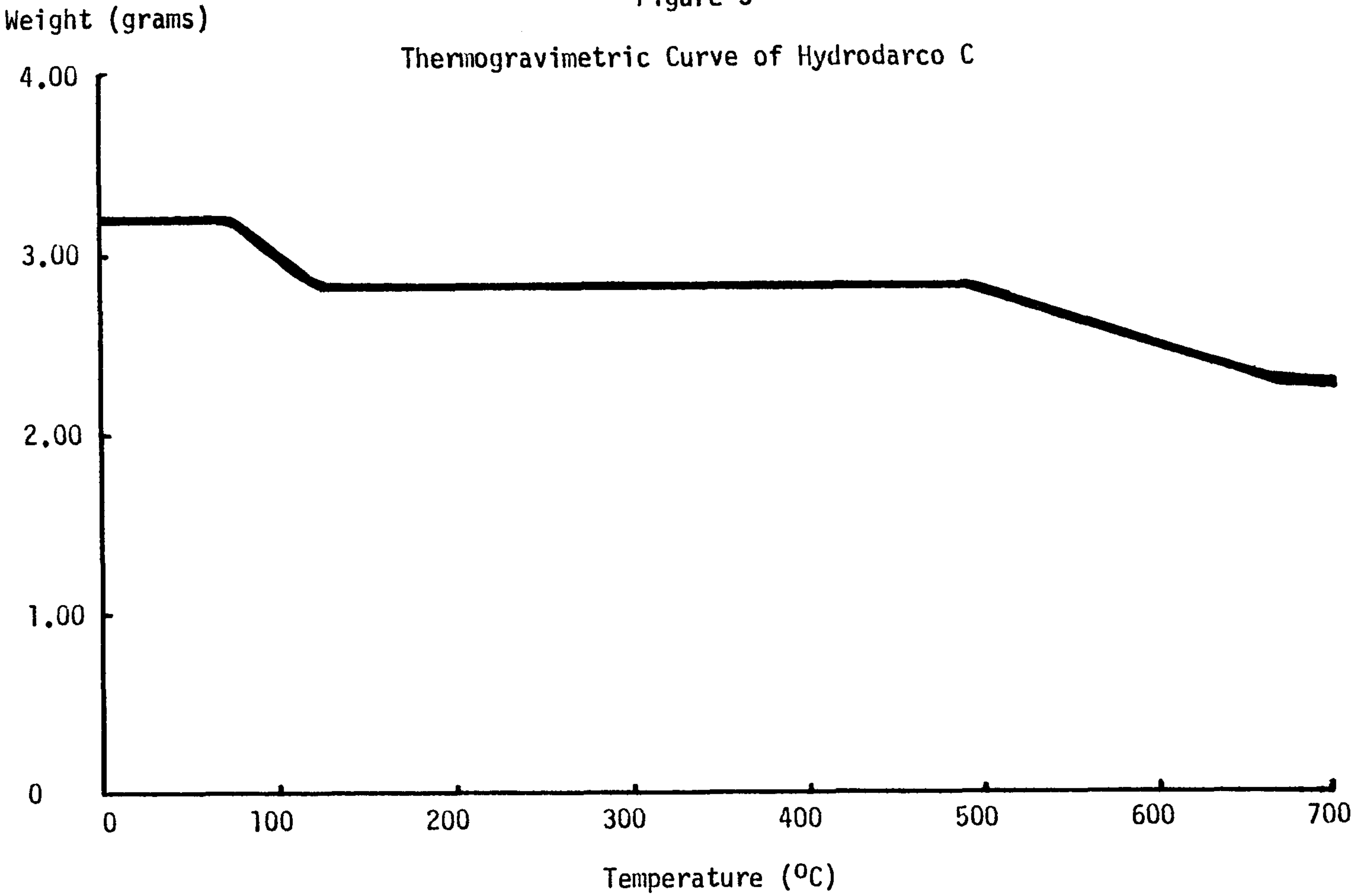


Table 5

Equilibrium Data - Grams of Disperse Dye Removed from Solution

Hours Stirred	Disperse Yellow 54	Disperse Red 73	Disperse Blue 7
0	0.025	0.025	0.025
0.5	0.024	0.022	0.020
1.0	0.023	0.020	0.019
4.0	0.023	0.016	0.015
8.0	0.022	0.015	0.013
16.0	0.021	0.016	0.012
24.0	0.021	0.015	0.012

Determination of Concentration Curves

The adsorption of the dye onto powdered activated carbon was determined by spectrophotometrically measuring the amount of dye remaining in solution before and after adsorption had occurred. The loss in color was directly proportional to a corresponding amount of dye which was adsorbed on the activated carbon. For this assumption to be valid there had to be a direct relationship between the concentration of dye in solution and the intensity of that solution when measured spectrophotometrically. The relationship between the amount of light absorbed and the concentration of a dye in solution is given by the Lambert-Beer Equation, which can be stated in its simplest form as:

$$A_s = a_s bc$$

A_s = the absorbance of the solution derived from:

$$A_s = \log 10 \frac{1}{T}$$

T = transmittance

as = constant, dependent upon the wave length

b = path length

c = concentration of the solution

From the data in Table 6 and from the linearity between the concentration of the dyestuff and the absorbance values determined spectrophotometrically as shown in Figure 6, it followed that Beers Law was obeyed over the dyestuff concentration range of 50-200 ppm. The adherence to Beers Law indicated that Disperse Yellow 54, Disperse Red 73 and Disperse Blue 7 were probably present in molecular solution.

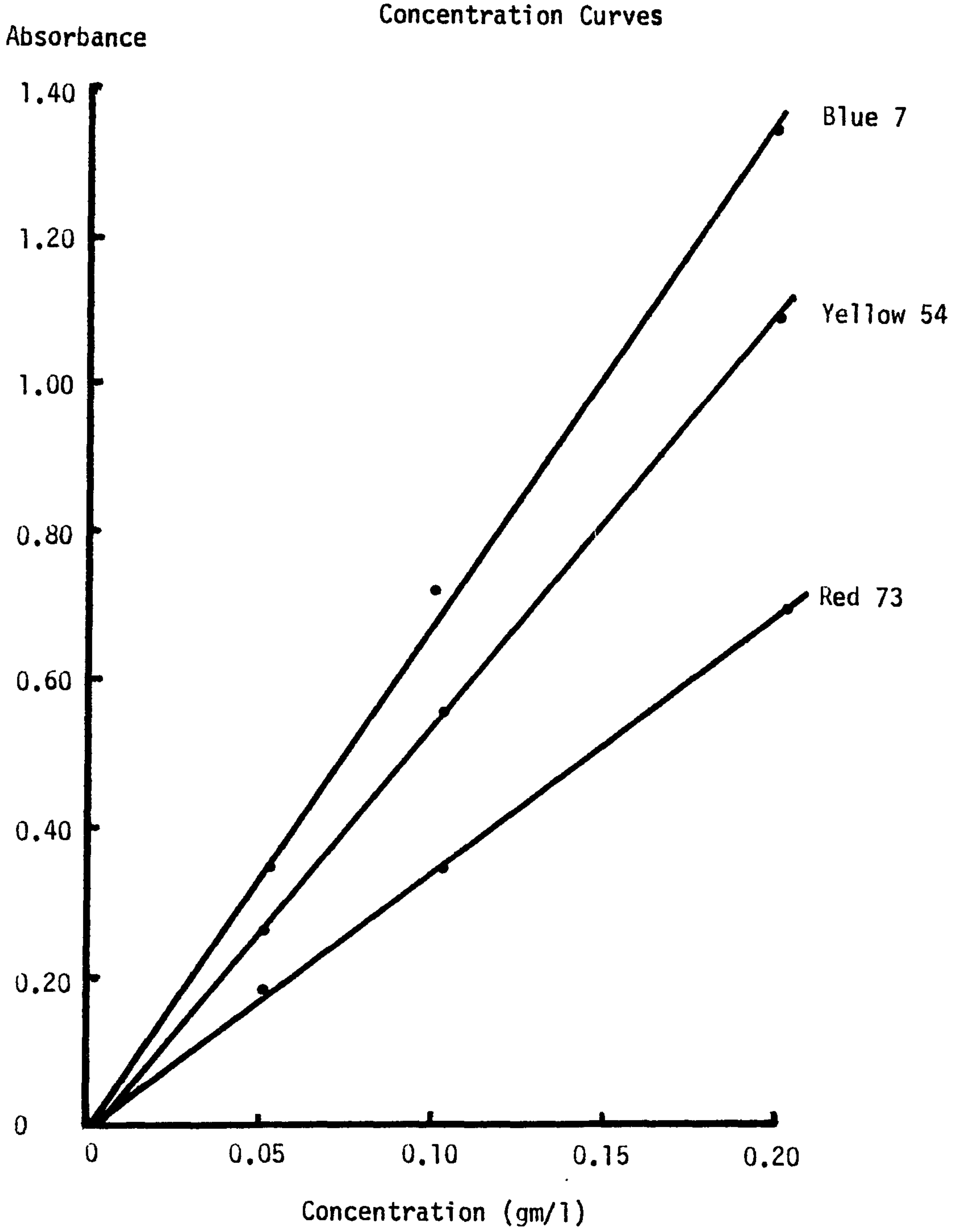
Table 6

The Relationship Between the Concentration of Dye in Solution and the Absorbance of Dye in Solution

Concentration (gm/l)	Absorbance Value
Disperse Blue 7	
0.2	1.35
0.1	0.69
0.05	0.35
Disperse Red 73	
0.2	0.68
0.1	0.35
0.05	0.18
Disperse Yellow 54	
0.2	1.05
0.1	0.55
0.05	0.26

Figure 6

Concentration Curves



Determination of Dye Solubility

The aqueous solubilities of Disperse Blue 7, Disperse Red 73 and Disperse Yellow 54 were in agreement with previously published data by Bird (70) for similar disperse dyes. The solubilities were 23.1 mg/l for Disperse Blue 7, 11.5 mg/l for Disperse Red 73 and 17.8 mg/l for Disperse Yellow 54.

Determination of the Filtration Effect

Since all dye samples were filtered prior to analysis on the UV-Visible Spectrophotometer it was necessary to determine how much of the dye was physically removed by this procedure. The amount of dye removed by filtration was related to the aqueous solubility of the dye, molecular size and configuration of the dye molecules, the dispersing characteristics of the dye in aqueous media, and the adsorption properties of the dye on the glass fiber filter. The average molecular size of the dyestuff tended to increase with time when dispersed in aqueous media. This was due to molecular aggregation, a common characteristic of disperse dyestuffs. From Table 7 it can be seen that there was a relatively large amount of color physically removed by filtration through a Gelman Type A glass fiber filter. The data indicates that filtration is one means by which disperse dyestuffs can be partially removed from solution.

Adsorption Experiments

The adsorption isotherm data for Disperse Yellow 54 at concentration levels of 200 ppm, 100 ppm and 50 ppm are tabulated in Table 8.

Table 7

The Amount of Dye Physically Removed by Filtration

Absorbance Before Filtration	Absorbance After Filtration	% Dye Removed by Filtration
	Disperse Blue 7	
0.80	0.58	27.5
0.80	0.57	28.8
0.80	0.57	28.8
	Disperse Red 73	
0.43	0.35	18.6
0.43	0.36	16.3
0.43	0.35	18.6
	Disperse Yellow 54	
0.73	0.57	21.9
0.73	0.55	24.7
0.73	0.58	20.6

Table 8

Adsorption Isotherm Data - Disperse Yellow 54

Carbon Concentration (gm/l)	Dye Concentration Remaining in Solution (gm/l) C	Dye Adsorbed on Carbon (gm/l) Xm	Amount of Color Removed (%)
	200 ppm Initial Dye Concentration		
0.1	0.185	150.0	7.5
0.3	0.172	92.0	14.0
0.5	0.164	72.0	18.0
1.0	0.145	55.0	27.5
5.0	0.102	19.6	49.0
	100 ppm Initial Dye Concentration		
0.1	0.0903	97.0	9.7
0.3	0.0835	55.0	16.5
0.5	0.0741	51.8	25.9
1.0	0.0645	35.5	35.5
5.0	0.0360	12.8	64.0
	50 ppm Initial Dye Concentration		
0.1	0.0416	84.0	16.8
0.3	0.0333	55.7	33.4
0.5	0.0287	42.6	42.6
1.0	0.0222	27.8	55.6
5.0	0.0000	10.0	100.0

The isotherm data were determined by stirring the Disperse Yellow 54 with a range of Hydrodarco C additions for 24 hours at a temperature of 22°C ± 2°C. The concentration of the Disperse Yellow 54 in solution was determined by spectroscopy as previously discussed. The experimental data were interpreted according to the Langmuir Adsorption Theory and were subjected to mathematical treatment by substituting the experimental data into the Langmuir Equation.

$$\frac{1}{X} = \frac{1}{kXmC} + \frac{1}{Xm}$$

From Figures 7, 8 and 9 it is evident that a plot of the reciprocal of the dye concentration remaining in solution $(\frac{1}{C})$ versus the reciprocal of the dye adsorbed on the carbon $(\frac{1}{X})$ indicates a linear relationship between these two factors. This relationship proved that the physical adsorption of Disperse Yellow 54 on Hydrodarco C, at dyestuff concentration levels of up to 200 ppm, was consistent with the Langmuir Theory. The fact that Langmuir adsorption was followed indicated that maximum adsorption corresponds to a monolayer of dye molecules on the carbon surface, the energy of adsorption was constant for each experiment, and there was no transmigratory activity of the dye on the surface of the activated carbon.

Adsorption isotherms have been determined for various synthetic fibers which have been dyed with disperse dyestuffs. From experimental adsorption-desorption data it has been shown that Langmuir adsorption was also valid for interpreting a disperse dye/synthetic fiber system in much the same way as the disperse dye-carbon system has been interpreted (71). The linear adsorption isotherm for disperse dyes in

Figure 7

Adsorption Isotherm
Disperse Yellow 54
200 ppm

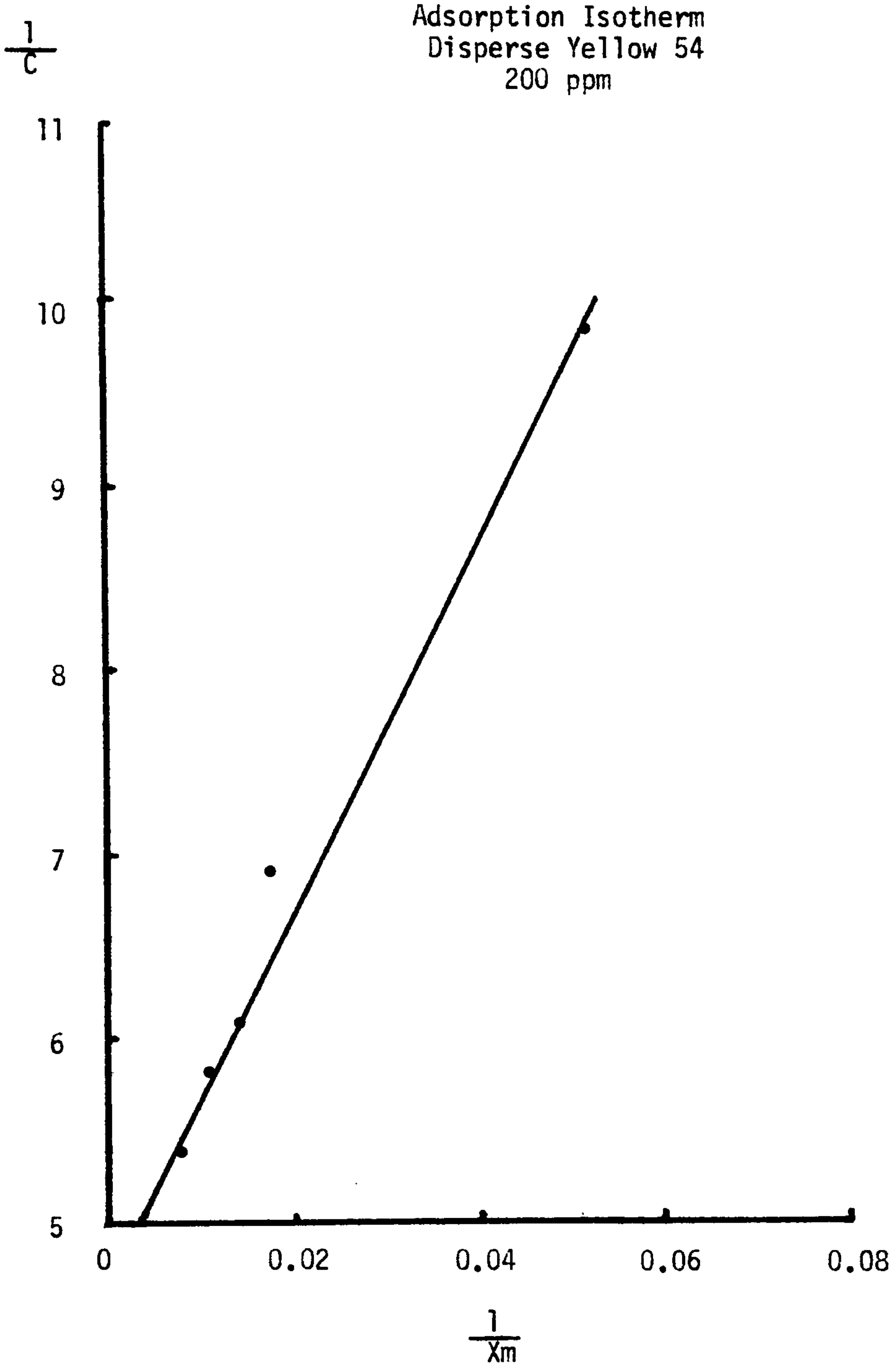


Figure 8

Adsorption Isotherm
Disperse Yellow 54
100 ppm

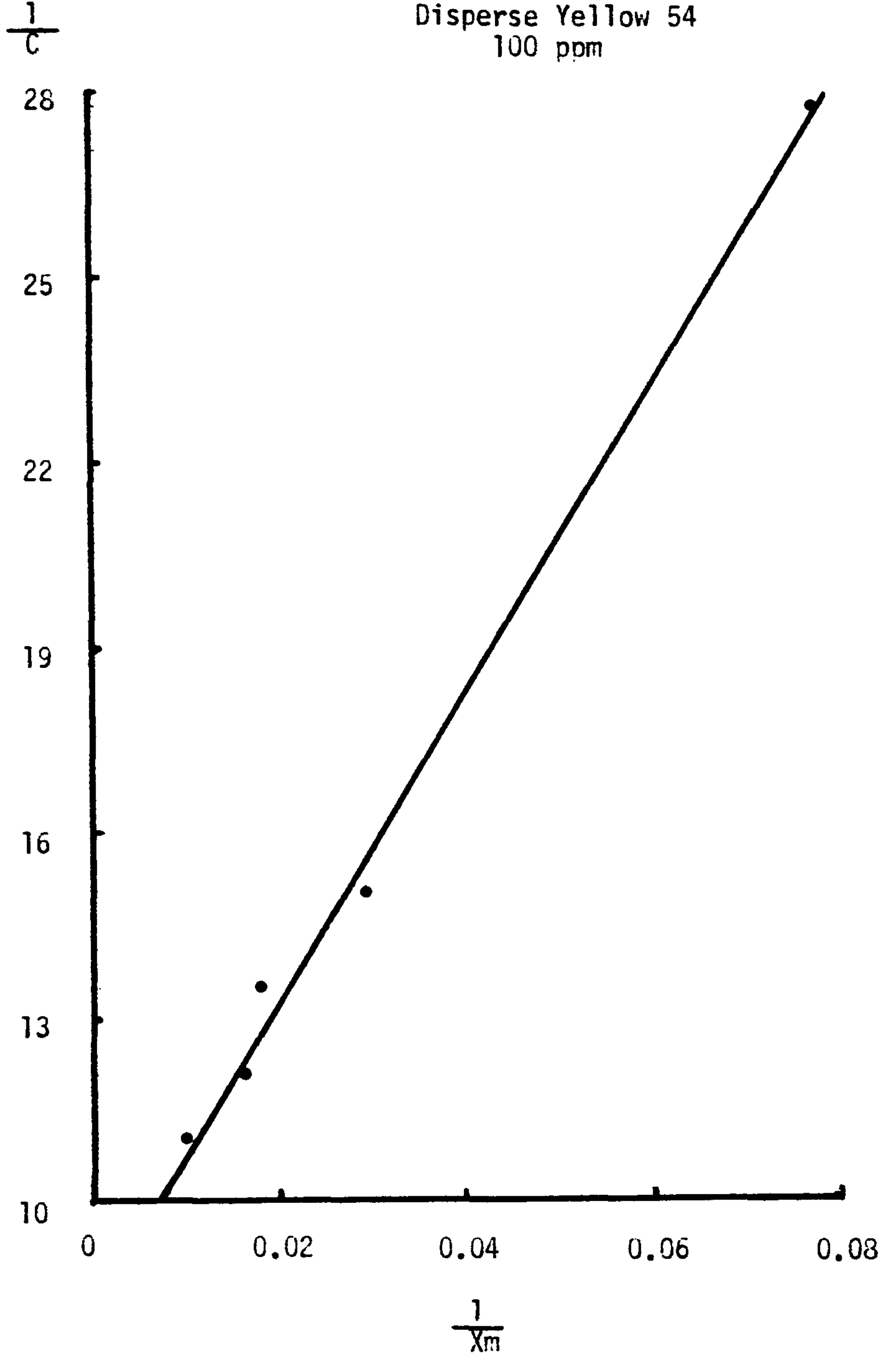
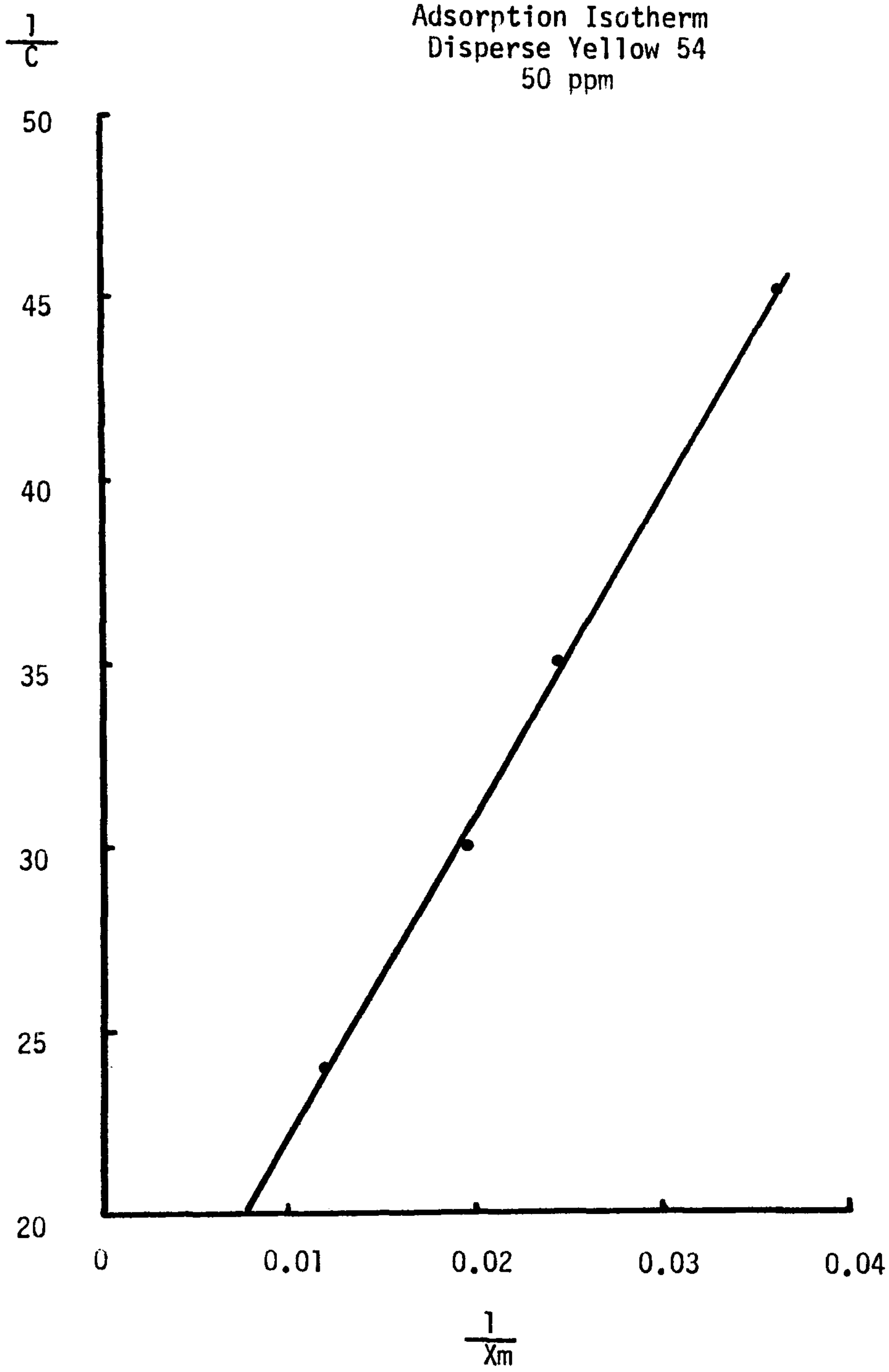


Figure 9

Adsorption Isotherm
Disperse Yellow 54
50 ppm



synthetic fibers indicated that the partition coefficient of the system did not change with a change in the concentration of the disperse dye. This means that over the concentration range being studied, as long as a linear adsorption isotherm was obtained then the concentration of the dye on the fiber was proportional to the concentration of the dyebath. This follows normal solution theory and is expressed by:

$$\frac{\text{Dye on fiber}}{\text{Dye in dyebath}} = \text{K (Partition Coefficient}$$

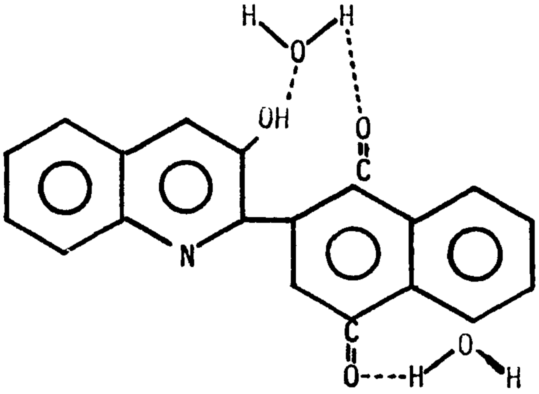
This same fact holds true for the adsorption of disperse dye on powdered carbon. A constant must be obtained for the amount of dye on the carbon-amount of dye in dyebath since there was a linear adsorption isotherm for the disperse dye on the carbon over the concentration ranges studied.

There are four stages in the mechanism of dyeing synthetic fibers with disperse dyestuffs: Only a small portion of the disperse dye is in the water soluble state, the dissolved dye is adsorbed on the fiber surface unimolecularly in accordance with the Langmuir Theory of Adsorption, and the soluble dyestuff migrates from the surface of the fiber into the amorphous regions of fiber and the exhausted dye is replaced in solution by more disperse dyestuff. The mechanism of adsorbing disperse dyes on activated carbon consists of three stages: A large portion of the available dye is in the water soluble state due to the fact that carbon treatment occurs after dyeing and the water soluble dye which is easily removed from the fiber is available to the carbon for adsorption, the water soluble dye is adsorbed unimolecularly on the surface of the activated carbon in accordance with the Langmuir

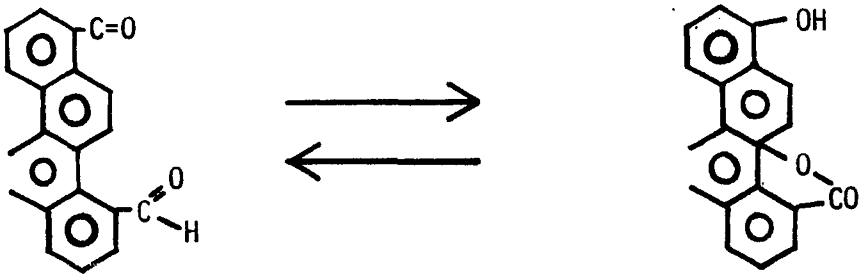
Adsorption Theory, and the dye which is removed by adsorption on activated carbon is replaced from the dye reservoir. The fact that disperse dyes are of low water solubility accounts for their being present in solution in the dispersed state with a particle size of 1-2 microns (72). Therefore, it can be stated in general terms that the dyeing of synthetic fibers with disperse dyes and the adsorption of disperse dyes on activated carbon involves a mechanism of adsorption of the disperse dye from its water solution to the solid substrate. The substrate being a fiber in the case of a dyeing procedure or activated carbon in the case of color removal experiments. The solubility of the dye is to a large extent a controlling factor for adsorption equilibria and the dyeing of synthetic fibers. In general, it has been observed that a direct relationship exists between the extent of adsorption of a disperse dye on activated carbon and the solubility of the dye in aqueous media.

From Table 8 it can be seen that the percentage of Disperse Yellow 54 which could be removed from solution by Hydrodarco C increased with decreasing dye concentration and increased with increasing carbon additions. The same phenomenon has been observed during the dyeing of synthetic fibers with disperse dyestuffs, for the percentage of dye exhausted onto the fiber increased with decreasing amounts of dye in solution or with increasing amounts of fiber available for dyeing. At a dye concentration level of 50 ppm, all color could be removed from solution with 5,000 ppm Hydrodarco C while at a dye concentration level of 200 ppm only 49% of the color could be removed with 5,000 ppm carbon.

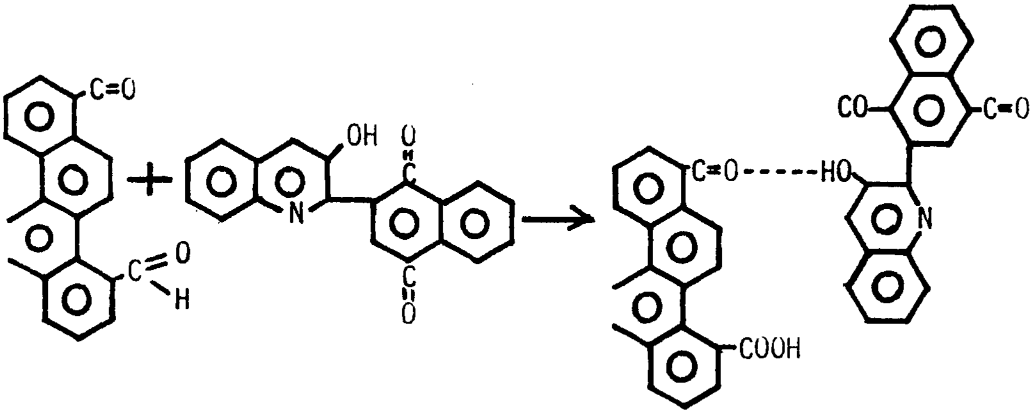
The structure of Disperse Yellow 54 indicates that there are some points for hydrogen bonding to take place:



The hydrogen bonds form in water and must be broken in order to reform and be adsorbed on the surface of the activated carbon. The production process of powdered activated carbon creates such groups as carbonyl and carboxyl on the carbon surface. These groups are somewhat unstable and tend to revert to the more stable lactone tautomer structure but are still available for hydrogen bonding with the Disperse Yellow 54. The reversion toward the lactone tautomer structure can be shown as follows:



The Disperse Yellow 54 can react with the activated carbon in the following manner:



The adsorption isotherm data for Disperse Red 73 at concentration levels of 200 ppm, 100 ppm and 50 ppm are tabulated in Table 9. The isotherm data was determined by stirring the Disperse Red 73 with a range of Hydrodarco C additions for 24 hours at a temperature of 22°C ± 2°C. The concentration of the Disperse Red 73 in solution was determined by spectroscopy as previously discussed. The experimental data were interpreted according to the Langmuir Adsorption Theory. The data were subjected to mathematical treatment by substituting the experimental data into the Langmuir Equation. From Figures 10, 11 and 12 it is evident that a plot of the reciprocal of the dye concentration remaining in solution ($\frac{1}{C}$) versus the reciprocal of the dye adsorbed on the carbon ($\frac{1}{X}$) indicates a linear relationship between these two factors. This dyestuff behaved similar to Disperse Yellow 54 and therefore, the previous discussion on Disperse Yellow 54 holds true

Table 9

Adsorption Isotherm Data - Disperse Red 73

Carbon Concentration (gm/l)	Dye Concentration Remaining in Solution (gm/l) C	Dye Adsorbed on Carbon (gm/l) Xm	Amount of Color Removed (%)
	200 ppm Initial Dye Concentration		
0.1	0.1938	62.0	3.1
0.3	0.1850	50.0	7.5
0.5	0.1760	48.0	12.0
1.0	0.1610	39.0	19.5
5.0	0.1134	17.3	43.3
	100 ppm Initial Dye Concentration		
0.1	0.0875	125.0	12.5
0.3	0.0764	78.7	23.6
0.5	0.0631	73.8	36.9
1.0	0.0590	41.0	41.0
5.0	0.0307	13.9	69.3
	50 ppm Initial Dye Concentration		
0.1	0.0377	123.0	24.6
0.3	0.0300	66.7	40.0
0.5	0.0260	48.0	48.0
1.0	0.0200	30.0	60.0
5.0	0.0000	10.0	100.0

Figure 10

Adsorption Isotherm
Disperse Red 73
200 ppm

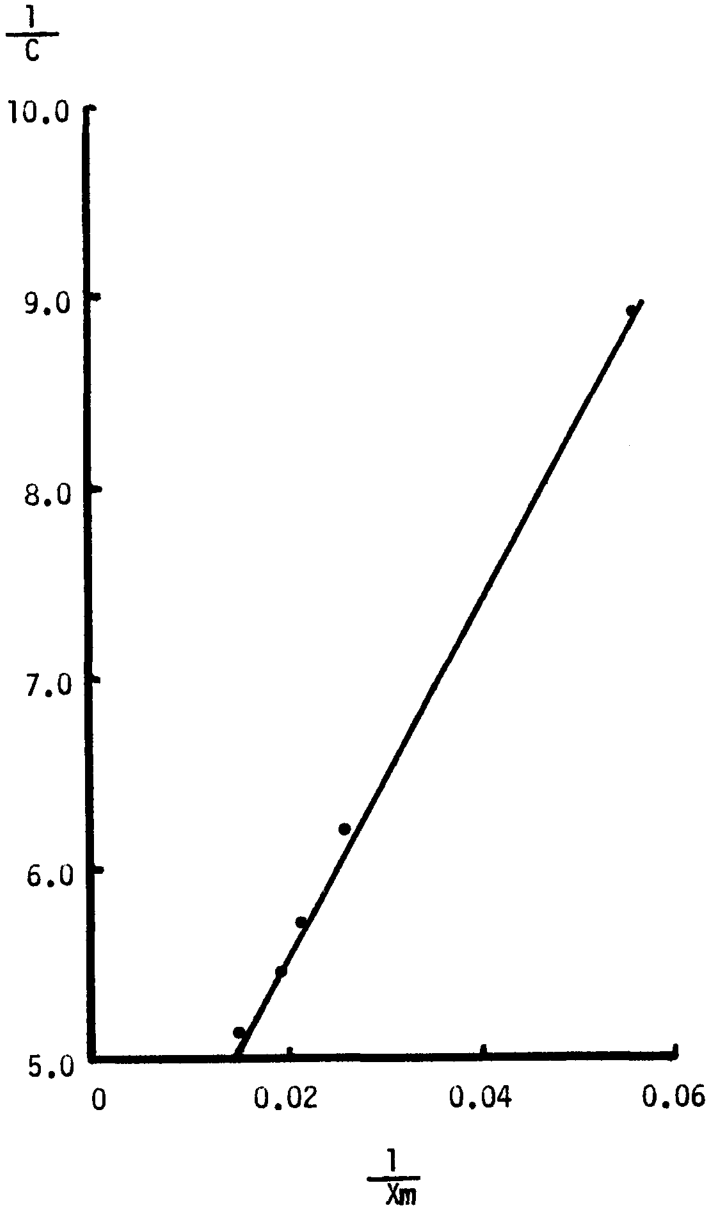


Figure 11

Adsorption Isotherm
Disperse Red 73
100 ppm

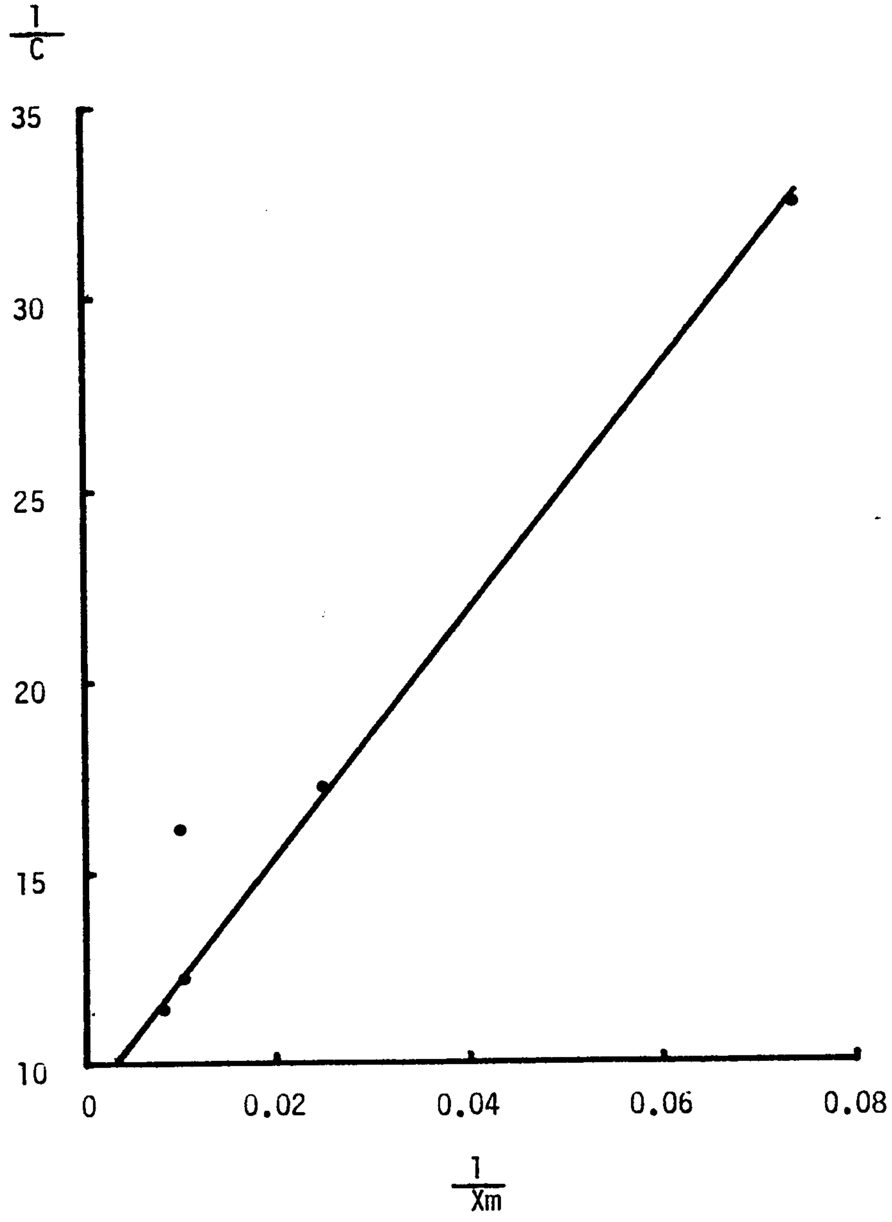
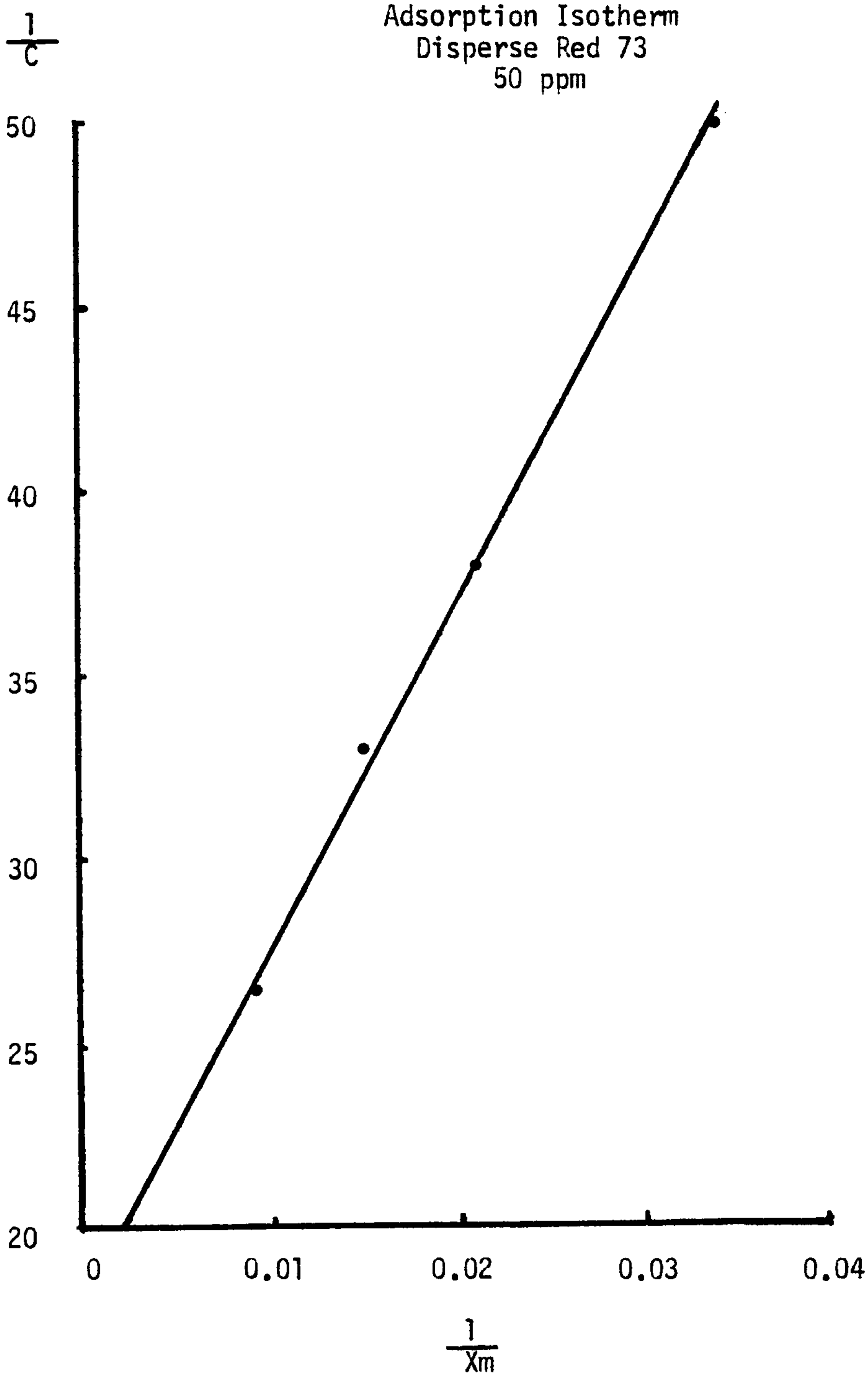
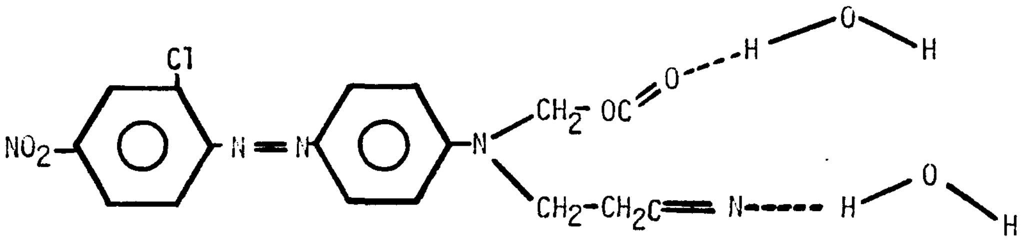


Figure 12

Adsorption Isotherm
Disperse Red 73
50 ppm

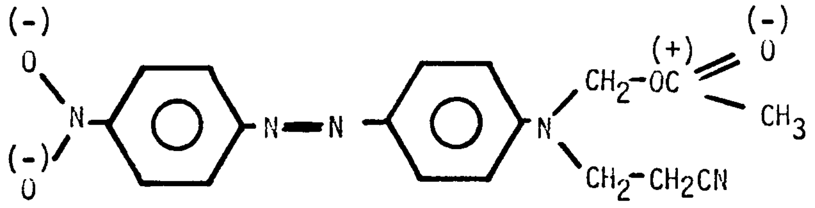


for Disperse Red 73. The structure cf Disperse Red 73 shows some capability for forming hydrogen bonds as shown by:



The dye can, therefore, combine with the active sites on the carbon and be removed from solution in much the same way that Disperse Yellow 54 was removed.

Additionally, Disperse Red 73 also has the ability to combine with carbon because of dipole-dipole interaction. This is due to the unequal attraction for the electrons of different atoms which cause some parts of the Disperse Red 73 molecule to be positively charged and others negatively charged. When these two charges are separated the molecule is said to be a dipole. Snoeyink (73) reported that the surface of activated carbon is slightly electronegative and should, therefore, be susceptible to dipole interaction with disperse dye molecules. The dipole behavior of Disperse Red 73 is shown as follows:



The adsorption isotherm data for Disperse Blue 7 at concentration levels of 200 ppm, 100 ppm and 50 ppm are tabulated in Table 10. The isotherm data were determined by stirring the Disperse Blue 7 with a range of Hydrodarco additions for 24 hours at a temperature of 22^{o}C ± 2^{o}C. The concentration of the Disperse Blue 7 was determined by spectroscopy as previously discussed. The experimental data was interpreted according to the Langmuir Adsorption Theory. The data were subjected to mathematical treatment by substituting the experimental data into the Langmuir Equation. From Figures 13, 14 and 15 it is evident that a plot of the reciprocal of the dye concentration remaining in solution ($\frac{1}{C}$) versus the reciprocal of the dye adsorbed by the carbon ($\frac{1}{X}$) indicates a linear relationship between these two factors. Therefore, the previous discussion on the Langmuir Adsorption Theory for Disperse Yellow 54 is also valid for the Disperse Blue 7/Hydrodarco C adsorption system.

The adsorption data showed that Disperse Blue 7 had a greater affinity for Hydrodarco C than either Disperse Yellow 54 or Disperse Red 73. At most levels of Hydrodarco C and at all dye concentrations the amount of Disperse Blue 7 removed from solution was approximately double the amount of the other dyestuffs. This phenomenon can be related to two main characteristics in the structure of the dyestuff. First the dye has a high tendency to form hydrogen bonds through the large number of hydroxyl groups present in the molecule. Secondly, the anthraquinone structure of the dye tends to present a planar configuration to the activated carbon which allows the dye molecule

Table 10

Adsorption Isotherm Data - Disperse Blue 7

Carbon Concentration (gm/l)	Dye Concentration Remaining in Solution (gm/l) C	Dye Adsorbed on Carbon (gm/l) XM	Amount of Color Removed (%)
	200 ppm Initial Dye Concentration		
0.1	0.1664	336.00	16.8
0.3	0.1144	285.30	42.8
0.5	0.0882	223.60	55.9
1.0	0.0622	137.80	68.9
5.0	0.0178	36.44	91.1
	100 ppm Initial Dye Concentration		
0.1	0.0785	215.00	21.5
0.3	0.0490	170.00	51.0
0.5	0.0242	151.60	75.8
1.0	0.0191	80.90	80.9
5.0	0.0027	19.46	97.3
	50 ppm Initial Dye Concentration		
0.1	0.0247	253.00	50.6
0.3	0.0120	126.00	76.0
0.5	0.0076	84.80	84.8
1.0	0.0042	45.80	91.6
5.0	0.0000	10.00	100.0

Figure 13

Adsorption Isotherm
Disperse Blue 7
200 ppm

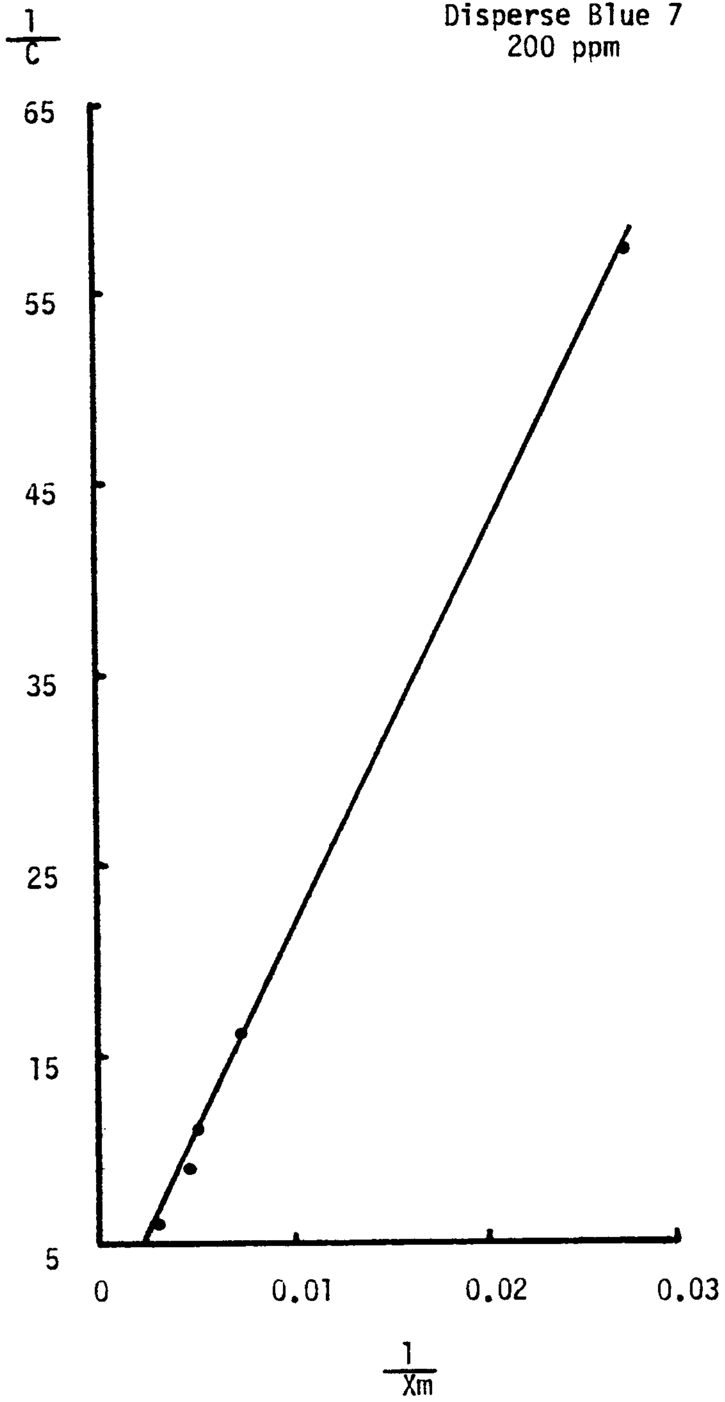


Figure 14

Adsorption Isotherm
Disperse Blue 7
100 ppm

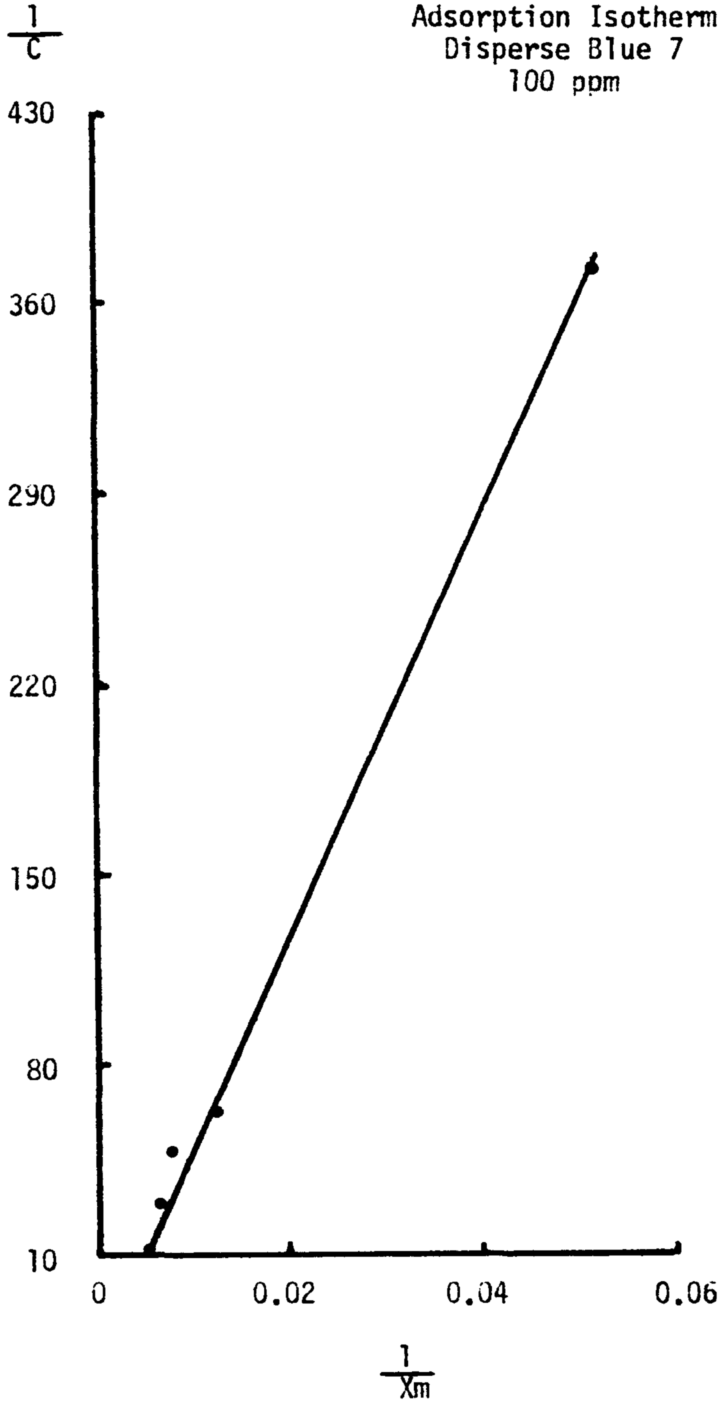
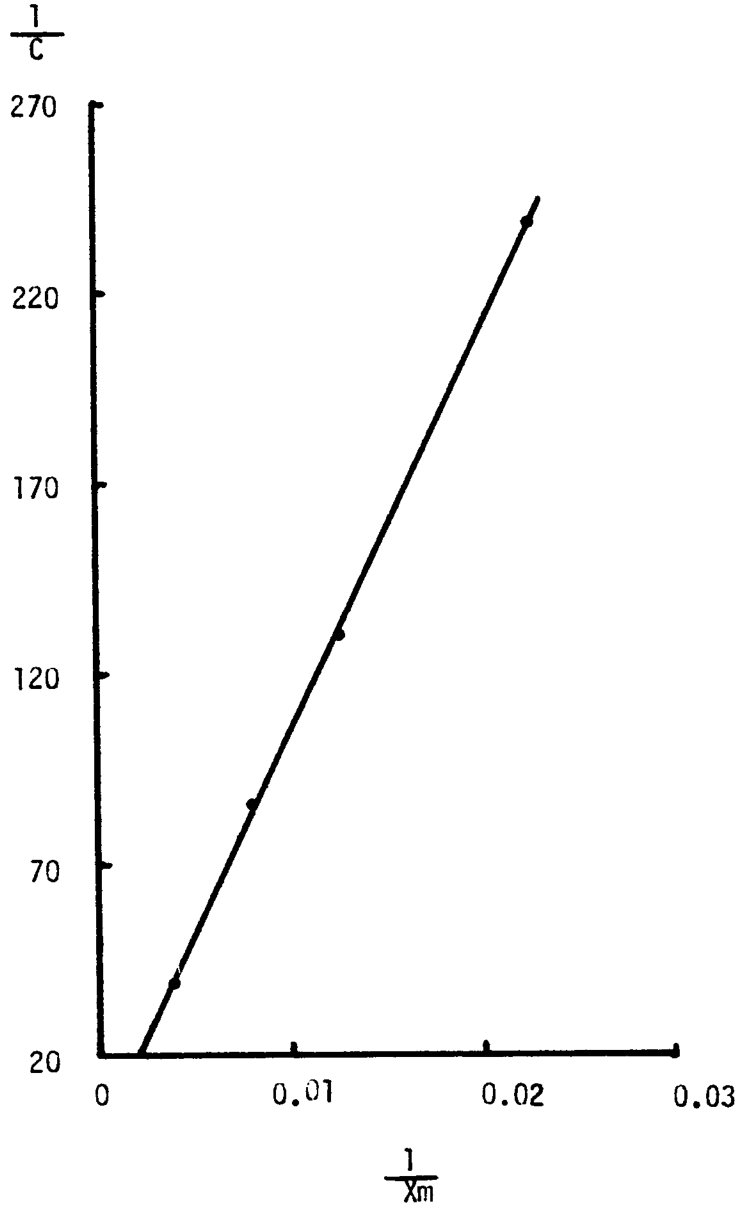
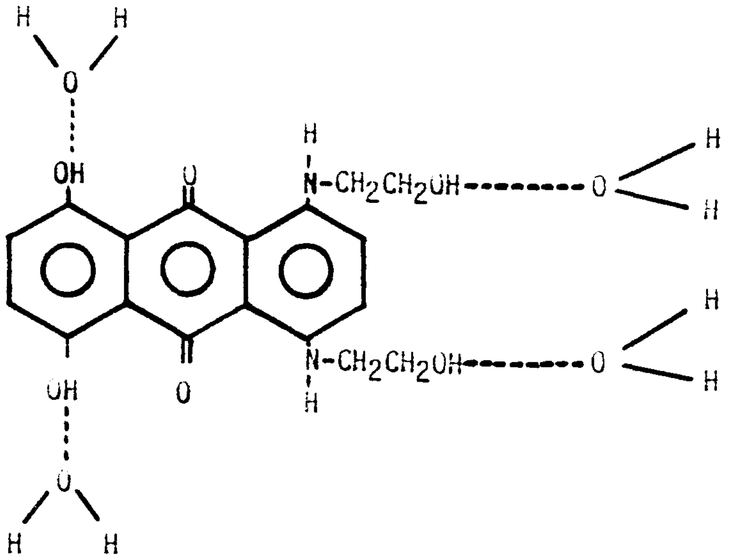


Figure 15

Adsorption Isotherm
Disperse Blue 7
50 ppm



to come into close proximity with the surface of the activated carbon. This type of configuration allows for van der Waals forces of attraction to take place. The anthraquinone structure and the ability for Disperse Blue 7 to form hydrogen bonds can be seen by the following:



Effect of pH on Adsorption

The adsorption of color can be influenced by changes in the pH of the solution. Hassler (74) stated that a pH above neutral was seldom favorable for color removal and in many applications it was found to be detrimental. In contrast, an acidic pH frequently aided decolorization, the optimum pH being dependent upon the particular system being studied. It is not unusual in decolorization processes to alter the amount of color removed by 10-20% depending upon the pH of the system. A low or acid pH usually promotes the adsorption of organic acids; whereas an alkaline pH is most often favorable for the removal of organic bases. The pH of most commercial carbons is due to the inorganic constituents of the initial source material or some added ingredient during manufacture. After the activation process most commercial carbons are alkaline but the pH can be altered by washing and reacting the carbon with various acids such as sulfuric or phosphoric.

Table 11 shows the effect of changes in pH on the amount of Disperse Yellow 54, Disperse Red 73 and Disperse Blue 7 removed from solution by stirring with Hydrodarco C for 24 hours. The pH of the dyestuff-Hydrodarco C solutions were adjusted by additions of sodium hydroxide and hydrochloric acid to simulate a pH range of approximately 4-10 which was characteristic of a dyehouse effluent. There was some degree of reactivity with each of the dyes at both acid and alkaline pH levels as evidenced by the shift to a pH of seven after stirring for 24 hours. This can be interpreted as an acid-base equilibrium and results when an acidic substance comes in contact with a substance possessing basic properties. In any equilibrium system there will be two pairs of conjugate acids and bases and the position of equilibrium will be dependent upon the electron affinity of the bases (75). In the experimental work with Disperse Yellow 54, Disperse Red 73 and Disperse Blue 7, it was found that the solutions were proceeding toward neutralization. Since the disperse dye molecules contain one or more acid or basic groups, or both, several equilibria are possible depending upon the pH, temperature, and concentration of the dyestuff in aqueous media.

Table 11

The Effect of pH on the Removal Properties of Hydrodarco C

pH - Original	pH - After Aeration	% Color Removed
	Disperse Yellow 54	
3.71	6.84	5.12
4.15	7.21	17.83
5.29	7.44	20.81
9.00	7.58	28.32
9.96	8.88	33.74
	Disperse Red 73	
3.91	7.01	6.65
5.14	7.36	23.12
10.21	9.23	40.16
	Disperse Blue 7	
4.42	7.40	47.60
5.92	7.45	51.60
10.12	9.19	56.80

At very low pH and at very high pH it was found that Disperse Yellow 54 precipitated from solution. Approximately 70-80% of the dye was precipitated from solution at a pH of 2.85 and 11.06, respectively. Figure 16 shows the effects of extreme pH on the dye spectra. The altered spectra and the fact that the dye precipitates from solution indicates that the dye tends to agglomerate at extreme pH levels. At a pH range of approximately 4-10 the three disperse dyes remained in solution. However, it was found that as the pH increased toward 10 a greater amount of color was removed from solution than at lower pH levels. This was contrary to what normally happens in color removal systems with activated carbon and was probably due to the tendency of the dyestuffs to begin to agglomerate as the pH of the solution was increased. As agglomeration proceeded the molecular weight and size of the molecules increased which probably caused the dyestuffs to be removed physically by filtration which was carried out prior to determining the amount of color in solution.

Both Disperse Red 73 and Disperse Blue 7 flocked at low pH levels with changes in spectra as shown in Figures 17 and 18. However, both dyestuffs were able to withstand a pH of approximately 11.0 without precipitating from solution. Although agglomeration was taking place with an increase in pH, some balance of time, temperature and concentration was preventing these dyes from precipitating from solution.

Figure 16

Normal and Altered Spectra
of Disperse Yellow 54

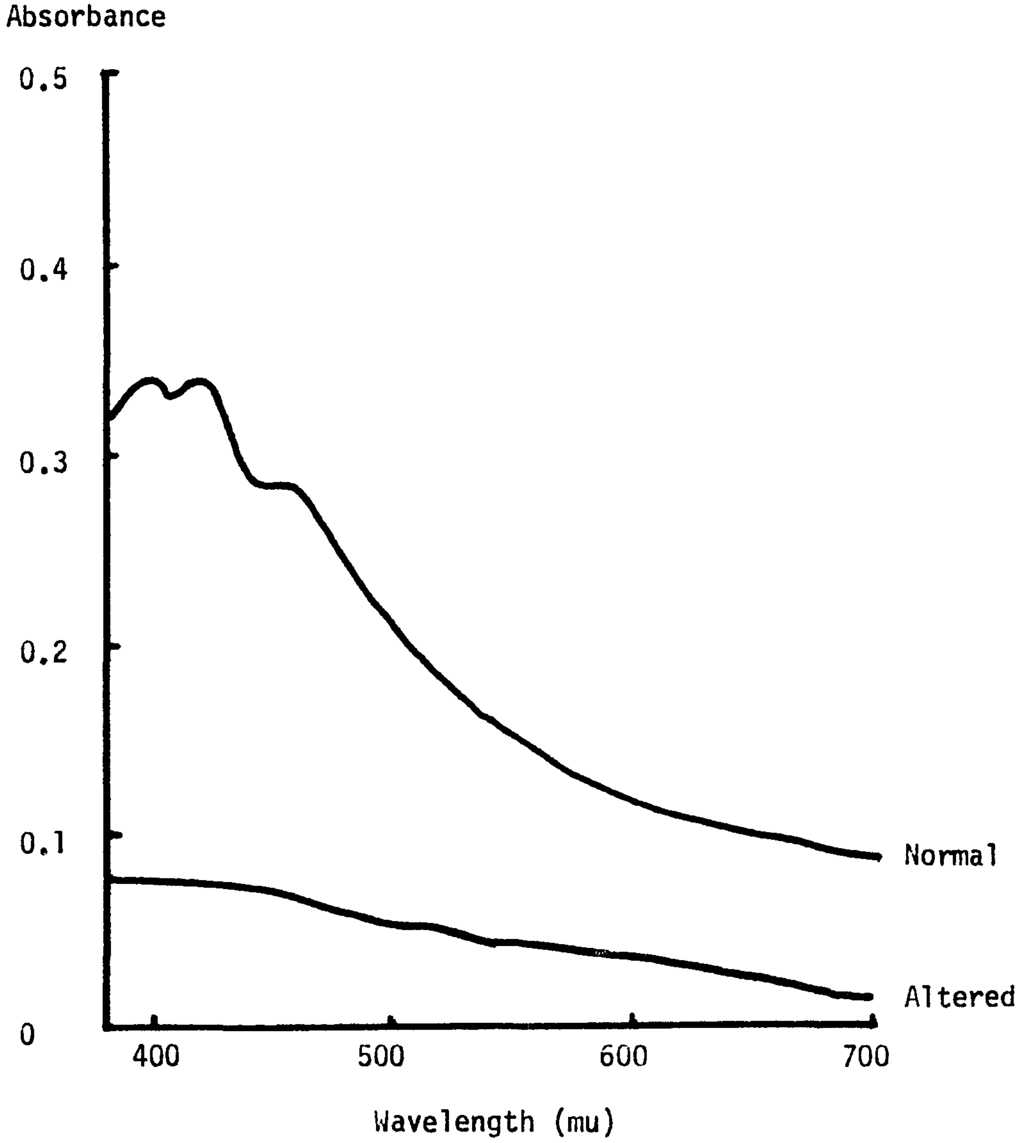


Figure 17

Normal and Altered Spectra
of Disperse Red 73

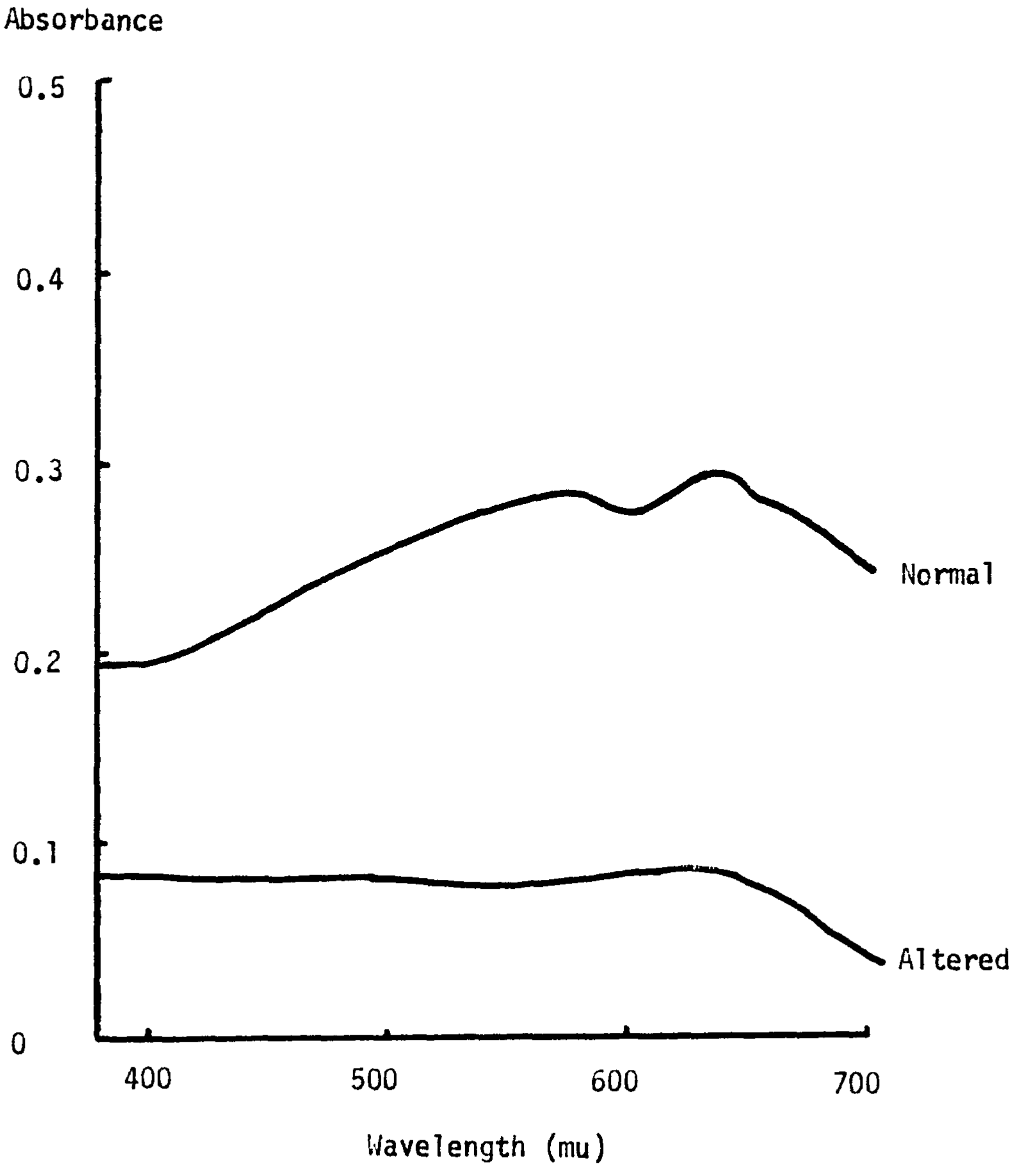
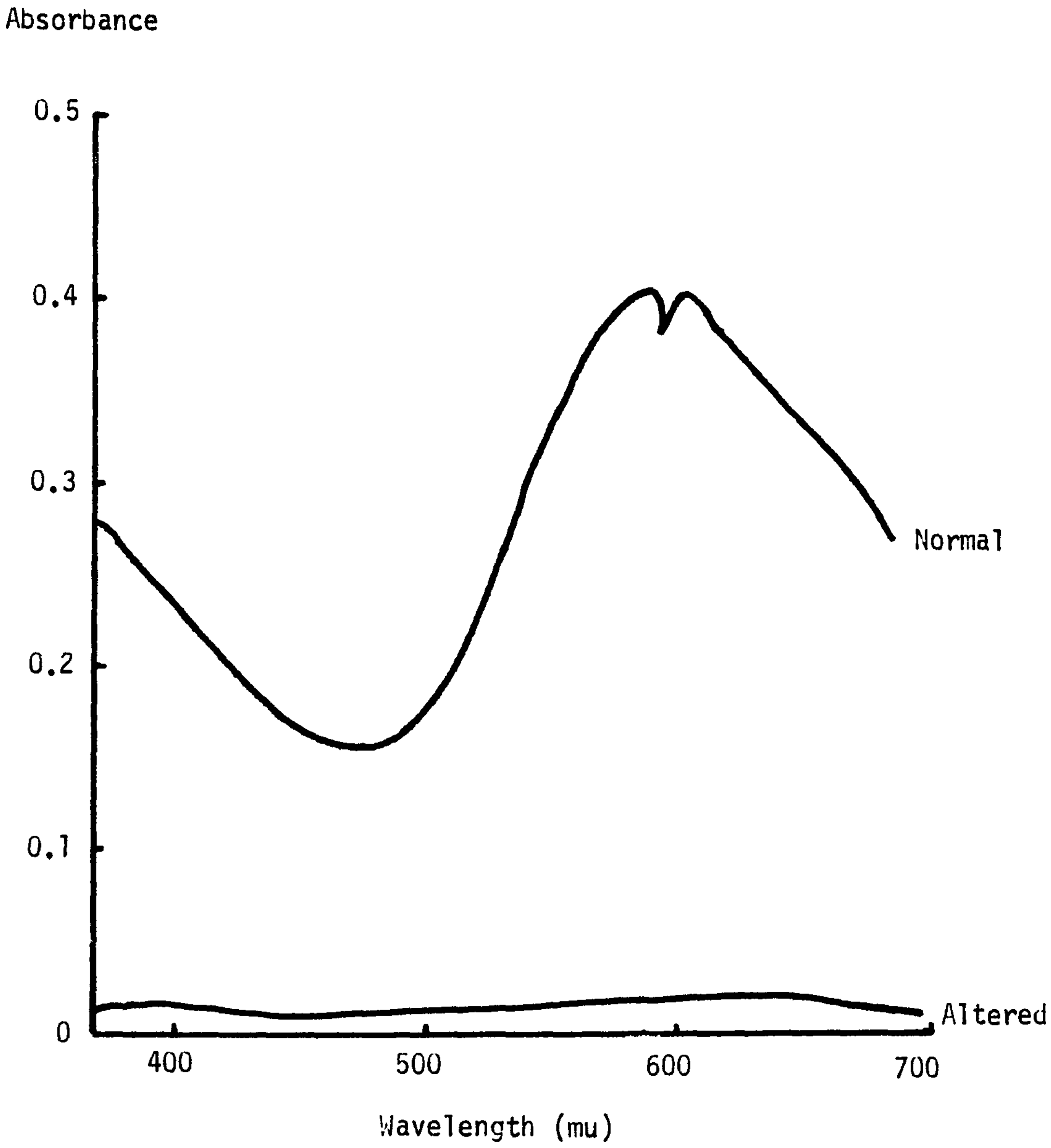


Figure 18

Normal and Altered Spectra
of Disperse Blue 7



Effect of Nonionic Surfactant on Adsorption

In order to determine what effect, if any, a nonionic surfactant had on the color removal properties of powdered activated carbon the following work was carried out. Solutions of Disperse Yellow 54, Disperse Red 73, and Disperse Blue 7 were stirred for 24 hours with 300 ppm of Hydrodarco C to which varying concentrations from 0 ppm to 1,000 ppm of Triton X-100, an octylphenoxynonylethoxyethanol obtained as a 99% minimum active ingredient solution, was added. After stirring, the solutions were filtered and the color was determined spectrophotometrically as discussed previously.

The data in Table 12 shows that the addition of octylphenoxynonylethoxyethanol greatly reduced the color removal properties of the Hydrodarco C. With high concentrations of nonionic surfactant no Disperse Yellow 54 color was removed and lesser amounts of Disperse Red 73 and Disperse Blue 7 color were removed. Only 15.33% of Disperse Red 73 and 17.71% of Disperse Blue 7 were removed from solution when 1,000 ppm Triton X-100 was added.

Based on the theory of dyeing synthetic fibers with disperse dyestuffs, it is known that dispersing agents such as nonionic surfactants can act on the dyestuff (76). Since the solubility of disperse dyes are extremely low, the surfactant tends to prevent aggregation or crystallization which would naturally occur. The surfactant tends to solubilize the dyestuff by forming micelles which can be considered to be tiny drops of hydrocarbons in which disperse dyes can dissolve. The dispersing agent competes with the dyestuff for the fiber just as it

Table 12

The Effect of Nonionic Surfactant on the Removal Properties of Hydrodarco C

Amount of Triton X-100 (ppm)	% Color Removed
Disperse Yellow 54	
0	18.37
50	15.08
100	15.08
500	0
1,000	0
Disperse Red 73	
0	23.98
50	23.43
100	20.44
500	16.35
1,000	15.33
Disperse Blue 7	
0	49.83
50	29.67
100	26.39
500	24.92
1,000	17.71

likewise competes with the disperse dyes for the surface of the activated carbon. By competing for the carbon it therefore increases the amount of dye remaining in solution which in dyeing of fibers reduces the partition coefficient and lowers the percentage exhaustion of the dyebath. Similarly with activated carbon, it greatly reduces the percentage of dye which can be adsorbed on the activated carbon. In a recent study by Weber (77), he experimentally determined that Triton X-100 attained an equilibrium position of greater adsorption than did any of the other surfactants which were tested with activated carbon. He found that 15 to 25% by weight of these materials could be adsorbed on activated carbon. It is reasonable to conclude, based upon the experimental data presented in Table 12 and from the work done by Weber, that the Triton X-100 reduced the adsorptive capacity of the Hydrodarco C by solubilization of the dyestuff and competitive adsorption for the surface of the activated carbon.

Effect of Anionic Surfactant on Adsorption

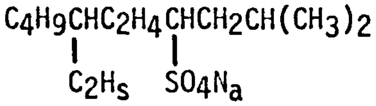
The results obtained from stirring varying amounts of Tergitol Anionic 4 with 100 ppm of Disperse Yellow 54, Disperse Red 73 and Disperse Blue 7 in the presence of 300 ppm Hydrodarco C for 24 hours is shown in Table 13. The data indicates that at low concentrations the Tergitol Anionic 4 had little or no effect on the color removal properties of the Hydrodarco C. However, a small increase in the color removal properties of the Hydrodarco C appears at 500-1,000 ppm Tergitol Anionic 4. The increase is most pronounced for Disperse Yellow 54 and relatively insignificant for Disperse Blue 7.

Table 13

The Effect of Anionic Surfactant on the Removal Properties of Hydrodarco C

Amount of Tergitol Anionic 4 (ppm)	% Color Removed
Disperse Yellow 54	
0	16.96
50	17.13
100	19.06
500	25.20
1,000	26.93
Disperse Red 73	
0	18.98
50	18.82
100	19.95
500	25.00
1,000	25.00
Disperse Blue 7	
0	54.52
50	49.53
100	40.15
500	56.57
1,000	60.53

Tergitol Anionic 4 is a sodium sulfate derivative of 7-ethyl-2-methyl, 4-undecanol, a fatty alcohol sulfate with the following formula:



$$C_4H_9\underset{C_2H_5}{\underset{|}{C}}HC_2H_4\underset{SO_4Na}{\underset{|}{C}}HCH_2CH(CH_3)_2$$

This particular material acts as a wetting agent and when placed in solution tends to dissociate into a negatively charged fatty alcohol sulfate and a positively charged sodium ion. The surface of the activated carbon is negatively charged (78), therefore, the Tergitol Anionic 4 has a tendency to be repelled from the surface of the carbon and to remain in solution. The competition for surface active sites on the carbon between the surfactant and the disperse dyestuff is negligible and one would expect little or no change in the adsorption characteristics of the Hydrodarco C for disperse dyestuffs in the presence of this anionic surfactant. However, the experimental evidence indicated that at very high anionic surfactant concentrations the color removal properties of the Hydrodarco C slightly increases. This could be due to a shift in the equilibrium of the system, whereby the increased amount of anionic surfactant in solution tends to increase the accessibility of the disperse dyestuff for the carbon surface, hence better color removal. An equilibrium shift of this nature is not uncommon and will be affected by changes in pH, temperature and solution concentrations.

Effect of Alkaline Salt on Adsorption

To determine what effect the addition of an alkaline salt has on the equilibrium of a disperse dye/activated carbon system, the following experiments were conducted. Varying concentrations of tetrasodium pyrophosphate ($Na_4P_2O_7$) were stirred for 24 hours with 100 ppm of Disperse Yellow 54, Disperse Red 73 and Disperse Blue 7 in the presence of 300 ppm Hydrodarco C. From Table 14 it can be seen that additions of tetrasodium pyrophosphate increase the color removal properties of the Hydrodarco C for all of the disperse dyestuffs. The effects of pH on the adsorption characteristics of Hydrodarco C, as previously discussed in conjunction with Table 11, is of primary consideration in trying to explain the effects of tetrasodium pyrophosphate on the dye-carbon system.

Tetrasodium pyrophosphate is an alkaline salt that at 25°C produces a pH of 9.5 for a 100 ppm solution and increases to a pH of 11.31 for a 1,000 ppm solution. The amount of color removal obtained with Hydrodarco C in the presence of tetrasodium pyrophosphate is similar to the color removal obtained in the presence of sodium hydroxide. A comparison of the data in Table 11 with the data in Table 14 shows a great similarity for equal pH levels. Disperse Yellow 54 was reduced 30.98% with 100 ppm tetrasodium pyrophosphate (pH = 9.5). Disperse Red 73 was reduced 36.73% with 100 ppm tetrasodium pyrophosphate and Disperse Blue 7 was reduced 70.99% with 100 ppm tetrasodium pyrophosphate. The tendencies of the dyes toward agglomeration with increasing pH is responsible for the high color removal properties of the Hydrodarco C in the presence of increasing

Table 14

The Effect of Alkaline Salt on the Removal Properties of Hydrodarco C

Amount of TSPP (ppm)	% Color Removed
Disperse Yellow 54	
0	15.31
50	24.44
100	30.98
500	51.11
1,000	49.39
Disperse Red 73	
0	20.92
50	32.40
100	36.73
500	40.05
1,000	42.86
Disperse Blue 7	
0	53.02
50	68.63
100	70.99
500	74.96
1,000	76.19

amounts of the alkaline salt. Rutkowski and Martin (79) reported on the ability of tetrasodium pyrophosphate to function as a detergent builder and as a sequestering agent for magnesium and calcium salts in water. However, neither of these factors could be responsible for the color removal properties of the Hydrodarco C since distilled water was used to disperse the dyes and calcium and magnesium ions would not be expected to be present. Furthermore, although the building action of tetrasodium pyrophosphate tends to keep the dye molecules in solution, the fact that the dyes agglomerate with increasing pH tends to nullify the building action of the alkaline salt.

Combined Effects of Anionic Surfactant and Alkaline Salt on Adsorption

The results obtained from stirring varying amounts of Tergitol Anionic 4 and tetrasodium pyrophosphate with 100 ppm of Disperse Yellow 54, Disperse Red 73 and Disperse Blue 7 in the presence of 300 ppm Hydrodarco C for 24 hours are shown in Table 15. Even with the addition of 50-100 ppm tetrasodium pyrophosphate the data followed very closely the results reported in Table 13 for Tergitol Anionic 4 by itself.

The effect of increased pH on the dye-carbon system was negligible in the presence of the anionic surfactant. From previous data it has been shown that increasing pH significantly improved the color removal properties of the system. This was probably due to the fact that the disperse dyestuffs have a tendency to agglomerate at extreme pH levels. From the data in Table 15, it can be seen that there is no

Table 15

The Combined Effects of Anionic Surfactant and Alkaline Salt on the Removal Properties of Hydrodarco C

Amount each of Tergitol Anionic 4 and TSPP (ppm)	% Color Removed
Disperse Yellow 54	
0	16.43
50	18.88
100	17.13
500	23.25
Disperse Red 73	
0	22.00
50	23.00
100	28.00
500	30.25
Disperse Blue 7	
0	51.24
50	56.08
100	56.08
500	56.08

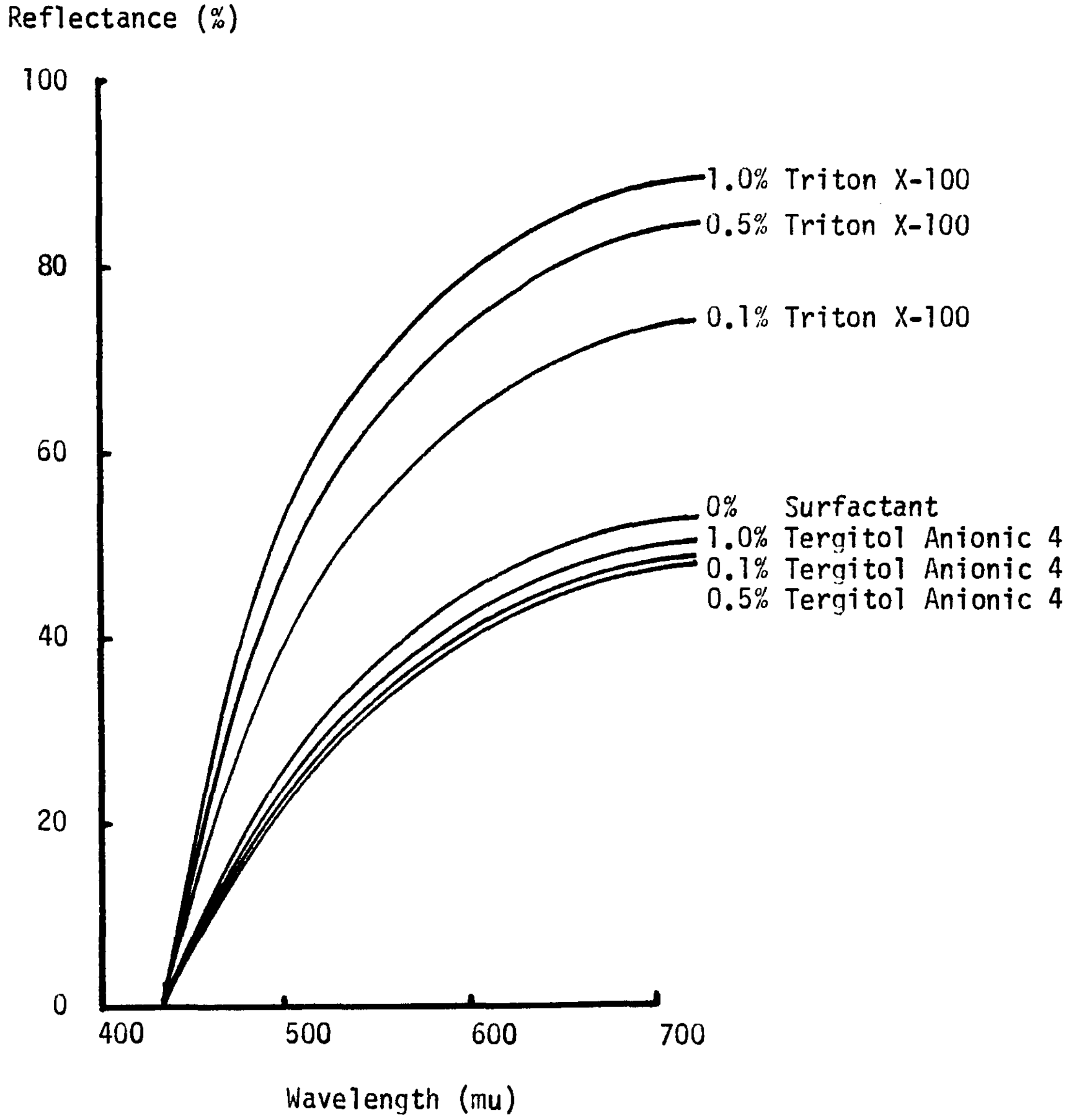
sharp decrease in the color content of the system with increasing additions of tetrasodium pyrophosphate in the presence of Tergitol Anionic 4. The Tergitol Anionic 4 is keeping the dyestuff in solution and preventing agglomeration which would normally occur due to the increased pH from the addition of the tetrasodium pyrophosphate. As long as agglomeration is prevent there will be no color removals as high as was reported either in the previous pH experiment or the experiments with the tetrasodium pyrophosphate alone. This is the same effect which takes place during the dyeing of synthetic fibers with disperse dyestuff, whereby a surfactant is added to the dyebath to prevent agglomeration of the dyestuff and to produce a more level dyeing effect.

Effect of Nonionic and Anionic Surfactants on the Dyeing Properties of 100% Polyester Fabric

The results shown in Figure 19 for the dyeing of 100% polyester fabric with Disperse Yellow 54 in the presence of varying amounts of Triton X-100 and Tergitol Anionic 4 are in agreement with the previously reported data for Hydrodarco C. The percentage reflectance increases with increasing amounts of Triton X-100. Therefore, the Triton X-100 is decreasing the amount of dye adsorbed on the fabric just as it decreased the amount of dye adsorbed on Hydrodarco C. The Triton X-100 solubilizes the disperse dye and competes for the surface of the polyester causing a higher concentration of dye to remain in solution. This reduces the partition coefficient and the amount of dye which is exhausted onto the fabric.

Figure 19

Reflectance Curves for 100%
Polyester Fabric Dyed with
Disperse Yellow 54



The reflectance data for dyeing 100% polyester fabric in the presence of varying amounts of Tergitol Anionic 4 closely follows similar data obtained with Hydrodarco C. In both cases there was a slight increase in the adsorption of Disperse Yellow 54 which was probably due to a shift in the equilibrium of the dye system.

Chapter 5

SUMMARY AND CONCLUSIONS

The adsorption characteristics of Disperse Yellow 54, Disperse Red 73 and Disperse Blue 7 in water were determined by stirring with Hydrodarco C at 22°C ± 2°C to reach equilibrium followed by filtration and spectrophotometric analysis. The following variables were investigated as to their effect upon the removal of disperse dyes by powdered activated carbon: Concentration, pH, surfactants, and alkaline salt. The experimental data led to the conclusion that by controlling the above variables a high degree of adsorption was possible for Disperse Yellow 54, Disperse Red 73 and Disperse Blue 7 on Hydrodarco C.

In a preliminary evaluation of a series of powdered activated carbons, Hydrodarco C a lignite type was found to be suitable for further experimental work. This was based on the adsorption properties of Hydrodarco C as evidenced by its effect on reducing the color, phosphorus, nitrogen and chemical oxygen demand of textile dyeing and finishing waste water.

Three typical disperse dyes were chosen for the experimental portion of this study: Disperse Yellow 54 a quinonapthalone type, Disperse Red 73 a monazo type and Disperse Blue 7 an anthraquinone type of disperse dyestuff. All three dyes attained equilibrium at 8-16 hours of stirring with Hydrodarco C and obeyed Beers Law at dyestuff concentrations of 50-200 ppm. The solubilities of these dyes were found to be 17.8 mg/l for Disperse Yellow 54, 11.5 mg/l for Disperse Red 73, and 23.1 mg/l for Disperse Blue 7. When these dyes were filtered through a Gelman Type A glass fiber filter approximately 20-30% of the color was reduced indicating that a portion of the disperse dyestuff could be physically removed by filtration procedures.

Linear Langmuir adsorption isotherms were obtained for Disperse Yellow 54, Disperse Red 73 and Disperse Blue 7 at concentrations of 50, 100 and 200 ppm dyestuff after stirring for 24 hours in the presence of varying amounts of Hydrodarco C. The fact that the dye-carbon system was explained in accordance with the Langmuir Theory of Adsorption suggested that maximum adsorption corresponded to a monolayer of disperse dye molecules on the carbon surface and that the energy of adsorption was constant. The adsorption isotherms obtained for disperse dyes on activated carbon were similar to those obtained for disperse dyes on synthetic fibers. It therefore followed that the adsorption of disperse dyes on activated carbon took place in three stages: The water soluble dyestuff migrated to the carbon and was available for adsorption, the dye was adsorbed unimolecularly on the surface of the activated carbon in accordance with the Langmuir Theory of Adsorption and the dye which was removed by adsorption was replaced from the dye reservoir to establish an equilibrium within the dye-carbon adsorption system.

Hydrodarco C was able to successfully reduce Disperse Yellow 54, Disperse Red 73 and Disperse Blue 7 from solution by adsorption in much the same way as fibers exhaust disperse dyes from solution during the dyeing process. The percentage of Disperse Yellow 54, Disperse Red 72 and Disperse Blue 7 which was removed from solution by Hydrodarco C increased with decreasing dye concentration and increased with increasing carbon additions. However, the adsorption data indicated that Disperse Blue 7 was more readily removed from solution than were the other dyes. At most levels of Hydrodarco C and at all dye concentrations the amount of Disperse Blue 7 removed from solution was approximately double the amount of the other dyestuffs. This was explained in terms of the large number of hydroxyl groups present in the dye molecule which were available for hydrogen bonding and the planar configuration of the anthraquinone structure which allowed the dye to come into close proximity with the surface of the activated carbon so that dispersion forces became important.

At a pH range of approximately 4-10, Disperse Yellow 54, Disperse Red 73, and Disperse Blue 7 tended to remain in solution. However, as the pH increased a greater amount of the dyestuff was removed from solution. This was contrary to what normally happened in color removal systems with activated carbon and was probably due to the tendency of the dyestuffs to agglomerate as the pH of the solution increased. Since the weight and size of the dye particles increased as agglomeration proceeded the dyes were physically removed by filtration, which at extreme pH levels had a much greater effect on color removal than did adsorption on activated carbon.

The presence of Triton X-100 greatly reduced the color removal properties of Hydrodarco C. The surfactant tended to solubilize the dyestuff and altered the equilibrium of the dye-carbon system by competing with the disperse dye for the available surface sites on the activated carbon.

Low concentrations of Tergitol Anionic 4 had little or no effect on the capacity for Hydrodarco C to remove disperse dyes from solution. However, there appeared to be a slight increase in the color removal properties of Hydrodarco C when high concentrations of Tergitol Anionic 4 were added to the system. This was explained by considering an equilibrium shift, whereby the increased amount of Tergitol Anionic 4 was increasing the accessibility of the disperse dyestuff for the carbon surface thus increasing the amount of color removed.

The surfactant effects were confirmed by dyeing a 100% polyester fabric with Disperse Yellow 54 in the presence of Triton X-100 and Tergitol Anionic 4. The dyeing results were in agreement with the adsorption data obtained with Hydrodarco C.

The effects of an alkaline salt such as TSPP on the dye-carbon system were explained due to the fact that the disperse dyes tended to agglomerate with increasing pH. The data from the TSPP experiments were extremely similar to previous data dealing with the effects of increased pH on the dye-carbon system. However, when Tergitol Anionic 4 was added to the dye-carbon system along with TSPP a sharp decrease in color removal was noted. This was probably due to the Tergitol Anionic 4 preventing agglomeration of the dyes with increasing pH.

From the data obtained in this study the following hypotheses were supported:

1. The adsorption of disperse dyes on powdered activated carbon follow physical adsorption laws and can be characterized by adsorption isotherms.

2. Deviations from the physical adsorption laws occur as the dye-carbon system becomes more complex by the addition of surfactants, alkaline salt, acids and bases.

3. Disperse dyes exist in equilibrium with the powdered activated carbon.

4. The presence of surfactants change the equilibrium characteristics of the dye-carbon system in relation to the solubilization effect of the surfactant with the dye.

5. The structural characteristics of the dye influence the adsorption equilibrium of the dye on the carbon.

It is recommended that future researchers investigate the following:

1. The effects of temperature on the ability of powdered activated carbon to remove the disperse dyes from solution

2. The possibility of desorbing and reusing the disperse dye

3. The effects of carbon mixtures, whereby carbons with different physical and chemical properties would be used to treat textile mill effluent

4. The economics of using powdered activated carbon for removal of disperse dyes from solution versus other known treatment methods

5. The feasibility of developing a specific type of powdered activated carbon which would selectively remove disperse dyestuffs.

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