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PACKED BED HYDRODYNAMICS OF AN ACID HYDROLYSIS PERCOLATION REACTOR

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ABSTRACT

This project is concerned with an experimental and analytical study to develop a predictive model for acid hydrolysis percolation reactors of the type being considered by SERI for conversion of lignocellulosic materials to fuel ethanol. The modeling approach proposed is an adaptation of stochastic percolation theory to the wood chip bed. Essentially, the theory provides for the volume-averaging of random local hydrodynamic phenomena on the particle scale, to the bed scale.

The experimental work will be accomplished primarily in a 6-inch diameter reactor of the type currently in use at SERI, on loan to Brown University for the duration of the contract. The reactor has been received and is currently in the process of installation at Brown. This reactor will be used for both wood chip conversion and inert tracer studies of liquid holdup, an indicator of liquid-solid contacting. The latter data are needed for the development of the percolation model. In addition to providing a convenient, nondisruptive method for measuring liquid holdup, the tracer data can also be interpreted to yield the effective intraparticle diffusivity in the wood chips.

One important aspect of the experimental work involves characterization of the wood chips as a function of conversion. Work along these lines thus far has shown that both flow BET (N_2 and CO_2) and mercury intrusion porosimetry are not suitable for characterizing the internal structure of the aspen wood chips. However, monolayer adsorption of cationic dyes (i.e., methylene blue and crystal violet) has been shown to yield reasonable and reproducible results for internal surface areas.

Following the experimental and theoretical work at Brown University, the resultant hydrodynamic reactor model will be tested for predictive capability on the SERI PBR system.

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INTRODUCTION

The modeling of packed bed reactors is a relatively straightforward procedure when the reactor operates as a single phase system and when the packing does not change with extent of reaction. However, for multiphase flow situations and/or when the condition of the packing is strongly affected by the extent of reaction, the modeling process becomes significantly more complicated by the random local bed hydrodynamics (e.g., see Calo, 1981). The situation of acid percolation through a packed bed of lignocellulosic material, such as in the SERI progressing batch reactor (PBR), or acid hydrolysis percolation reactor (AHPR), as used here, is an example of the latter type of behavior.

Primarily due to hydrodynamic complexities, the design and prediction of the operating performance of such reactor systems has been, for the most part, semi-empirical in nature. Approaches range from purely empirical correlations of experimental observations of conversion as a function of the primary system parameters (usually over a very limited operating range), to more careful treatments of the transport phenomena involved in the fluid-solid interactions; including, for example, axial and radial dispersion. However, even models of the latter type adopt a fundamentally homogeneous continuum description; i.e., the liquid (and, if applicable, gas) volume-averaged flow rates are assumed to be completely independent of location in the packing. However, even a cursory observation of the actual physical situation readily reveals that the random nature of the packing causes the fluid flow rates to vary spatially, resulting in flow maldistribution. All the continuum models fail to take this very important characteristic into account; namely, that the distribution of flow in the bed packing, as well as the transport and reaction phenomena are controlled *locally* on the scale of the particle size, and that they must be properly volume-averaged in order to enable an accurate description of reactor behavior at the bed level. It is this latter, intrinsically more faithful, description of packed bed hydrodynamics that is provided by the stochastic percolation theory.

In the current project it is planned to apply the percolation theory to describe the hydrodynamics of acid hydrolysis of lignocellulosic materials in reactors of the type planned for use in the progressing batch reactor (PBR) system of SERI. The experimental and analytical research program described herein has been designed to attain the objective of developing a predictive model of the behavior of this type of reactor system.

BACKGROUND

Percolation Theory and Packed Bed Hydrodynamics

In general terms, percolation theory is a mathematical description of the processes associated with fluid spreading randomly through a medium. Whereas the process of diffusion may very well describe the *fluid* behavior, percolation theory focuses on the *medium* which is recognized to be stochastic in nature. That is, the probability density function for flow distribution is dependent on the local random characteristics of the medium. This type of medium is also known as a random maze, and it can be viewed as composed of *sites* and *bonds*. The basic elements of percolation theory as used here are primarily those set forth by Frisch and Hammersley (1963) and Broadbent and Hammersley (1967).

A packed bed of particles exhibits the property that it is globally homogeneous (due to the relatively small [i.e., particle] scale of transport and reaction phenomena), but is highly

heterogeneous at the particle scale. It is this local irregularity, however, that controls the bed hydrodynamics and determines how fluid flows through the random network comprised of particles and pores. It is this physical picture that ideally lends itself to description via the percolation theory. Essentially, the number of channels [i.e., pores] entering and leaving a cell region [on the particle scale] varies randomly from point to point, and the clustering of these channels is responsible for generating the various macroscopic flow structures observed.

Recently, this approach has been successfully applied to the description and modeling of three-phase *trickle bed reactors* by Crine and co-workers at the Universite' de Lie'ge (Crine et al., 1981-83). The trickle bed model is based on a representation of the packed bed as a scattering medium or lattice where the *sites* correspond to contact points between particles, and the *bonds* correspond to pores connecting neighboring contact points. The percolation process is realized by randomly distributing blocked and unblocked pores within the lattice. In one particular version of this model (Crine and L'Homme, 1982a), developed for the low interaction gas-liquid trickle flow regime, the flow was assumed to occur in laminar films in the unblocked pores, driven by a combination of gravity and pressure drop. It was further assumed that the pores were randomly distributed with respect to angular orientation, with equal flow for all unblocked pores of the average angular orientation. No flow occurs in the blocked pores.

Even though this is an intuitively pleasing qualitative description of the flow behavior, it would not be very useful for reactor modeling were it not for the quantitative results that it allows. Essentially, the local flow rate is determined by the density of connection via the pores, denoted as α_i , for $i = 1, 2, \dots, \infty$ connections. By maximizing the configurational entropy of this system, Crine and Marchot (1984) showed that:

$$\alpha_i = \exp(a+bi)$$

where $\exp(a) = 1/[\langle i \rangle + 1]$ and $\exp(b) = \langle i \rangle / [\langle i \rangle + 1]$, and $\langle i \rangle$ is the averaged value of i for the entire bed. The corresponding superficial flow rates are given by:

$$L_i = i L_m; \text{ and } \langle L \rangle = \langle i \rangle L_m,$$

where L_m represents the minimum flow rate in a single pore.

In order to model global rates of transport and reaction, these processes must first be modeled at the particle scale and then appropriately averaged to the bed scale. Volume averaging occurs via the flow distribution presented above. Transport properties, Γ , are bed-averaged simply according to:

$$\langle \Gamma \rangle = \sum_{i=0}^{\infty} \Gamma(L_i) \alpha_i$$

In this manner, Crine and co-workers determined bed-averaged values of the irrigation rate (Crine and Marchot, 1984), and the dynamic liquid holdup and reaction rate (Crine and L'Homme, 1982a). Crine et al. (1982b, 1983) also derived a theoretical expression for the axial dispersion coefficient (or the axial liquid phase Peclet number) based on the particle irrigation rate. Good agreement was obtained for the variation of dispersion coefficients, determined in this manner, with liquid viscosity and particle irrigation rates.

In addition to the preceding, Crine and co-workers demonstrated that the trickle bed percolation model results can be interpreted in terms of the size and compactness of the liquid flow structures (i.e., irrigated and nonirrigated zones), and liquid distribution between rivulet and film flows (Crine and Marchot, 1983a). Another application of the same model involved its extension to

the description of heat transfer in trickle bed reactors (Crine, 1982c).

Measurement of Liquid Holdup Via Tracer Methods

Liquid holdup is the key variable in determining liquid-solid contacting effectiveness, and, consequently, in determining the overall reaction rate and reactor performance. The total liquid holdup, H_t , is made up of two major contributions: the static liquid holdup, H_s , and the dynamic liquid holdup, H_d , such that $H_t = H_s + H_d$. The static liquid holdup is defined as the total amount of liquid retained in the porous packing after the liquid has been drained from the reactor, divided by the total bed volume. Thus, this parameter depends primarily on the nature and the state of the packing. The dynamic (or operating) holdup is then the liquid external to the packing, residing in the bed voidage. In the AHPR, due to the changing bed state (e.g., its progressive compaction and local collapse), the accessible bed volume may vary significantly over the course of the reaction, thereby also varying the contacting effectiveness of the liquid phase with the solid packing. These variations will be reflected in the liquid holdup.

Various methods have been proposed in the literature for the determination of wetting of the bed packing. These may be generally classified as destructive and nondestructive methods. Among the former are reactive and nonreactive dissolution techniques, and permanent dye adsorption. The nondestructive techniques rely primarily on inert tracer response. Due to the reactive nature of the packing in the AHPR of interest here, the tracer techniques seem to be the most appropriate, since continual variation in bed state can be monitored directly without disrupting the bed.

The method proposed for the current study is basically an adaptation of the technique presented by Mills and Dudukovic (1981). These authors presented an expression for the first moment of the impulse response of a partially-wetted, packed bed to a nonvolatile inert tracer in terms of measurable system parameters. This same expression is also applicable to liquid-full operation upon appropriate substitution of parameters. The total liquid holdup, H_t , can be determined from the first moment of the tracer response using a nonadsorbing tracer. The static liquid holdup can then be separated from this value by assuming a suitable correlation for the dynamic liquid holdup, such as the one suggested by Mills and Dudukovic (1981). The dynamic liquid holdup is then determined by difference, $H_d = H_t - H_s$. Once the liquid holdup is determined, the method of Colombo et al. (1976), for example, can be used to assess the *internal* wetting. This method relies on the ratio of the second (i.e., the variance) and first moments of the tracer impulse response.

RESEARCH PLAN

Application of the Percolation Theory to the Acid Hydrolysis Percolation Reactor

The AHPR is not operated as a trickle bed reactor; i.e., the bed runs liquid-full. Even so, the basic principles of the percolation theory remain applicable and provide a useful theoretical framework for the development of a predictive model. In fact, some of the results already derived by Crine and co-workers for trickle bed operation may also be applicable to the AHPR under certain operating conditions.

For liquid downflow, an approach similar to that of Crine and co-workers will be pursued for the laminar flow regime in the bed pores. [Note: Here the term *pore* is used to designate the channels in the bed voidage external to the packing, as well as the internal structure of the wood chips. The precise meaning can be inferred from the use of the term in context. Both the internal pore structure of the wood chips and the bed voidage as a function of conversion will be determined in separate batch studies.] As indicated by Crine and L'Homme (1982a), the percolation theory is not limited to the local laminar film flow pore model. Therefore, a local flow model, dependent on the actual operating flow rates and the pore structure determined for the external bed voidage, will be formulated for the

AHPR. In any case, the resultant theoretical formulation will have a parameter (or parameters), analogous to L_m , related to $\langle i \rangle$, the bed-averaged number of interconnections of the flow cells. This parameter can then be evaluated by comparison of the resultant predictions with liquid holdup data.

Another major difference between the AHPR and the catalytic trickle bed case is the crucial added dimension of continuous variation of the state of the reactive packing. The percolation theory has not yet been applied to any type of reactor approximating this situation. In terms of a formulation like the one presented by Crine and co-workers for trickling liquid downflow, it is expected that the bed-averaged connectivity, $\langle i \rangle$, will vary with extent of reaction. However, as shown above, $\langle i \rangle$ is directly proportional to $\langle L \rangle$ for this model, and thus any variation in $\langle i \rangle$ can be detected simply by measuring the total bed-averaged flow rate, $\langle L \rangle$.

For situations where the bed is running full, as in the AHPR, the total, bed-averaged flow rate will depend on both the total bed voidage (as previously), as well as the bed (external) pore size distribution, or mean pore diameter, which will vary in accordance with the opposing effects of pore enlargement due to exterior reaction and shrinkage of the wood chips, and pore compaction and collapse due to degradation of the wood chips. The former effect will cause the local flow rate to increase, while the latter will cause it to decrease, and, ultimately, degenerate to a blocked pore. In addition, the possibility remains that the nature of the bed-averaged connectivity may vary with extent of reaction.

In order to investigate these phenomena, both reaction and liquid holdup measurements will be conducted with beds that have been reacted to varying extents. Tracer studies on these beds will then be used to generate an appropriate model, the hydrodynamic parameters of which will vary as a function of conversion. For example, in terms of the Crine et al. model, a different value of $\langle i \rangle$ will be determined for each level of conversion for incorporation into the model.

Liquid Holdup

The bed liquid holdup is the primary measurement that will be used in the model development. It is proposed to measure liquid holdup as a function of: liquid flow rate; flow direction; and bed state (i.e., extent of reaction and compaction). These measurements will be interpreted in terms of the percolation theory. In order to apply this technique in downflow, experiments must be conducted under both liquid-full and percolation flow regimes (Mills and Dudukovic, 1981). In upflow, the effect of varying liquid holdup with bed state will be interpreted in terms of packing compaction and varying accessibility.

The reactor for both the reaction and liquid holdup tracer studies is a 6-inch diameter vessel of the same type currently in use at SERI, on loan to Brown University for the duration of the contract. In this manner, beds of the same type as experienced in current use will be produced *in situ* for subsequent tracer studies.

Wood Chip Characterization

Wood chips of three different sizes will be reacted to varying extents. Samples of these materials will then be characterized with respect to both external void fraction and internal pore volume and pore volume distribution. These data are necessary in order to guide the application of the percolation theory and to correlate bed state with the liquid holdup and contacting measurements. In addition, some knowledge of the internal pore structure is required for correlation of the effective intraparticle diffusivity to be determined from the tracer tests.

RESULTS

Since this contract has only recently been initiated (1 September 1987), almost all the work described above has yet to be performed. However, some work has already been accomplished nonetheless. During this past first month, the SERI reactor has been received, and we are currently in the process of installation. In addition, we have been examining techniques for wood chip characterization. Initial results concerning these efforts are reported below.

SERI Reactor

The 6"-diameter SERI reactor has been received at Brown, and is currently in the process of being installed in a new laboratory. The heat exchange and flow schematics for the reactor system are presented in Figures 1 and 2, respectively. Much of the necessary piping and fittings have been ordered, and installation is proceeding according to expectations.

Characterization of Aspen Wood Chips

Certain aspects of the internal structure of the aspen wood chips must be known in order to determine reaction and transport parameters for the reactor model. The principal characteristics of interest are surface area and pore size distribution. The measurement of these properties is not always straightforward due to the complex pore structure of wood; and, of course, they must also be determined as a function of conversion in the present context. The development of a reliable technique for the determination of total surface area has already been initiated.

Internal Surface Area Determination in Porous Solids. Many methods have been employed for the determination of the internal surface area of porous solids; the most common being gas adsorption, mercury intrusion porosimetry, gas permeability, adsorption of a solute from solution, and, depending on the nature of the material, optical and electron microscopy. Of these, nitrogen physisorption, interpreted according to the BET equation, is, perhaps, the most common (e.g., see Lowell, 1979). The basic principle of adsorption techniques is that the adsorbate (e.g., nitrogen, carbon dioxide, and other solutes) lowers its energy by adsorbing onto the sample surface. Knowing certain properties of the adsorbate and in what manner it attaches to the surface, the amount of adsorbate uptake can be interpreted in terms of a surface area. The simplest type of adsorption behavior is known as a Type I, or Langmuir isotherm, which can occur when the adsorbate sorbs as a monolayer. In this case the surface area is simply equal to the number of sorbed species multiplied by the area a single adsorbate molecule occupies on the surface. If, on the other hand, the adsorbate appreciably adsorbs onto itself, something like the multilayer BET theory must be used to interpret the uptake data. The latter is the usual case for both nitrogen and carbon dioxide adsorption isotherms.

BET Results. Both nitrogen and carbon dioxide BET surface analysis was performed on a sample of 1/8" aspen wood chips using a Quantachrome Quantasorb surface area analyzer. The sample was prepared by drying in a vacuum oven at 80°C for 1 hour. The nitrogen analysis indicated that no measurable amount of nitrogen was adsorbed, thereby implying zero surface area. Adsorption of carbon dioxide was observed, but no subsequent desorption was detected when the sample temperature was increased. The latter may imply that carbon dioxide does not physisorb, but rather dissolves or otherwise interacts chemically with the wood. Therefore, neither of these adsorbates yielded any surface area information. On a preliminary basis, this behavior is attributed to the pyrophoric behavior of aspen; i.e., essentially the pores collapse upon drying, which is a necessary preparatory step for adsorption at low temperatures. This is well known behavior for lignites, peat and some woods (e.g., see Gauger, 1945).

Monolayer Dye Adsorption Technique. Upon failure of the gas adsorption BET technique to yield surface areas, it was decided to try dye adsorption techniques from solution. Actually, this technique is perhaps the most relevant to the reaction environment of the wood chips in

Figure 1. AHPR Heat Exchange Schematic

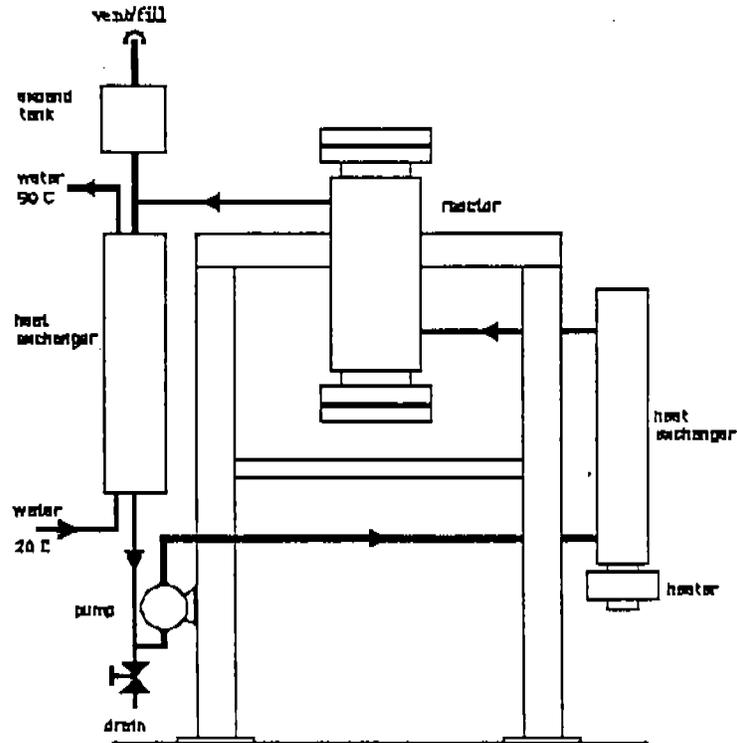
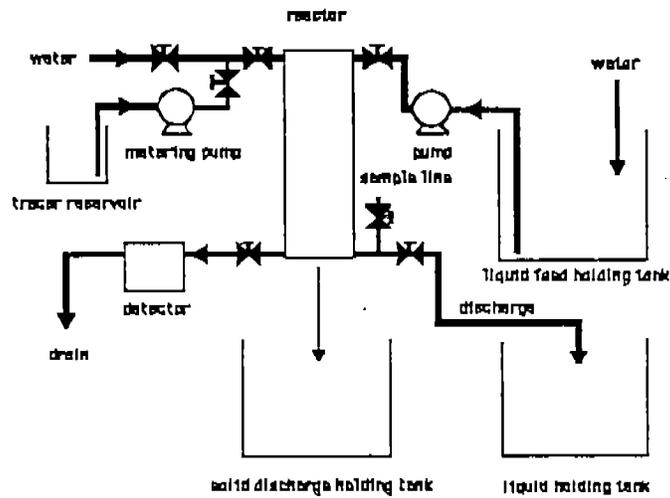


Figure 2. AHPR Flow Schematic



the AHPR. This method was used by Giles and Nakhwa (1962) to measure surface areas of various porous materials, and was applied specifically to wood by Poots and McKay (1979). The method involves immersing wood chip samples in a series of dye solutions of increasing concentration, and allowing the adsorption of dye to come to equilibrium. The equilibrium dye concentration is measured using a spectrophotometer. For monolayer adsorption, this results in a Langmuir-type isotherm, from which the covered surface area can be easily calculated. Giles and Nakhwa (1962) discuss the characteristics of desirable candidate adsorbate dyes. To date we have used two cationic (basic) dyes: methylene blue and crystal violet. Both of these dyes have the desired characteristics, and their aggregation numbers (to correct for non-planar packing on the sample surface) have been measured by Giles et al. (1974).

Experimental Procedure. The experimental procedure is fairly straightforward, but is rather sensitive to errors in laboratory technique. First, a calibration curve is determined relating concentration to optical transmittance for the particular dye used. A series of dye solutions is prepared with the highest concentration selected to yield a point on the constant asymptotic region of the isotherm. The wood is dried and stored at 100°C to standardize the weight. About 0.5 g of wood is then weighed out into a 15 ml sample bottle, and 10 ml of dye solution is added. The samples are then allowed to equilibrate for approximately 48 hours. It was found useful to place the samples in an ultrasound bath during equilibration in order to increase the rate of solution uptake into the wood. The resultant equilibrium dye solutions are decanted and centrifuged for 20 minutes. The samples are then diluted, as needed, and the concentration determined spectrophotometrically.

Results. Some typical Langmuir-type dye isotherms are presented in Figures 3, 4, and 5. The surface areas obtained using the asymptotic equilibrium dye uptake of methylene blue range from 40 to 45 m²/g, and do not seem to vary significantly with wood chip sizes of 1/4" and 1/8"; which is to be expected since the surface area is almost completely internal. The crystal violet isotherm yielded a surface area of 60 m²/g, which is in fair agreement with the methylene blue results, and also with the results of Poots and McKay (1979) for spruce.

FUTURE WORK

Since this project has only recently gotten underway, almost all the work described above lies ahead of us. Therefore, future work essentially involves implementing the research plan outlined in this paper. However, some progress has already been made. Concerning the development of a reliable surface area measurement technique, it is planned to determine some isotherms using an anionic (acid) dye for comparison to the two cationic dyes that have already been used. In addition, the dye adsorption technique must be tested for the determination of wood chip surface areas at varying extents of conversion. Based upon these results, a standard dye will be selected with which to perform all the diagnostic surface area determinations. Also, as indicated above, the SERI reactor, which has been received, will be installed and begin operation.

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Figure 3. Methylene blue isotherm for 1/4" aspen wood chips.

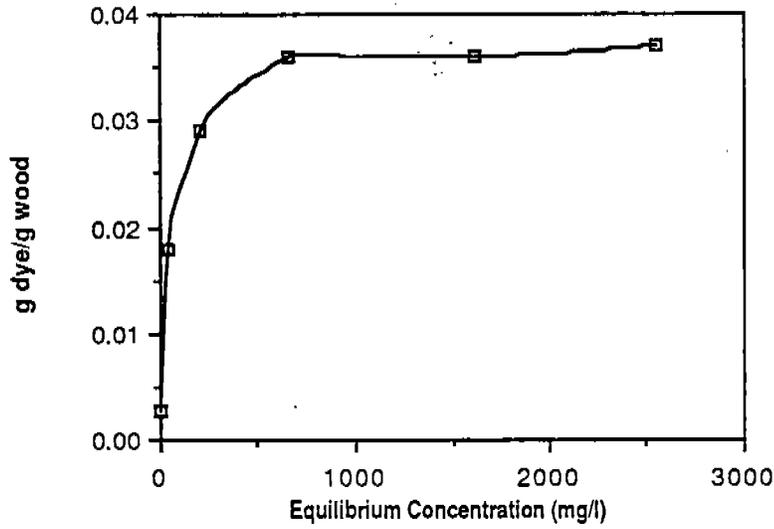


Figure 4. Methylene blue isotherm for 1/8" aspen wood chips.

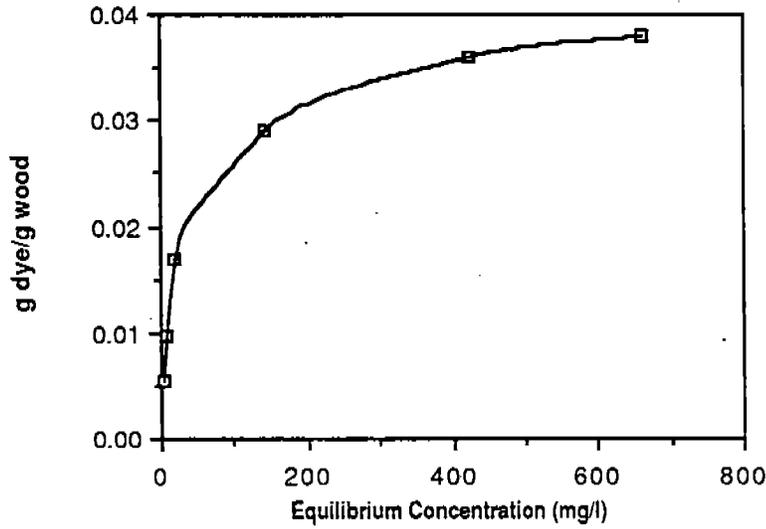
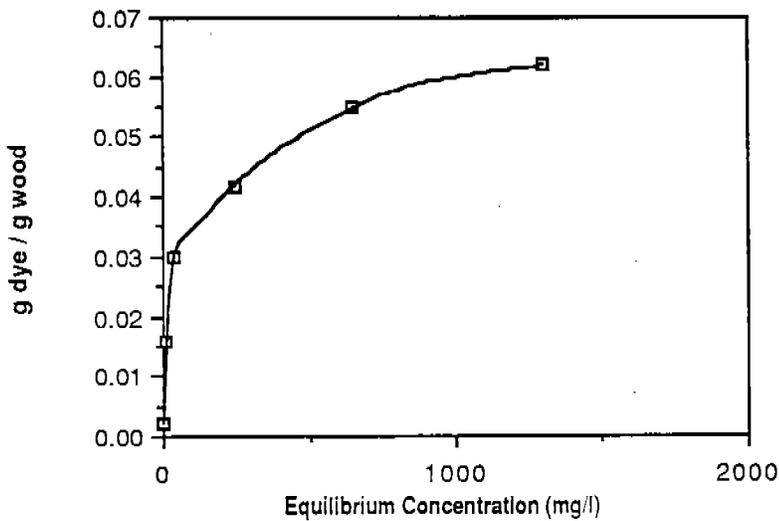


Figure 5. Crystal violet isotherm for 1/4" aspen wood chips.



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