

AN ABSTRACT OF THE THESIS OF

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Batch sorption tests were conducted using 3,4-DCP and cellulose triacetate as the sorbate/sorbent pair. Sorbate concentrations in the liquid were sampled with time and analyzed by electron capture detector gas chromatography. Sorption was found to be a two stage process characterized by a rapid initial uptake followed by a extended period of slower sorption. A fully reversible two step sorption model was applied to the results of batch sorption tests and sorption rate constants were determined. Although sorption equilibrium was not reached during the time scale of this study, it appears that the equilibrium partition coefficient, K_p , was not dependent upon sorbent concentration. Due to the extended period needed to reach sorption equilibrium, the kinetic approach to modeling sorption in subsurface environments may be more accurate than the use of local equilibrium assumptions.

The Effect of Organic Sorbent Concentration
On Sorption Kinetics

by

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TABLE OF CONTENTS

INTRODUCTION AND OBJECTIVES	1
LITERATURE REVIEW AND THEORETICAL CONSIDERATIONS	4
EXPERIMENTAL METHODS AND MATERIALS	10
Materials	10
Experimental and Analytical Apparatus	11
Experimental Method	12
RESULTS	16
Batch Sorption	16
Batch Sorption/Desorption	27
Microparticle Quantification	33
DISCUSSION	38
SUMMARY AND CONCLUSIONS	45
SIGNIFICANCE AND RECOMMENDATIONS FOR FUTURE STUDY	47
BIBLIOGRAPHY	48

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Batch Sorption Results of 10 mg/l 3,4-DCP Tests	18
2. Batch Sorption Results of 100 mg/l 3,4-DCP Tests	19
3. Batch Sorption Results of 1000 mg/l 3,4-DCP Tests	20
4. Solids Effect Summary at 96 Hours	22
5. Time Dependent Solids Effect Using 100 mg/l 3,4-DCP Test Data	24
6. Model Prediction of Time Dependent Solids Effect for 10 mg/l 3,4-DCP Tests	25
7. Model Prediction of Time Dependent Solids Effect for 100 mg/l 3,4-DCP Tests	26
8. Batch Desorption at 10 hours for 10 mg/l 3,4-DCP, 10 g/l Solids	28
9. Batch Desorption at 100 hours for 10 mg/l 3,4-DCP, 10 g/l Solids	29
10. Batch Desorption at 10 hours for 100 mg/l 3,4-DCP, 10 g/l Solids	30
11. Batch Desorption at 10 hours for 100 mg/l 3,4-DCP, 10 g/l Solids	31
12. Microparticle Quantification for 100 mg/l Solids Concentration	34
13. Microparticle Sorption Analysis for 150 mg/l Suspended TOC Concentration	36
14. Model Prediction of Solute Distribution at 10 g/l Solids Concentration, 10 mg/l 3,4-DCP	43

The Effect of Organic Sorbent Concentration On Sorption Kinetics

INTRODUCTION AND OBJECTIVES

The fate of organic chemical pollutants in aquatic and groundwater environments has become the object of increasing concern in recent years. It is important to gain an accurate quantifiable understanding of chemical behavior in the environment to assess the potential hazards of current use and disposal practices. Organic chemicals are introduced to the environment through application of pesticides, leachate from sanitary landfills, disposal of primary and secondary sewage treatment sludge and effluent, and hazardous waste spills. Groundwater contamination occurs when these pollutants are transported through the soil matrix to useable groundwater reserves.

Biodegradation and sorption are the most important processes in determining the fate and availability for transport of nonvolatile compounds in subsurface environments (1). Many toxic organic compounds have been shown to be biodegraded in actual or simulated subsurface environments (1,2,3,4). Degradation conditions range from fully aerobic to anaerobic and from primary metabolism to cometabolism depending upon the type of organic compound, its concentration, the physical conditions and the population of microorganisms present.

Sorption in subsurface environments includes ion exchange, chemical sorption, adsorption to surfaces, and partitioning through solid surfaces. Sorption reactions are modeled as reversible, where the organic contaminant is chemically unaltered in the process, or as irreversible, where the chemical fate of the contaminant is unknown. Often sorption is described not as a specific reaction, but by an equilibrium partition coefficient, K_p , which relates the equilibrium concentration of the solute in the liquid and solid phases.

Transport models involving reactive solutes in soils often assume local chemical equilibrium in describing sorption reactions. The validity of this assumption depends upon a variety of parameters including the groundwater flow rate and the rate of sorption (5). Previous research on sorption kinetics indicates two components in the reaction. First is a rapid or "labile" sorption followed by a much slower sorption reaction (6,7,8). The use of local equilibrium assumptions may produce substantial errors if the second slower stage of organic sorption is considered to be complete in the time scale of the transport model.

Recent studies have shown a dependence of the equilibrium partition coefficient on the concentration of sorbent in the system: a "solids effect" (9,10,11). Various explanations and models have been proposed regarding this observed phenomena. While some investigators feel the effect is caused by a third phase of non-settleable sorbed microparticles incorrectly measured as dissolved

solute (11,12,13), others have introduced evidence that it is an actual particle interaction phenomena (10,14). Depending upon the reason for these observed effects, serious errors in the prediction of sorption behavior in natural systems could occur due to variations between sorbent concentrations in the field and in the laboratory.

The objectives of this study were:

1. To determine if the sorption of hydrophobic organic solutes to organic sorbents can be described as a two step procedure of a rapid initial step followed by a slower long term second step.
2. To investigate the dependence of the equilibrium partition coefficient, K_p , on the organic sorbent concentration.
3. To develop a mechanistic kinetic sorption model that adequately fits the experimental data with varying solids concentrations.
4. To quantify the presence of suspended microparticles in the system, to determine if solute sorbed to these microparticles is mistakenly quantified as "free" solute, to estimate the sorption capacity of the microparticles, and to evaluate the role of sorption to microparticles to any observed "solids effect".

LITERATURE REVIEW AND THEORETICAL CONSIDERATIONS

Sorption refers to a combination of reactions including ion exchange, physical adsorption, chemisorption and absorption occurring at or through the solid surface. Because of the difficulties in identifying and evaluating the importance of each process, the term sorption is generally used.

The solid-liquid interaction is usually described by an equilibrium isotherm which relates the sorbed concentration to the liquid concentration. Numerous fitting equations are used to model the data including the Freundlich and Langmuir isotherms. Both have been theoretically derived from kinetic or thermodynamic considerations. However, questions remain about the meaning of the fitting parameters in these models. Good discussions of this problem have been offered by Harter (15) and by Veith and Sposito (16).

At low liquid concentrations, the sorption isotherm is often observed to be linear. The slope is called the sorption partition coefficient, K_p , which is defined as:

$$K_p = \frac{C_s}{C_L}$$

where C_s : mass of sorbed sorbate per unit
mass of sorbent, (mg sorbate/g
sorbent) and

C_L : liquid concentration in mg sorbate/l.

The units of K_p are consequently the inverse of sorbent concentration (l/g).

The first reports concerning the solids effect described sorption to soils and lake sediments (17,18,19). Certainly, many reports of solids effect may result because of experimental errors. However, improvement of experimental methods and apparatus have confirmed this unexpected dependence of sorption on solids concentration. Data from various sorption studies exhibits this apparent dependence of K_p on solids concentration (9).

Applications of the sorption partition coefficient have increased the importance of understanding the solids effect. This is especially true in the area of groundwater quality modeling where K_p values are determined at low solids concentrations in batch reactors and are used to describe sorption in soil systems. Solute transport is often modeled assuming local equilibrium in subsurface systems of porous media where high solid concentrations are present.

O'Connor and Conolly (9) have surveyed the literature data and compared them with an empirical model:

$$K_p = K_{p\#} + \frac{b}{c + S^a}$$

where $K_{p\#}$ = limiting partition coefficient at high
solid concentration in l/g

S = solid concentration in g/l

a, b, c = empirical fitting constants

In most cases, due to the relatively low values of K_p and c , this equation can be reduced to:

$$K_p = \frac{b}{S^a}$$

O'Connor and Conolly's study revealed that empirically derived constants are a function of the sorbate-sorbent couple.

An alternate explanation of the solids effect is the concept of a nonseparable third phase, where the solute is complexed or sorbed on colloids or microparticles which have a concentration proportional to the solids concentration. Solid separation techniques such as centrifugation or filtration always leave microparticles in suspension. As is well known, the sorption activity increases as the radius of the particle decreases, and so the saturation capacity expressed per unit weight of these small particles increases. A solids effect is created when sorbate sorbed to these microparticles is mistakenly quantified as free sorbate due to the analytical method used.

Voice and Weber (11,13) proposed that the partitioning of hydrophobic solutes associated with nonseparable colloids is empirically related to the organic solid concentration by the equation:

$$TOC = E * S^F$$

where

TOC = total organic carbon in solution

S = solid concentration

E, F = empirical constants.

Including this relationship and developing the equations required to

describe the three phases (liquid, solid and microparticles), Voice and Weber proposed a complex model which was able to fit literature experimental data, but is difficult to use because of the number of parameters involved. After making simplifying assumptions, Gschwend and Wu (12) developed a simple model which strongly supports the third phase hypothesis.

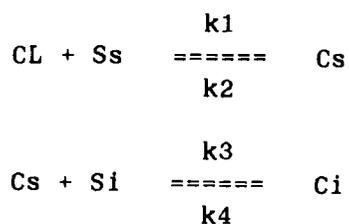
The desorption of hydrophobic solute often exhibits a hysteresis effect in which desorption and sorption have different isotherms. Several authors have investigated the possibility of two different kinds of reactions sites: one assumed to be irreversible and another with forward and reverse velocities. This concept of an irreversible site explains the observed hysteresis, but the same effect can be observed if the experimenter with a completely reversible sorption mechanism assumes equilibrium before true desorption equilibrium is reached.

DiToro et al. (10,14) have described this hysteresis effect with a particle-particle interaction model occurring only at high solids concentrations. As the collisions occur between solids, the free particles are thought to destabilize the bound particles, thus lowering the K_p value and suggesting the observed solids effect. The model developed fitted experimental data. In a later publication (10), DiToro, working with glass beads as solids for which no microparticles and no colloids occurred, showed that although the third phase hypothesis does not apply in the completely reversible situation of heavy metals sorption, the solids effect was still

observed.

This described solids effect becomes important when the K_p value obtained under laboratory conditions (i.e. low solids concentration) is applied to models to assess the contamination risk of aquifers under the assumption of local equilibrium. If the observed solids effect is a result of particle interaction the question is raised as to the degree this interaction occurs in field situations. If, on the other hand, the effect is caused by sorption to a third phase in the system, the question of mobility of this third phase is raised.

The sorption model chosen for use in this study is a variation of a standard two-box model (8). Sorption from the liquid phase to a particle exterior is followed by partitioning of the sorbate into the particle interior. Both reactions are considered to be essentially Langmuirian, completely reversible and can be written as follows:



where:

- CL = free (liquid) DCP concentration, mg/l
- S_s = available exterior sorption sites, mg/g
- C_s = DCP sorbed to surface, mg/g
- S_i = available interior sorption sites, mg/g
- C_i = DCP sorbed to interior, mg/g
- k₁ = forward exterior sorption constant, g/(mg*hr)
- k₂ = reverse exterior sorption constant, g/(l*hr)
- k₃ = forward interior sorption constant, g/(mg*hr)
- k₄ = reverse interior sorption constant, 1/hr

At the beginning of a sorption test, the available free sorption sites S_s and S_i are set equal to the maximum available sites C_{smax} and C_{imax} respectively. The numerical model equations were then developed as follows:

$$dCL/dt = -k_1*CL*S_s + k_2*Cs$$

$$dCs/dt = (k_1*CL*S_s - k_2*Cs)/S - k_3*S_i*Cs + k_4*Ci$$

$$dCi/dt = k_3*Cs*S_i - k_4*Ci$$

$$S_s = C_{smax} - Cs$$

$$S_i = C_{imax} - Ci$$

where: C_{smax} = maximum exterior sorption sites, mg/g

C_{imax} = maximum interior sorption sites, mg/g

S = sorbent concentration, g/l

The six unknown model parameters are then C_{smax} , C_{imax} , k_1 , k_2 , k_3 , and k_4 . An iterative approach is used to solve for the unknown parameters.

EXPERIMENTAL METHODS AND MATERIALS

Materials

The purpose of this study was to develop a better understanding of the effects of concentration of an organic sorbent on sorption kinetics and equilibrium partitioning of a hydrophobic organic solute. These experiments represent a portion of a larger study involving the determination of the relationship between sorption kinetics and the kinetics of biodegradation in a simulated subsurface environment.

The sorbate 3,4 Dichlorophenol (3,4-DCP) was chosen because of its hydrophobic character, its ability to be biodegraded (2), and because it is representative of a class of compounds, chlorophenols, which are known groundwater contaminants (23). The pKa and water solubility of 3,4-DCP are 8.59 and 4000 mg/l, respectively (22). Solutions were prepared with 99% pure 3,4-DCP purchased from Aldrich Chemical Company and glass distilled water. Solution pH ranged from 4.2 to 4.6 throughout the experiments, thereby eliminating any need to quantify phenolate sorption.

Researchers often correlate the amount of sorption to the organic content of the soil or sediment. Cellulose triacetate was chosen as the sorbent because of its organic nature, its insolubility in water, and its interstitial structure. Greater than 93 percent of the hydroxyl groups of cellulose are replaced by acetate groups in forming cellulose triacetate resulting in an

organic carbon content between 45 and 50 percent. The cellulose triacetate was purchased from Eastern Kodak Company and ranged in size from dust particles to irregularly shaped "beans" approximately 1 cm in length. The cellulose was ground, sieved, and washed with glass distilled water. The portion retained on the 100 mesh per inch sieve was dried in a vacuum oven at approximately 60 C for several days and then stored in a desiccator for future use. This particle size was chosen in an attempt to maximize surface area, while maintaining its rapid settling behavior in solution.

Experimental and Analytical Apparatus

The batch reactors used in this experiment consisted of 100 ml clear glass serum vials sealed with aluminum crimp-top caps and teflon faced rubber cap liners. The vials were placed at a 45 degree angle in a Blue M constant temperature shaker bath. All experiments were conducted with the shaker set at approximately 150 oscillations per minute, and at a temperature of 20 C.

Samples were taken using either a Gilson micropipetor with a polypropylene tip or a Wheaton micropipetor with a glass barrel and a teflon tipped plunger. The Gilson pipetor was used to take 200 ul samples of 10 mg/1 or less 3,4-DCP solution. Samples were taken with the polypropylene tips were compared to samples taken with a microsyringe and no detectable difference in 3,4-DCP concentration was observed. The Wheaton pipetor was used to take 25 ul samples of 100 mg/1 3,4-DCP solution and 5 ul samples of 1000 mg/1 3,4-DCP solution. The samples were placed in glass vials containing 1.8 ml

of glass distilled water and sealed with teflon lined screw caps. At the end of each experiment, an internal standard was added to the sample which was then acetylated and extracted into 2 ml of hexane. The hexane extract was placed into 1.5 ml amber glass vials with teflon lined caps and refrigerated until analyzed.

The hexane samples were analyzed on an HP 5890A gas chromatograph using a splitless injector system, an electron capture detector, and a 10 m long, 530 um diameter HP-1 methyl silicone gum capillary column with a 2.65 um film thickness. The 3,4-DCP concentration in the hexane sample was determined by calculating the ratio of the 3,4-DCP peak area over the internal standard peak area and comparing it to a standard curve. The detection accuracy was found to be approximately $\pm 5\%$.

Total organic carbon analysis was conducted on a Beckman Model IR315 Infrared TOC Analyzer using 30 ul sample injections. The results were accurate to approximately ± 5 mg/1 TOC. Filtration of 10 ml samples was conducted using a teflon filter apparatus with a 0.25 mm thick, 1-2 mm porosity teflon filter.

Experimental Methods

Three types of experiments were conducted; batch sorption, batch sorption/desorption, and microparticle quantification. All three experiments used essentially the same equipment under the same environmental conditions. Before any experiment was started, all of the glass equipment to be used in the experiment was soaked in a 25%

sulfuric acid bath for at least 24 hours and then consecutively rinsed with tap, distilled, and finally glass distilled water and left to air dry. Stock 3,4-DCP solutions of 10 mg/l, 100 mg/l and 1000 mg/l were prepared in advance and refrigerated until use.

At the beginning of a batch sorption experiment a quantity of cellulose triacetate was removed from the desiccator, weighed on an analytical balance, and placed in a reactor vial. A stock 3,4-DCP solution was warmed to 20 C and an initial ($t = 0$ hr) sample was taken. Eighty ml of 3,4-DCP stock solution was added to the cellulose triacetate in the vial, the top was crimped on, and the vial was placed in the shaker bath. Samples were taken by removing the vial from the shaker, taking the cap off, pipeting off a sample, and placing a new top on the vial. The entire sampling procedure required about 30 seconds. The samples were not filtered or centrifuged as the cellulose triacetate settled rapidly.

Blanks were run at 3,4-DCP concentrations of 10 mg/l and 100 mg/l. These blanks were subjected to the same conditions and sampling regimen as the reactors containing solids and were found to exhibit negligible losses due to volatilization, sorption to reactor components, or photodegradation. By limiting the number of samples taken from a reactor to 20 samples of 200 ul each, the greatest volume change during an experiment was limited to 4 ml or 5% of the total volume. This restriction allowed the sorbent concentration to be assumed constant over the duration of the experiment. Due to a fairly high solids density, approximately 1.3 g/ml, the volume of

sorbent was neglected in all concentration calculations.

Batch sorption/desorption experiments began using the same procedure described in the batch sorption tests. At a given time, either 10 or 100 hours, 70 ml of solution was removed from the reactor and replaced with 70 ml of glass distilled water. The reactor was replaced in the shaker and samples were taken over a period of up to 230 hours. Although the cellulose triacetate settles quickly, it was difficult to remove 70 ml of liquid from the reactor without disturbing the solids and possibly removing some of the finer solid particles. Approximately 4 minutes were required to complete the liquid exchange procedure. Sample volumes taken after the exchange were twice the original size, either 400 μ l or 50 μ l, so that the eventual concentration in the hexane extractions would be within the detection limit of the gas chromatograph.

A microparticle quantification experiment was conducted using 8 g of cellulose triacetate in 80 ml of glass distilled water. The solution was shaken in the constant temperature water bath and samples were taken and analyzed on the Beckman TOC Analyzer for a period of 100 hours. At this time approximately 65 ml of supernatant was removed from the vial and replaced with 70 ml of glass distilled water. The vial was shaken for another 150 hours with periodic sampling before ending the test. In addition to charting the suspension of microparticles as TOC with time, 10 ml of the supernatant removed at 100 hours was filtered and the "dissolved" portion or DOC was determined. The rest of the supernatant, 54 ml,

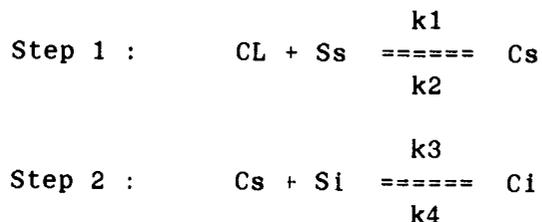
was placed in a serum vial along with 6 ml of 100 mg/l 3,4-DCP. The vial was shaken for 101.5 hours with samples removed periodically for GC analysis. In an attempt to quantify sorption to micro-particles and to determine whether the sorbed fraction registered as "free" DCP in the GC analysis, 10 ml samples were removed at 75 hours and again at 101.5 hours. A portion of each sample was filtered and both the filtered and unfiltered samples were tested for TOC and extracted into hexane for GC analysis.

RESULTS

Batch Sorption

The first step in the experimental plan was to conduct batch sorption experiments to establish the general nature of sorption kinetics and the effect sorbent concentration had on both sorption kinetics and the equilibrium partition coefficient, K_p . With this objective in mind, sorption experiments were conducted using initial 3,4-DCP concentrations of 10 mg/l, 100 mg/l and 1000 mg/l and sorbent concentrations of 1, 3, 7, and 10 g/l cellulose triacetate. The proposed sorption model shown below and discussed in a previous section was then applied to the data gathered from these tests.

Two-step fully reversible kinetic sorption model:



An iterative approach was used in an attempt to find one set of model parameters that would fit all the data. The following model parameters were used in model application to batch sorption data:

k_1	=	0.0267	g/(mg*hr)
k_2	=	1.40	g/(1*hr)
k_3	=	0.00018	g/(mg*hr)
k_4	=	0.005	1/hr
C_{smax}		7.5	mg/g
C_{imax}	=	100	mg/g

The results of the batch sorption experiments are presented in Figures 1 through 3 and indicate a two stage sorption phenomena in which the first stage of rapid sorption is followed by slower, prolonged sorption. Sorption tests initiated at 3,4-DCP concentrations of 10 and 100 mg/l are fit well by the predictive model. The initial sorption rate appeared to be fairly constant over the range of solids concentrations tested. However, both tests showed that the lower the solids concentration, the sooner the initial rapid sorption step was completed. Lower solids concentrations also exhibited a more uniform second step sorption rate when compared to the curvature seen in the 7 and 10 g/l solids tests. In all cases, the addition of more solids caused increased sorption.

The chosen model parameters did not fit the data from sorption tests of 1000 mg/l initial 3,4-DCP concentration. The model predicted significantly less sorption than actually took place. Model parameters could not be found that would fit both the 1000 mg/l data and the data from the lesser 3,4-DCP concentration tests. It was uncertain whether this was a fault with the model or if the sorption characteristics of the system changed at high 3,4-DCP concentrations. Solubility of 3,4-DCP is in the range of 3 to 4 g/l. It was observed during the 1000 mg/l 3,4-DCP tests that an emulsion formed at the air-solution interface and air bubbles clung to the particles causing them to float. Neither of these phenomena occurred at lower DCP concentrations.

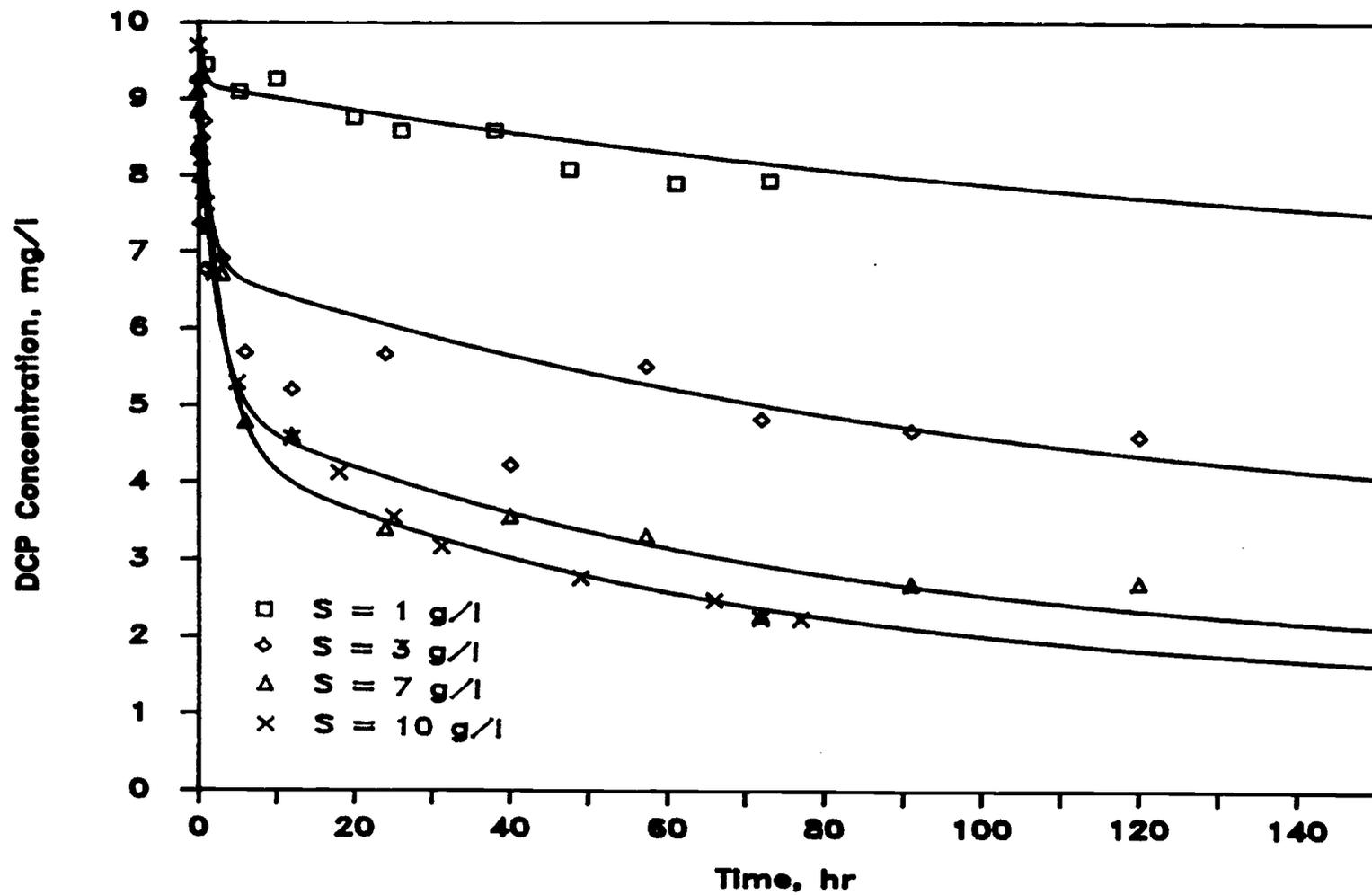


Figure 1. Batch Sorption Results of 10 mg/l 3,4-DCP Tests

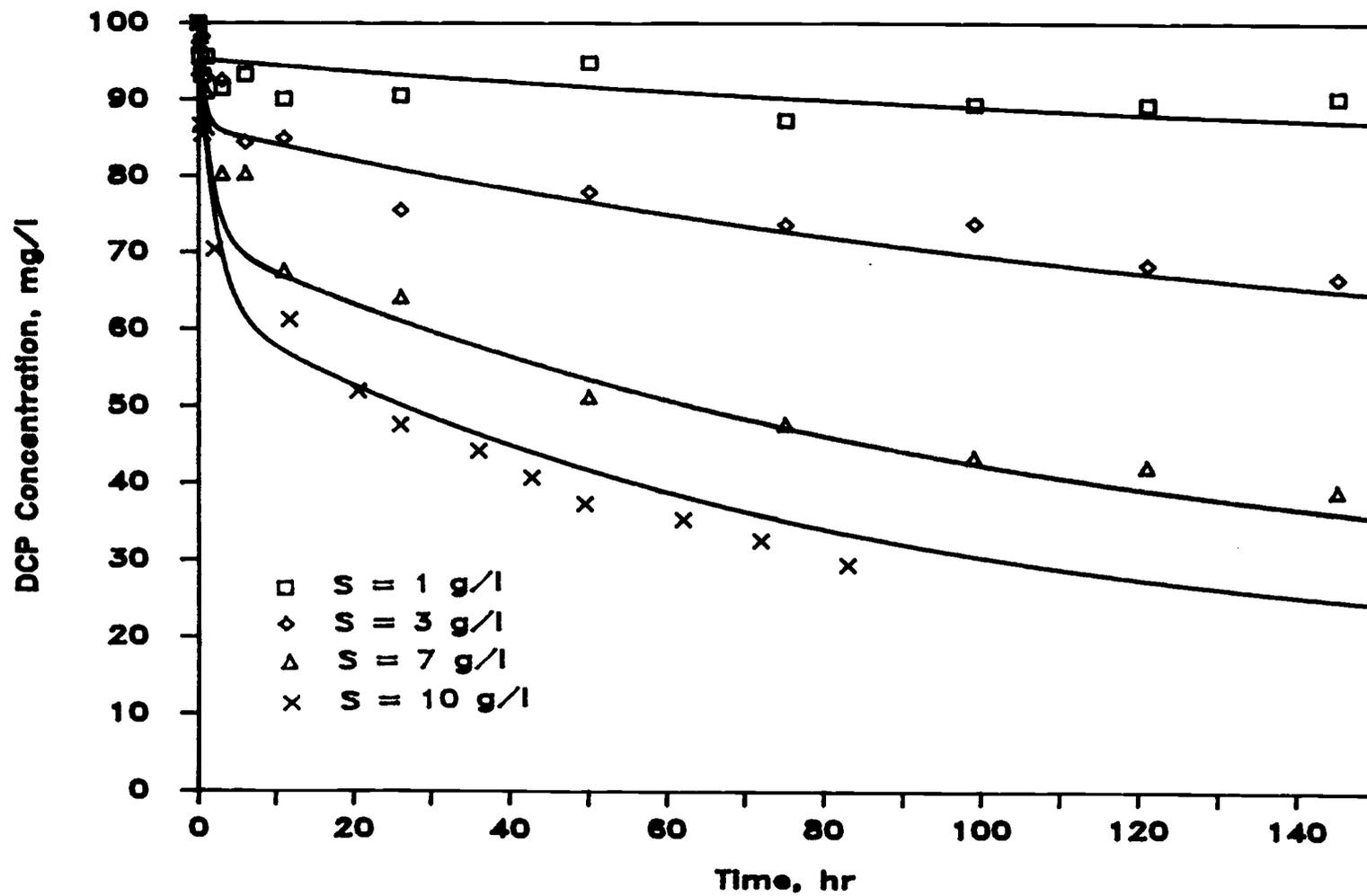


Figure 2. Batch Sorption Results of 100 mg/l 3,4-DCP Tests

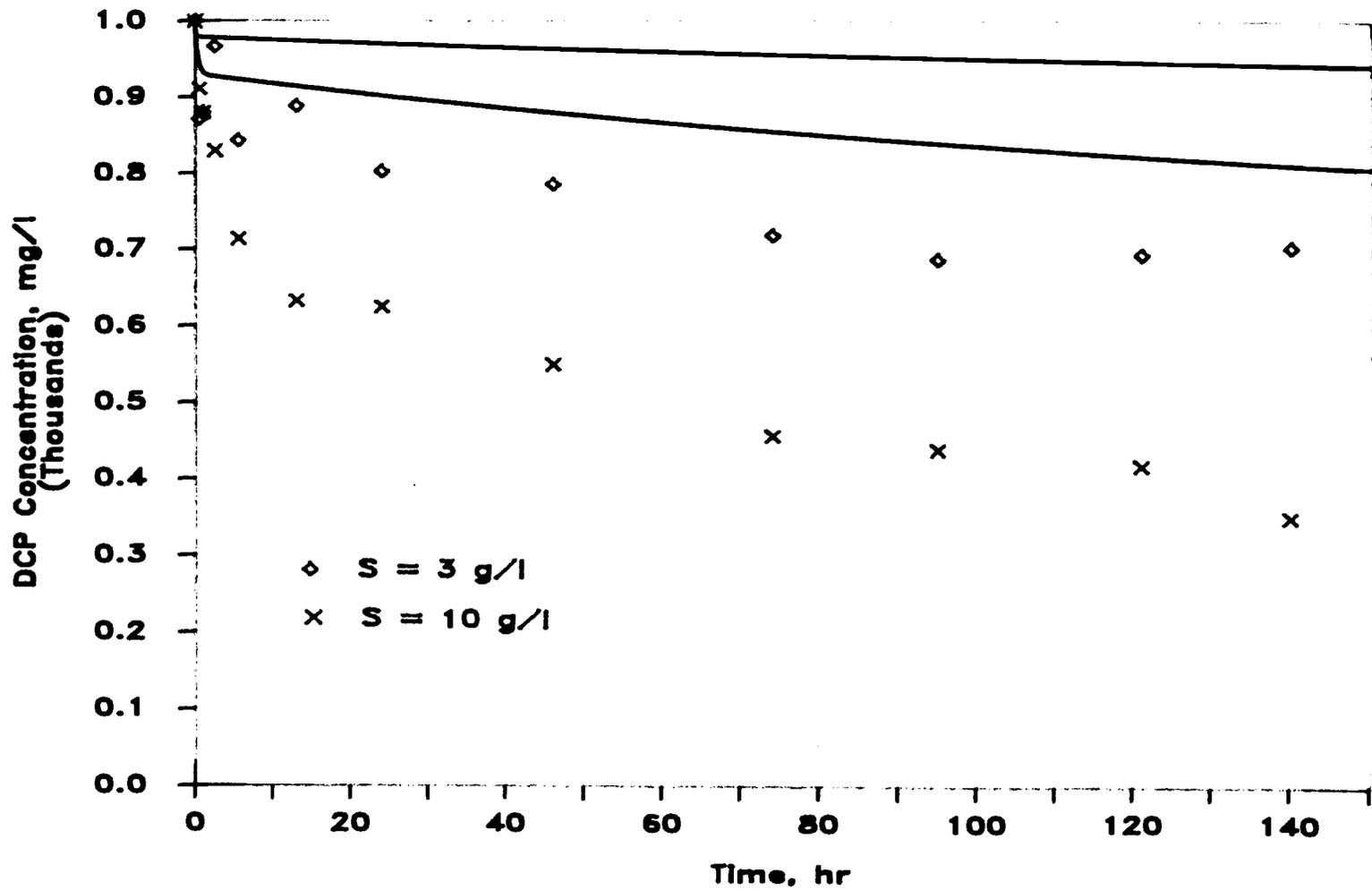


Figure 3. Batch Sorption Results of 1000 mg/l 3,4-DCP Tests

It can be seen from the experimental data that true equilibrium had not been reached by the end of the tests. This makes evaluation of an equilibrium partition coefficient for the various tests difficult. For batch sorption tests, the equilibrium partition coefficient can be expressed as:

$$K_p = \frac{(C_{Lo} - C_{Le})}{C_{Le} * S}$$

where: K_p = equilibrium partition coefficient, l/g

C_{Lo} = initial 3,4-DCP concentration, mg/l

C_{Le} = equilibrium 3,4-DCP concentration, mg/l

S = sorbent concentration, g/l

The term "solids effect" describes the observed phenomena of the log of the partition coefficient varying approximately linearly with the log of the solids concentration. Reported solids effects appear to exhibit linear relationships with slopes between -1 and 0. The above equation can be rewritten as:

$$\text{Log } K_p = \text{Log } (C_{Lo}/C_{Le} - 1) - \text{Log } S$$

To produce a slope of -1, the equilibrium sorbate concentration, C_{Le} , must be constant over the range of solids concentrations tested. This indicates that the solids concentration has no effect on the amount of sorbate removed from solution. This was not the case in the batch tests performed in this study. The relationship between the partition coefficient and the solids concentration after approximately 96 hours of sorption is shown in Figure 4. K_p appeared to be approximately constant over the range of solids concentrations

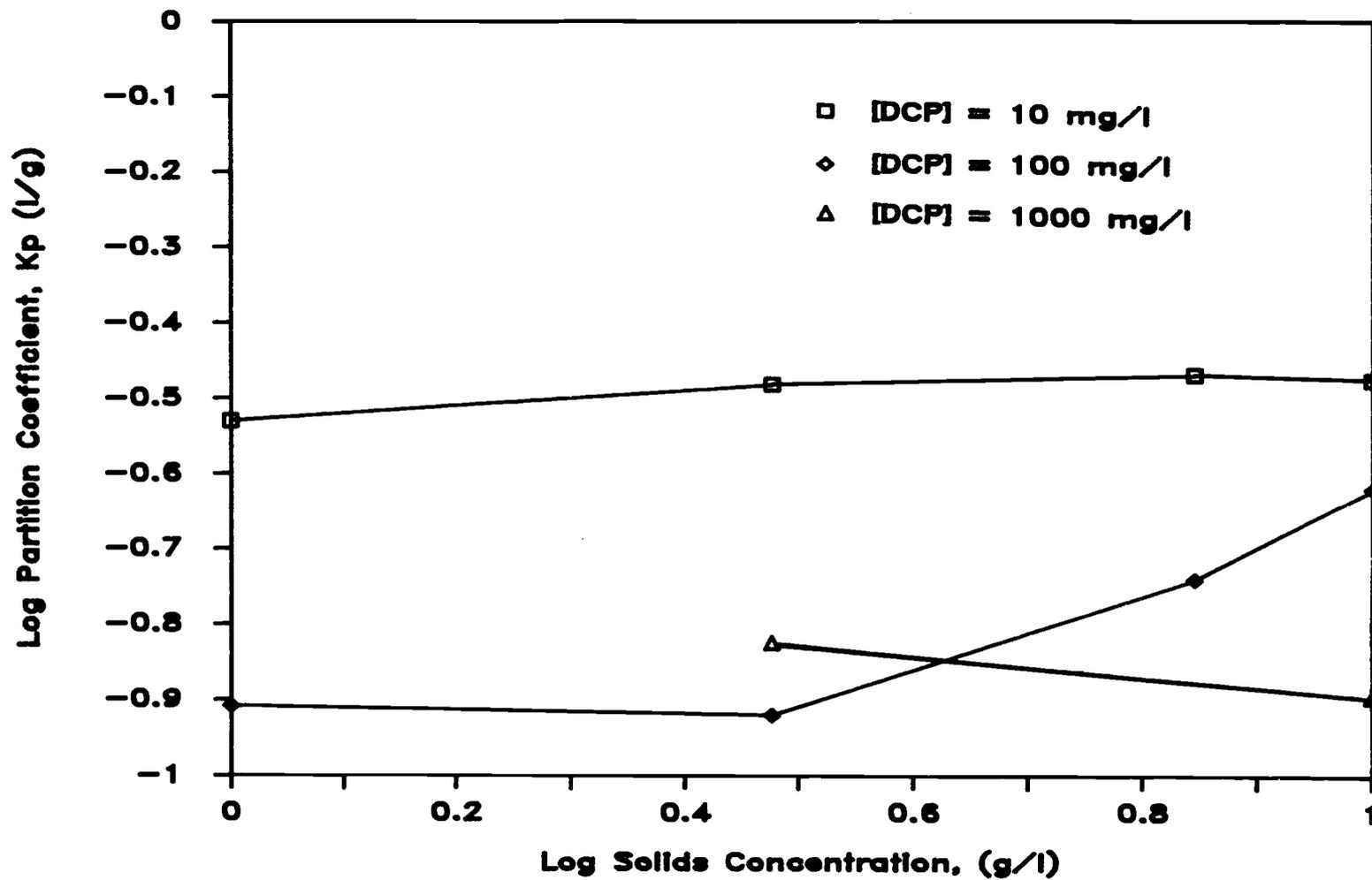


Figure 4. Solids Effect Summary at 96 Hours

in the 10 and 1000 mg/l 3,4-DCP tests, but the value for K_p in the 10 mg/l test was about twice of that in the 100 or 1000 mg/l tests. The 100 mg/l test showed an increase in K_p as solid concentration increased which is opposite to previously observed solid effects. However, it is evident from Figures 1 and 2 that the system was not at equilibrium at 96 hours. It can also be observed that the second step sorption rate was lower in the 10 mg/l 3,4-DCP test at 96 hours than in the 100 mg/l test. This may indicate that the 10 mg/l test was closer to equilibrium than the 100 mg/l test and therefore closer to the true equilibrium partition coefficient.

Since true equilibrium was not attained in the time scale used for the tests, an "apparent" partition coefficient was evaluated and plotted versus time and solids concentration. This was done with the contention that other studies reporting an apparent solids effect might possibly be examining a system that has not yet reached true equilibrium. The apparent partition coefficient, K_{ap} , was calculated in the same way as the true coefficient except the equilibrium values, C_{Le} , are replaced by the time dependant values, C_L .

The results shown in Figure 5 are data obtained from the 100 mg/l 3,4-DCP batch sorption tests. The lines are least square linear regression of the data for a given time. At the beginning of the sorption process, when the rapid sorption step dominates, a solids effect appears and gradually lessens in effect until an approximately constant K_{ap} over the solids range is attained. This

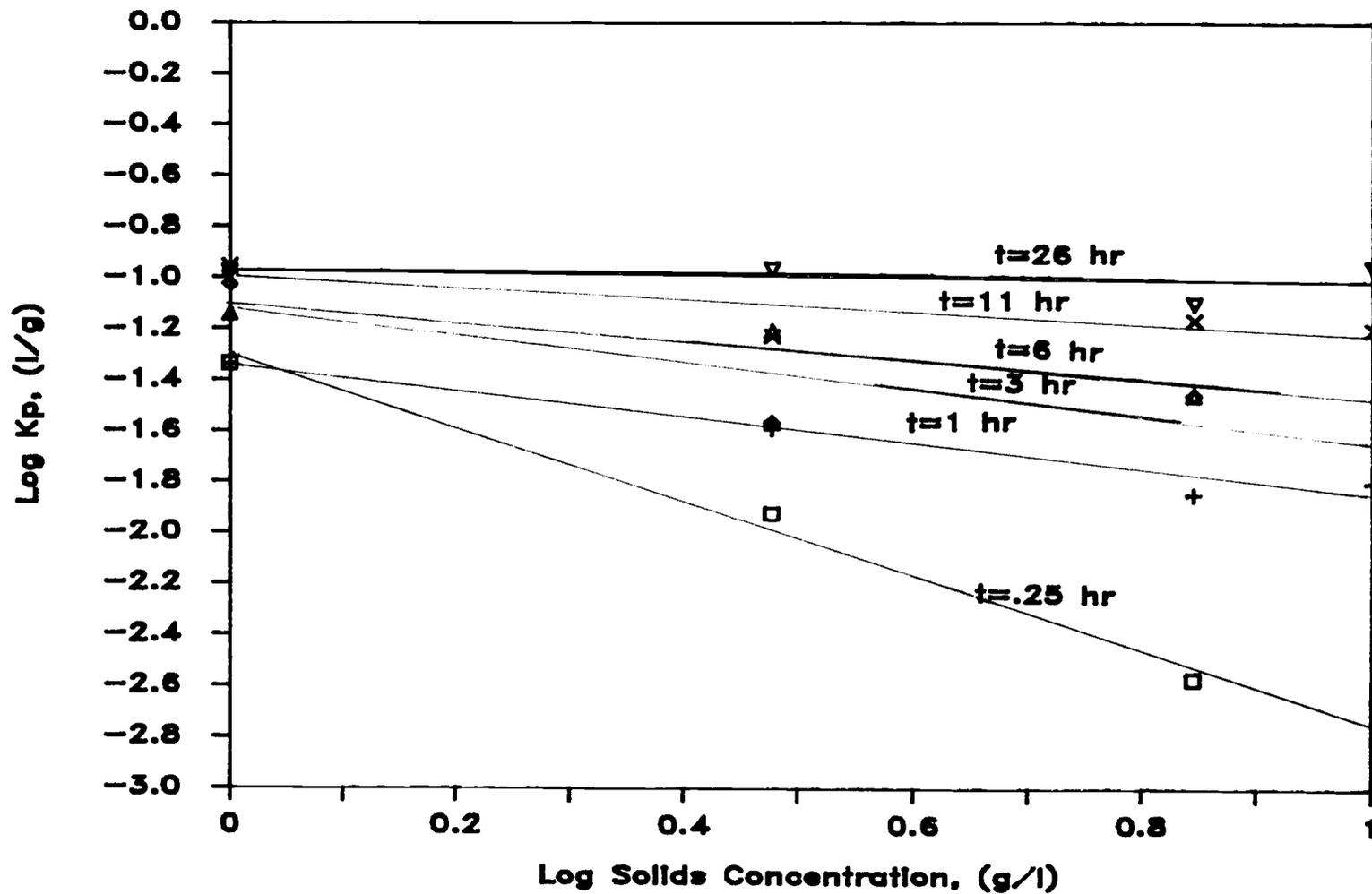


Figure 5. Time Dependent Solids Effect Using 100 mg/l 3,4-DCP Test Data

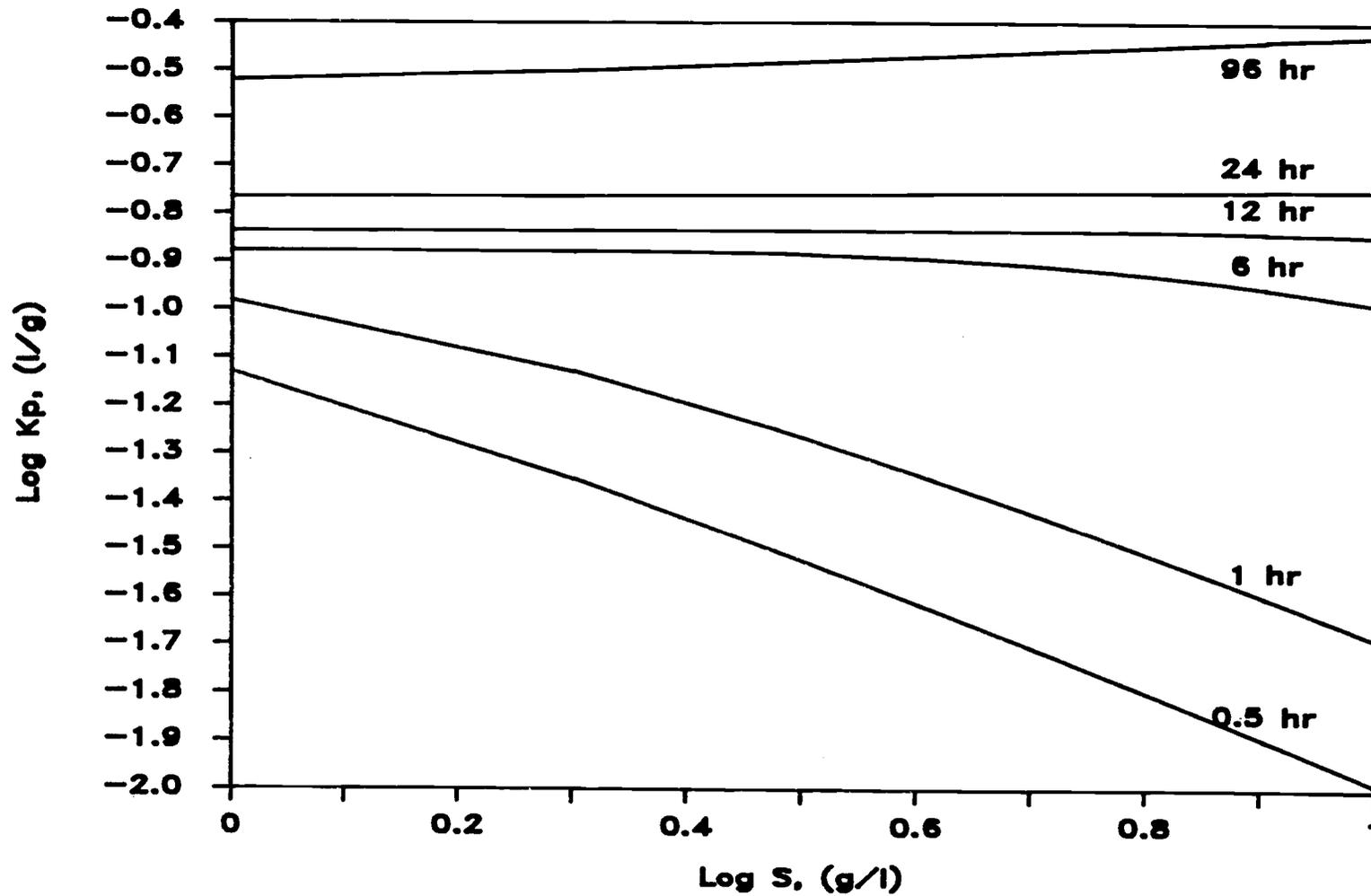


Figure 6. Model Prediction of Time Dependent Solids Effect for 10 mg/l 3,4-DCP Tests

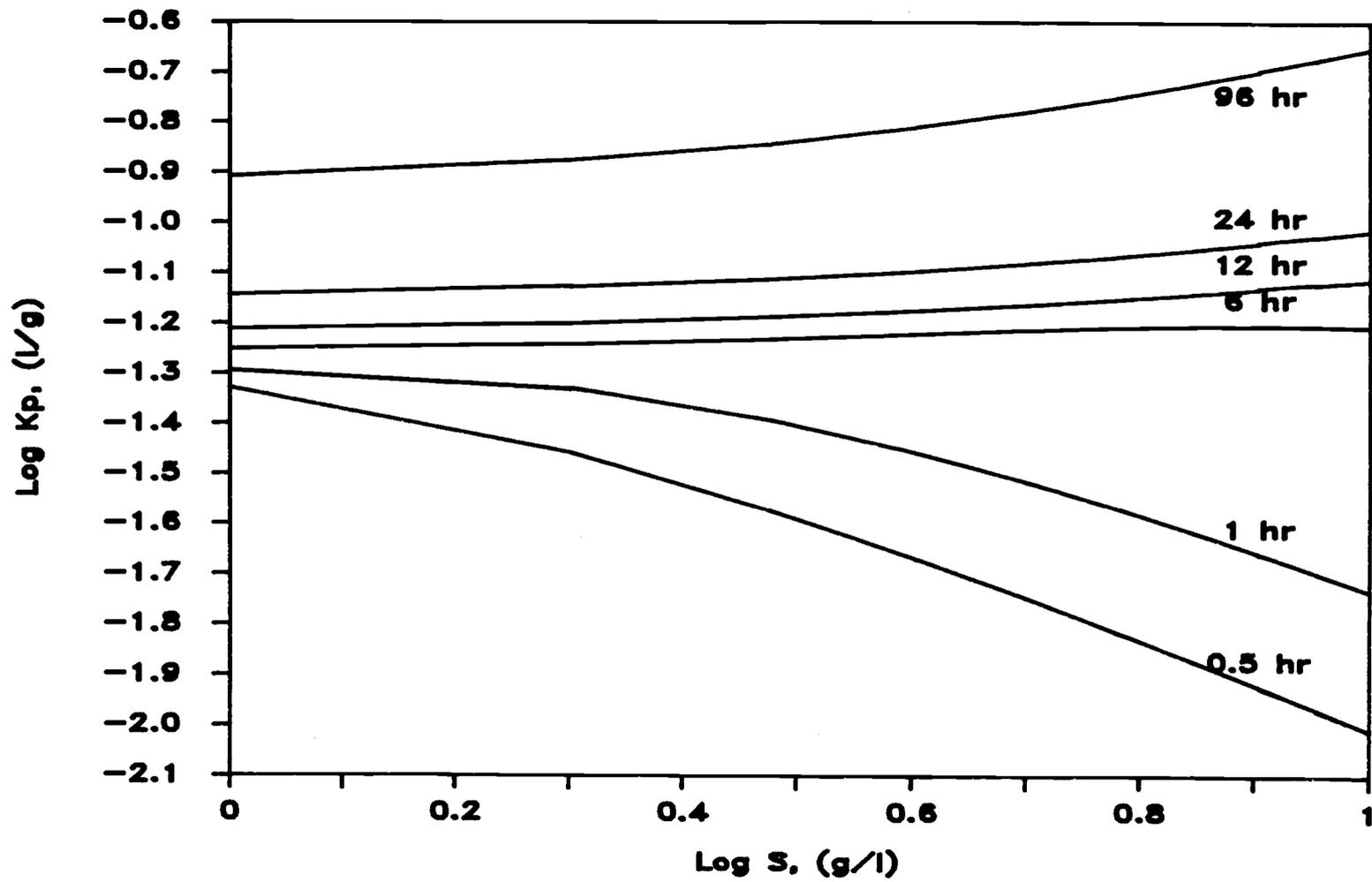


Figure 7. Model Prediction of Time Dependent Solids Effect for 100 mg/l 3,4-DCP Tests

appeared to be complete in the first 6 to 12 hours after which the partition coefficient continued to increase as sorption continued, but was approximately constant over the range of sorbent concentrations.

Figures 6 and 7 are model predictions of a time dependent solids effect. Figure 6 shows an approximate -1 slope at 0.5 hours gradually disappearing to a constant or slightly positively sloped K_p relationship at 96 hours. The predicted effect for the 100 mg/l 3,4-DCP tests showed an initial negative slope which rapidly levels off and became a decidedly positive slope at 96 hours.

Batch Sorption/Description

Desorption experiments were conducted with the objective of further defining the kinetic behavior of sorption and hopefully increasing the resolution of the proposed sorption parameters. Due to the number of parameters used in the sorption model, it was difficult to find a single combination of values that would adequately fit all the data and yet provide a unique solution. By conducting desorption tests, the validity of the parameters chosen in the sorption experiments as well as the validity of the model itself could be further tested.

A sorbent concentration of 10 g/l was chosen for all desorption tests because, of the four concentrations previously used, it was the only one that provided enough sorption to allow for measurable quantities of desorption. Initial 3,4-DCP concentrations

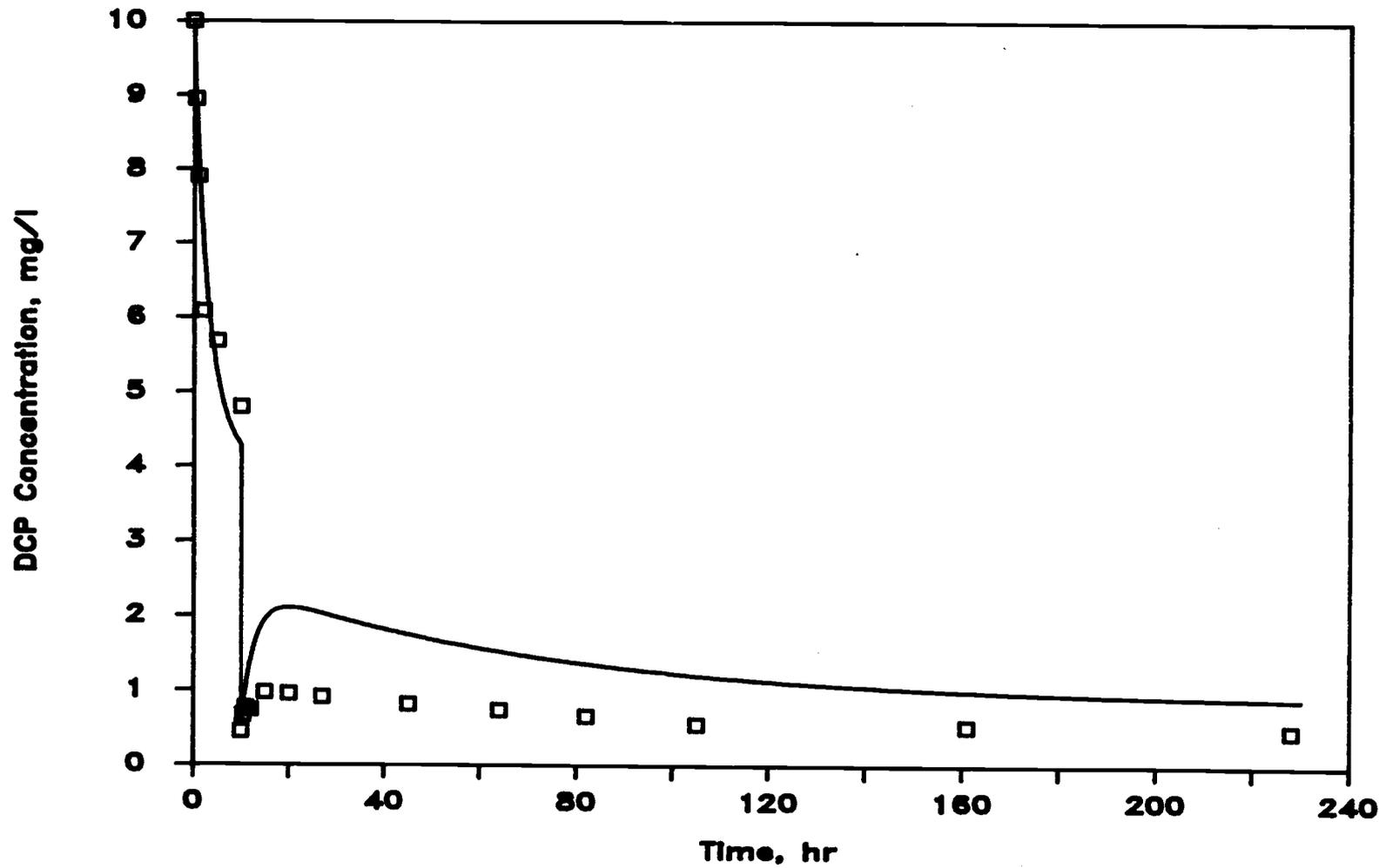


Figure 8. Batch Desorption at 10 Hours for 10 mg/l 3,4-DCP,
10 g/l Solids

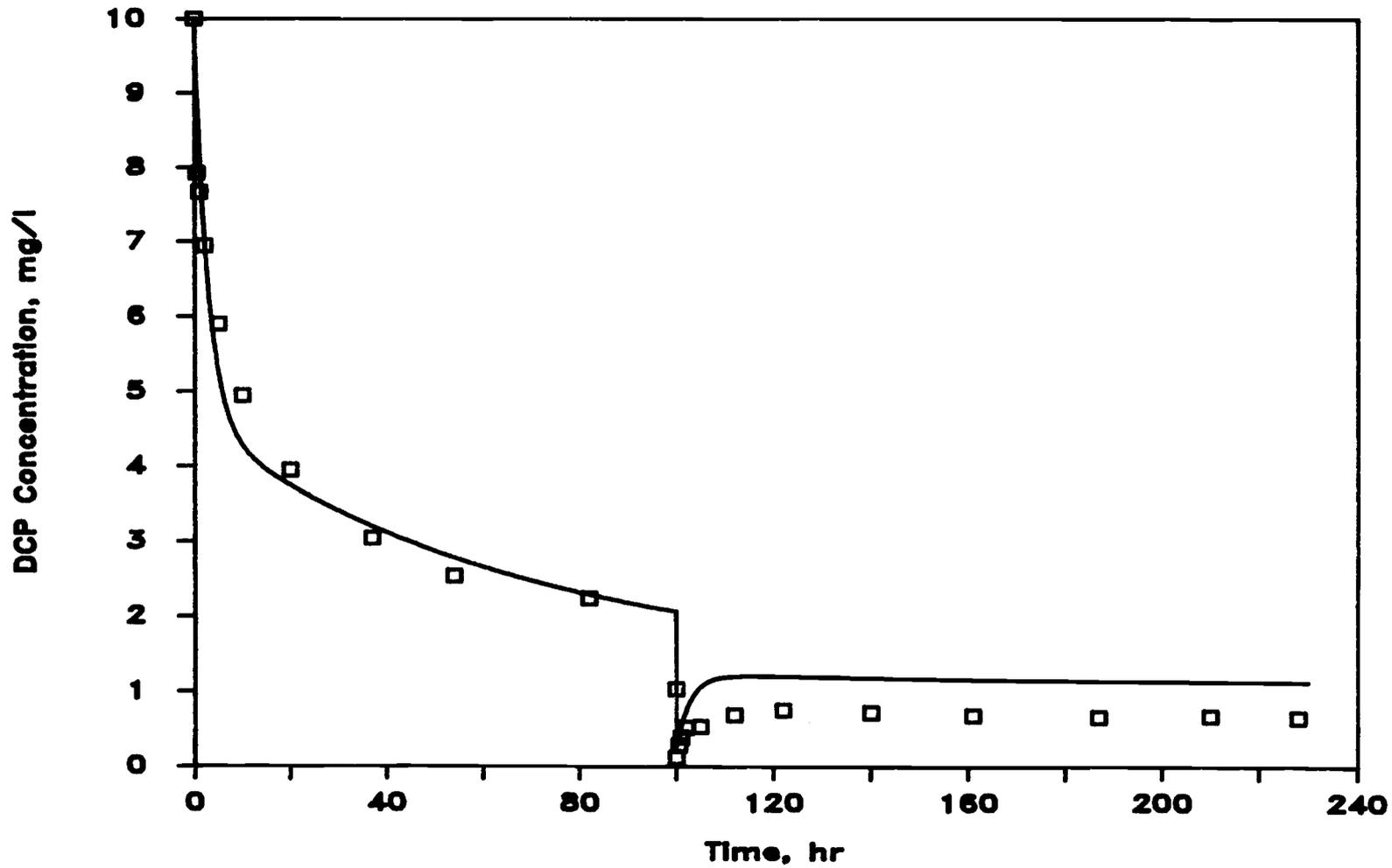


Figure 9. Batch Desorption at 100 Hours for 10 mg/l 3,4-DCP,
10 g/l Solids

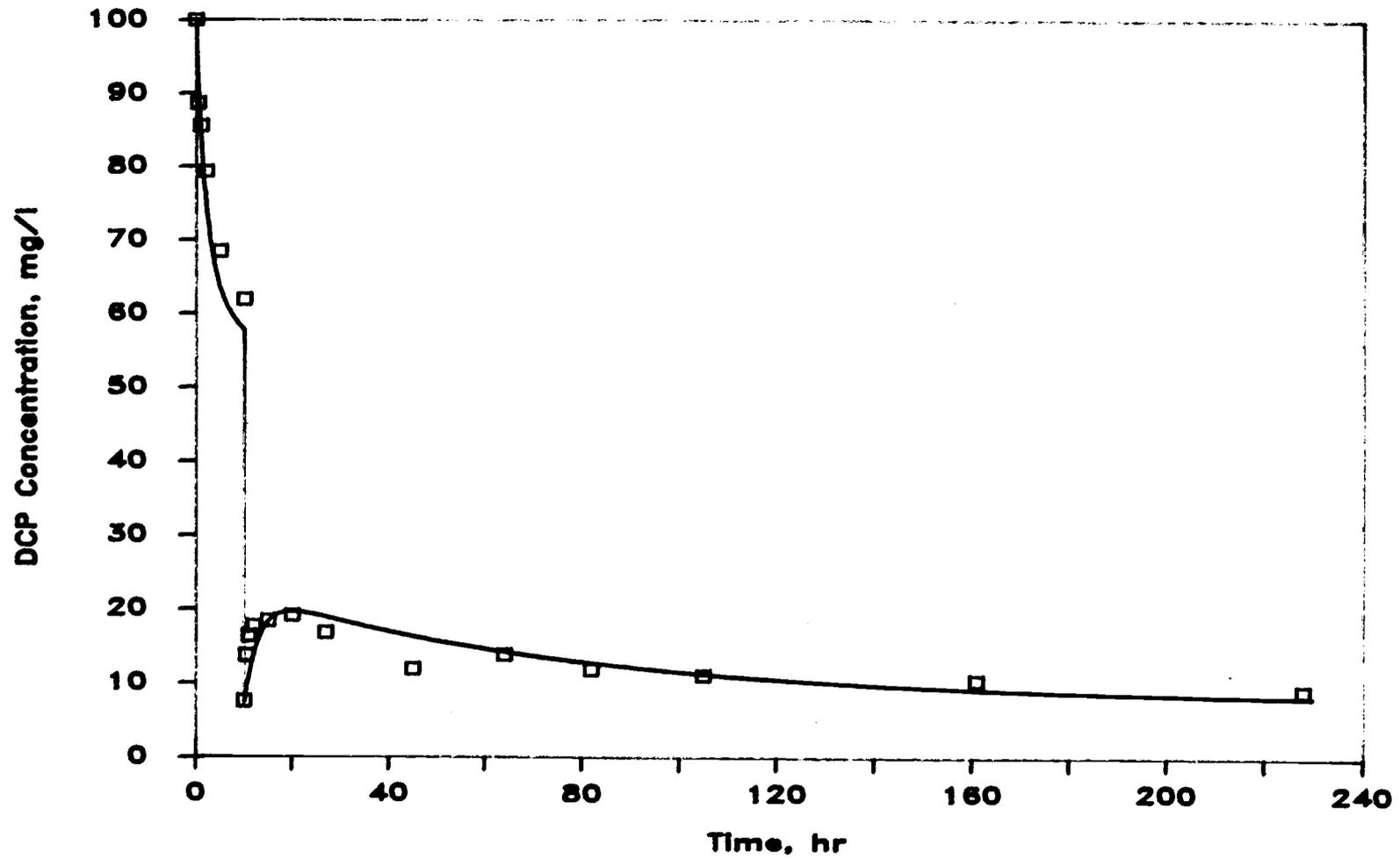


Figure 10. Batch Desorption at 10 Hours for 100 mg/l 3,4-DCP,
10 g/l Solids

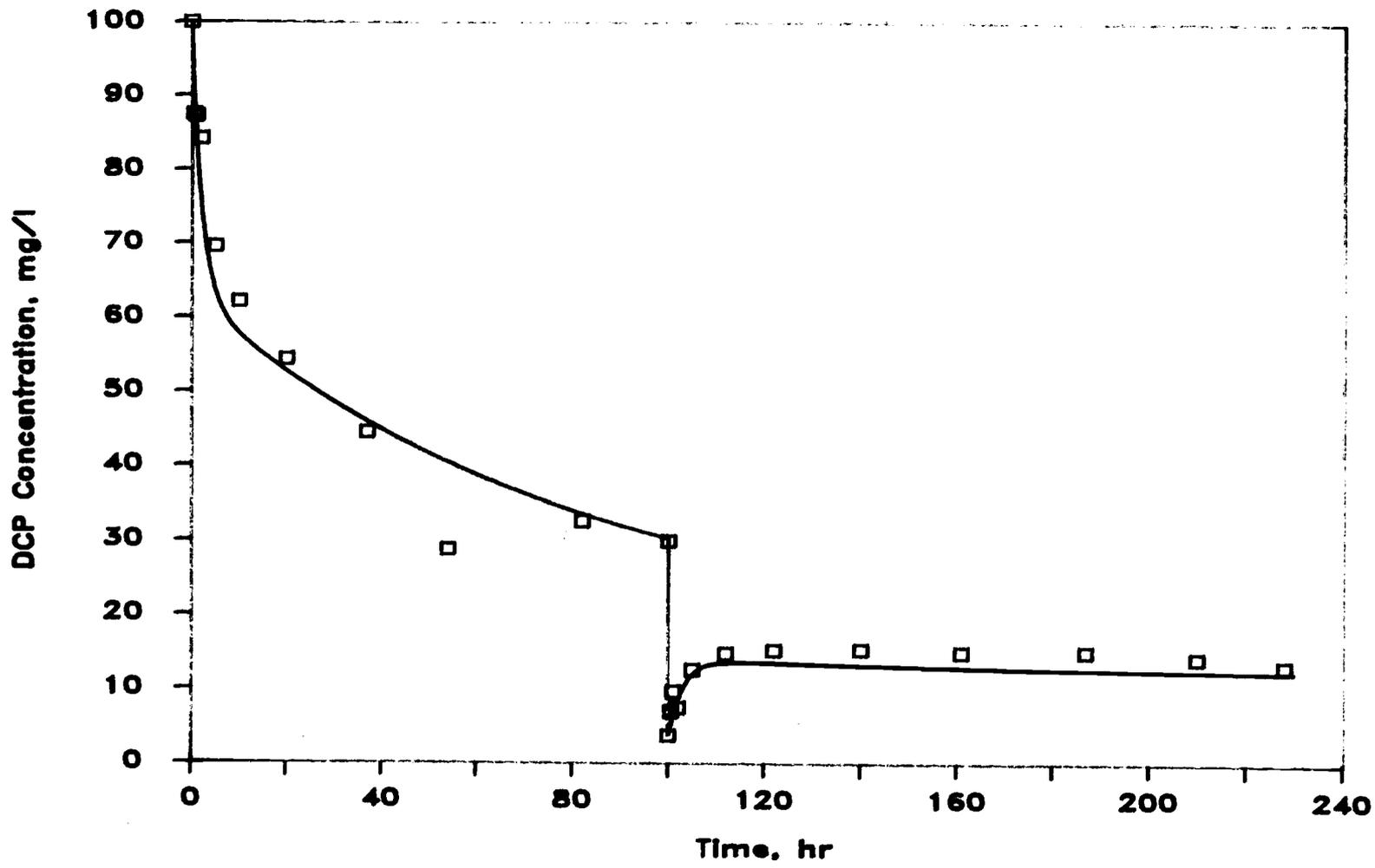


Figure 11. Batch Desorption at 100 Hours for 100 mg/l 3,4-DCP, 10 g/l Solids

of 10 and 100 mg/l were used and desorption began at times of 10 hours and 100 hours. These times were chosen so that desorption could be observed after the rapid stage of sorption and again after extended long term sorption in hopes of establishing reversibility or irreversibility to both stages of sorption.

The results of the 10 mg/l 3,4-DCP desorption experiments are presented in Figures 8 and 9 and showed actual sorption to be less than the model predicted. The general shape of the model and the experimental data agreed, but the model significantly overestimated the initial amount of desorption. This would most likely be attributed to the model overestimating the amount of solute sorbed to the particle surface and underestimating diffusion of solute to the interior. However, result from the 100 mg/l 3,4-DCP tests, presented in Figures 10 and 11, showed very good agreement between the experimental data and the model prediction. Another possibility is that some irreversibility existed in the sorption process. However, it would have to be a small to not show up in the 100 mg/l tests.

All four tests show an initial rapid desorption followed by continued slow sorption further corroborating the theory of a two stage sorption reaction. Continued manipulation of the model parameters in an attempt to further refine the values to better fit the data did not produce values that could better describe both the desorption and the sorption tests. However, this does not necessarily mean that such values do not exist, since the interplay

of the six parameters is fairly complex and the search was conducted only by manual trial and error.

Microparticle Quantification

One of the more popular theories discounting observed solids effects is the presence of a "third phase" of dissolved or non-settleable microparticles in solution. It is proposed that solute is sorbed to these microparticles, but due to sampling technique and analysis the sorbed solute is incorrectly measured as free solute. Cellulose triacetate was chosen as the sorbant for this study because of its insolubility in water, its particle stability, and its rapid settling characteristics. Microparticle concentration and sorption capacity was quantified to determine if a significant amount of sorbed third phase existed in the batch sorption tests and its effect on the sorption results.

A solution of high solids concentration, 100 g/l, was tested to determine if a breakdown of the particles occurred over the time scale of a sorption test. The solution was shaken and tested for total organic carbon content periodically over a 100 hour time period. At the end of this period, the supernatant was removed, replaced with fresh water, and the shaking and testing resumed for another 150 hours. The results of this test are shown in Figure 12.

In the first 100 hours, the suspension of microparticles rose from 0 to 160 mg/l TOC. In the later 150 hours, the change was a lesser 15 mg/l to 85 mg/l TOC. A constant or "equilibrium" TOC value

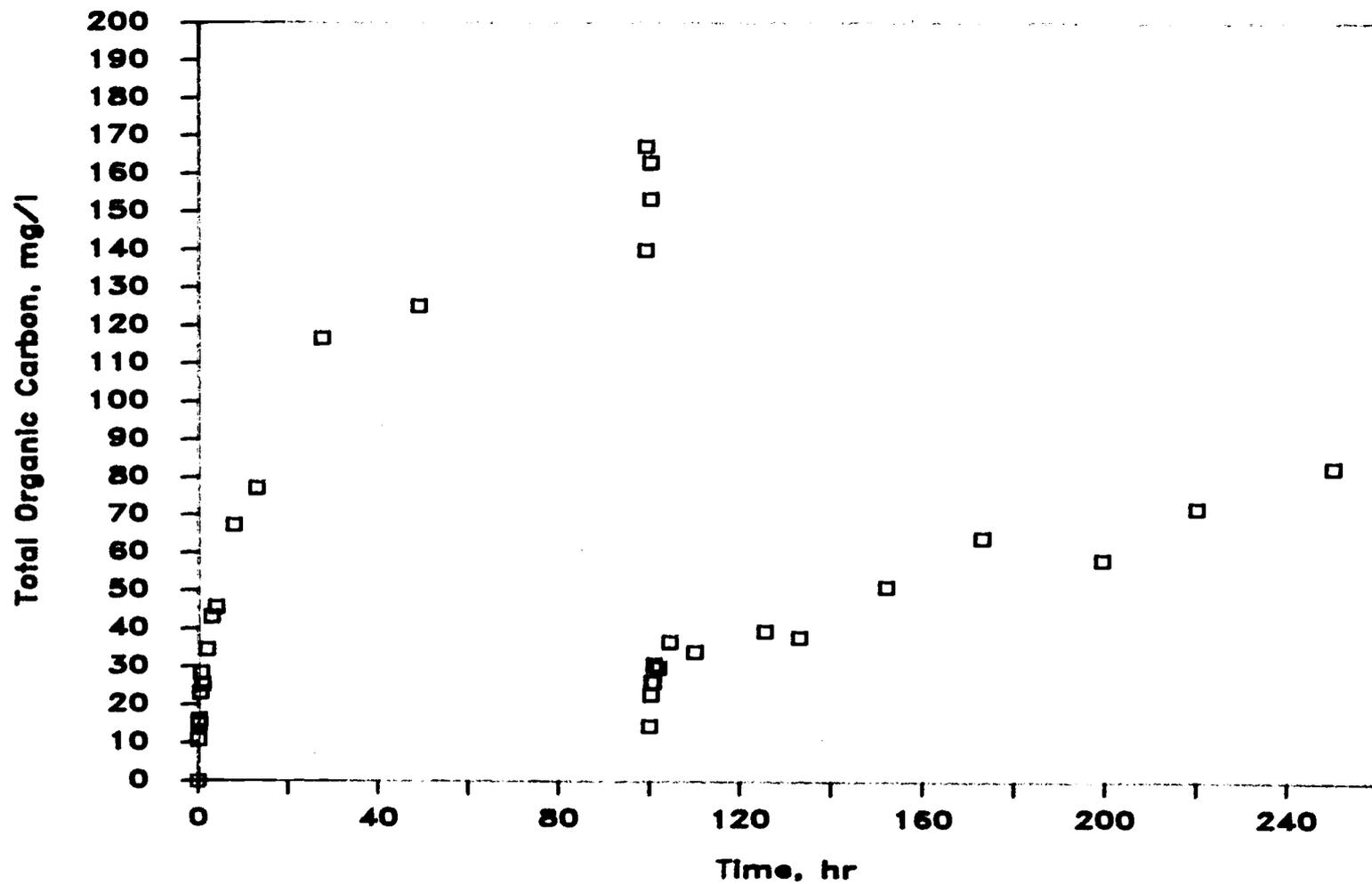


Figure 12. Microparticle Quantification for 100 g/l Solids Concentration

was not attained in either leg of the test, but the majority of microparticles appear to be produced in the first few hours. The higher TOC values in the first leg of the test could be due to fines that were not completely removed during the initial solids washing and screening. Cellulose triacetate has a plate-like, angular structure. It is possible that the first 100 hours of agitation could have rounded the particles to a point where the second test would produce less TOC. Of most importance however, is that the suspended microparticles comprised only a very small portion of the total solids in the system. At the highest point, only 340 mg/l or 0.34% of the cellulose was present as microparticles. Approximately 20% of these microparticles were found to be less than 1 μm in size and were operationally defined as dissolved organic carbon (DOC).

The supernatant from the first 100 hour TOC test was dosed with 3,4-DCP, shaken and sampled for TOC and free DCP over a 101.5 hour period. At 75 hours and again at 101.5 hours, a sample was removed, filtered and tested for DOC and free DCP. The results of this test, shown in Figure 13, indicated that 3,4-DCP was indeed sorbed to microparticles and that under the sampling conditions used in the sorption tests this sorbed fraction would be represented as free DCP. A blank sample containing 10 mg/l 3,4-DCP, but no microparticles, was filtered and analyzed to quantify sorption to the filter apparatus and is presented at 110 hours on the test scale. If approximate equilibrium is assumed at the 101.5 hour mark, the partition coefficient can be calculated to be about 0.90 l/g which

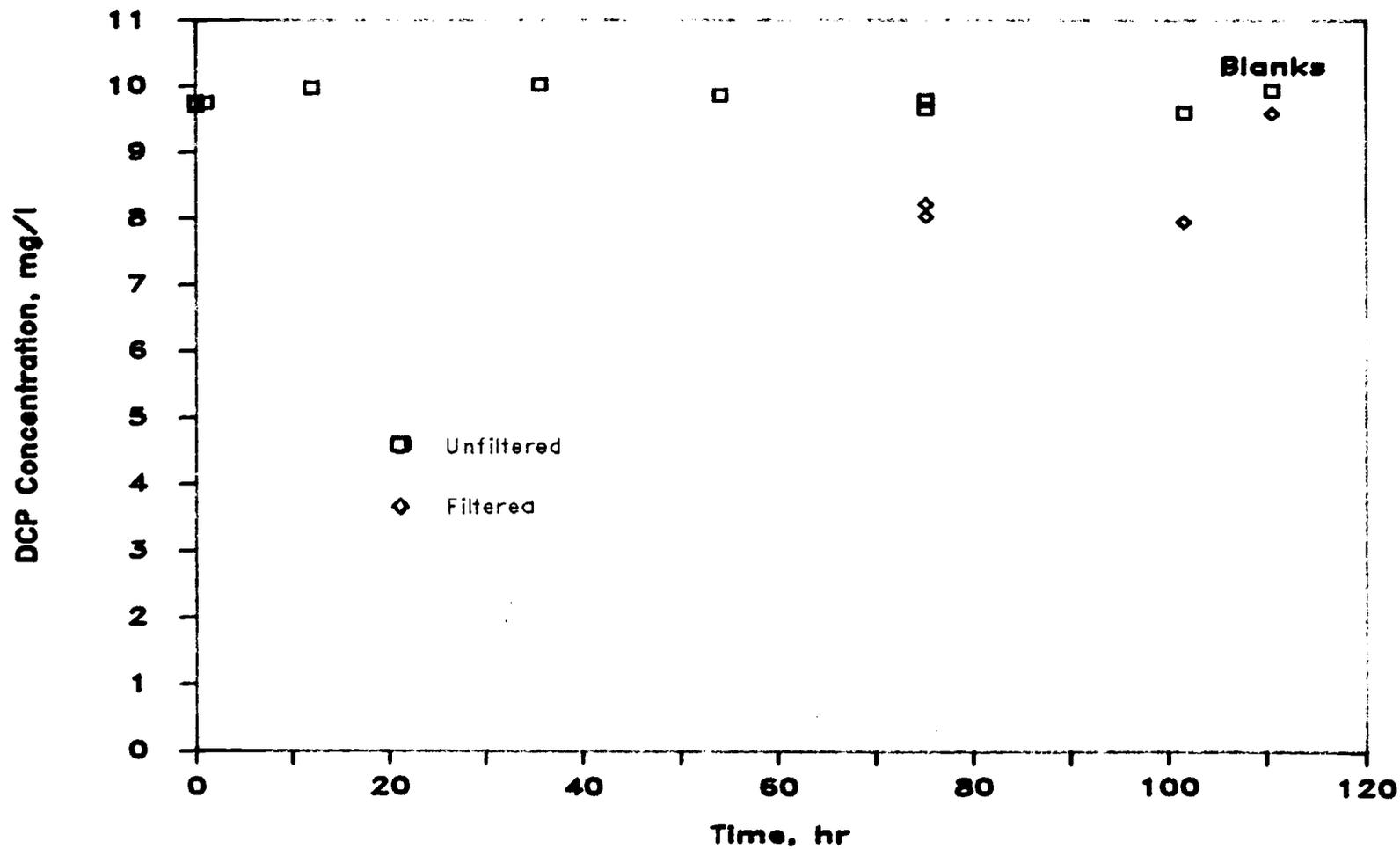


Figure 13. Microparticle Sorption Analysis for 150 mg/l Suspended TOC Concentration

is about three times larger than the values calculated for the bigger particles. Some of this difference could be due to the increased surface area per unit weight of the microparticles. There could also be the effect of faster sorption since more of the sorption sites will be on the surface and the diffusion paths to the interior sites will be shorter.

Sorption to the microparticles in the DOC size range was not quantified in this test. Dissolved organic carbon was tested at 0, 75, and 101.5 hours during the microparticles sorption test, but there was no way to differentiate between free and sorbed DOC. Since the amount of DOC was small and the partition coefficient did not change radically for the large particles to the microparticles, it is reasonable to assume that sorption to DOC is small and probably negligible.

DISCUSSION

The results of the batch sorption experiments confirmed the general nature of hydrophobic organic solute sorption to an organic sorbent as being a two stage process. An initial stage of rapid uptake was followed by an apparently long term stage of slower sorption. Conceptually, this seemed to represent an initial equilibrium being established between the bulk liquid concentration of solute and the solute sorbed to the solid surface followed by a long term step of intraparticle solute diffusion.

It is the second step of the sorption reaction which is the most difficult to model. An accurate knowledge of the reaction mechanisms involved is required to develop a reliable predictive model. However, the ability of a model to adequately fit a series of experimental data does not provide absolute verification of the mechanisms assumed in the model. This is especially true when there are a large number of fitting parameters within the model and when the range of experimental conditions is limited.

The model fit the experimental data fairly well in both the sorption and desorption tests for 3,4-DCP concentrations of 100 mg/l and less. The greatest deviations were observed in the desorption cycle of the tests conducted with an initial 3,4-DCP concentration of 10 mg/l. The general shape of the curve was accurate, but the predicted desorption was substantially greater than that observed. It was difficult to assess whether the discrepancy was due to a

fault with the model or to the possibility of some irreversible sorption. The same discrepancy did not appear in the desorption results for the tests conducted at initial 3,4-DCP concentration of 100 mg/l. This would seem to indicate that if irreversible sorption was indeed involved, its ultimate capacity is quite low. It is interesting to note that a period of rapid desorption was followed by a longer period of gradual continued sorption. This adds further credence to the assumption of a rapid equilibrium between the bulk liquid and the solid surface and a retarded equilibrium between either the bulk liquid or the particle surface and the particle interior.

The model severely underestimated the amount of sorption in the tests using an initial 3,4-DCP concentration of 1000 mg/l. One possible explanation for this could be multilayer sorption on the surface of the cellulose triacetate. Formation of a froth at the liquid-air interface and air bubbles clinging to the surface of the cellulose triacetate were observed at this 3,4-DCP concentration but not at the lower test concentrations. The solubility of cellulose triacetates in chlorinated hydrocarbons is well established and perhaps becomes a significant factor at these higher solute concentrations (20,21). High local concentrations of 3,4-DCP at the solid surface could have induced multilayer sorption that does not occur at lower 3,4-DCP concentrations. This type of sorption is often described by a B.E.T. isotherm. Values taken from the model fit of experimental data at time equal to 140 hours, using actual data for

the 1000 mg/l 3,4-DCP tests, showed a feasibly linear isotherm. However, not enough information was gathered to develop a completely reliable isotherm since only three initial solute concentrations were used and true equilibrium was not established by the end of the tests.

The time scale of sorption kinetics was important in the evaluation of experimental data and the application of those results to field situations. Although the second stage of sorption occurs at a slower rate, the ultimate intraparticle sorptive capacity can be very high. The time interval between samples and the accuracy of sample analysis were very important in determining the extent of reaction. If data was collected quite frequently, a leveling off effect would appear as soon as the first stage sorption equilibrium was established. To detect further removal, sampling would have to be retarded to the point where sorption in the time scale between samples is greater than the combined sampling and analytical errors. The problem increased the closer the reaction came to equilibrium and the more the sorption rate was reduced. The sorption time scale evidenced in this experiment should not be considered predictive of the time scale of hydrophobic organic sorption to natural soils and sediments. However, the general shape and proportion of the sorption curves developed in this study should be very applicable to natural sorption systems, especially those where sorption is correlated to soil organic carbon content.

Since equilibrium was not achieved during these tests, it

cannot be stated with complete certainty that a solids effect did not occur. However, the indication from both the experimental data and the descriptive model is that while a solids effect phenomena was observed in the initial stages of sorption, it gradually disappeared as the first stage of sorption was completed. Since both steps in the model sorption reaction are essentially Langmuirian, there is no possibility of achieving an equilibrium solids effect that exhibits a negative slope using this model. The equilibrium partition coefficient can be expressed as:

$$K_p = (k_1/k_2) * S_s * (1 + k_3/k_4 * S_i)$$

Both S_s and S_i will increase or remain approximately constant, depending on what portion of the isotherm is applicable, as solids concentration increases.

Model prediction of a time related solids effect shown in Figures 6 and 7 was based on the kinetics of reaction, not particle interaction, and is in itself not evidence of an actual phenomenon. Data gathered in the initial sorption stage was most susceptible to error in both sampling and GC analysis. Sorption in this stage was fairly rapid and therefore the possibility of local variations in the bulk liquid was greater. Analysis by gas chromatography yielded results that were accurate to approximately $\pm 5\%$ of the peak area. This resulted in larger magnitude deviations at higher liquid concentration such as occur in the initial stages of the tests. The experimental data suggested a possible phenomena, but would have to

be classified as inconclusive due to the inconsistency of the observed effect in the 10 and 1000 mg/l 3,4-DCP tests.

The competition between interior and exterior sorption can be seen in Figure 14 which shows the liquid, exterior, and interior 3,4-DCP concentrations with time as predicted by the model. If this model is an accurate portrayal of a sorption reaction, it can be seen that the possibility for a significant particle interaction effect occurs early in the reaction when more solute is sorbed to the exterior of the particle than to the interior. As partitioning to the interior of the particles becomes the dominant reaction, the effect of exterior destabilization is reduced.

Results of the microparticle quantification experiment indicated that little third phase sorption would be expected at the low solids concentrations used in the sorption tests. Observation of the test showed that the solution became noticeably cloudy at TOC levels of approximately 20 mg/l. This corresponded to a cellulose triacetate concentration of approximately 40 mg/l. Using a K_p of 0.90 l/g as calculated from the microparticle sorption experiment, only 3.5% removal of 3,4-DCP would be expected from a solution containing a microparticle concentration of 40 mg/l and less than 1% removal at a concentration of 10 mg/l. The solutions with sorbent concentrations of 10 g/l or less produced no visible signs of microparticles and were expected to be well below 20 mg/l TOC and, consequently, well below the 3% removal mark. Since the GC analysis

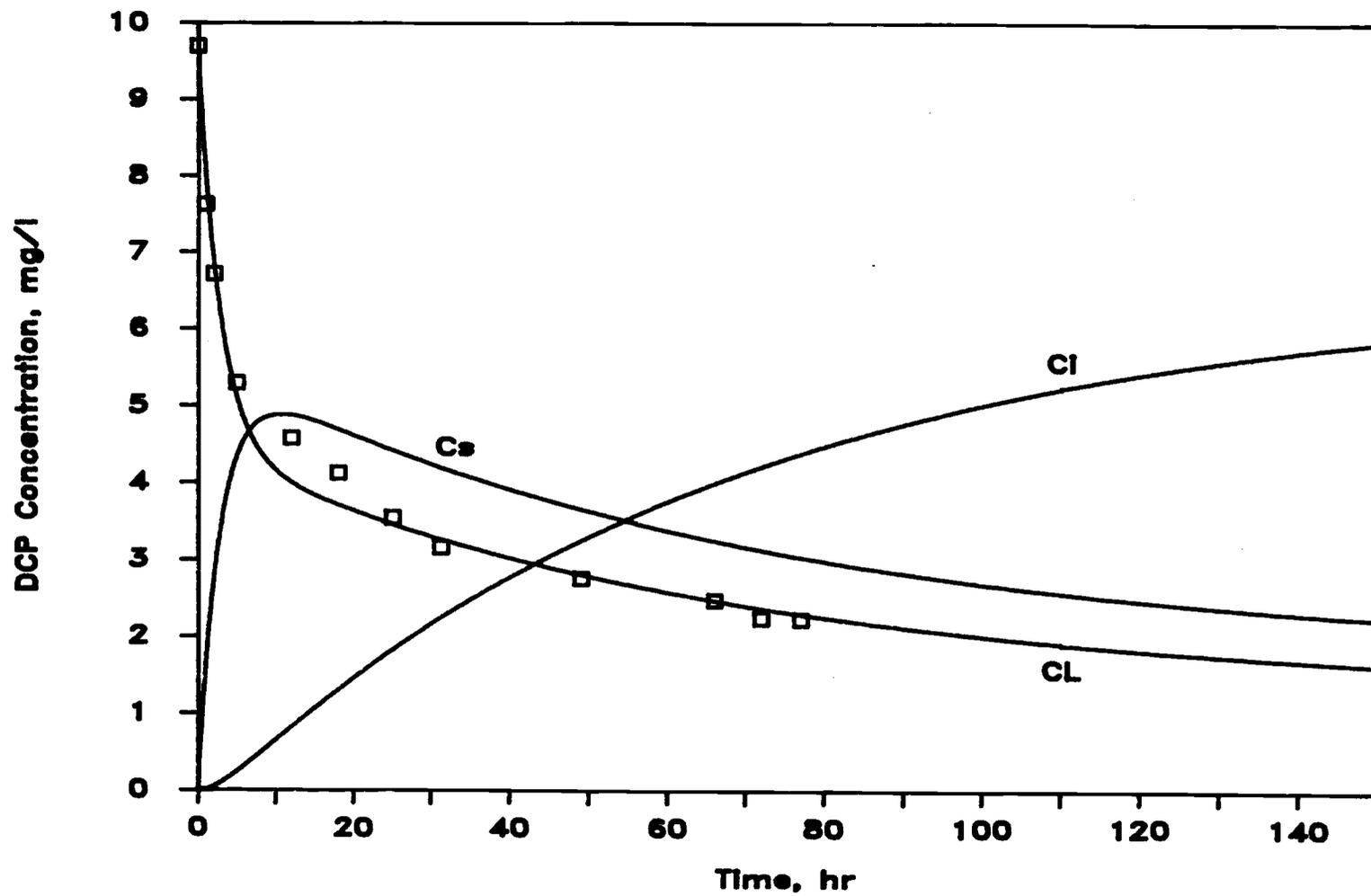


Figure 14. Model Prediction of Solute Distribution at 10 g/l Solids Concentration, 10 mg/l 3,4-DCP

accuracy is $\pm 5\%$, any third phase effect would be virtually undetectable. The lack of a substantial third phase adds little to the discussion since no solids effect was observed.

SUMMARY AND CONCLUSIONS

This study shows the sorption of a hydrophobic organic solute to an organic sorbent to be a two step process. Sorption is characterized by an initial rapid uptake followed by an extended period of slow sorption. The initial step appears to be a fairly rapid equilibrium between the solute in the bulk liquid and that sorbed to the exterior of the sorbent particles. The slower second step follows the pattern of intraparticle diffusion either from the bulk liquid or from the particle surface. A model is proposed that fits the experimental data for 3,4-DCP concentrations up to 100 mg/l using one set of values for the model parameters. The model is unable to fit the data from tests using 3,4-DCP concentrations of 1000 mg/l with the same parameter values.

Although the model does an adequate job of fitting the data, its accessibility is low. It is a nonlinear model with six parameters that are not easily related to measurable physical characteristics of the solute/sorbent system. The sorption rates observed in these experiments indicate the need for an accessible kinetic model for sorption that can be applied in solute transport models. Equilibrium is not attained in any of the tests due to the long term slow sorption into the cellulose triacetate polymer. Although the rate of long term sorption is slow, the high ultimate intraparticle sorption capacity seriously challenges the validity of using local equilibrium assumptions when modeling the transport of

hydrophobic organic compounds in soils.

Since equilibrium is not attained in the time scale of these experiments, it cannot be stated conclusively that sorbent concentration had no effect on the equilibrium partition coefficient, K_p . However, if an apparent partition coefficient, K_{ap} , is defined as the ratio of the amount of solute sorbed per unit mass of sorbent divided by the concentration of solute in solution at time, t , a time dependent solids effect can be observed. Both the experimental data and the predictive model suggest an inverse dependency of K_{ap} on the sorbent concentration that is greatest as sorption begins and completely disappears in about 6 hours. However, the inconsistency of the effect in the observed data combined with the inability for a time dependent effect to explain solids effects observed at equilibrium in other research suggests caution in accepting these apparent phenomena.

Tests results did confirm that 3,4-DCP sorbed to microparticles suspended in solution are mistakenly quantified as free 3,4-DCP under the sampling and analysis procedures used. Sorption to microparticles was quantified and considered negligible at the levels found in this study. Since no equilibrium solids effect was observed, no relationship between a solids effect and the presence or lack of a third phase could be established.

SIGNIFICANCE AND RECOMMENDATIONS FOR FUTURE STUDY

The kinetic approach to the study of sorption phenomena has been shown in this and other studies to be an important and valuable tool. Weaknesses of this study have been the failure to test to equilibrium and perhaps the use of a specific solute/sorbent system without analog in natural sorption situations. Future studies would be most applicable if they focused on the development of a kinetic sorption model with high accessibility using model parameters that have specific physical significance. One such modeling approach currently being developed by Gschwend and Wu is an intraparticle diffusion model (8). If the calculation for the flux of solute across a theoretical boundary could be simplified, the diffusion approach appears to have much promise.

There is also a need for extensive kinetic studies using both batch and transient or continuous flow conditions to evaluate the nature of hydrophobic organic solute transport and sorption in subsurface environments. The results from this study indicate that the nature of organic solute sorption into organic sorbents invalidates the use of local equilibrium assumptions in solute transport models unless the flow is very slow. More work needs to be done to quantify the error involved by neglecting the kinetics of sorption and the impact that has on groundwater risk assessments.

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