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The Use of Activated Carbon for Removal of Dyestuffs from Secondary Paper Mill Effluent

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THE USE OF ACTIVATED CARBON
FOR REMOVAL OF DYESTUFFS
FROM SECONDARY PAPER MILL EFFLUENT

by

Duane L. Zomer

A thesis submitted to the
Faculty of the Department of Paper Science and Engineering
in partial fulfillment
of the
Degree of Bachelor of Science

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ABSTRACT

Adsorption of colored materials, dyestuffs, from simulated paper mill effluents by activated carbon columns appears to be a very effective method of removing color from waste effluents. Laboratory investigations have indicated that materials commonly encountered in paper mill effluents tend to slow the adsorption of color molecules. This phenomenon is overcome by allowing more time for adsorption. This lends itself to a diffusion-limited type adsorption mechanism with multi-layering adsorption on the carbon surface.

Using carbon of not less than 45 mesh, carbon adsorption columns appear to become feasible for large volume color removal. There appeared to be no significant head loss or plugging problems when countercurrent flow columns were used to remove color from the mill effluents. The columns also appeared to remove rosin from the waste while filtering out fiber fines. While contact time of the effluent with the carbon was shorter than usual (2 minutes as compared with 17 minutes commonly used today), color adsorption appeared very good.

A cost estimate of the carbon was also made. Since the adsorptive capacity of the carbon was not completely utilized, the estimates are high. The adsorption cost was \$5,590 per million gallons of effluent treated for discard-type applications and \$888 per million gallons of effluent treated for regenerated carbon.

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HISTORICAL BACKGROUND & DEVELOPMENT OF THE PROBLEM

HISTORY

Activated carbon is a compound that has been around for centuries, although its isolation was only accomplished in the past century. Wood ashes, a very crude form of active carbon, were used for many years around the sixteenth century. This was at one time considered the best method for improving the palatability of water (1). The ability of charcoal, an unpurified form of activated carbon, to decolorize solutions was known in the fifteenth century. The earliest recorded use of charcoal for decolorizing solutions was in 1785 when Lorwitz (2) investigated the decolorizing and deodorizing effects of carbonized plant tissue. Later, the use of bone char for decolorizing sugar solutions was common. In 1905, Glassner and Suida (3) investigated the properties of lamp black and acetate soots, analyzing them for chemical content, effectiveness, release of adsorbates, and possible uses.

To meet the increasing need for color adsorbents in the sugar industry, Raphael von Ostreiko developed and patented (4) a process for carbonizing a mixture of vegetable type materials with metal chlorides or with carbon dioxide and steam on charred material (5). This was the industrial basis of many of the activated carbon preparations to follow. Among these were Eponet (Fanto Works in Stockerau, near Vienna) in 1911, Norit (Norit Company of Amsterdam) in 1911, Carboraffin (Bayer Company of Leverkusen, Germany) in 1913, Radit (Prague, Czechoslovakia) in 1918, and Active Carbon

(National Carbon Company, United States of America) in 1919. The studies in reactivation of spent carbon led to further refinements in the products and newer production techniques, especially with those using zinc chloride (5). The specialized manufacture of these activated carbons continues today.

The use of carbon has been studied very closely since early industrialization caused its manufacture to be economical. During World War I, the use of granular and then pelletized carbons for gas masks was very thoroughly examined. By these studies, efficient gas masks are available today (6). After World War II, industry started to apply carbon to specific tasks. Large gains were made in solvent recovery using active carbon. Other gains were made in the sugar industry, where active carbon replaced bone char. Carbon was also applied to the textile and the pulp and paper industries. This has continued to meet wide spread approval up to today, when mixed municipal and industrial wastes are being removed at Lake Tahoe, California and at Fitchburg, Massachusetts by carbon adsorption columns (7-8).

CARBON STRUCTURE

Activated carbon is an imperfect and therefore porous crystal lattice. It is prepared by carbonization of carbon containing materials, usually by pyrolysis in a low oxygen atmosphere. The pores left behind after carbonization give activated carbon its adsorptive properties.

Activated carbon has characteristics closely resembling those of graphite, although less perfectly oriented (9). The

atoms are in a planar hexagonal arrangement of about 3.35 \AA of separation. The parallel planes of activated carbon are not perfectly aligned with respect to their common perpendicular axes. Layer overlapping and combining is quite common, giving the carbon a random planar structure (10). Also, activated carbon has other groups, like oxygen and nitrogen, in the lattice which cause a deflection of the graphite planes.

The structure of activation varies from carbon to carbon. Detailed X-ray studies by Franklin and others (11) have indicated that about 65% of wood charcoal is an ordered, planar structure, 55% of which is parallel plane oriented, and the remaining fraction is completely unordered. The unordered fraction is not graphitized and is harder than the rest of the carbon, i.e., not as apt to be torn apart by abrasion. It is a combination of the unordered and the highly ordered areas with some mixing of the planar layers that give activated carbon a basic porous structure.

The activation process removes most of the unordered carbon as well as any residual hydrocarbon materials. This introduces voids in the carbon structure, commonly called pores. The inner surface of these pores is large, thus giving activated carbon its high adsorptive capacity. Investigations indicate that concentrated entrance structures, straight through capillary type structures with closed ends, regular slit openings, V-shaped pores, tapered pores, and other structural formations are common in the carbon particles (12-15).

The pore sizes of carbon vary and are usually divided

into three areas: micropores, transitional pores, and macropores. Micropores are usually classified as less than 18 to 20 Å in radius and fill very quickly (16).. The transitional pores range in radius size from 20 to 500 Å and are filled by capillary condensation. The macropores are usually those above 500-1000 Å in radius and are defined as those pores not fillable by capillary condensation. Most carbons contain a mixture of all three types of pores, usually predominating to a limited extent in one type of pore.

While carbon is the predominant material in activated carbon, other compounds are also present and influence the adsorption by it. Common contaminants found in and on commercial activated carbon are hydrogen, oxygen, nitrogen, chlorine, combined sulfur, organic materials, and trace metals.. Groups formed in the carbonization process, commonly called tar and tarry products, limit the adsorption of some compounds. Also, entrapment of compounds like oxygen, nitrogen, and metallic elements limit the adsorption of some materials.. Trace groups of incompletely combusted materials around the pore openings can slow or limit the entrance of certain compounds. This is why a pure carbon is sought for active carbon.

MECHANISM OF ADSORPTION

The mechanism of adsorption on the surface of activated carbon particles has been studied extensively and has been fairly well defined. Proposed mechanisms include monomolecular solid surface adsorption, multi-layer molecular layering

of adsorbate molecules, molecular screening, capillary adsorption, and limited secondary chemical bonding. The multilayer theories and the capillary adsorption theories are the most widely accepted ones at present. These theories lead to empirical equations which will be discussed later.

There are five steps relating to a mechanism (17):

These are:

1. Transfer from the medium to the carbon particles of the medium-material mixture.
2. Adsorption of the material in solution onto the carbon surface.
3. Penetration of the material in solution into the capillaries of the carbon.
4. Adsorption with the solid carbon or possible chemical reaction.
5. Mixing and possible equalizing of the concentrations of the adsorbed materials.

These, combined with layering of the adsorbed material on the carbon particle surface, give a good general concept of an adsorption mechanism. Specific things tend to be more common to the adsorption of one phase than to the others. These will be discussed in more detail in the following sections.

Mathematical Models

In any adsorption reaction, there are three things that influence adsorption. These are the amount of adsorbent, the amount or concentration of the adsorbate in close contact with the adsorbent, and the temperature of the adsorption. Since the adsorption mechanism involves an energy change, conditions favoring exothermic reactions are also important.

Historically, the first experimenter to find an equation applicable to adsorption was Gibbs (18).. While his equation dealt with concentrations in a solution, this was quite hard to apply to adsorption applications.. Soon after Gibbs equation emerged and applications were tried, Langmuir found a more easily applicable theory..

Langmuir postulated that the adsorption rate of a material from solution was proportional to the pressure of the adsorption and a fraction of the surface of the carbon occupied by it. He also postulated that desorption, also known to be present, was proportional to the surface area occupied. With a knowledge of the weight of the substance adsorbed per unit weight of adsorbate, the Langmuir equation was developed (19). It states:

$$\frac{C}{X/M} = \frac{1}{a} + \frac{bC}{a} \quad \text{or} \quad \frac{P}{X/M} = \frac{1}{a} + \frac{bP}{a}$$

where

$X/M = \theta$ = the amount of solute adsorbed per unit weight of adsorbent

a = the activity of the solute

b = a constant

C = concentration of solute

P = partial pressure of the gaseous component

The Langmuir equation is restricted by many things. It must be assumed that no interaction of the adsorbed molecules takes place; that no tarry products or non-adsorbent materials are on the adsorbent surface; that the adsorbed molecules do remain on the surface of the adsorbate a "sufficiently long time"; that there is no multi-layer adsorption; and that there is no capillary migration and condensation. By assuming that all adsorption energies are from $\theta = 0$ to $\theta = 1$, substitution

into the Langmuir equation gives the simpler Freundlich equation for equilibrium conditions (5):

$$X/M = K C^{1/n}$$

where K and n are constants characteristic to the system.

For very dilute solutions of organic compounds, a diffusion reaction of the type::

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2} - \frac{\partial S_o}{\partial t}$$

where S_o is an adsorption site term, as found by simple integration of Henry's law with respect to heterogeneous equilibria, is very useful and applicable. By substituting the Freundlich equation into the above equation, an expression easily recognizable as Fick's Law results..

$$\frac{\partial S_o}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) = \frac{\partial}{\partial x} \left(\frac{D}{n K S_o} \right)^{1/n} S_o^{(1-n)/n} \frac{\partial S_o}{\partial x}$$

where:

t = time

D = Diffusion constant

x = adsorbate distance from adsorbent

By integration, it is found that a modified diffusion coefficient results, or::

$$(D/N) (1/KS)^{1/n} S_o^{(n-1)/n}$$

These equations lay the fundamentals of all modern adsorption rate equations. They represent the case of only one component adsorbed on carbon. When more adsorbates are involved, the equations become unweildy and can not be resolved in the general case. For instances dealing with these, work has been done in this area and it is advisable to check reference material for them (5).

Adsorption of Liquids from a Liquid Medium

Many studies have been done in the past fifty years to apply activated carbon to specific uses (12-17). These have led to some end use applications as well as long term data gathering. This gathering of data has brought about a group of proposed theories and a resulting set of new facts.

A first for liquid adsorption is the initial wetting of the carbon. While this first appears insignificant, it should be noted that air and gases are trapped in some surface imperfections. These gases greatly decrease the liquid contact surface area and also the carbon efficiency (20).

The liquid adsorption theories tend to favor an initial monolayer adsorption. As the solute molecules are taken from the solvent, they diffuse across the surface of the carbon particle. The adsorbed molecules next fill the porous structure of the carbon particle, beginning with the large macropores, next to the transitional pores, then finally the micropores. After this happens, a less strongly held second layer follows the same procedure.

Adsorption of weak- and non-electrolytes gives a good understanding of adsorption. These materials are believed adsorbed mainly by physical forces, as indicated by a low or negligible enthalpy change. This is an extremely rapid adsorption and is believed limited only by molecular diffusion over the carbon particle. This also is the nature of the multi-layers of adsorbate covering the particle's surface. But, in some instances, a slow and large enthalpy change process called chemisorption takes place. This process involves

coulombic attraction through oppositely charged particles, allowing a large enthalpy change. Chemisorption, if present, takes place almost solely on the particle's surface and requires a large amount of free area to occur. While there is no complete means of differentiating how much of each type of reaction occurs with present techniques, they will be assumed to take place simultaneously with more physical than chemisorption taking place.

Adsorption of molecules tends to be influenced by a change in pH (21). Adsorption of acids in low concentrations ($<0.01N$) seems to proceed as previously described. Stronger amounts of acids tend to increase chemisorption with the molecules being neutralized during adsorption. This is believed due to the hydrogen present in the acid and on the outer surface of the carbon (22). After the first layer is chemisorbed, other layers of unneutralized acid are adsorbed, oriented with the cationic end of the first layer adsorbed to the anionic end of the next. There is also evidence that indicates functional group branching from the carbon particle surface has an influence on the adsorption and adsorption rates (22).

Adsorption by various carbons in changing pH has also been studied. It has been found that adsorption drops at a certain pH, due to the isoelectric effect. By decreasing the pH even further below this adsorption drop point, the adsorption rises slightly. This is believed due to the Frumkin phenomenon. These values change from carbon to carbon, but all tend to be in the acidic region of pH (22-24).

While diffusing into the porous areas of the carbon, adsorbed molecules become limited as to their porous accessibility; carbon acts as a molecular sieve (5). While carbon is not as effective as other molecular sieves, it does screen out certain sized molecules and compounds with specific functional groups.

Molecular screening on activated carbon has two well founded theories. The first theory uses only capillary action (23). The surface opening in the capillary structure limits the molecular mass and the amount of material that can be adsorbed. The second theory allows for only limited capillary action, favoring the influence of surface groups on the adsorption of molecules (24). Recent studies have shown that only the change of free energy during the adsorption affects the groups adsorbed, allowing different chemical groups and compounds of markedly different size to be adsorbed simultaneously (24).

The screening properties of carbon are very good for selective organic adsorption. Carbon exhibits a concentrative effect on specific sized molecules by limited capillary adsorption. This has been found to be a useful process in special applications in both gas and liquid chromatography (25). This special use of carbon can be easily applied to large scale projects, although it may be economically infeasible for some applications (21).

It was found that carbon had a special affinity for solutions (26). This affinity applies to all components of the solution, both the solvent and the solute. There is a compet-

itive adsorption between the two. Therefore, an initial equilibrium must be established, usually by wetting the carbon in the solvent. This gives the impurity a higher attraction to the carbon than the liquid has. Carbon has a higher affinity for certain materials than it has for others (21). Therefore, a solvent with low affinity, like water, is recommended. The adsorptive properties on a one pass carbon system commonly allow one to two parts in twenty thousand for most common inorganic impurities to pass through the carbon column (27).

Studies have indicated that adsorption is greatly influenced by many factors. A decrease in temperature tends to increase adsorption (5). Pressure also tends to influence adsorption in a positive manner. Also, with fixed temperature and pressure, the amount of contaminant removed varies logarithmically with the percentage of carbon present, by weight percentage (21). This shows that the more dilute a contaminant is, the easier and more efficiently it is removed. The time the carbon is in contact with the contaminant also exhibits a logarithmical proportion as to contaminant removal (5). Contact time equilibrium varies from carbon to carbon and from solution to solution, usually taking days to accomplish (28). It is this time lag that makes carbon hard to fill, therefore increasing its economic favor.

Polarity of materials and solvents has also come under careful study. Initial findings, as reported by Pouchly and Vavruck (29), give a general rule of mutual affinity of substances with similar polarity. Traube's rule (30), similar

to that mentioned before, states that the adsorption of organic molecules from aqueous solution increases strongly and regularly with an increase in molecular weight in a homologous series. These observations suggest that non-polar substances will be adsorbed better than polar molecules, which may still be adsorbed to a smaller extent. For this reason, polar solvents dispersing less polar molecules are an optimum condition. Also, from the general rules, it can be seen that the adsorbed material will increase its solubility as it is concentrated on the carbon. This is not necessarily of any importance since the material is held there by other strong forces.

Other things have also been studied as to their effect on carbon adsorption. The surface tension of the solution (surface energy) has also been found to play a role in adsorption (18). Another factor is steric and blocking effects caused by branching and cyclic molecules (31). This tends to influence the solubility of the molecule, and therefore, the resulting adsorption. These effects are important, remembering that the carbon adsorption is reversible.

The reversibility of carbon adsorption is very important in all recovery processes. The recovery of adsorbed molecules can easily be done by using a more adsorptive compound. In many cases, a steam or hot solvent treatment is very effective. This can also separate various components from the carbon with good results, especially purity.

Adsorption of Colloids and Solids from Solution

Solids and colloids are removed effectively from solution by activated carbon. These adsorptions tend to follow two separate processes. While the processes are different, they tend to combine as the solid and colloidal particle size approach each other.

The mechanism of colloidal adsorption is one of surface adsorption. The colloidal group is adsorbed on the surface of the carbon. After this initial adsorption, the colloid structure breaks down and the material then diffuses into the macroporous structures of the carbon (5, 31).

The mechanism of solid adsorption is mainly one of filtration. The solid particles are passed between the carbon particles, where they become trapped. Depending on the size of the particles, they may be adsorbed by the carbon or just held from passing through the carbon mass. This is usually followed by a large flow rate and adsorption efficiency drop, possibly blocking further carbon adsorption. While active carbon is not widely used for filtration of solids, it is possible, through special adaptations discussed later in this report, to efficiently use carbon for this purpose.

A third area, combining solid and colloidal materials removal, is that of bacterial and micro-organism removal (32-33). Carbon has exhibited good results in this area. The adsorbed microbes are not harmed. They remain active while adsorbed by the carbon and appear to have no ill effects when released from it.

After adsorption and filtration of particulate and colloidal dispersions, the carbon loses much of its liquid, solution, and gaseous adsorptive properties. This has been found true in the case of several governmentally subsidized water filtration plants, causing them to be designed away from bed type carbon adsorption (33).

Adsorption of Gaseous Contaminants

As in the case of colloidal adsorption, gaseous adsorption parallels the adsorption of molecular contaminants from a liquid medium. The gas is adsorbed on the surface of the carbon and diffuses into the porous structures. After an initial layering, restricted multi-layering takes place.

Some very different things do happen with gaseous phase adsorption. There is a tendency for gaseous (vapor) condensation in the pores of the carbon (34). This is thermodynamically favored and, therefore, occurs easily. A more open and therefore, less expensive, larger particle carbon can be used for gases than is used for liquids. Reversibility with gaseous components seems to be a larger problem than with solventized and solid adsorption, eliminating some gas adsorption applications from practical consideration (35). Adsorption of gaseous components is usually more detrimental to the carbon than is any other phase; this is the case with SO_2 , reacting with the carbon and decreasing the carbon's surface area and resulting efficiency (36).

WASTE REMOVAL

The paper and paper related industry relies heavily on the use of water as a medium for transporting paper fibers and various additives for the paper system. These additives and other water components are divided into four classes: organic compounds, dissolved and colloidal; dissolved inorganic compounds; suspended solids; and pathogenic organisms (21). While it is possible for these to have a high degree of adhesion on paper fibers, there is also a good deal of them not attached to the fibers and are eventually passed to the sewers. With closing of the white water systems in many mills, an efficient cleaner is needed for this material. This cleaner may very well be activated carbon.

Dyestuffs fall into the category of paper mill "wastes". Most dyestuffs are either anionic or cationic organic salts or colored pigments. These are added to the fiber-water system as solutions or as pigment dispersions. They adhere to the fiber by electrostatic attraction, weak chemical and secondary bonding, or fiber entrapment. Being in solution, all material is not retained by the paper fibers or the fibrous mat they form, with the excess being commonly passed into the waste water system. The waste water may be recycled or passed into the sewer. These color bodies have a high degree of coloring possibility and can cause extensive visible contamination of water at low concentrations.

Other problems associated with dyestuffs include those of optical brighteners. These increase the nitrate and phosphate levels of mill effluents. Microbiological degradation

and settling can remove some of these, and are presently being used, but they can not economically remove 99+% of all wastes.

Activated carbon filters are an efficient answer to this. Activated carbon can remove organic and inorganic materials, including dyes and other additives, and filter out larger materials, like pigments and fibers, remaining in suspension in the water. Adsorption and blocking by active carbon columns are good, although possible carbon adsorption overloading tends to offset this (an increase in an optimal 0.1% contaminant level to a 3.5% contaminant level decreases carbon efficiency to unusable amounts (37)). This is why activated carbon is used in secondary and tertiary applications instead of primary and secondary ones (38).

Applications of Active Carbon

There are several methods used for applying activated carbon for waste treatment. All methods have favorable and unfavorable factors. Modifications and additions to these means have allowed them to keep up with the high volumes of preparatory and waste waters needed by modern industry.

The first method of activated carbon use was the addition of dry powdered carbon to a body of liquid. This is now called the batch contact method. This method is still very common in the sugar industry and in using activated silica from alum plants for cleaning pulpmill wastes. In the 1930's, a wetting and metering machine was very common in pipeline addition before settling area applications (1). The addi-

tion of the carbon in pipelines has lowered head losses and saved related horsepower requirements for water movement (39). Presently, most activated carbon is used in other large scale application methods, but when it is applied in pipeline type applications, the carbon is added just ahead of large settling basins. This is also modified in preliminary water treatment to add dry carbon on the top of the water in settling ponds to shield sunlight, then fall through and adsorb organic materials and micro-organisms, especially algae, which cause foul taste in water (40). Other applications usually involve updating existing machinery to meet present higher volumes of water needed by industry..

The problems of this method lie mainly in recovery.. Fine carbon particles, while aiding in some contaminant flocculation, remain in solution for long periods of time before settling out (5).. Also, there is a chance that a contaminating molecule may never come close enough to an active carbon particle for adsorption, and, if it does, there is another good chance that the carbon particle may already be loaded. Problems also occur in the recovery of the spent carbon, often with results detrimental to its end use (41).. These problems have led to the use of carbon bed filtration.

Fixed bed carbon filtration, with its modifications, has found the widest acceptance of all methods currently used (5). The advantages of this type process include having all carbon in one finite space, conserving the area needed for the process.. It allows easier carbon recovery. It also allows filtration by the carbon of particles not usually

adsorbed, i.e., leaves, weeds, pollen, dust, etc.

Dry bed carbon filtration is an old and important process. It has been used effectively in gas masks, hospital air filtration systems, and cigarette filters (42-52). Dry carbon beds are often used for vapor and volatile solvent recovery systems. While they are of little use in paper mill effluent waste removal, they could be useful in stack gas and pulp mill odor elimination.

The method that has met with the widest acceptance in the water treatment area in recent years is the fluidized carbon bed. The use of a low adsorbance medium, like water, or a very dilute contaminant, <2.0%, has allowed carbon to become known as an economic adsorption and filtration medium. This has also met with widespread investigation as a possible means of water pollution abatement (53).

The fluidized carbon bed method is usually divided into two major areas, fixed and moving bed adsorption (54). The use of fixed fluidized carbon bed has met with much widespread acceptance, becoming very common (7). The moving beds, a basic modification of the fixed bed system, have good flow and solid filtration capabilities, but seem to be meeting less acceptance. Both methods are presently used and warrant dissertation.

The fixed bed method is one of the easiest methods of adsorption. The contaminated material is passed through a column at a common rate of 4 gpm/ft.² carbon. The contact time in the column is generally high, 15-30 minutes, with total color removal reached only through the column layering

of theoretical carbon beds. The contaminated matter is usually monitored at influent and effluent ports. Exceeding maximum acceptable effluent levels usually causes column shutdown. Most present fixed fluidized bed systems contain several (usually four) columns. Waste effluent enters one column, with the column effluent used as influent for the next column. As the first column exceeds maximum effluent standards, influent is changed to the second column, which then becomes the primary adsorption unit. The first column is then emptied and refilled with fresh carbon. The fresh column is then placed at the end of the effluent line, working its way back to the primary adsorption unit as preceding columns become loaded.

The advantages of the countercurrent type systems are numerous (8). The space saved from the non-bed systems is enormous. The carbon is easily recovered with almost negligible losses. Also, if something does happen to one column, it can be shut down and another easily put in its place without closing down the entire system.

To further conserve space, the moving bed carbon column was developed. There are two common types of moving bed columns, the cocurrent and the countercurrent methods. With the cocurrent method, fresh carbon is added to the influent and most contaminated end of the column. With the countercurrent method, the fresh carbon is added at the effluent end of the column. Of the two methods, the most popular is that of countercurrent addition, with it also being the easiest to operate (55-56).

The application of these column types has been very popular.. While,, with no regeneration, carbon is a more expensive means of adsorption and filtration than the others commonly used today, regeneration has brought these costs down to a cost competitive with other adsorbents like clay,, activated silica,, and others. Also,, the possibility of reusing instead of discarding the carbon saves on the land needed for waste disposal. These things,, combined with automation, have given carbon a potential for leading the field of adsorbents and purification resins..

CARBON REGENERATION.

Cost wise,, carbon is a good adsorbent,. The initial costs of equipment for carbon adsorption is approximately the same as most other processes.. But the high initial and make-up costs of fresh carbon eliminate it from a discard-type system. This necessitates the reactivation of spent carbon to make the entire system economical, as compared with other waste removal and adsorption systems.

The regeneration of the carbon is a very critical process (21). The adsorbed materials must be carbonized. This must be done with the lowest possible loss of carbon but with the highest loss of contaminants. To accomplish this, the process is carried out in a low or oxygen deficient atmosphere.. Next, the purified carbonaceous material is activated or formed into a purer, crystalline oriented product.. Since the activation processes are identical in procedure and mechanism during the initial and the reactive phases of carbon

processing, the initial phase will be discussed in detail here. It must be stressed that the two mechanisms are identical, with only the overall amount of activation being the difference between the two; a limited amount of activation takes place in the capillaries and on the surface of carbon particles in regeneration while capillaries and surface imperfections are formed in initial activation phases.

Carbonization is usually done by one of two methods, heat in a low oxygen atmosphere or by heat in chemical surroundings (57-58). In the first method, an oven, usually with multiple plates or hearths, is used in a nitrogen, carbon dioxide, or steam atmosphere. Since hydrocarbon molecules tend to be oxidized at lower temperatures than the pure carbon is, the oven temperature is kept below the combustion point of carbon, 500-600° C. When multiple hearths are used in a furnace, the fresh material is added near the top and removed from the bottom of the furnace, giving the carbonaceous materials less chance to react with oxygen as they become purified. The second method involves mixing of chemicals, usually including zinc chloride, in a paste with the carbonaceous base. This is then heated to around 600° C., liberating gasses and causing an oxygen free atmosphere. This may also allow chemical activation of the carbon to occur.

Activation of the carbon is the second step in the process, although often included in one step in most modern processes. Activation is usually accomplished by controlled oxidation or by chemical reaction (5, 57-58). The first method of activation, as outlined by Ostrejko, was by addition of super-

heated steam during a carbonization process. This has been modified in some processes to use air at 600° C. in limited amounts to give a controlled exothermic reaction. Chemical reaction usually lessens the amount of control needed for activation at carbonization temperatures. Chemical activation materials (metallic salts, cyanides, nitric and sulfuric acids, sulfur, and others) are added in specific amounts and mixed thoroughly with the carbonaceous materials before heating. After the activation process is complete, the final material is washed to remove excess chemicals, then ground to the specific coarseness desired.

The mechanism of the activation process is believed to be that of the removal of uncrystalline and a limited amount of crystalline carbon. The main activation reactions usually involve oxygen from air, water molecules, or organic molecules. The activation reactions are easily performed on the non-crystalline carbon regions, although they may also occur to a limited extent on the crystalline areas (5). If the activation reactions are not well controlled, the amount of micro and transitional pores, as well as total surface area, are decreased, thereby decreasing the amount of carbon adsorptive capacity (5). This undesirable side effect calls for the extremely close regulation found in all carbon activation and regeneration facilities in operation today.

While the degradation by activating agents is detrimental on virgin material, this could be beneficial to regenerated carbon. The Taft Water Research Center has found a decrease in the adsorptive capacity in regenerated carbon (7).

This was found to be large enough to warrant dumping the carbon after eight to ten regenerations by pyrolysis. While this preliminary finding was poor, work at the Lake Tahoe PUD project showed that this was not as detrimental as first indicated and has had no effect on plant operation (59). The use of superheated steam in the Tahoe regeneration furnace is an activation-type system used in many virgin material activation facilities. While data on the use of chemical activation on in plant use is not available at present, this is a possible means of reactivating the low efficiency pyrolytically regenerated material to that comparable to the virgin material.

The economics of regeneration of spent carbon is a great concern. Solvent removal of adsorbed material is industrially unfeasible due to high cost factors, except for very expensive chemicals (5). The regeneration by pyrolysis has an optimum material loss of 3-10% (5% at Lake Tahoe), with approximately 50% of virgin material loss required for an acceptable initial product and a loss of over 60% of adsorbed materials required for a good second product (60). Regeneration problems also include loss of iodine number and color removal efficiency. Also, the cost of regeneration and make-up carbon, plus instrumentation, accurate control and increased manpower are other costs associated with carbon systems. At the Lake Tahoe PUD project, these were found to be \$36.11/MG waste treated. While the total overall cost is not extremely high, it is in a 6% cost deficit when compared to costs of silica, alumina, resins, talc, clay, or other common adsorbent systems (7). Where carbon costs are expected to decrease in future years,

this problem will be eliminated. Also, esthetically speaking, carbon can be made reusable, eliminating the land fill needed for the other spent adsorbents. These costs must be studied well before any installation is made and will show the true long-term low cost of an activated carbon system.

CARBON APPLICATION TO PAPER MILL EFFLUENT SYSTEMS:

While carbon is an excellent means of color removal from solutions, as yet, there has been no recorded evidence of a paper mill using active carbon filters, although it has been used in integrated pulp-paper mill set-ups (61). This is partially due to the different color problems encountered in pulp mill effluents and partially due to the fact that lignin, a major byproduct from the pulping of wood, is one of the best carbonizing materials known. The use of carbon in these applications is mainly for the removal of lignin products (color) from the pulp mill effluents, although some paper mill wastes may also pass through the carbon columns for purification. The removal of pulp mill color bodies from effluent is fairly well related to the problems encountered with removal of color from paper mill effluents.

Paper mill effluents are different from those encountered from pulp mills. They have a different pH, higher concentrations of fillers, optical brighteners, and different additives. Paper mill wastes also contain more cellulose fibers, an excellent carbonizing medium, than is commonly encountered with the pulp mill waste. These all affect the adsorption by active carbon columns and should be eliminated as much as possible.

The carbon should be used as an additional treatment (secondary or tertiary) and not used to replace the primary treatment or clarifier (21). Most paper mills have primary and secondary treatments in current operation which drop contaminant levels appreciably. Since carbon adsorbs better at lower adsorbate concentrations, this is very beneficial. Also, large amounts of fibers and fillers do tend to block flow through the carbon. These problems indicate that carbon should not be used for primary paper mill effluent treatment.

The system used should be a bed type system. The countercurrent moving bed type, as described in Smisek and Cerny (5,62), with gravity flow of carbon is also recommended. The countercurrent flow method would lower the plugging at the beginning of the column. Also, technology allows a fewer number of columns than with fixed bed systems, since the one constantly on stand-by would not be mandatory. The recycling of the carbon would also be automated as facilitated by the counterflow design. One man could run the columns and the regeneration furnace from one central control room. The manpower savings would warrant this type of set-up, not to speak of the power savings from the unblocked filters.

Problems for the individual system must still be solved. First, the maximum adsorbing rate and amounts must be found. Second, the affects of fibers and additives on the adsorption by the carbon must be found. Third, the ability of the regeneration furnace to carbonize adsorbed wastes and revitalize the carbon without excessive carbon loss must be found. It should also be found if the cellulose fibers are sufficient

in quantity and quality to make up any part of the carbon lost in the recovery operation.. Fourth, it should be determined if the additives, fillers, and optical brighteners commonly found in the paper system will have a detrimental affect on the adsorptive and regenerative capacities of the carbon..

These questions must be answered to check the economics of the carbon system. At present, there is no published material on these topics, so further work must be done in these areas before a good appraisal can be made. Also, a check on mill conditions should be made and the above questions answered before an accurate appraisal of the carbon can be made for the actual properties sought.

EXPERIMENTAL

EXPERIMENTAL APPROACH

The purpose of this study is to determine if activated carbon is an efficient and economical means of removing dye-stuffs and other coloring materials from paper mill effluents. This was accomplished using simulated mill conditions with a laboratory prepared primary-treated paper mill effluent and down and countercurrent flow carbon bed systems. Due to the limited nature of this report, only one dyestuff was evaluated. The dyestuff was used in evaluating three different types of carbon. Rosin, alum, and fiber fines were also added to the dye solution to approximate actual paper mill effluent conditions.

MATERIALS

The materials used in this experiment were, for the most part, very common to present paper mills. They consisted of an acidic dyestuff, Cyanamid-Calco Water Green SX Conc., Dustless; a standard rosin sizing agent, Pexol, by Hercules; a standard technical grade solid paper maker's alum; and a standard paper making fiber, Weyerhaeuser bleached hardwood kraft, specially treated to represent fiber fines. The carbons were slurried in water before addition to the columns. The preparation of each of these materials will be discussed later.

Preparation of Solutions

All solutions were prepared in a weight to volume relation. All solids were oven-dried to remove loose moisture. Common analytical techniques were used in all preparations.

The solutions were prepared in concentrated stock quantities, then diluted when needed. Solutions of one and two grams per liter of solution were used. Due to the breakdown of some materials, all solutions were discarded when extreme optical variances and precipitates were noted.

To obtain paper fiber fines similar to those found in mill effluents, the fibers used in this project were specially prepared. The Weyerhaeuser bleached hardwood kraft pulp was dispersed in distilled water by a high speed disperser, then classified with a Bauer-McNett Fiber Classifier. The fraction between 48 and 200 mesh was collected. These fines were wet-lapped and stored until needed for use in the stock solutions.

The stock solutions were diluted to proper concentration in a fifty-four liter Nalgene carboy. These concentrations were derived from operational data on a primary paper mill clarifier operating at 3 MGD and emitting six hundred pounds of paper fibers and an additional six hundred pounds of BOD to receiving waters. The concentrations used in this study, as derived from this data, were 200 ppm dyestuff, 100 ppm rosin, 100 ppm alum, and 200 ppm (in weight/volume) fiber fines. Stock solutions were diluted to the above consistency in the column feeding carboy, agitated by mechanical means

and by compressed air. The solutions were agitated for a minimum of one hour before treatment by the carbon columns.

Carbon

Three carbons were used in these experiments. They were Carbon 1, Filtrasorb 400, made by the Calgon Corp.; Carbon 2, Philterkol SP#1, marketed by the Olin Company; and Carbon 3, Norite, manufactured by the Norit Company. The mesh sizes used were 12 X 40 for Carbon 1, 8 X 60 for Carbon 2, and 200+ for Carbon 3. The carbon hardness ranged from that of charcoal for Carbon 2 to that of an expensive coal-based carbon for Carbon 1.

INSTRUMENTATION

Instruments used in these experiments were for color measurement and for flow rate determination. A Hitachi-Perkin-Elmer UV-Vis Spectrophotometer, model 139, with recorder, photomultiplier and wave length drive units, was used to measure color. A matched set of 1.008 cm. quartz cells were used in this instrument. Due to the low volume of flow, a stopwatch and a graduated cylinder were sufficient to measure the flow rate.

Color was detected by the spectrophotometer. After an initial instrumental standardization and calibration, dyestuff adsorption plots were made. From these, areas of maximum adsorption were compared to a distilled water standard curve for the maximum adsorption region to be used as the standard for this experiment (Figure 2). This demonstrated the useful-

ness of the recorder and wavelength drive units, giving quickly interpretable results in a minimum of time and with a minimum of effort.

Concentration calibration of the dyestuff was done both before and after adsorption by carbon. This procedure showed a shift in the maximum adsorption area, causing an ultraviolet region at 249 μ to be used as the standard wavelength, Figures 3 and 4. Addition of rosin-alum and settled fiber-rosin-alum solutions made only slight deviations in instrument readings at this wavelength (Figure 2). Visible color limits were found. Graphs of concentration curves and wavelength changes on dye solutions were also made (Figures 1-4).

Flow measurement on the columns were very simple. Times were recorded for one hundred milliliters of effluent to pass through the column. All readings were done manually.

ADSORPTION EXPERIMENTS

Three basic types of experiments were made. The first experiment was an equilibrium study using carbon and dyestuff only. The second study involved using a fixed bed downflow carbon column. The third study involved the use of counter-current flow columns. Depending on the results of the first and second tests, the third test was optional.

The equilibrium test was done in beakers with stirring. These tests were made initially to check the amount of color adsorption by the carbon. This was accomplished by adding fifty milliliters of standard 200 ppm dye solution to vari-

ous amounts of carbon. To obtain more accurate data, the carbon was not pulverized, as is common practice. The settling of the carbon particles, as well as the effect of agitation, was noted to see how the carbons would perform in the columns.

The downflow column studies were done next. These used 20 X 400 mm. fritted glass chromatography columns as carbon holders. The columns were filled with forty grams of oven-dried carbon, wetted, and added to the columns filled with distilled water. The columns were kept full of water until the water was displaced by the dye solution. The columns were made continuous by lifting the column effluent to the top of the column with compressed air. The recycling technique was used only when needed to further clarify column effluent.

If successful downflow studies were accomplished, counter-current flow studies were then done. These studies used cork-affixed water cooled condenser jackets with Y-tubes serving as dual action water inlet and carbon outlet connections. Column effluent was removed from the top water feed outlets of the columns. Two columns were used, being connected in a tandem system. The first column contained twenty-five grams of carbon and the second column contained fifteen grams of carbon. The flow through the columns was kept uniform.

The experiments with the three columns were based on carbon adsorption and dyestuff removal efficiency at a standard flow rate of 3 liters/hr./column, or 12 gal/hr/ft². When excess visible color was noted leaving the columns or when a large flow drop indicated column plugging, the columns

were shutdown. After being shutdown for specific short periods of time, the columns were restarted as a check on the regenerative properties of the carbon. This will be discussed in more detail later.

DISCUSSION AND PRESENTATION OF RESULTS

The effect of carbon toward two major things was studied in these experiments: the removal of color in the column and flow changes while the column was in operation. Also, any pertinent or visual observations were noted.

MESH

Carbon mesh is very important to liquid flow through the carbon bed and to the amount of color adsorbed. Finer mesh carbon particles adsorb more color per unit weight than do the larger carbon particles. But, small mesh carbon particles also tend to increase head loss through a carbon column. In addition, the finer carbon particles tend to wash out of column beds. These tend to pack near the bottom of the carbon column or may leave the column with the treated effluents. This increases the adsorption of treated effluents and increases the amount of make-up carbon necessary to maintain proper bed depth. These both lower the apparent carbon efficiency. To compromise for this, a suitable mesh size with acceptable color removal and head loss characteristics had to be found.

With Carbon 2, Philterkol SP#1, an acceptable mesh for a paper mill application was found to be 45 mesh. Using 60 and 80 mesh carbon, the fine particles passed to the bottom of the downflow column where they decreased effluent flow and increased instrumental adsorption readings. At 45 mesh, as seen in Figure 5, this was held to a minimum. Also,

using the 45 mesh carbon in a taller column, this effect was not noticed. This ^{made} #45 (U.S. Bureau of Standards) mesh the smallest acceptable carbon particle for adsorption column applications..

DATA FROM FIGURE 5

Minimum Mesh Studies, Mixed Size

Adsorbance

80 mesh- .43
60 mesh- .39
40 mesh- .35
40 mesh, tall column- .22

Lowest Adsorbance

80 mesh- .43
60 mesh- .39
40 mesh- .29
40 mesh, tall column- .22

Carbon mesh also appeared to be affected by carbon hardness.. When a soft, easily abraded carbon like Carbon 2 was used, general handling was sufficient to cause enough fine carbon particles to hamper flow through the carbon column. Investigation of samples of Carbon 2 after shipment showed carbon chips ranging from 60 to 200+ mesh. Harder carbon, Carbon 1, did not exhibit this property. This indicated that a harder carbon was more desirable for column applications.

Carbon hardness also appeared to have long term effects in column applications. Long term use of Carbon 2 in down-flow columns yielded some flow loss. While part of this could be attributed to the density increase due to adsorption by the carbon, a definite amount of fine particle carbon was noted after it washed out of the carbon bed. The longer the

column was operated, the more fine carbon particles were noted. This could mean a long term loss of carbon passing to receiving waters, increasing the amount of make-up carbon needed.

EFFECT OF PAPER MILL ADDITIVES

Carbon has had well known applicability to color removal processes for many years. Unfortunately, carbon also adsorbs other things besides color at varying rates, thereby lowering its apparent adsorptive capacity for color. For paper mill applications, these facts plus the high cost of the carbon have kept active carbon from finding its proper position as a pollution abatement material.

As evidenced from Figure 6, additives tended to decrease the color adsorption of the carbon. Addition of rosin and alum to the standard dye solution decreased the initial noticable color point from 23 liters to 11. But the rosin-alum addition, after being shutdown for $\frac{1}{2}$ hour, decreased the color passing through the column, and, after a shutdown of 10 hours, brought the color adsorption level back to a non-visible amount. The total color adsorbed before this phenomenon was no longer observed was 23 liters, the same amount as with the dye solution alone.

Rosin appeared to cause the biggest problems for the columns. Adsorption of dye solutions containing rosin-alum impurities tended to form colloidal masses. In the downflow column, this was seen as a crust; in the countercurrent flow column, this was seen as fiber-like materials and as "blue clouds". Upon the first visual indications of these masses

color adsorption by the columns tended to decrease from the amount when they were not noticed.

DATA FROM FIGURE 6

Carbon Adsorbance Studies

Initial Color Visible After

22½ l. for Dye only
10½ l. for Dye-Rosin-Alum
15 l. for Dye-Rosin-Alum-Fiber

Other Color Visible at

22½ l. for Dye only
15, 30 l. for Dye-Rosin-Alum
30 l. for Dye-Rosin-Alum-Fiber

Columns Shutdown After

12, 24, 31 l. for Dye only
12, 18, 31 l. for Dye-Rosin-Alum
13, 23, 34 l. for Dye-Rosin-Alum-Fiber

While the rosin colloid did decrease the amount of color adsorbed before colored column effluent was noted, by simply allowing more time for adsorption, this was overcome. By shutting the column down for an initial ½ hour on the down-flow rosin-alum addition, (Figure 6), an adsorption increase was noted at 10½ liters. After shutting the column down for 10 hours (overnight), an even larger increase was noted. This was repeated two more times during the column's operation with similar results. Similar results were also found with the addition of fiber fines to the rosin-alum-dye solution.

Addition of paper fiber fines also created unexpected results. They were expected to further decrease the adsorptive capacity of the carbon, but they did not. They tended to counteract the detrimental effect of the rosin, allowing

more effluent to be treated before color was noticed. This is believed due to an increased surface area for the rosin to fill before filling and plugging the carbon particles.

Fiber fines increased the amount of color removal capability for the columns, but had a detrimental effect on them. The flow through the columns was decreased by addition of fiber fines, as seen in Figures 9 and 10. This was believed due to the filling of the passages used by the liquid to flow through the carbon column. This phenomenon was bad enough in the case of the downflow system to cause the abandonment of this type column for any practical consideration in treatment of paper mill waste effluent.

The flow rate through the columns tended to be influenced by three major things: the size of the carbon used, the amount of fiber present, and the amount of material adsorbed. Fine carbon particles tended to allow only a limited amount of effluent to pass through the column, as previously discussed. Fiber fines tended to plug the passages open to flow in the column. But the decrease in flow rate due to material adsorption is not as easily explained.

Two major factors appear to influence the decrease in flow as materials are adsorbed. These are a blocking of the effluent passages around the carbon by a multi-layering effect noticed with the rosin-alum additions, and an increase in particle density as material fills the internal cavities of the carbon particle. As rosin is adsorbed, it is packed in layers, forming the multi-layer phenomenon. The filling of passages by multi-layering accounts for the increase in

(velocity needed to maintain constant flow through the counter-current columns, but does not explain the slight flow change noted in the downflow columns, as seen in Figure 9, especially when no additives were used with the dyestuff solution. This was due to the particle plugging of some of these passages with the weight increase from the adsorbed material. Of the two flow loss factors, the multi-layer blocking was the most significant.

The multi-layering of adsorbed material, as noted by the rosin colloid, is not a tightly held adsorption. Flow around carbon particles in the countercurrent columns was sufficient to recover the colloids, as seen by fiber-like materials in the effluent. These colloids may also be removed by air bubbles or massive carbon movement, forming the "blue cloud" phenomenon. While this did not appear to be a major problem in this study, it may be a source of BOD and COD passing on to receiving waters.

ADSORPTION OBSERVATIONS

While watching the columns during adsorption and analyzing the data obtained from them, many things were noticed. They give a good understanding of what is happening during the adsorption by the carbon column. Unfortunately, they were not extensive enough to warrant a theory, while they do tend to support many theories common today.

The most probable mechanism derivable from the observations in this study is one of a multi-layering type of diffusion controlled adsorption. This is seen by the large

groups of rosin forming the multi-layers on carbon particles during column adsorption. This is further shown by a lowering of color adsorptive properties by column operation and a return of these by shutting down the column.

While a detailed discussion of the multi-layering phenomenon has been given previously, a recapitulation is in order. When rosin and alum were added to the dye solution, a mass became noticable on the carbon particles. When the mass was observed, a color adsorption decrease was noted. By shutting the column down for varying periods of time, the adsorption was increased. In countercurrent type flow columns, material believed to be multi-layered rosin colloid was removed by flow of effluent around the carbon particles.

These observations indicate that, after an initial adsorption of materials on the carbon surface, other layers of material are also adsorbed. They are not tightly held, being removed by normal and abnormal flow through the carbon column. The mass formed, or the multi-layers, can block the carbon, allowing less color to be adsorbed.

Allowing more time for adsorption increased the amount of color removed from solution. This indicates more than an initial and multi-layer adsorption takes place on the carbon particle. This also indicates a diffusion into the carbon particle. This diffusion appears to be time dependent, with different materials being diffused into the carbon particle at different rates.

The diffusion of materials into the carbon particle can account for many things found in this study. Knowing that

the dyestuff chosen as the color standard was a mixed dye, this accounted for the color shift noticed upon adsorption by the carbon. It may also account for the blocking of color when rosin was added to the standard dye solution. The larger rosin molecule is diffused into the carbon particle more slowly than the dye molecule. While waiting to be diffused into the carbon particle, the rosin colloid multi-layers fill all free area around the carbon, allowing no other materials to be adsorbed. After sufficient time for diffusion has elapsed, adsorptive areas are again open on the carbon particle, allowing more adsorption to occur. This can give the impression that the carbon has regenerated itself (Figure 6).

Carbon ~~was~~ also good for filtering. The carbon effectively blocked all fiber fines from passing through the column. The blocking associated with the carbon column can be detrimental, causing flow loss sufficient to discontinue the use of the carbon column. This is a phenomenon associated with particulate beds and commonly used for solids removal from liquids. It is also useful in the overall view of a carbon column mechanism.

With all the observations in mind, a mechanism of the multi-layer type, controlled by diffusion, was indicated. The adsorption of materials on the surface of the carbon seems to be the first step. While materials must diffuse into the openings inside the carbon particles, their diffusion into the carbon particle seems to be the rate-determining step of the adsorption mechanism. Waiting to be diffused into the carbon particle, materials are adsorbed in multi-layers on

the carbon surface. When the adsorbed multi-layers become thick, they tend to decrease the adsorption of further materials. Removing these multi-layers by diffusion or by mechanical means allows more material to be adsorbed. When materials are too large to be adsorbed, they are blocked from passage through the carbon bed by the carbon particles, or filtered out of suspension. This type mechanism best explains all the adsorption observations seen in this study.

COLUMNS

Two column types were studied in this report: downflow and countercurrent flow types. Carbon 1 was used exclusively in the countercurrent flow studies. Special characteristics of these columns make them useful for various types of adsorption, especially when used for paper mill waste treatment.

Downflow carbon columns were found very effective in color and colloidal material removal. As seen from Figure 6, color adsorption was nearly linear. When colloidal blocking did occur, it was not as pronounced as with the countercurrent flow column, as seen in Figure 7. Adsorption of materials, excluding solids and particulate matter, was found to be superior to that of the countercurrent flow columns.

The downflow carbon column had one major flaw, it became plugged when fiber fines were added to the system. It can be seen from Figure 9 that flow through the column remained fairly constant during the dye solution and dye-alum-rosin trials. But the addition of fines plugged the column for all practical purposes in less than $2\frac{1}{2}$ liters of treated

effluent. This flow problem was not found with the counter-current type flow columns, as evidenced from Figure 10.

The countercurrent flow columns performed quite well in adsorption of solid and dissolved materials from paper mill effluents. While total material adsorption was not as complete as that of the downflow column, adsorption was good, as evidenced by Figures 6 and 7. While regenerability of the carbon by standing was not as great for the rosin-alum-dye trials, (Figure 7), the addition of fiber tended to counteract this.

Flow through the countercurrent column was more controlled than through the downflow column. When a flow drop was noted, more liquid was allowed to flow through the column to overcome this. This could not be done with the downflow column. Changes in the column flow rates are indicated by variances in the flow lines in Figures 10 and 11. The data shows that as more materials were adsorbed, the flow rate had to be changed more often. This appears to be an efficient method of monitoring the amount of material adsorbed by the carbon.

DATA FROM FIGURES 10 AND 11

Countercurrent Flow Studies

Dye-Rosin-Alum

Velocity Increase Needed After
4, 11, 19, 25 l.

Dye-Rosin-Alum-Fiber

Velocity Increase Needed After
6, 10, 18, 26, 28, 30, 33 l.

Countercurrent Flow With and Without Carbon Addition

With No Addition

Velocity Increase Needed After
10, 18, 21, 24 l.

With Carbon Addition

Velocity Increase Needed After
3, 10, 22, 27, 29 l.

As a final check of the systems, a check was made to see how continuous operation of the countercurrent type column system would affect color adsorption. For this, one gram of carbon was added to the column for every liter of effluent treated. This was added in five gram doses, with carbon removed from the bottom of the column to maintain proper carbon bed depth. This proved quite effective, with color remaining more uniformly adsorbed than with no carbon addition, as seen in Figure 7.

COST

To bring this study into its proper perspective, cost calculations for a column were made. While the carbon was not used to its total capacity, as seen by the amount of color still being removed from solution when the columns were shut down, the visual detection of color was used as the end point of this study. The amount of useful life still remaining in the carbon after column use was greater than expected from batch studies, but is felt to be near half the actual capacity of the carbon. While this study can not yield an accurate actual cost figure, it is an estimate for a one column adsorption system.

Costs of the carbon are important. Recent market values for the carbons were found to be 32¢/lb. for Carbon 1, Filtrasorb 400, and 9¢/lb. for Carbon 2, Philterkol SP#1. The cost difference is due mainly to the amount of processing done to each carbon.

For a theoretical carbon adsorption, the results of the equilibrium study were used. For this, using one million gallons of effluent as a basis, the carbon needed for Carbon 2 is 1,823,000 lbs. and for Carbon 1, 19,390 lbs. The cost for these would be \$164,070 for Carbon 2 and \$6,205 for Carbon 1 for sufficient carbon to treat one million gallons of effluent. This cost removed Carbon 2, Philterkol SP#1, from economic competition for column use.

Using the actual data found in the countercurrent flow column studies, the economics of Carbon 1 appear better. 16,845 lbs. of carbon (8.42 tons) were needed to treat one million gallons of effluent. This costs \$5,590/MG treated, or \$5.59/1000 gal. of effluent treated. This cost is extremely high when compared to other systems (2.59), but is believed due to fractional utilization of the carbon and to no attempt to regenerate the carbon.

COST OF THE APPLICATION OF CARBON

	Cost of MGD, NO NO Regeneration	Cost of Regeneration	Cost With Regeneration
Experimental Values	\$5,590/MG	-----	\$888./MG *
Actual, as found at Lake Tahoe	-----	\$0.0323/lb.	\$35.00/MG

* Using the Tahoe Regeneration Cost.

Regeneration lowers the process cost. While it was not studied here, pyrolytic and chemical treatment do revive the carbon to a state similar to that of virgin carbon. The mechanism and problems with regeneration have been previously discussed, showing the favorability of regeneration. The cost of regeneration of the carbon used in water purification at the South Tahoe P.U.D. was found to be \$.0323/lb. (59). For the paper mill system, this would be \$888/MG purified effluent, assuming a 7% carbon loss during regeneration. This figure also reflects the incomplete utilization of the carbon. Costs of regeneration and make-up carbon at the South Tahoe project were found to be \$35/MG effluent treated, a figure which should be approached in paper mill applications. (59).

SUMMARY AND CONCLUSIONS

Color can be removed effectively by activated carbon columns. Laboratory investigations have indicated that materials encountered in paper mill effluents slow the rate of adsorption by carbon slightly. They have indicated that complete utilization of the color adsorbing capacity of the carbon is necessary for economic feasibility of a carbon system.

Mesh size of carbon particles was important in the adsorption of color. Smaller particles adsorbed more color than the larger ones, but smaller particles tended to wash out of carbon beds and plug downflow type carbon columns. For this reason, a mesh study was done on Carbon 2. These

showed that a maximum color adsorption with a minimum of plugging was found with 45 minimum mesh as the smallest size particle in the column.

Mesh was also related to carbon hardness. A soft, carbon, like Carbon 2, may be broken into smaller pieces and chips with simple handling of dry or wet carbon. This was noted by the plugging of the column in long time studies of Carbon 2, but was not noted with Carbon 1, a harder carbon.

Components common to paper making systems tended to have detrimental effects on the adsorptive properties of carbon columns. This was noted in a decreased initial color visible point, as seen in Figure 6. This appeared to be due to a competitive adsorption by the carbon, with additives being adsorbed more slowly than the dyestuff. Concentration of material on the surface of the carbon encouraged the growth of multi-layers. In the case of rosin, this was a visible colloid. These colloids plugged the surface of the carbon, allowing only very limited adsorption of color. Given sufficient time, these multi-layers were also adsorbed. The additives appeared to have no effect on the amount of color adsorbed, only on the rate at which it was adsorbed.

Paper mill additives had strange effects on color adsorption. Components of the standard dyestuff were adsorbed at different rates, causing a color shift. The addition of rosin decreased the initial visible color point, while addition of fiber fines to the solution increased it slightly. This is believed due to an increased area the colloid must cover before multi-layering and its resulting carbon blocking occur.

The above observations are best explained by a possible multi-layering adsorption mechanism. This tends to be a mechanism of initial surface adsorption and diffusion into the carbon, followed by a surface multi-layering, due to a slow diffusion into the carbon particle. After filling the carbon pores, the multi-layers can remain or may be removed by flow around the carbon particles. The multi-layers can also block or slow the adsorption of other components into the carbon particle. By giving the carbon more time to adsorb material, the multi-layers may be removed and allow more material to be adsorbed and diffused into the particle.

The type of flow through the carbon column is also important to paper mill effluent applications. The downflow-type bed carbon column appeared very effective in removing color and colloidal matter, but was quickly plugged by normal concentrations of fiber fines encountered in paper mill waste effluents. The countercurrent flow-type columns appeared to be less efficient in color and colloidal material removal, but were not plugged with fiber fines. While the total differences in material removal appeared quite small (Figure 7), the plugging characteristics of the downflow column rule it out of most applications in the paper industry.

Economically, carbon adsorption columns can not be used to remove color and discarded when the effluent becomes colored. From calculations made in this study, the carbon cost for this type system would be \$5,390/MG effluent treated. By pyrolytic regeneration of spent carbon, using actual cost figures found at Lake Tahoe P.U.D. (59), this figure dropped

to \$888/MG effluent treated. In more continuous operations with a more total utilization of the carbon, this figure can be expected to drop even further, approaching the \$35/MG effluent treated figure found at Lake Tahoe (59).

The following conclusions can be drawn from this study:

1. The adsorption and filtration of paper mill wastes by activated carbon columns is a promising method of removing colored material from paper mill effluent.
2. #45 (U.S. Bureau of Standards) mesh sized carbon granules appear to be the smallest size particle acceptable in a carbon column.
3. Paper mill effluent components tend to slow the adsorption of color by active carbon particles.
4. A multi-layer diffusion type adsorption mechanism best explains color adsorption in carbon columns.
5. Countercurrent or upflow columns are best suited for use in paper mill applications.
6. Carbon costs for non-total utilization of color adsorption by carbon particles make this type application economically prohibitive.

SPECULATIONS ON THE APPLICATIONS OF ACTIVE CARBON TO PAPER MILL USES

Application of carbon to paper mill waste effluent can be a very economical one. By using all the properties of carbon, further effluent treatment may be unnecessary. It is quite possible to obtain water pure enough for process reuse, boiler make-up, and even drinking.

The process used would most probably be in a three stage loop, including an initial filtering, a second adsorption, and a regeneration phase. Since countercurrent columns are the most suited to use in a paper mill system and also to automation, they should be used in most stages of column operation. While downflow columns may be more efficient in the polishing stages of carbon usage, they may be used near the end of the column systems. The first stage should be used mainly for particulate and solids filtering. The second stage should be used mainly for soluble material adsorption and for colloidal material removal. The third stage should be used for regeneration by pyrolitic or superheated steam type regeneration furnaces.

A filtration type first stage is necessary. This stage would remove fiber fines, fillers, and any other particulate material. Since these materials tend to plug downflow columns, the countercurrent or upflow column should be used. This stage would also allow some coagulation and possible adsorption of materials which tend to lower the adsorption of the second phase.

To aid the effectiveness of the first stage, the carbon

can be removed, washed or screened, and returned to the first stage. Since the carbon is acting primarily as a filter, its adsorptive capacity is of only secondary importance, making this type operation permissible. The water used to wash the carbon can be untreated effluent. This water can then carry the removed waste back to the primary clarifier for disposal, or can be removed, allowing the wastes to be used as a possible source of fresh carbon.

The second stage is the adsorption phase. Most color and colloidal matter should be removed here. The columns should be the countercurrent flow type in the initial phases with polishing columns being either downflow or upflow. For proven processes, a system similar to that used at Lake Tahoe P.U.D. (8,59) would be very good for this phase. After the carbon is used, it can then be sent to the first stage for completion of its effective life and for regeneration.

Twin columns are suggested for the first few columns in the second phase. It has been shown that rosin is more slowly adsorbed than is color. To take care of this, more contact time and slower effluent speed through the columns is called for. This can be accomplished by either allowing more adsorption surface area to become available or for more columns to be used to take care of the increased holding time necessary. Separate columns allow more complete utilization of the carbon and different flow rates to keep the total volumes through the columns uniform.

A second alternative is also possible. This is to simply pump the carbon out of the columns and place it in a separate

holding tank where the carbon can self-regenerate in sufficient time for this. It can then be pumped into the column for further use in adsorption.

The columns should be monitored as to their effectiveness. This is best done by color monitoring for immediate results and COD testing for quicker long term results. Due to the variety of color mixtures encountered in most mills today, a computerized scan of all wavelengths commonly encountered for a maximum adsorption area should be made during every sampling period. Also, using countercurrent flow type columns, monitoring the power and velocity requirements of the effluents and head and velocity drops of entering and leaving effluents from the column can be used as a check as to the amount of life remaining in the carbon columns.

Carbon movement should be carried out with a minimum of mechanical attrition. Since carbon particles are easily broken down, carbon movement should be kept to a minimum. To decrease mechanical breakdown of the carbon, it should be moved as much as possible by water pressure. Screens should be used to keep carbon out of pumps. This type movement would also decrease abrasion of the carbon on the pipes and pumps used in the system.

The third step is the regeneration phase. This should be a continuous multi-hearth type pyrolytic or superheated steam method of activation. As this arrangement is a heat loss type installation, placing this unit near the boilers in the plant and utilizing the lost heat for processing uses would be in order. The hot, regenerated carbon

carried to the columns on a conveyor, wetting the carbon before addition to the columns. This phase appears to be the greatest money saving step of the entire system, so it should be engineered sufficiently for the greatest use of its placement before the entire system is installed.

A final step needed in carbon regeneration is a screening of the final product. If the particles are too large, they should be ground down. If the particles are too small, they should be removed before they enter the column and increase the adsorption and COD levels of the leaving effluent. The fine particles could either be separated and sold as a more expensive waste product, or disposed of with the waste from the primary clarifier.

The use of activated carbon can be a very efficient and economical use of mill wastes. It can be used to enhance the esthetics connected with paper mill installations. It can also be used to further use water for paper mill installations, especially where systems are being closed up. This may be a very probable solution for pollution abatement by paper mills today, and we need them.

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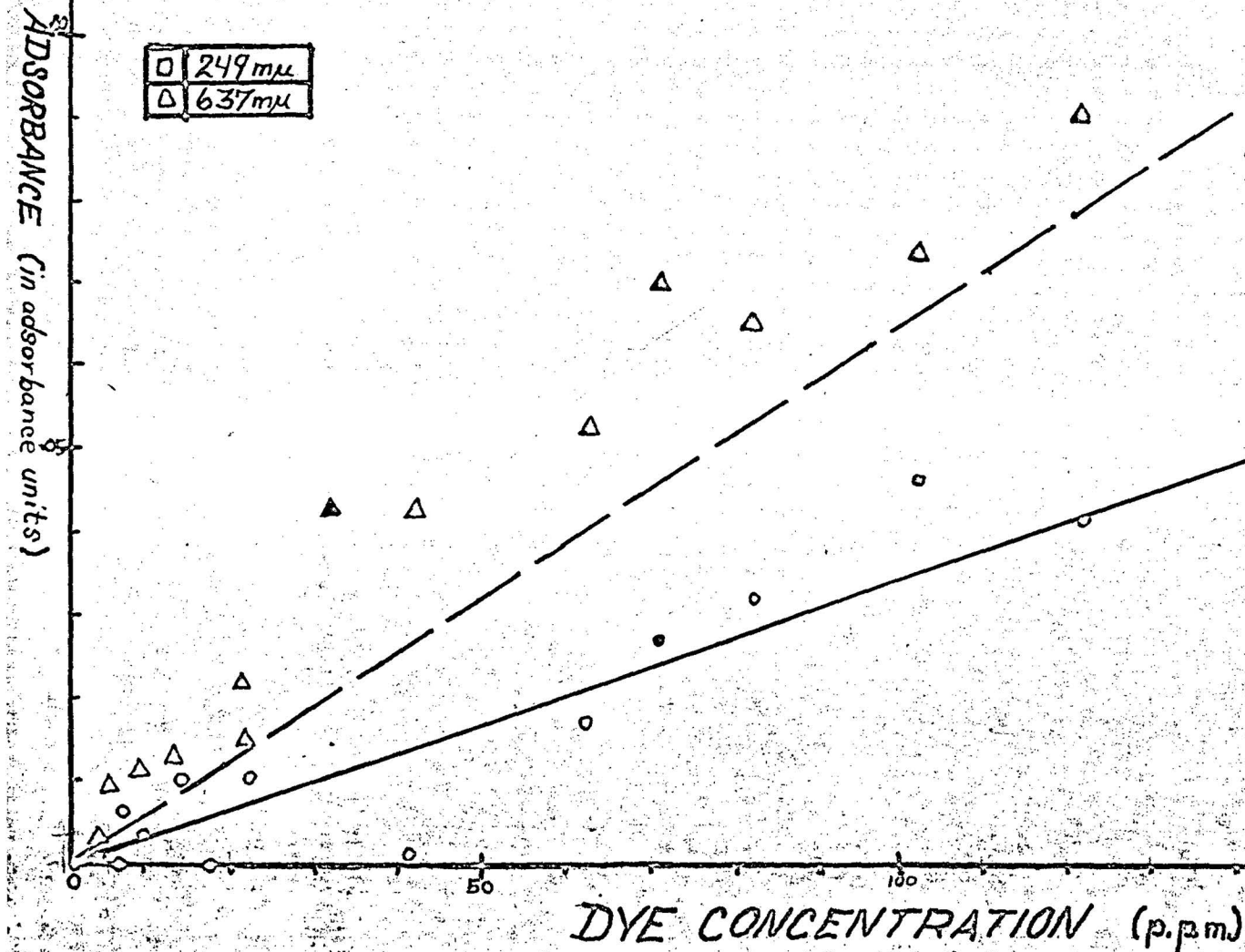
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APPENDIX I
GRAPHIC DESCRIPTION OF DATA

FIGURE 1
CONCENTRATION CALIBRATION CURVE
AT 249 AND 637 mμ wavelength



Calibration Curves

non-standardized recorder print
constant slit opening

—	Distilled Water
—	Purified Dye Sol'n
- - -	Dye Solution
...	Dye-Rosin-Alum-Fiber-Solution

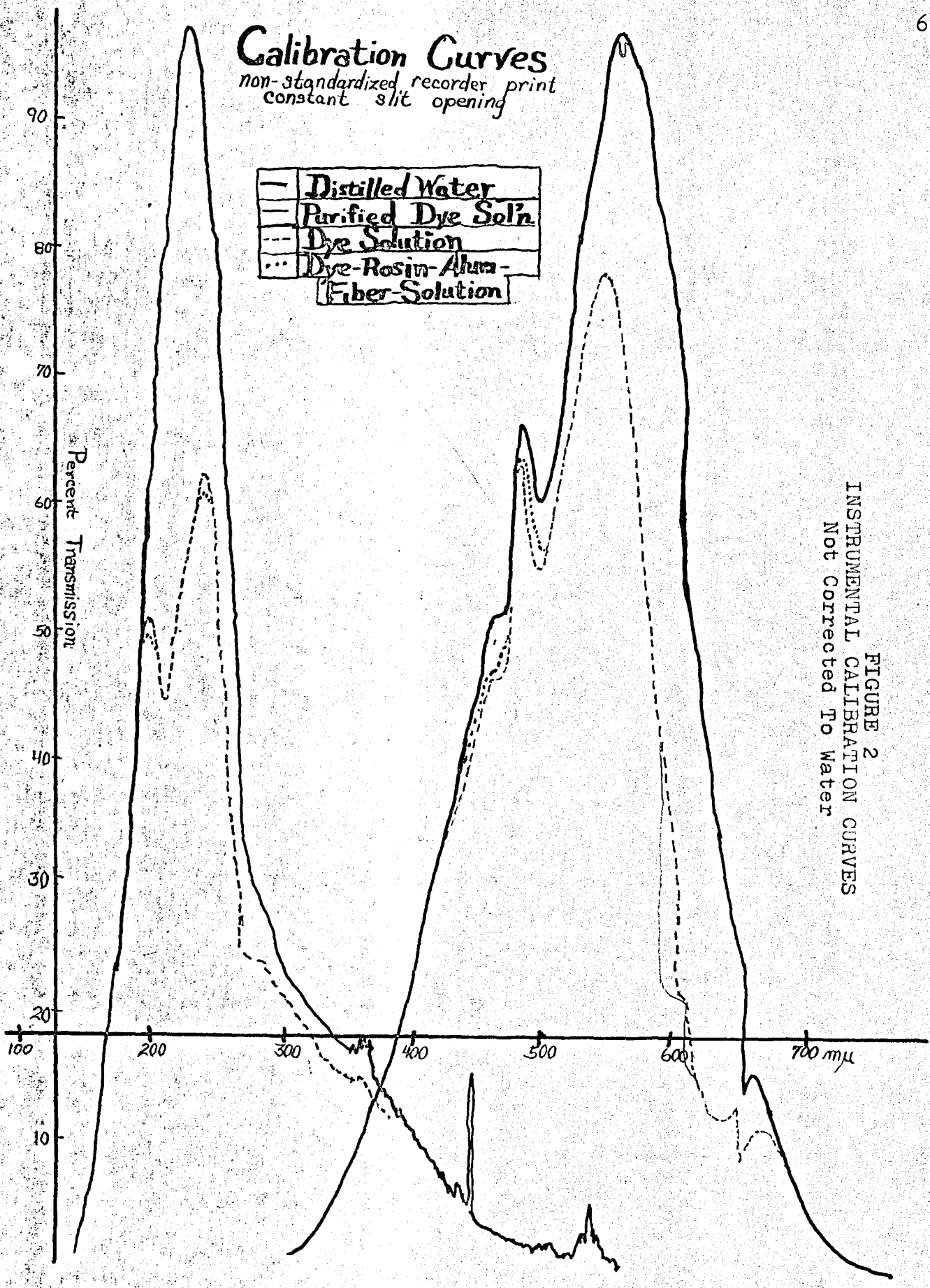
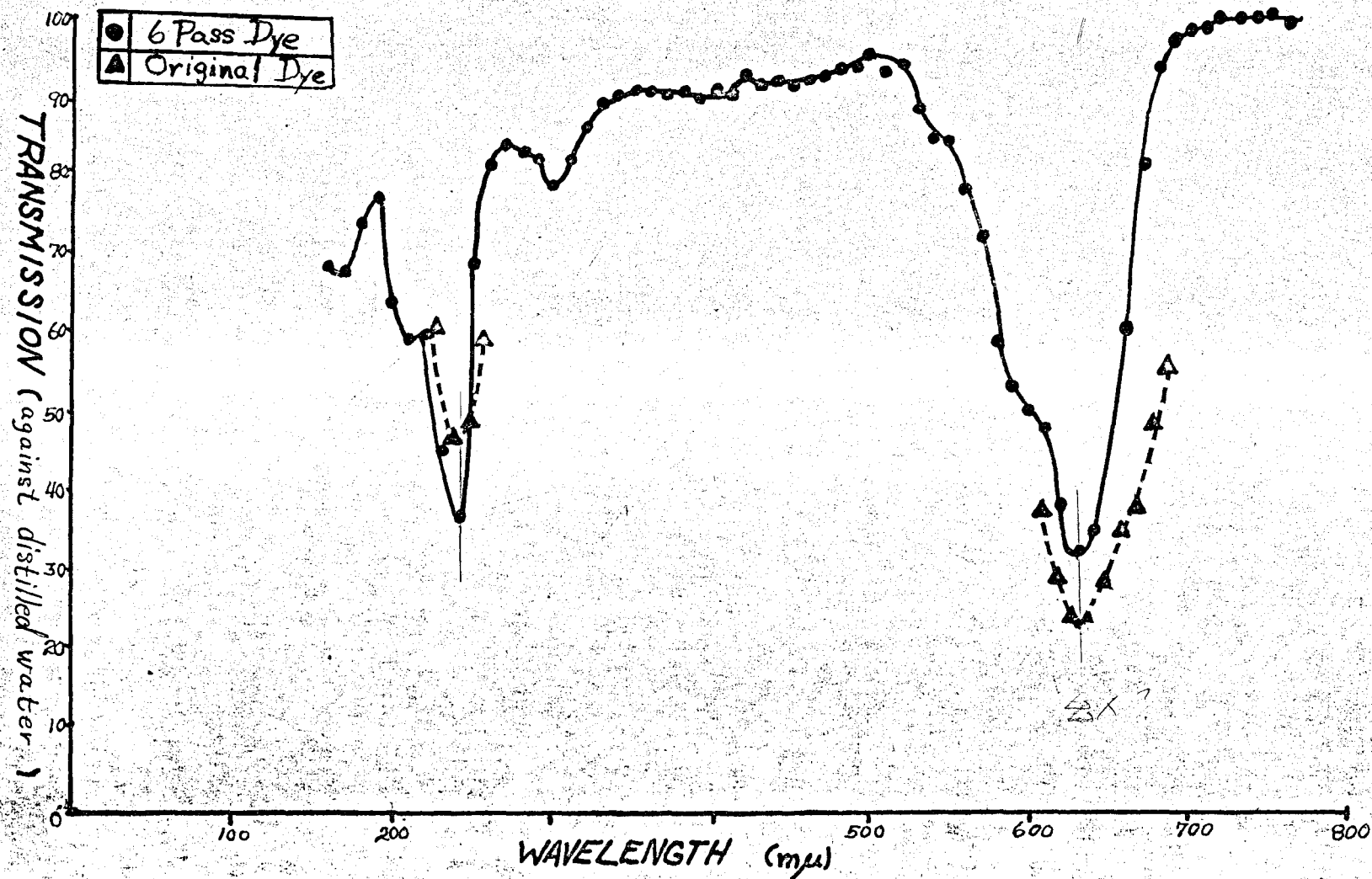


FIGURE 2
INSTRUMENTAL CALIBRATION CURVES
Not Corrected To Water

FIGURE 3
TREATED AND UNTREATED DYESTUFF CALIBRATION CURVES
Based On Distilled Water



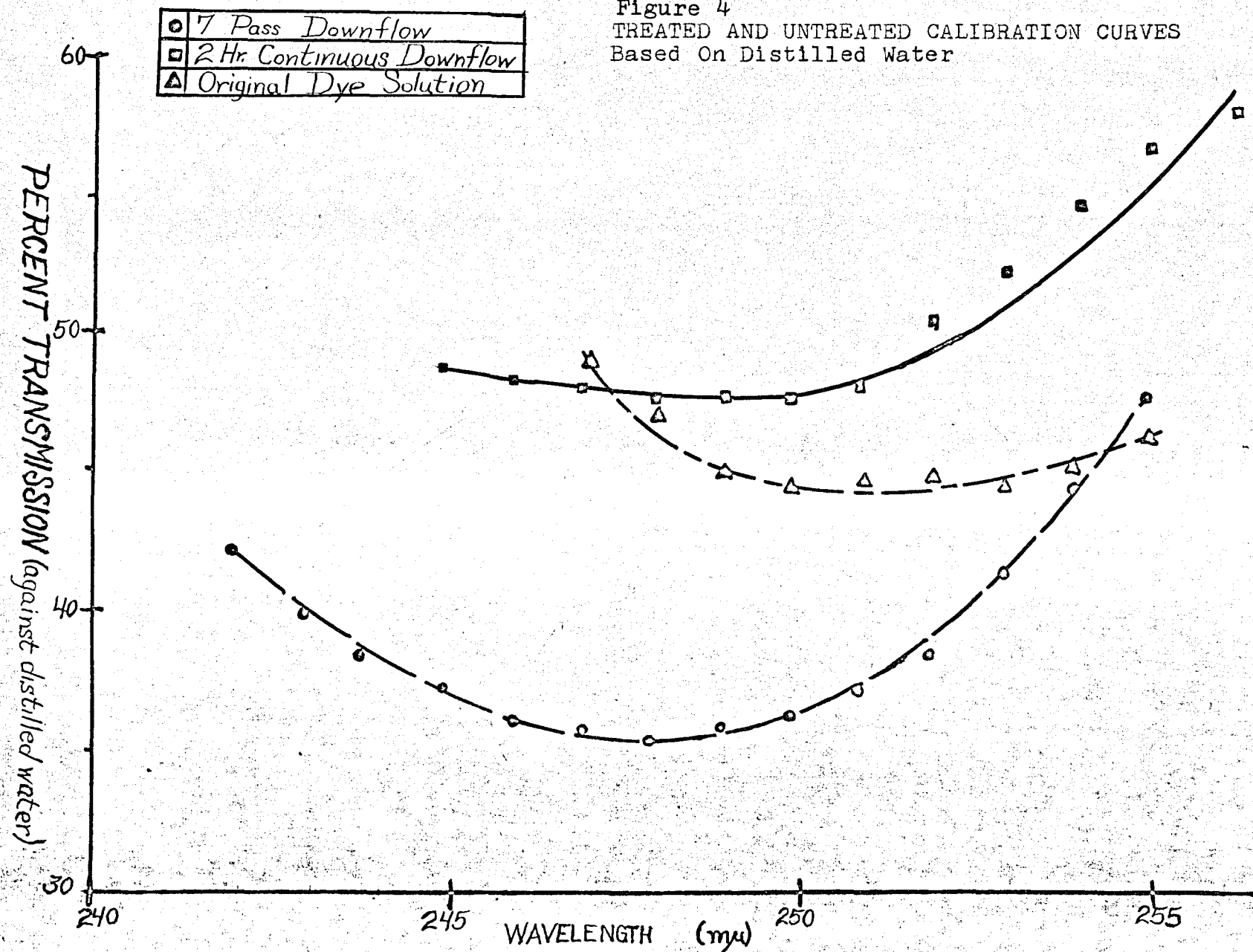


FIGURE 5
PHILTERKOL STUDIES
Mesh and Column Depth Studies

○	45 Min. Mesh
○	45 Min., Tall Column
△	60 Min. Mesh
□	80 Min. Mesh

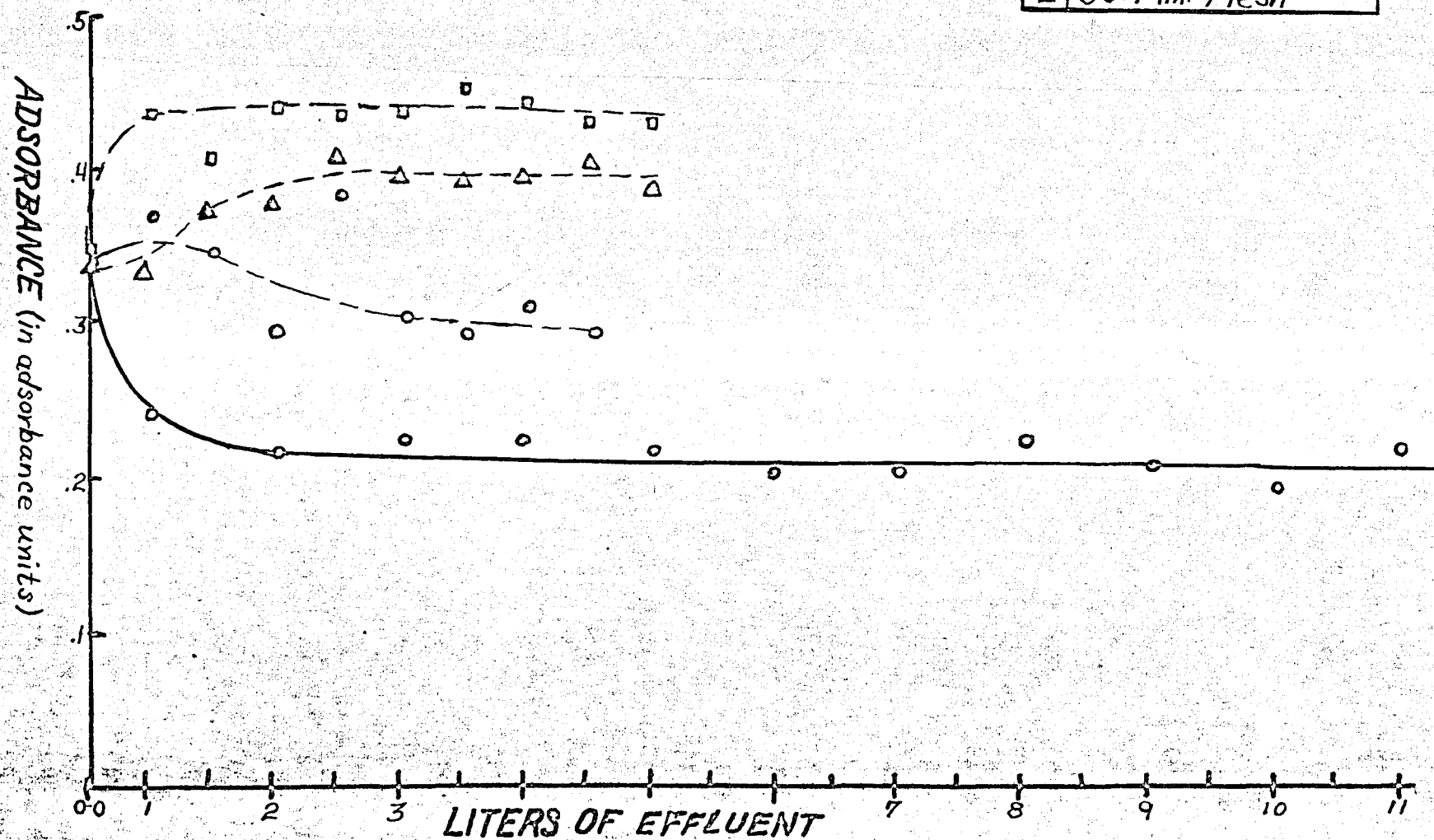


FIGURE 6
CARBON ADSORBANCE STUDIES
ACTUAL COLUMN PERFORMANCE STUDIES

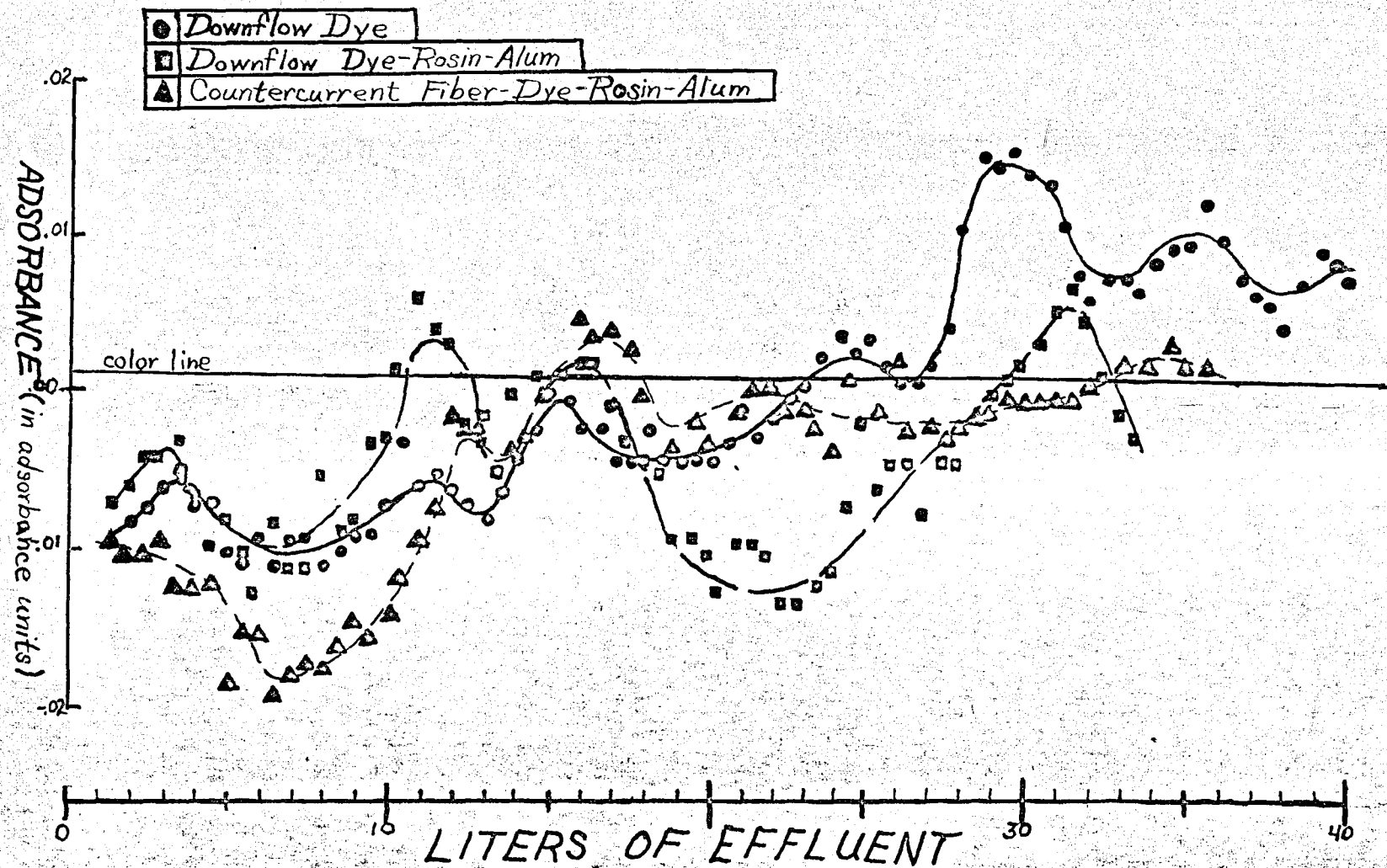


FIGURE 7
CARBON ADSORBANCE STUDIES
Downflow Versus. Countercurrent flow Studies

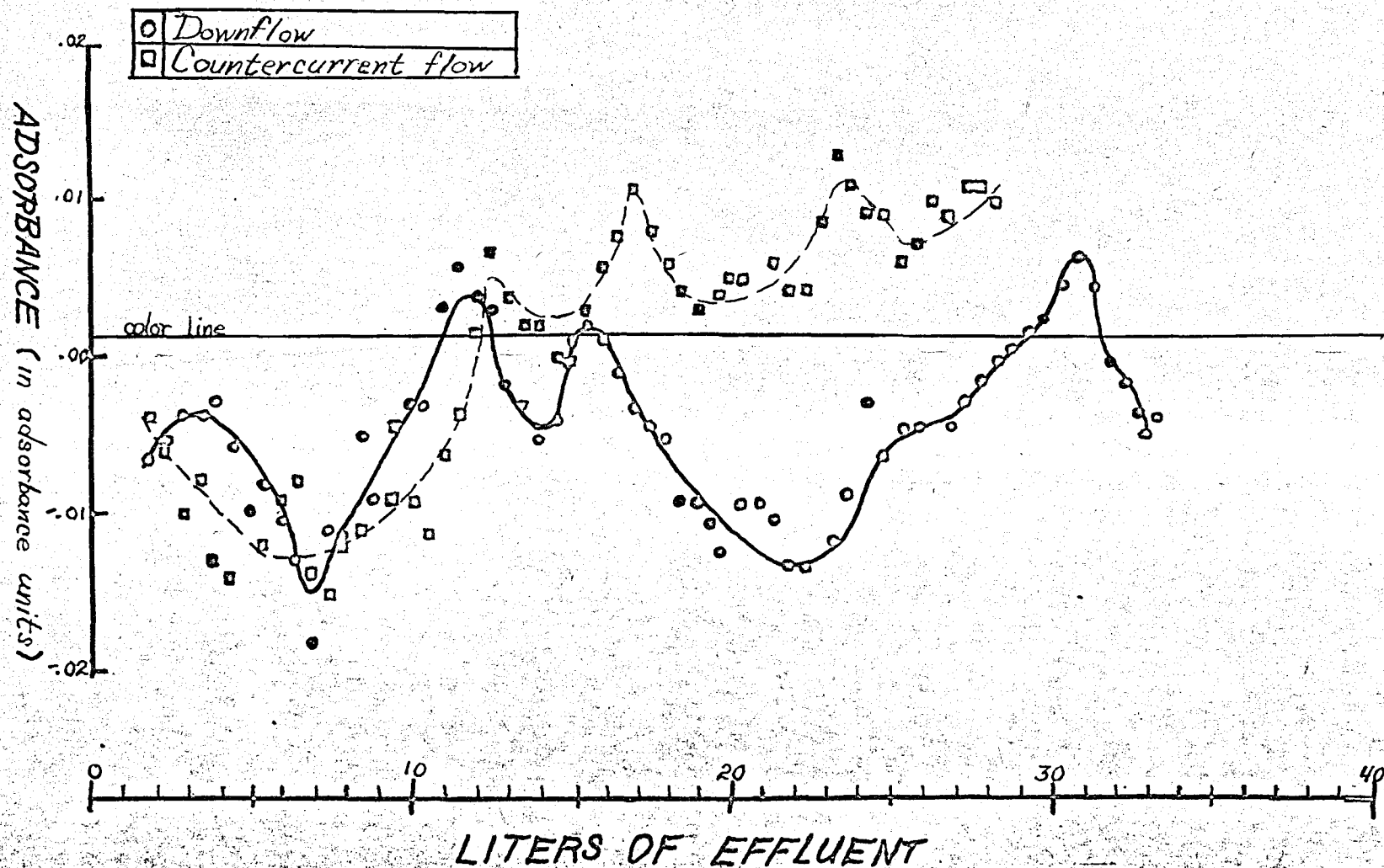


FIGURE 8
CARBON ADSORBANCE STUDIES
With and Without Carbon Addition Countercurrent Flow Studies

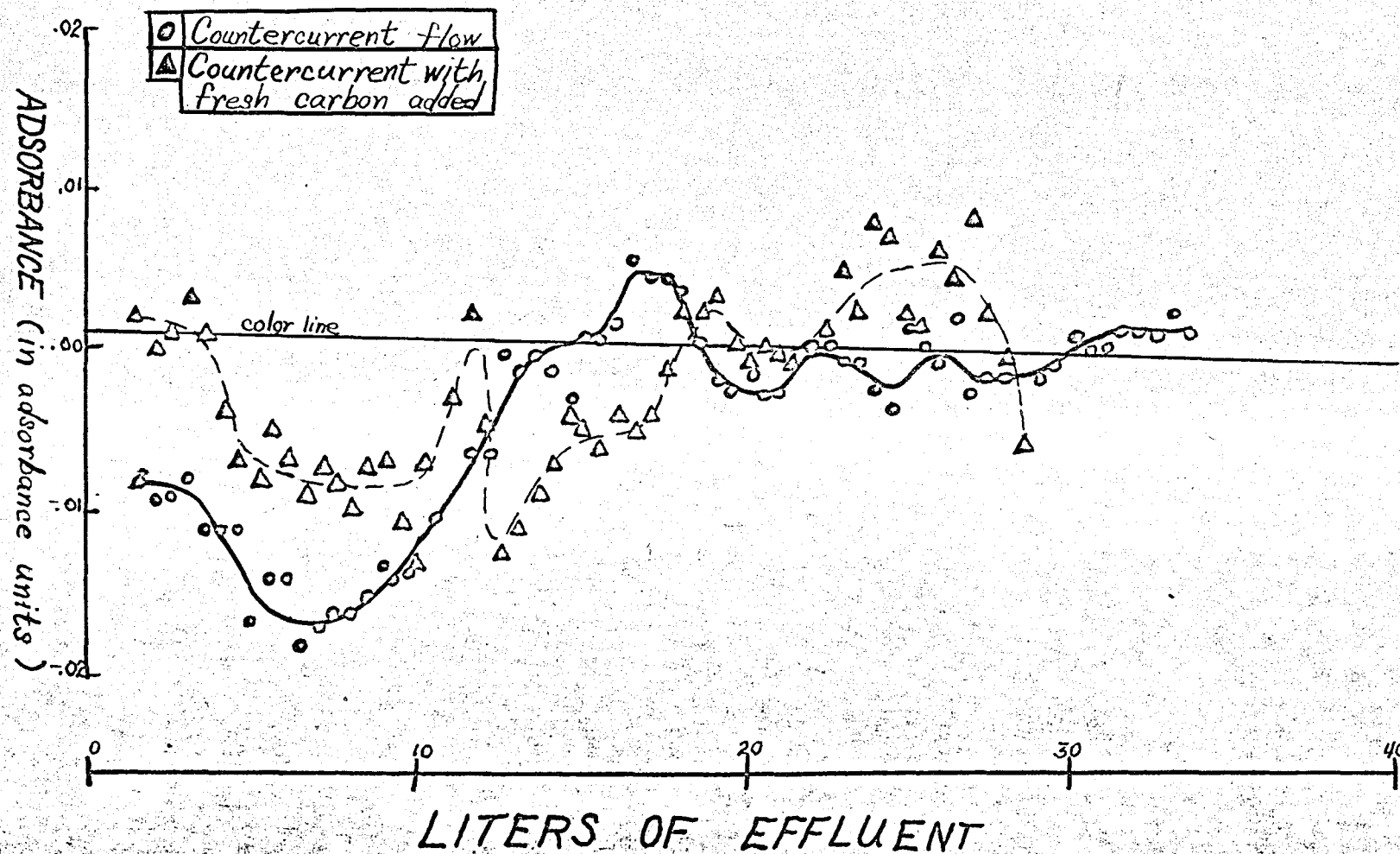
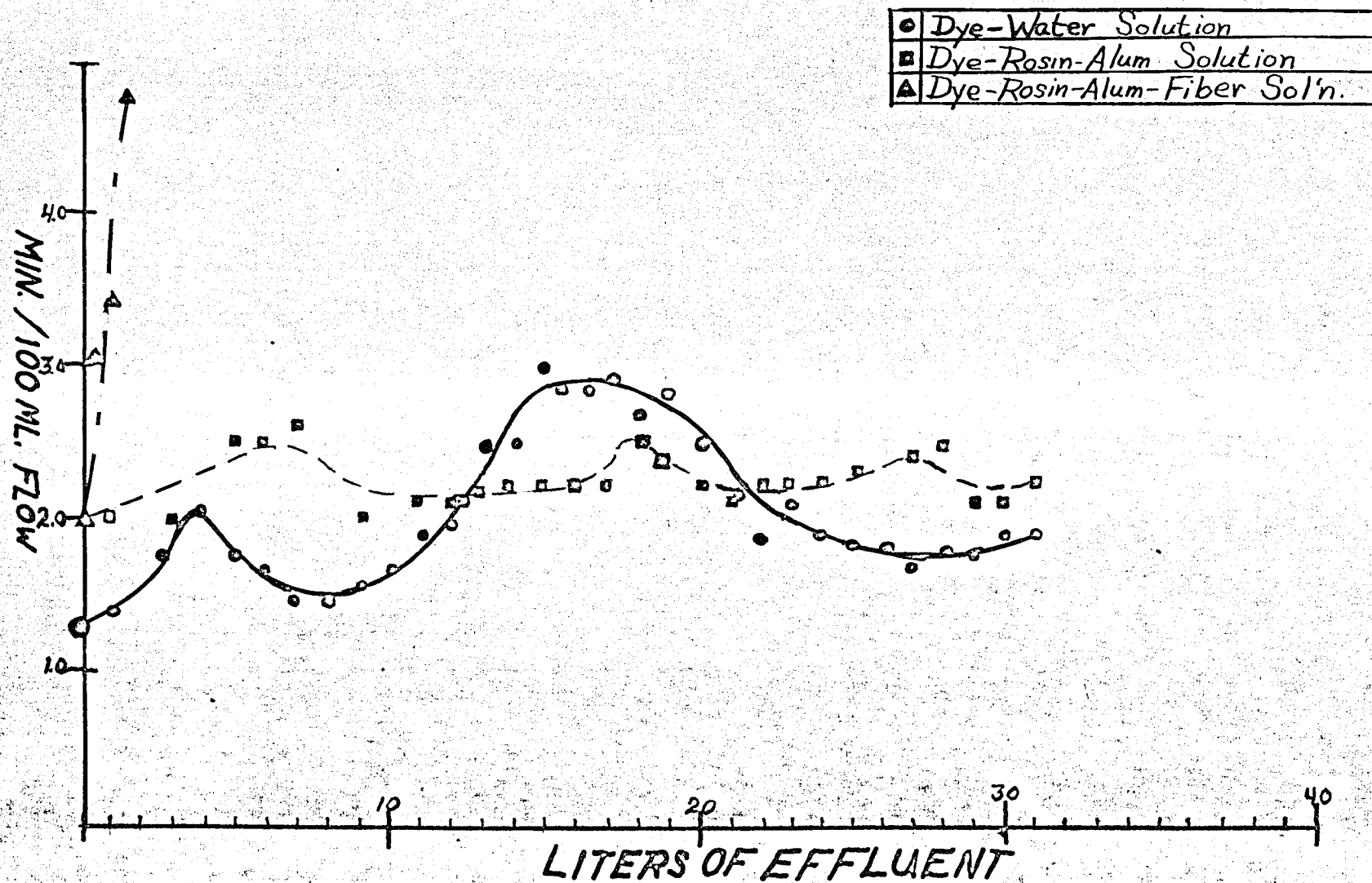


FIGURE 9
FLOW STUDIES
Downflow Column Additive Studies



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FIGURE 10
FLOW STUDIES
Countercurrent Additives Study

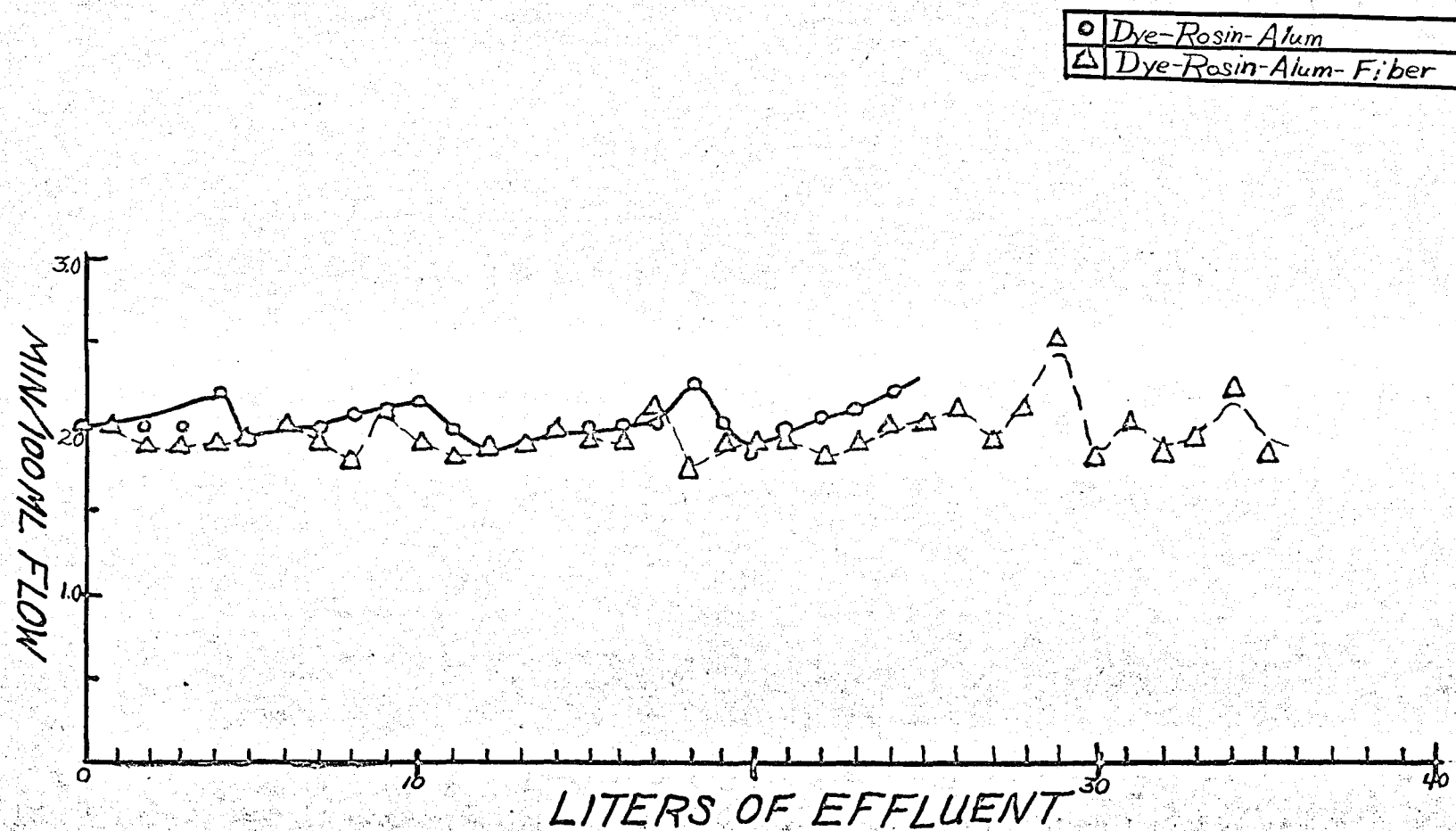
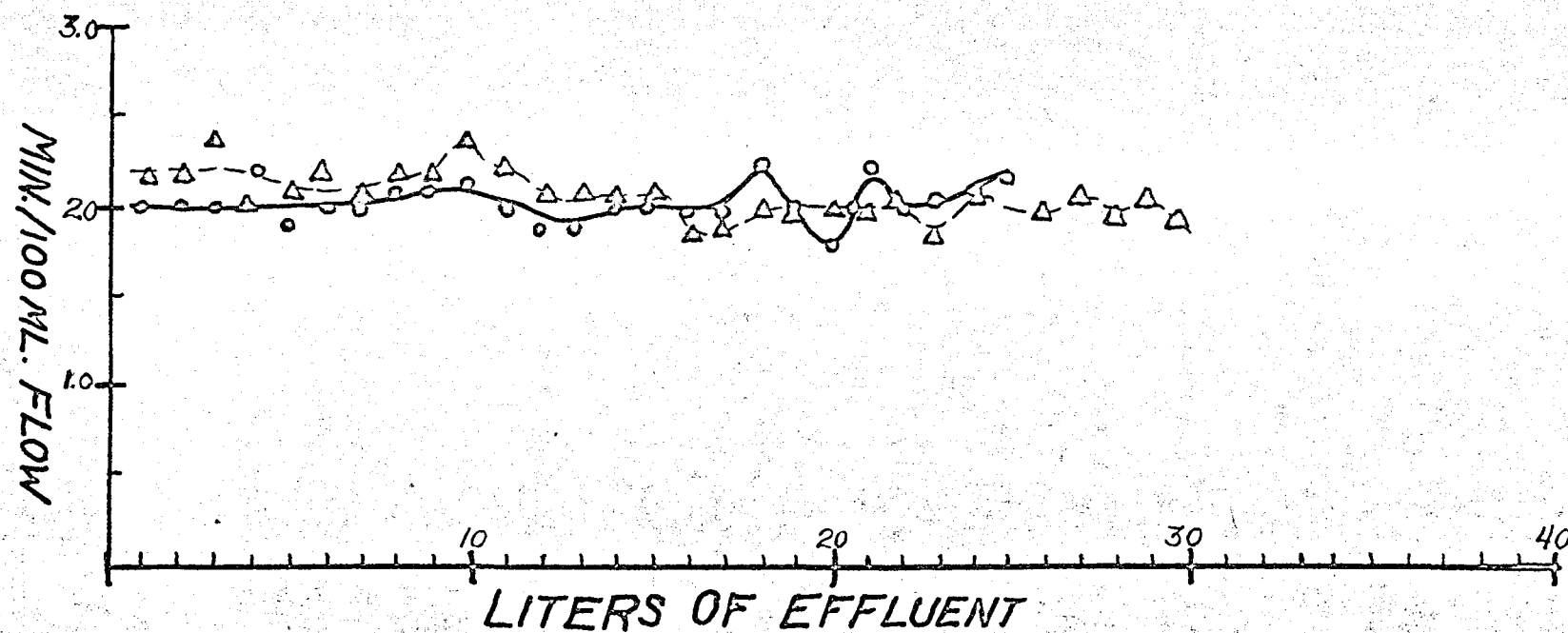


FIGURE 11
FLOW STUDIES
With and Without Carbon Addition Countercurrent Flow Studies

○	Countercurrent
△	Countercurrent with fresh carbon added



APPENDIX II
EXPERIMENTAL PROCEDURES

SOLUTION PREPARATION

I. Stock Solutions

A. Dyestuff

1. 2 g. dyestuff
2. dilute to 1000 ml. with distilled water
3. shake well before using

B. Rosin

1. 1 g. Pexol
2. dissolve in a small amount of water
3. dilute to 1000 ml. with distilled water
4. allow to stand min. 1 hr. before use
5. shake well before using
6. discard when cloudy

C. Alum

- 8 1. 1 g. granular tech. grade paper maker's alum
2. dilute to 1000 ml with distilled water
3. shake well before using
4. discard when oxides ppt. from solution

D. Fiber

1. Perpare fiber
 - a. slurry desired pulp
 - b. classify according to TAPPI procedures, accepting only paper fines
 - c. dry fibers in mat oven dry
2. 1 g. O.D. fibers
3. disperse in distilled water
 - a. add saturating amount of contaminant to be used in the column study

- 1). 10 ml. alum stock solution
 - 2). 10 ml. rosin stock solution
 - 3). 20 ml. dyestuff stock solution
- b. dilute mixture to 1000 ml. using distilled water

II. Dilution

- A. add enough stock solution to give desired contaminant concentration
1. 200 ppm dyestuff
 2. 100 ppm rosin
 3. 100 ppm alum
 4. 200 ppm fiber fines
- B. dilute to required volume
- C. Mix thoroughly
- D. with fiber fines or other settlable material, agitate constantly with either
1. mechanical stirrer
 2. air pressure
 - a. bubble air into the bottom of carboy
 - b. pressure should be sufficient to simulate a rolling boil

INSTRUMENTATION

I. Initial Calibration

- A. Make sure all moving parts on the spectrophotometer are lubricated properly
 - 1. no improper friction binding on recorder arm
 - 2. meter needle functions properly
- B. calibrate and check wavelengths according to instrumental instructions
- C. Check all instrumental operating procedures

II. Wavelength, Standard Selection

- A. Collect samples to be used
- B. Find maximum adsorption region for dyestuff
- C. Find maximum adsorption region for treated samples
- D. Compare these regions
 - 1. If data is acceptable, accept the wavelength
 - 2. If data is unacceptable
 - a. Find a wavelength where the data correlates
 - b. Find a usable concentration-adsorbance relationship
 - c. Pick another dyestuff

III. Correlation

- A. Prepare a concentration series
 - 1. Make concentrations similar to those expected
 - 2. Use small increment concentration differences
- B. Run samples
 - 1. Base readings on a standard, like the pure solvent
 - 2. Record data in adsorbance values

C. Plot data found

1. Interpolate results when needed
2. These results should be linear

APPENDIX III
POSSIBLE CARBON SOURCES

At present, carbon is obtained mainly from virgin materials, commonly wood and coal. While these materials are abundant, they do have a fairly constant market price. To bring the cost of active carbon down, new carbon sources, less expensive than those commonly used, must be found.

One of the first places to look for carbon sources is in industrial wastes. This has been done in the pulp and paper industry with pulp mill wastes (lignin) as basic carbon sources being realized already. This is the only industry known at this time to utilize its carbonaceous wastes in this way. While this is a source of less expensive carbon, it is not sufficient in volume to lower the carbon cost throughout the entire market.

To bring down carbon costs in the future, other sources must be investigated. To meet all requirements for a material to be a good source of active carbon, a large carbon source must be present. Unfortunately, only a few materials may meet this requirement. One source is human sewage. By burning solidified wastes, a possible well-ordered carbon may result. Another good source may be in the hard-to-decompose waste products of plastics. These are now used mainly in landfill and do not decompose. Burning these may give a possible source of carbon, which could then be activated relatively easily.

There are undoubtedly many other sources of carbon, which need only to be discovered. This does not mean that these materials can be economically handled under present conditions, but it is a beginning of complete reutilization of wastes.