BIODEGRADATION OF ALKYL BENZENE SULFONATE IN A VENTED SAND FILTER

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SUMMARY AND CONCLUSIONS

This project has been undertaken to study the efficiency in removing organic matter and synthetic detergents such as alkyl benzene sulfonate#, by means of sand filters, which would be normally encountered in sewage. The bulk of the organic matter usually encountered in sewage is readily biochemically oxidized. The ABS is not readily oxidized biologically due to its branch chain structure. Most organic matter is most effectively attacked by aerobic microorganisms and there are also indications from previous work (5) that an aerobic environment would be most conducive to the degradation of ABS.

In a properly constructed sand filter system there is high removal of the biochmical oxygen demand, generally above 90 per cent. This is achieved by the reduction of organic matter to CO_2 and H_2O by aerobic bacteria. The oxygen required to support this aerobic population is introduced through the surface of the sand filter and can penetrate only a certain distance, approximately 12 inches, regardless of the depth of the sand bed. This penetration controls the effective depth of the filter in a conventional system. However, Article 11 of the Massachusetts Sanitary Code (7) specifies a thickness that is two or three times the effective thickness. If the lower section of the sand bed were aerated by vents there would be a possibility that more of the sand bed would be utilized and that the increased contact time with the aerobic microorganisms may facilitate the breakdown of ABS.

This aeration of the lower section of the sand bed was attempted by installing a one half inch I.D. tube in a filter of 6" diameter. This tube was inserted in the subdrain and extended to the surface of

hereafter referred to as ABS

the filter. The sewage was applied at 2 gal/day/sq. ft. which is the maximum rate recommended by the Massachusetts State Department of Public Health.

Comparing the results obtained by vented and unvented sand filters using sand of effective sizes varing from 0.4 to 0.8 mm. the following conclusions were drawn:

1. The sand filters (vented and unvented) showed no degradation of ABS.
2. The filters adsorbed ABS. The adsorption capacity of a sand filter decreased with an increase of its effective sand size.
3. The adsorption of ABS ceased as the adsorption capacity of the sand filter was reached.
4. The vented filter packed with sand of 0.4 mm. effective size showed a small but significant increase in BOD removal.
5. The BOD removal decreased with an increase in the effective sand size.

It seems from these conclusions that sand filters are not effective in eliminating ABS. On the other hand, sand filters, if adequately vented, may have an improved efficiency in BOD removal.

INTRODUCTION

Synthetic detergents have been in use in this country since shortly before 1940. This broad class of washing products has rapidly gained popularity because they are able to maintain their efficiency in hard water. Today these synthetic detergents comprise 90 per cent of all household products marketed by the soap and detergent industry. Alkyl benzene sulfonates probably account for 70 per cent of the detergent volume likely to be disposed of in waste water. Detergents in waste water become problematic because the breakdown of these compounds is slower and less complete than for other organic wastes under the same conditions. Elimination of these surface active agents in waste water is much dependent upon the extent of treatment and exposure time to a mixed microbiological population.

For the most part of the concern for degradability of ABS has been aimed at avoiding the formation of foam, and the presence of off-taste (1). In studies made on the physical effects of ABS it was found that an off-taste was first noticed at 1.0 mg/liter. Frothing occured most frequently at concentrations of 1.0 mg/liter or higher. From the toxiological point of view an extremely high concentration of the surfactant is necessary to produce adverse effects. This concentration is in the vicinity of 10,000 mg/liter. It can be seen then that the criteria for contamination is the presence of off-taste and frothing (1). In any discussion of surfactants it will be noted that considerably more attention is given to alkyl benzene sulfonates than to other surfactants. Not only does this reflect the volume of ABS used but it also results from the fact that it is relatively easy to analyze for ABS. For non-ionic surfactants no simple, precise method has been found to determine the amounts present in sewage or raw water at low

concentrations. Since the amount of ABS can be determined and the bulk of detergents used are of this type, then for all practical purposes, the ABS content may represent the total detergent concentration in waste water.

It is primarily in areas utilizing subsurface sewage disposal and a well water supply located in a stratum nearby the disposal facility that ABS becomes a nuisance in drinking water. The surfactant passes, unaltered, through the septic tank and leaching field and seeps into the groundwater supply. There is nothing in the groundwater capable of achieving its biodegradation (6) and the ABS moves with the groundwater to the point where it is drawn up through the wells with the drinking water.

LITERATURE REVIEW

The biochemical breakdown of ABS has been extensively investigated by other researchers. Swisher (10) conducted experiments on the ability of a mixed microbiological population to break down (a) straight chain alkyl benzenes having the phenyl linked to the C_{12} chain at the 1, 2, 4, 5, and 6 positions, (b) branch chain alkyl benzenes with combinations of methyl group positions and phenyl positions. As a result of his studies he concluded that the rate of degredation of the straight chain compounds was increased as the distance between the sulfonate and the end of the chain was increased. This observation also held true in the branched chain alkyl benzenes. In addition it was reported by Swisher that the presence of a terminal quaternary group without an open end chain causes a pronounced retardation, if not a complete stoppage of the degradation.

Robeck et al (7) conducted similar experiments. Lysimeters packed with sand of effective size 0.11 to 0.28 mm were used as filter beds. With a loading of two gal/day/sq.ft. they managed to remove 90 percent to 96 per cent of the ABS which was applied. It was surmised that the biodegradation of ABS took place in the upper three inches of these lysimeters where the bacterial population was concentrated. Robeck et al attributed the fact that the microorganisms were confined to the top by a lack of both nutrients and oxygen in the lower section of the bed, while in the vented filters of this experiment it is surmised that only the lack of nutrients kept the microbiological population from extending through the entire depth of the bed. The BOD removal in both the lysimeters and the filters of this experiment is high.

THEORETICAL BACKGROUND

Biodegradation of Surfactants

The ease or difficulty of the biodegradation of surfactants is difficult to attribute to one general cause. One factor which effects the rate of biodegradation is the initial concentration of a surfactant. Also the biochemical behavior of surfactants varies a great deal depending upon the chemical structure of the surfactant in question. The chemical makeup of a surfactant varies diversly within the general structural catagories of the products commonly in use.

Surfactants may be divided into three basic types: anionic, non-ionic, and cationic. The cationic syndets are salts of quarternary ammonium hydroxide, with all the hydrogen ions of the ammonium having been replaced by alkyl groups. These detergents are noted for their bactericidal properties and will act as inhibitors to a certain segment of the microbiological population in a treatment system. The non-ionic detergents do not ionize and have to depend upon groups within the molecule to obtain their water soluble properties.

$$HO\ (C_2H_4O)_x\ H$$

solubility producing group

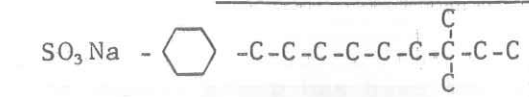
The non-ionics utilize polymers of ethelyene oxide to achieve this property. The syndets prepared from polymers of ethelyene oxide are highly resistant to biological attack presumably because of the ether bonds they contain.

The anionic syndets, of which alkyl benzene sulfonates are the most common, are sodium salts which ionize to yield sodium and a negatively charged surface-active ion. These anionic surfactants can generally be broken down into two catagories, the sulfates and the sulfonates.

The sulfates are inorganic esters with surface active properties produced from long chain alcohols and sulfuric acid. These sulphated alcohols are readily assimilated by bacteria and present no problem to biodegradation.

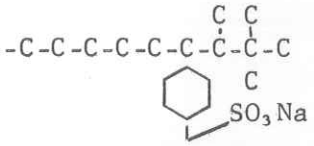
The important sulfonates are derived from esters, amides and alkyl benzenes. The esters and amides are of organic acids and the alkyl benzenes are derived largely from polymers of propylene. When the degradability of this group is examined, it observed that those formed with ester or amide linkages are readily hyrolyzed. The fatty acids produced are suitable for bacterial assimilation. However, the alkyl benzene sulfonates present a problem. In the polypropylene derivatives a branched chain alkyl group apparently blocks degradation completely (9). This, however, must be qualified. The presence of a branch chain is, in its self, not sufficient to retard degradation. The alkyl group must be positioned in such a way that it constitutes a terminal quarternary group and there must be no open end to the chain. In straight chain ABS compounds the biodegradation is hindered by decreasing the distance between the sulfonate group and the most remote end of the alkyl chain. On the following page are some graphic formulas of ABS molecules and their relative degradabilities.

Branched chain compounds of ABS



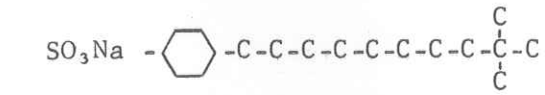
Degradable

The right end of the chain is open and susceptible to enzyme attack.



Degradable

The left end of the chain is open to attack. The right end is blocked by a terminal quaternary group. The biodegradation is hindered slightly by decreasing the distance between the sulfonate group and the open end of the chain.

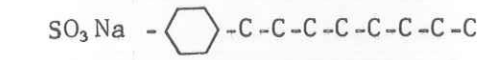


Not degradable

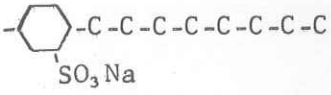
The right end is blocked by a terminal quaternary group and the left end is blocked by the phenyl group.

Straight chain compounds of ABS

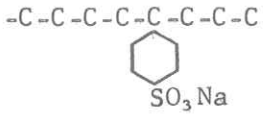
arranged in descending order of degradability.



The sulfonate in para placement with the chain and the phenyl group terminating the chain gives the greatest possible distance between the remote end of the alkyl group and the sulfonate group.



The sulfonate is in ortho placement with the alkyl chain. This lessens the distance between the remote end of the chain and the sulfonate group. This retards degradation somewhat.



The phenyl group has been moved from the extremity of the alkyl group to the center of the chain. This further decreases the distance between the sulfonate and the remote end of the chain.

EXPERIMENTAL PROCEDURE

Apparatus

The basic apparatus shown in Figure I used to conduct this investigation was six sand filters constructed of lucite cylinders. These cylinders were six inches in diameter and sixty inches high. A six inch layer of graded gravel served as underdrain, which was overlaid by a bed of sand four feet deep. The top of the sand was covered by a six inch layer of coarse gravel which acted as a distribution system to spread the influent over the surface of the sand bed. Three of the six filters were vented by inserting a one half inch vent pipe from above the surface of the filter into the subdrain system. Each filter that was vented had a corresponding filter of the same size but without a vent.

Filter Media

The material used in the filters was all obtained originally from a supply of clean sand with an effective size of 0.4 mm and a uniformity coefficient of 2.7. This sand was used, unaltered, for the first and second filter units. For the third and fourth filter units the fine fraction of the sand was removed from the original supply so that the effective size for these two units was 0.6 mm and the uniformity coefficient was 1.6. In a similar manner, sand of effective size 0.8 mm and a uniformity coefficient of 1.5 was obtained for the last two filters. The distribution of grain size and the physical and chemical characteristics of the test are shown in Figure 2 and Table I.

Filter Influent

The feed material for the filter was the unchlorinated effluent from the primary sewage treatment plant in Amherst, Massachusetts.

FIGURE I

Typical Filter Bed

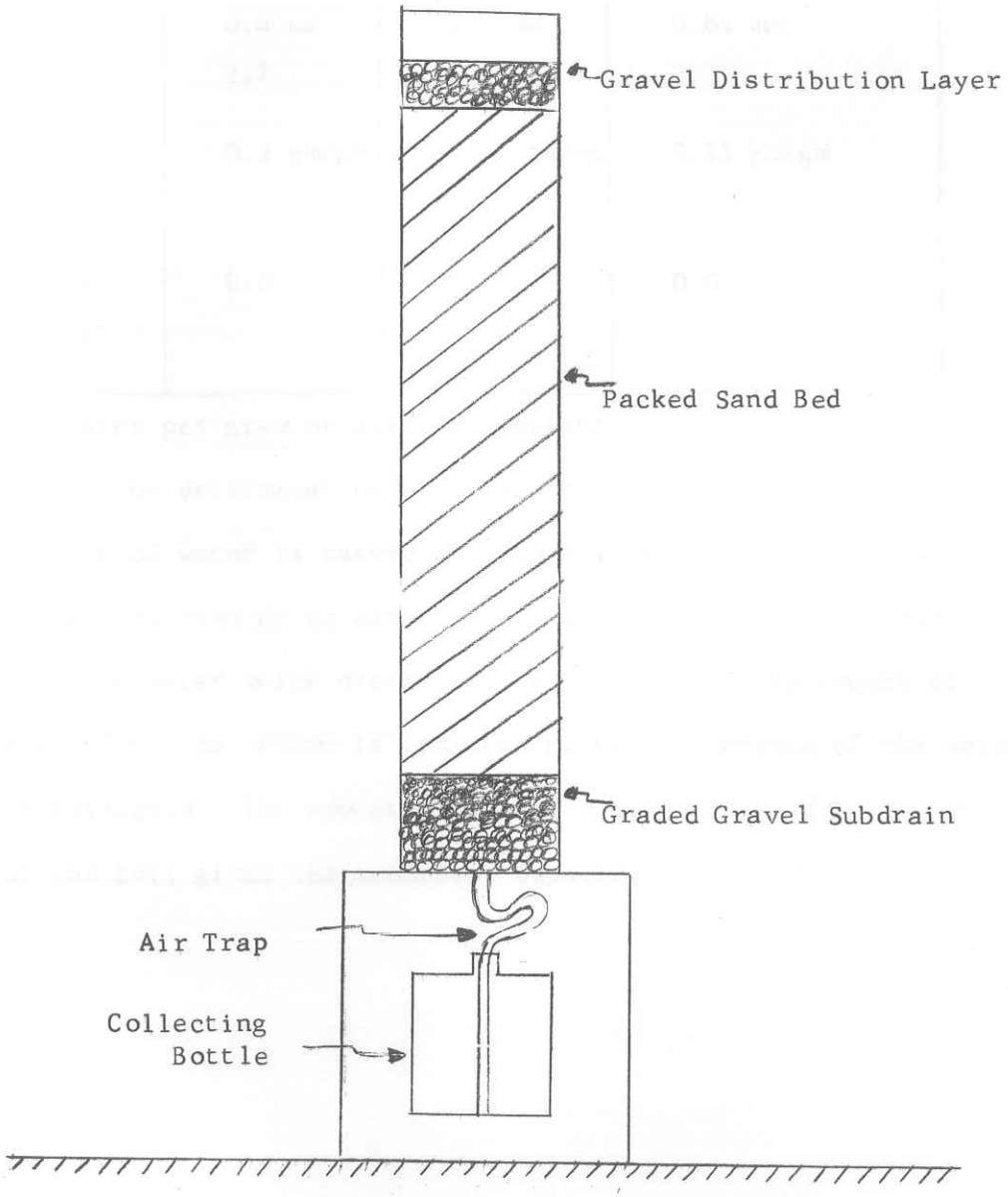


Table I

PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE TEST SAND

Characteristics	Filter 1 & 2	Filter 3 & 4	Filter 5 & 6
Effective size	0.4 mm	0.6 mm	0.84 mm
Uniformity Coef.	2.7	1.6	2.5
Adsorbent Capacity #	0.2 gm/gm	0.17 gm/mg	0.13 gm/gm
Silicone as Si O^2			
Acid Solubility	0.0	0.0	0.0
Organic Matter			

Grams of water per gram of soil, dry weight

Procedure for the determination of adsorbent capacity is as follows: A known volume of water is passed through a glass column packed with a known weight of oven dried sand. The column is allowed to drain by gravity and the water which drains out is collected. The amount of water retained in the column is computed by the difference of the water added and collected. The amount of retained water divided by the dry weight of the soil gives the adsorbent capacity.

This plant treats primarily domestic sewage with no industrial waste. The characteristics of its effluent during the time of the experiment are listed in Table II. (page 21)

One of the primary purposes of this project was to ascertain whether ABS could be degraded in a vented sand filter more efficiently than in an unvented sand filter. The effluent from the Amherst sewage treatment plant which contained a concentration of ABS varying from four to ten ppm was used without any supplementary ABS during the experiment. A concentration ranging from four to ten ppm is lower than would be expected for domestic sewage. However since the higher concentrations of ABS would be even more difficult to degrade (9), (10) it was decided to conduct the experiment within this range of ABS concentration.

Feeding Procedure

For the entire experiment the filter was dosed with a loading equivalent to two gal/day/sq. ft. This amounted to 1.7 liters applied once a day. The feeding was steadily applied over a fifteen minute period onto the surface of the filter. The effluent of the filter was collected at the bottom of the cylinder in such a way that the air would not be allowed to move up the discharge tube and provide venting. This was done by having a "U" shaped tube at the bottom which acted as a trap and prevented the air from flowing back up through the sand bed.

Sampling and Testing

An attempt was made to draw samples out through aeration stones which had been inserted in the filter at various depths. This procedure was abandoned because it had significant effect on the aeration of the beds and it drew off some of the pellicular water in which the microbiological population should have developed.

The ABS content of the influent and effluent of the filters was determined by the methylene blue method. Besides the BOD, turbidity, settleable solids, total solids and nitrogen content of the samples were analyzed during the experiment. The results are shown in Table I.

In order to determine how effective the vent was in introducing air into the subdrain system and the lower part of the filter, an impermeable clay layer was placed on the top of two of the filters. One of the covered filters was vented and one was unvented. The D.O. of the effluents was recorded for several weeks. The results thus obtained, shown in Table III indicated that the oxygen being introduced into the bed through the vent was slightly less than fifty per cent of the oxygen which was apparently supplied to the filter through the gravel surface of the filter unit. In the covered, unvented filter there was a gradual decrease in the oxygen content of the effluent as the available oxygen in the air spaces of the unsaturated sand was diminished. The method by which air was taken into the vented filter became quite obvious when the impervious cover was used. The filter "breathed" air out through the vent when the loading was applied and "inhaled" as the effluent discharged from the filter. The air was forced out of the filter as the influent was filling the soil interstices. Since the impermeable cover prevented the escape of any air through the surface of the bed, the air being discharged through the vent was more noticeable. In the same way air was drawn into the vent by a partial vacuum caused by the effluent leaving the filter.

Several modifications of the Standard Methods procedure for the methlyene blue determination of ABS were made to adapt the test for sewage samples with high suspended solids and a variable concentration of ABS. The suspended solids caused difficulty in the ABS determination by

VENTING EFFECTS ON COVERED
AND UNCOVERED FILTERS

DISSOLVED OXYGEN IN FILTER EFFLUENT PPM.

TABLE III

vented covered filter 0.8 mm effective size	unvented uncovered filter 0.8 mm effective size
2.1 ppm	3.7 ppm
2.1	4.1
2.0	4.2
1.9	4.0
2.2	4.6
1.6	4.3
1.9	3.9
2.2	4.5
2.0	3.9

unvented covered filter 0.4 mm effective size	vented uncovered filter 0.4 mm effective size
2.0	3.3
1.8	3.7
2.3	4.0
1.5	3.5
1.3	3.6
1.4	3.2
1.0	3.8
0.5	3.5
0.1	3.5
0.6	3.7

the formation of an emulsion of water in the chloroform which resulted in incomplete separation of the water. This problem was resolved by passing the chloroform extract through a packed column of anhydrous sodium sulphate, which effectively removed the water and the suspended particles, and enabled the spectrophotometric measurements to be carried out without interference.

There occasionally arose the problem that the chloroform solution contained too much methylene blue complex and the transmittance would fall below 20 per cent. Since the transmittance error becomes very large in this region dilutions were made with chloroform to bring the reading up into the range where the error is less. The results of the modified procedure showed the same experimental accuracy as the Standard Methods procedure of taking a smaller sample and repeating the test. This modification saved a considerable amount of time.

When the apparent ABS concentration, as determined by the methylene blue test is compared with the true ABS as determined by the infra-red method the apparent concentration is invariably one third higher than the actual concentration (7). All values of ABS presented in this paper are apparent concentrations.

Bacterial Analyses

Bacterial analyses were made on the influent and effluent and also of the sand at different levels of the filter bed. The total count was made on Triptone Glucose Extract agar at 20° C. The coliform count was made by the millipore filter method using MF Endo broth with an eighteen hour incubation period at 37° C. To analyze the sand samples a core of the filter material was taken, a portion of which was weighed and then was washed with sterilized water. The bacterial

population of the wash water was analyzed. There was some difficulty in obtaining sand from different depths because the distrubance of the filter bed during sampling tended to free some of the adsorbed water which flowed into a lower section of the bed and undoubtably carried microorganisms with it. There was no way to prevent this occurance so it must be noted that the bacterial population in the bottom portion of the bed might have been lower than the data had indicated.

BACTERIAL ANALYSIS RESULTS

Filter 1 vented

Colonies per gram of test sand

surface of bed	65×10^6
two foot level	21×10^4
four foot level	30×10^4
effluent	18×10^4

coliform per gram

Millipore filter m. Endo broth

Influent	4×10^6
Effluent	95

Filter 2 Unvented

Colonies per gram of test sand

surface of bed	92×10^6
two foot level	41×10^5
four foot level	15×10^5

RESULTS AND DISCUSSION

1. The data from this experiment, as shown in Figures 3, 4, 5, 6, 7, 8, and 9, gives the indication that venting the lower portion of the filter bed would not produce an appreciable increase in the removal of the ABS group of detergents. Both the unvented and the vented filters appear to be removing the ABS at the beginning of the experiment. The degree of removal seemed to be dependent upon the grain size of the filter media and was indifferent to whether the filter was vented or not. After thirty five days of operation the removal of ABS decreased sharply in all filters but most noticeably in those with the larger grain sizes. The fact that the filter was vented made no difference in the removal. The decrease in removal rapidly reached a point where the concentration of ABS in the filter effluent was much higher than that in the filter influent. All this made it apparent that the earlier removal of the ABS was due to adsorption and not to biodegradation. To confirm this fact two of the filters were fed with distilled water instead of sewage for several days. The ABS content of the influent was zero but the concentration of the surfactant in the effluent was consistently between three and four parts per million. This gave indication to the fact that the filter had reached its adsorptive capacity and the ABS was breaking through. On the other hand the BOD removal during the thirty five days of experimentation remained at 90 per cent or higher. Therefore it was apparent that a microbiological population had developed and was consistently active throughout the duration, and the microbiological activities were not able to breakdown the ABS.

2. The next logical step is to question why the microbiological population of the vented filter did not extend throughout the entire depth of the bed. It was determined that the vent in the filter did introduce ample air into the bed to prevent anaerobic conditions from occuring. In the analysis of this question it would be helpful to look at the distribution of the bacteria in the filter. The density of the bacteria drops off sharply as the distance from the surface of the filter increases. In a vented filter the distribution was 65×10^6 at the surface 21×10^4 at the two foot level from the surface, 30×10^4 at the top of the underdrain and 18×10^4 in the effluent. This seems to suggest that although there was sufficient oxygen in the lower portion of the bed not enough degradable organic matter was getting by the top third of the filter to support a large microbiological population. This seems to be a reasonable assumption since the BOD removal is high and the density of the microorganisms drops off sharply in the lower two thirds of the bed.

For further research on this project it would be interesting to determine whether this line of reasoning does explain the failure of the filter to remove ABS. This might be done by loading the vented filter bed from two levels and using the finer sand sizes such as 0.2 mm, 0.4mm and 0.6 mm. If sixty per cent of the total load was introduced at the surface and forty per cent was introduced at the two foot level it is possible that this might develop a large microbiological population throughout the entire depth of the filter. This, in turn, might provide the biodegradation of a portion of the ABS introduced into the bed.

TABLE II

CHEMICAL CHARACTERISTICS OF THE FILTER INFLUENT AND EFFLUENT

Determination	Influent	Effluent
total solids	159 ppm	37 ppm
pH	7.0	6.0 - 6.7
suspended solids	122 ppm	13 ppm
settlable solids	0	0
B.O.D.	200 - 350 ppm	5 - 40 ppm
D.O.	0.0	2.2 - 4.1 pp,
Nitrogen		
organic	23 ppm	0.0
ammonia	13 ppm	9.0 ppm
A.B.S.	2.3 - 8.7 ppm	0.5 - 11.7 # ppm

this high value occured at breakthough

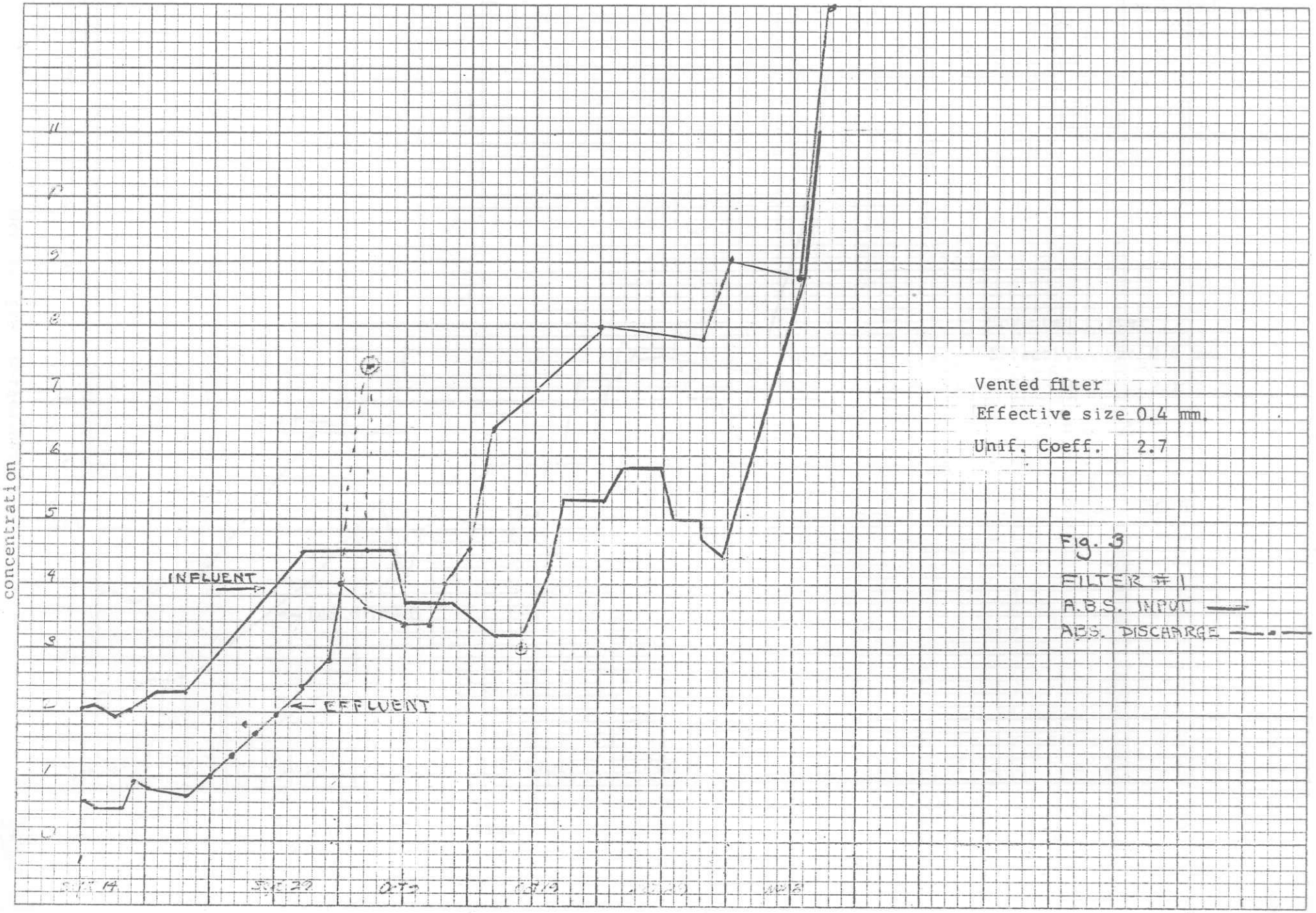
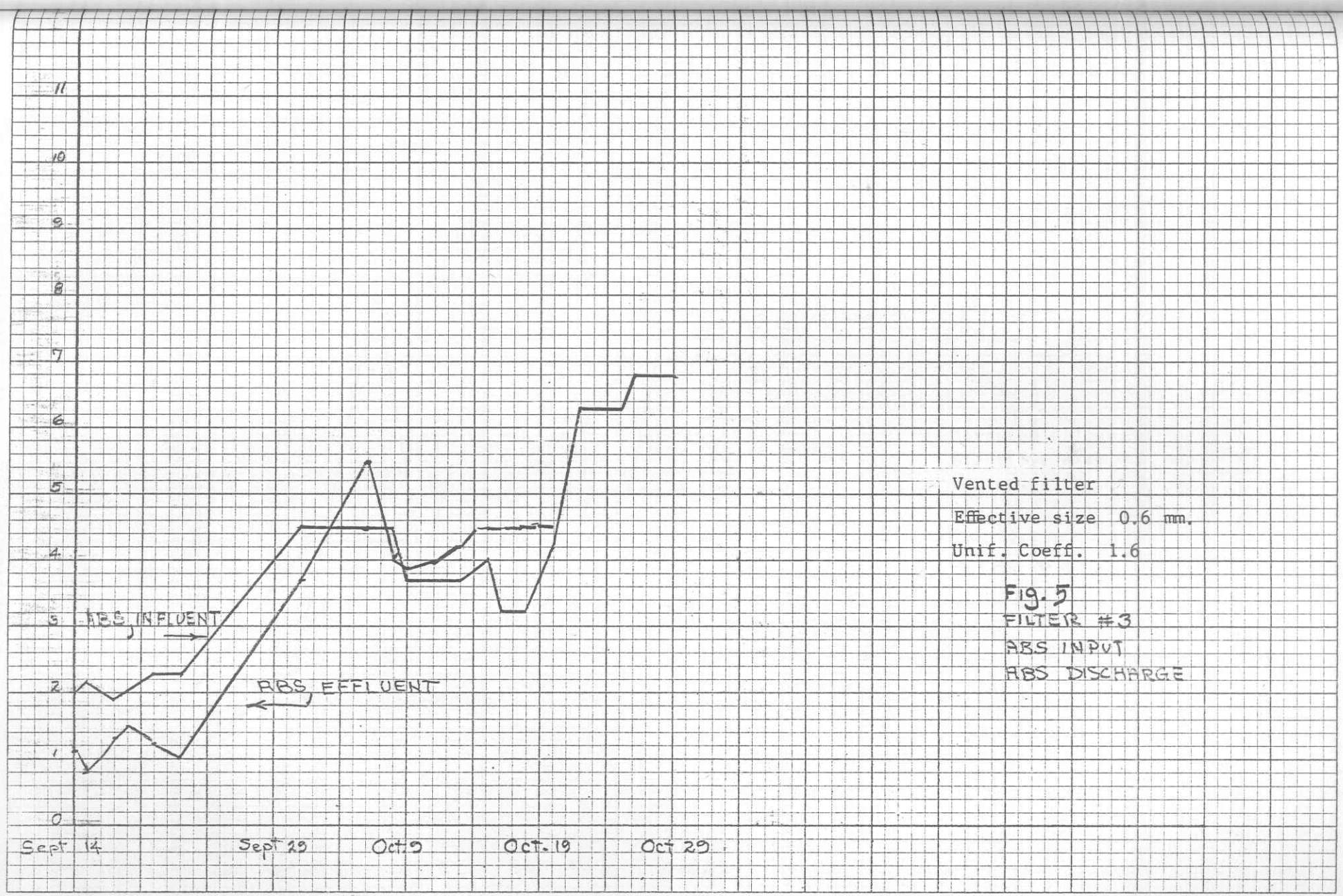
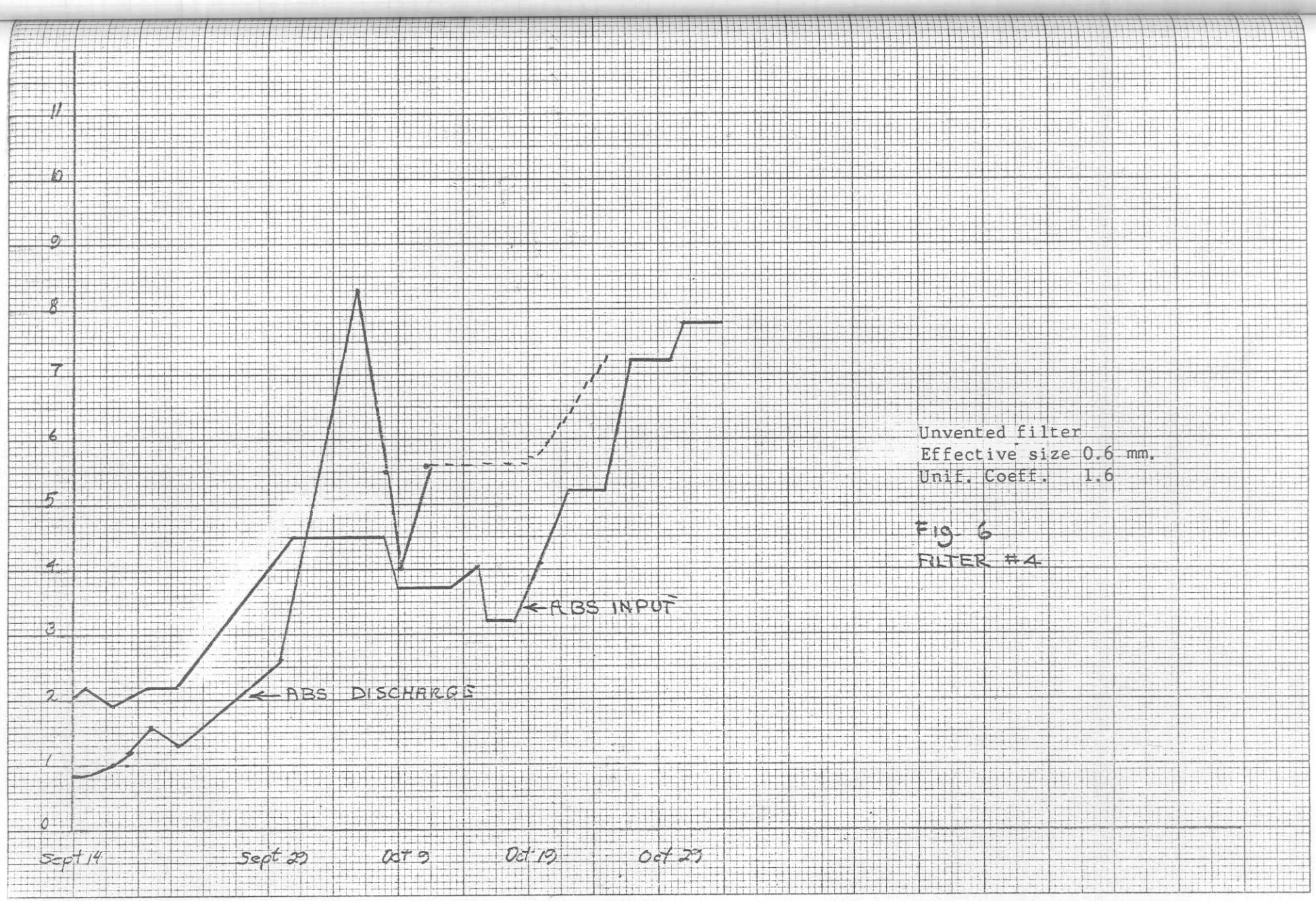
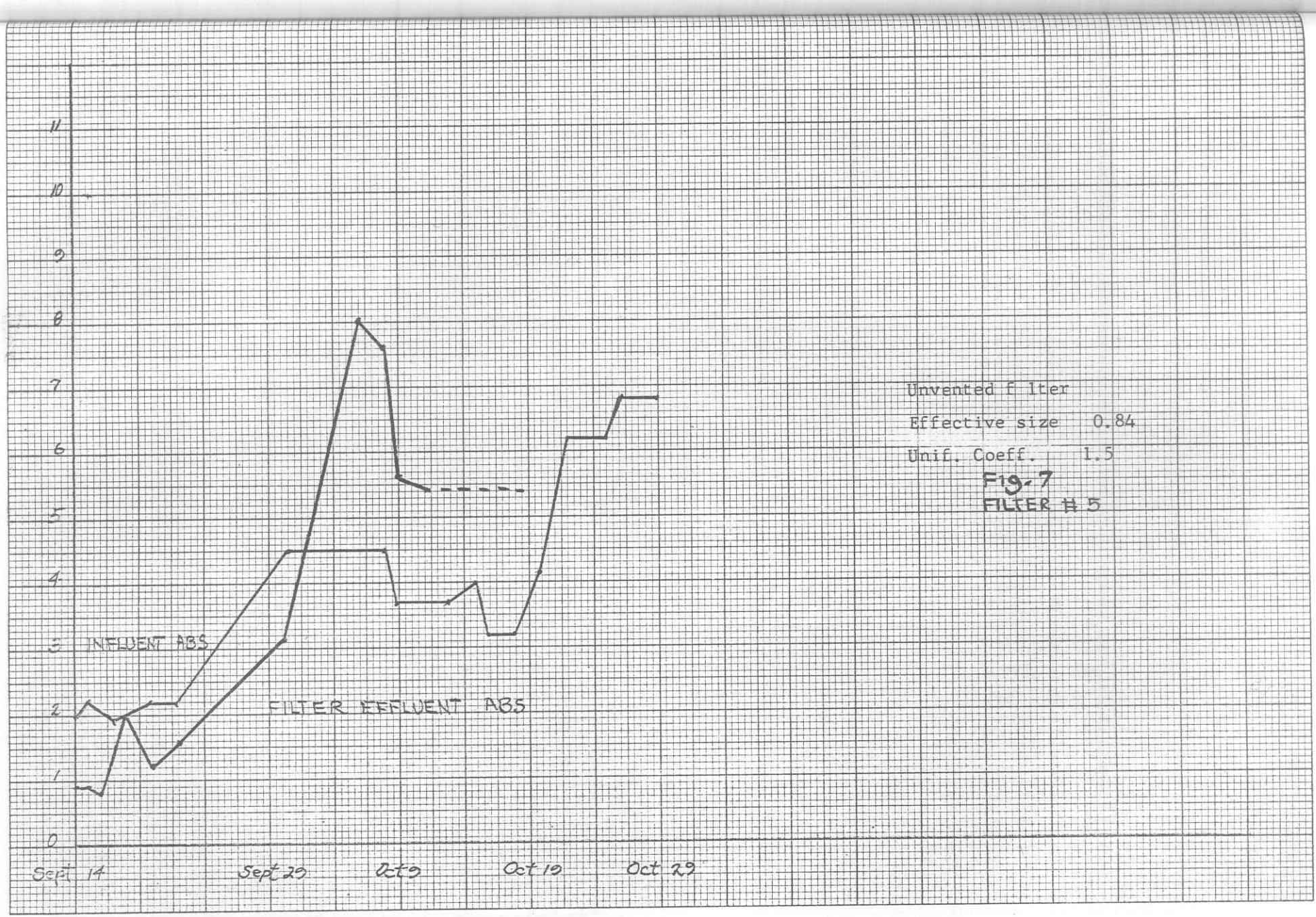
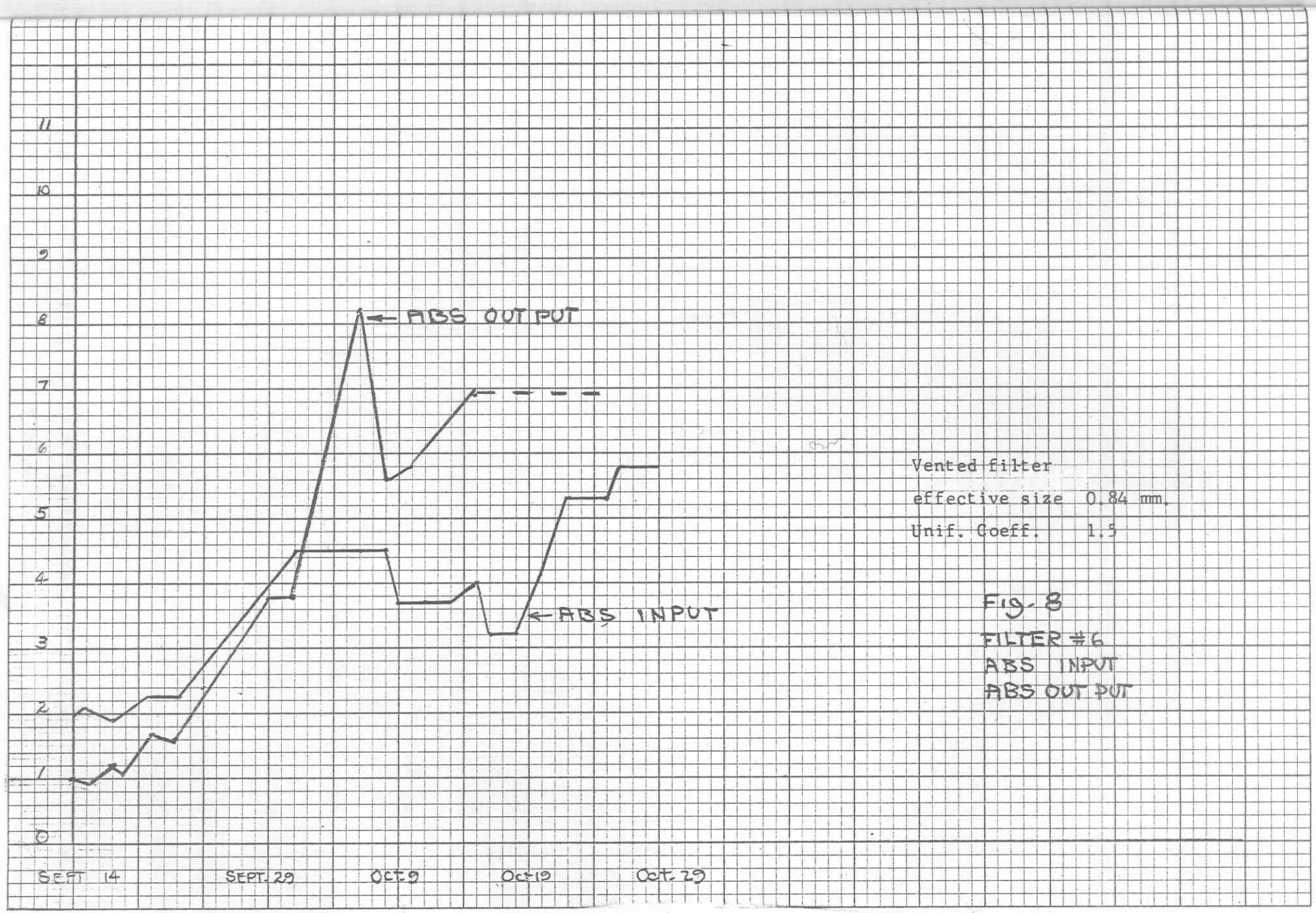


Fig. 3
FILTER # 1
A.B.S. INPUT ——
ABS. DISCHARGE —·—









Vented filter

effective size 0.84 mm.

Unif. Coeff. 1.5

Fig. 8

FILTER #6

ABS INPUT

ABS OUT PUT

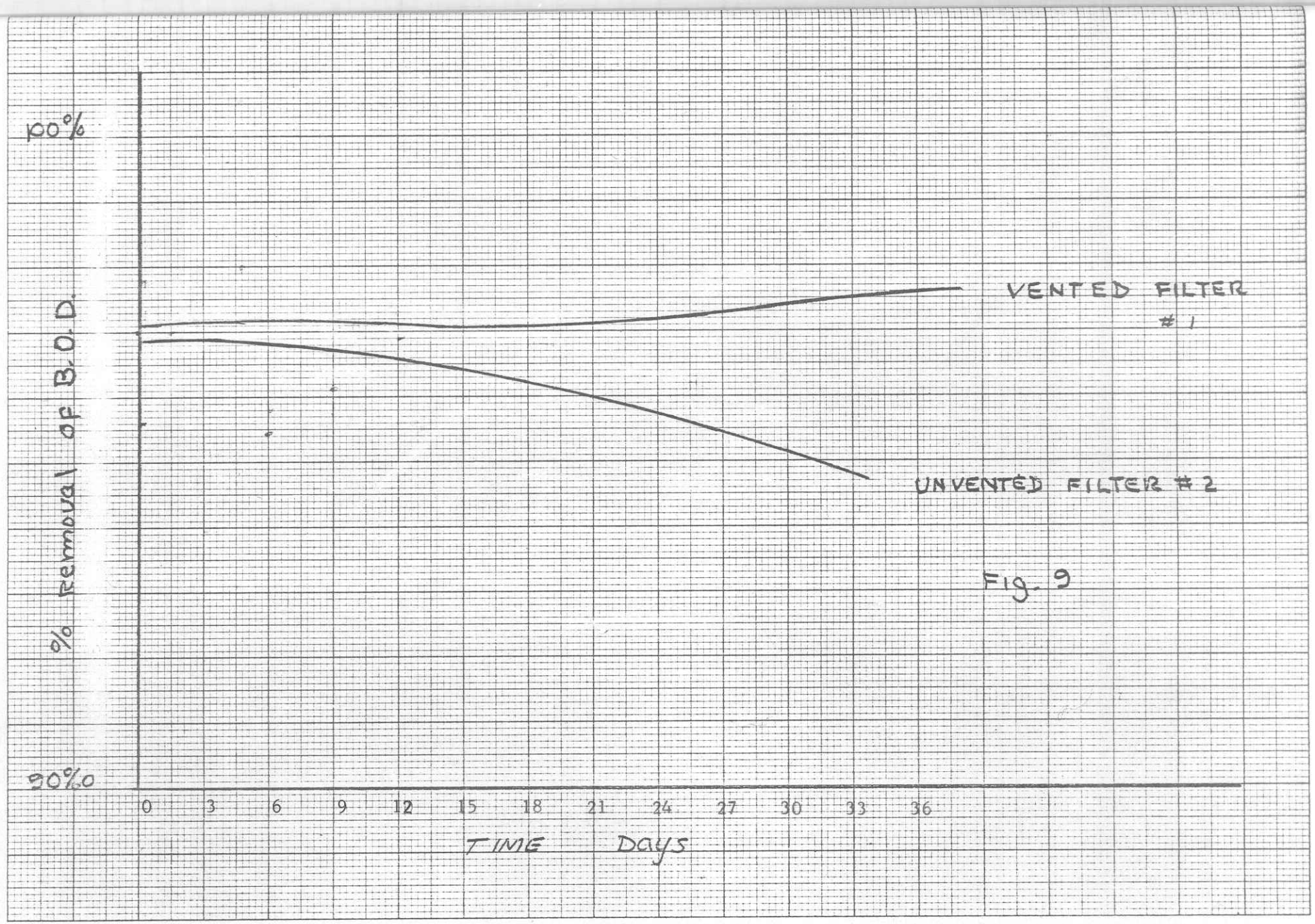


Fig. 9

APPENDIX

Methylene Blue Test

The procedure which was used is as follows. A calibration curve for the spectrophotometer was made by preparing a series of ten solutions of standard ABS in chloroform with concentrations ranging from 0.1 mg/liter to 2.0 mg/liter and measuring the per cent transmittance at 690 mu. A fifty milliliter sample was used for most of the determinations. First the solution was made alkaline with sodium hydroxide and then acidified with sulphuric acid. Next, ten ml of chloroform and twenty five ml. of methylene blue solution containing 0.03 gm/liter were added. The methylene blue forms a complex with the A.B.S. and this complex is more soluble in chloroform than in water. The aqueous solution is then washed three more times with ten ml. portions of chloroform to extract the methylene blue A.B.S. complex. Next the extract is washed with a sodium dihydrogen phosphate solution to remove any methylene blue that is in the chloroform extract and is not complexed with the ABS. To remove water and turbidity in the chloroform five grams of anhydrous sodium sulfate is added to the extract and mixed vigorously in a flask. The extract is then passed through a packed column consisting of several inches of sodium sulfate. The column is then washed with sufficient chloroform to bring the sample volume to one hundred milliliters. This procedure removes the water and turbidity which may interfere with the spectrophotometric measurements without lowering the concentration of the methelene blue complex. The most effective wave length to determine the transmittance of this solution is 690 mu.

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