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THE USE OF PERLITE AS AN ADSORBENT

BY

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A THESIS
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ABSTRACT

The adsorptive properties of perlite, an expanded volcanic glass, have been studied. Several activating treatments were investigated, air oxidation at 400 degrees Centigrade appears to be the best. The adsorption of the basic dye methylene blue yields a saturation value of 50 milligrams per gram of perlite. The acid dye cotton blue showed no measurable adsorption. A maximum adsorption of 15 millimoles of acetic acid and one milligram of iodine were found in aqueous solution. A high value of 1.33 milligrams of iodine per gram of perlite were found in methyl alcohol solutions. The surface area of perlite appears to be rather low. The material does not seem suitable for use as a commercial adsorbant.

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INTRODUCTION

This thesis is concerned with the problem of evaluating the material perlite as an adsorbent. Perlite has not previously been used as an adsorbent. Hence, the problem of evaluation presented an interesting challenge. The problem was divided into several phases for investigation.

The initial phase of the investigation was to conduct a thorough literature search in order to gain some knowledge as to the history, properties, processing, and uses of the material. It was felt that an insight in this area would give some clue as to the ultimate use of perlite as an adsorbent.

The second phase of the investigation was to investigate various activating treatments which seemed to promise a measure of success. The choice of these treatments was in part based on the work of other investigators on other adsorbents, and in part on the authors previous experience in developing cleaning techniques for metal, ceramic and glass components for vacuum tube use.

The third phase of the investigation was concerned with evaluating the activated perlites as adsorbents for specific materials. It was decided that the scope of this investigation would be limited to adsorption from solution.

The materials chosen for this evaluation were methylene blue, a basic dye; cotton blue, an acid dye; acetic acid; and iodine. Iodine was adsorbed from aqueous and methyl alcohol solutions.

A fourth phase of the investigation was an effort to estimate the surface area of the adsorbent from the data taken in the third phase. It was felt that surface area is one of the controlling factors in the evaluation of a material as an adsorbent.

PERLITE

Perlite is a mineral belonging to the granite-rhyolite family. This family may be subdivided into four groups: granitoid, felsitoid, tuffs, and glassy rocks. Perlite is a member of the latter sub-group, other members of this group are obsidian, pitch stone, and pumice. In general all members of the granite-rhyolite family have the same chemical composition, the composition of perlite (See Table I) is typical.

Perlite is a glassy rock more or less completely broken into globules somewhat resembling pearls, and made up of concentric shells. The structure of perlite is probably due to contraction at the time of cooling. The rock is commonly grey in color and has a pearly or waxy luster.

Perlite contains from two to five percent of dissolved or chemically combined water. King, Todd, and Kelley (1) report that water above 1.2 percent is very loosely held. M. T. Hunting (2) reported that only that water below 0.75 percent was firmly held.

Processing perlite (3, 4, 5) is a fairly simple operation. Mining is usually an open pit operation. On leaving the mine the ore is crushed, screened, and stored according to size. The ore is then passed into a preheating furnace at 800 to 1000 degrees Fahrenheit, then into a "popping" furnace at temperatures as high as 1800 degrees Fahrenheit. The product from the furnace is then separated and sized in a cyclone separator. 2600'

The operation of the "popping" furnace is interesting. As stated above the perlite has a certain amount of loosely bound water. On

heating the water vaporizes and causes the ore to burst, yielding a product of very low density. It is common for an ore with a density of from 68 to 74 pounds per cubic foot to yield a product with a density of from 5 to 7 pounds per cubic foot.

The product resembles small irregular bubbles of glass which are very fragile.

The processed perlite is used chiefly as an additive to cement or plaster, yielding a strong, low density mixture with good insulating properties (6). It has also been used as a soil conditioner with encouraging results (7).

TABLE I
PERLITE - COMPOSITION %

	A	B	C	D	E	F	G
SiO ₂	73.41	70.63	73.79	74.82	73.28	69.79	73.61
Al ₂ O ₃	12.34	13.36	12.40	13.61	12.55	14.72	12.17
Fe ₂ O ₃	1.33	2.23	0.52	0.25	0.58	2.07	1.51
FeO	-	-	0.62	0.89	0.63	-	-
MgO	-	-	0.11	0.04	0.08	1.08	-
CaO	0.75	1.69	0.80	0.68	0.80	1.49	0.84
Na ₂ O	2.95	2.93	3.16	1.98	2.97	2.79	2.97
K ₂ O	5.33	5.16	4.84	2.99	3.0	3.98	5.08
H ₂ O	3.70	2.84	3.24	3.86	3.60	4.00	3.34
H ₃ O	-	-	0.25	0.22	0.19		
TiO ₂	-	-	0.09	0.28	0.09	-	-
P ₂ O ₅	-	-	0.01	-	0.01	-	-
MnO	-	-	0.02	0.04	0.02	-	-
Fe ₂ S	-	-	-	-	-	-	-
Total	99.97	100.36	99.66	99.66	99.80	99.88	
Expansion							
T. °F	1751	1949	1700	2200			
Reference	(8)	(8)	(8)	(8)	(8)	(8)	(1)

A. Snowwhite Mine, Superior, Arizona.

B. Near Good Springs, Nevada.

C. Lady Francis Mine, Oregon.

E. Mutton Mountains, Oregon.

F. John Clark Mine, Colorado.

G. King, Todd, Kelley, U.S. Bur. Mines, RPTS. Invest. 4394, 1948.

TABLE 2PHYSICAL PROPERTIES OF PERLITE
BEFORE EXPANSION (9)

Hardness	5.5 - 7
Specific Gravity	2.25 - 2.40
Melting Point	1400 - 2400°F
Index of Refraction	1.483 - 1.506
Color	Grey to Grey black
Streaks	White
Luster	Pearly to Dull Glassy
Transparency	Translucent to opaque
Tenacity	Brittle
Fracture	Shelly, concentric, or columnar, or splintery

ACTIVATION AND PRETREATMENT

There seem to be no hard and fast rules governing the activation of an adsorbent. In fact, a survey of the literature leads one to believe that most activating treatments were developed by experience or trial and error.

A few principles may be followed, however. An adsorbent should be clean, that is, it should be free of contamination such as oils or greases or other debris which would tend to mask the surface from the adsorbate. Secondly, an activating treatment should, if possible, increase the surface by forming or exposing fine internal fissures or capillaries. This is probably the most important function of activation. Although there are inherent differences in the adsorption properties of many materials, they are to a large extent negligible in comparison with the effect of the specific area. A third function of activation may be the increase of surface forces due to changes in structure. In many cases, lattice dislocations are achieved by heating and rapid cooling.

According to Huttig (10) an active solid when heated tends to sinter with a reduction of its surface area. This, however, is not a continuous process, but shows increases in activity at $0.37X$, $0.50X$ and $0.80X$ where x is the melting point of the solid in degrees Kelvin. This rule was used as a guide in picking the temperature ranges used in these experiments, but since perlite has no definite melting point the figures could not be verified.

The work of several investigators shows the effect of activation of charcoal on its adsorptive properties (See Table III). This table illustrates the effect activation has on the performance of an adsorbent.

TABLE III

Effect of Activation on Sorption

<u>Activation at °C</u>	<u>Does it Sorb</u>		<u>Reference</u>
	<u>Acids</u>	<u>bases</u>	
air at 100°C	yes	no	11
air at 800°C	no	yes	12
air at 500°C	yes	no	12
O ₂ at 100°C	yes	no	13
O ₂ at 400°C	yes	yes	14
O ₂ at 1000°C thru 400°C	no	yes	15
CO ₂ at 1000°C	no	no	13
H ₂ at 1000°C	no	yes	13

As has been pointed out activation may be the crucial phase in developing an adsorbent. The work done on the activation of perlite may be divided into several phases: pretreatment, activation, and evaluation. The activation treatments employed were, air activation, dry hydrogen activation, wet hydrogen activation, nitrogen activation, vacuum activation, hydrogen peroxide activation, sulfuric acid activation, and sodium hydroxide activation. The balance of this section will deal with the techniques and equipment used in carrying out these treatments, and a preliminary attempt to evaluate the effect of these treatments.

PRETREATMENT

In all cases the perlite as received from the manufacturer was placed in a four liter beaker equipped with a close fitting screen at the top. Water was introduced into the beaker with a glass tube which extended to the bottom of the beaker. The system was allowed to overflow for at least thirty minutes. This treatment was designed to remove any readily soluble matter; also, dust and other debris. The batch was then

allowed to settle by halting the water flow. A good deal of sand was found at the bottom of the beaker in most of the samples. This sand was removed by scooping out the top seventy-five percent of the perlite and discarding the balance which contained the sand.

The material was then crushed and screened. That portion between 297 and 149 microns was retained for activation. The sample was crushed to make it easier to handle in later operations and to give a more consistent sample. The washed and crushed material was considered to be in the as received condition.

ACTIVATION

Air Activation. Samples of perlite were activated by baking in air at 350, 400 and 500 degrees Centigrade. This treatment was carried out in a heavily insulated, nichrome wound, muffle furnace. A Wheelco controller was used to regulate temperature.

The furnace was heated to the desired temperature and the perlite introduced in a ceramic boat. The ceramic boat containing the perlite was withdrawn from the furnace after the stated time and allowed to cool. Cooling was carried out in either a dessicator or in a room at 50 percent relative humidity.

Hydrogen Activation. Perlite samples were activated in wet hydrogen at 500 degrees Centigrade. Wet hydrogen describes a gas which was bubbled through water at 25 degrees Centigrade, - it is assumed to be saturated. Perlite samples were also activated in dry hydrogen with a dew point of minus 50 degrees Centigrade.

The equipment used for heat treating the perlite may be divided into several stages - a) furnace, b) dryer, c) saturator, d) controls, and e) gas supply (Figure I).

The furnace used was a 3000 watt Burrell tube furnace, a 36 inch quartz tube was used with a water cooled jacket at one end. The purpose of the cooler is to allow a sample to be cooled in a selected atmosphere after heat treating without removing from the furnace (see Figure II).

All gas passing into the system was passed thru a silica gel dryer to remove moisture. After leaving the dryer the gas could be run directly into the furnace or, via a bypass, into a bubbler for saturation with water vapor. The dryer (Figure III) consisted of a 4 inch diameter tube, twenty-nine inches high packed with silica gel. Fine nichrome screening was placed before the inlet and outlet ends to prevent the drying agent from escaping. The bubbler column (Figure IV) was glass, 2 inches in diameter, and 14 inches high. The gas passed down a center tube and through a fritted glass filter for better dispersion. On emerging from the water the gas was passed into a large chamber to eliminate any fine droplets of water which were carried from the saturator.

Temperature control was achieved using a Wheelco controller. The controller was set up in such a fashion as to bypass the furnace controls except those which provided a selection of the current flow. An iron-iron constantan thermocouple was placed on the outside of the quartz tube about 1/16th of an inch from the tube. This acted as the sensing element for the controller (Figure V).

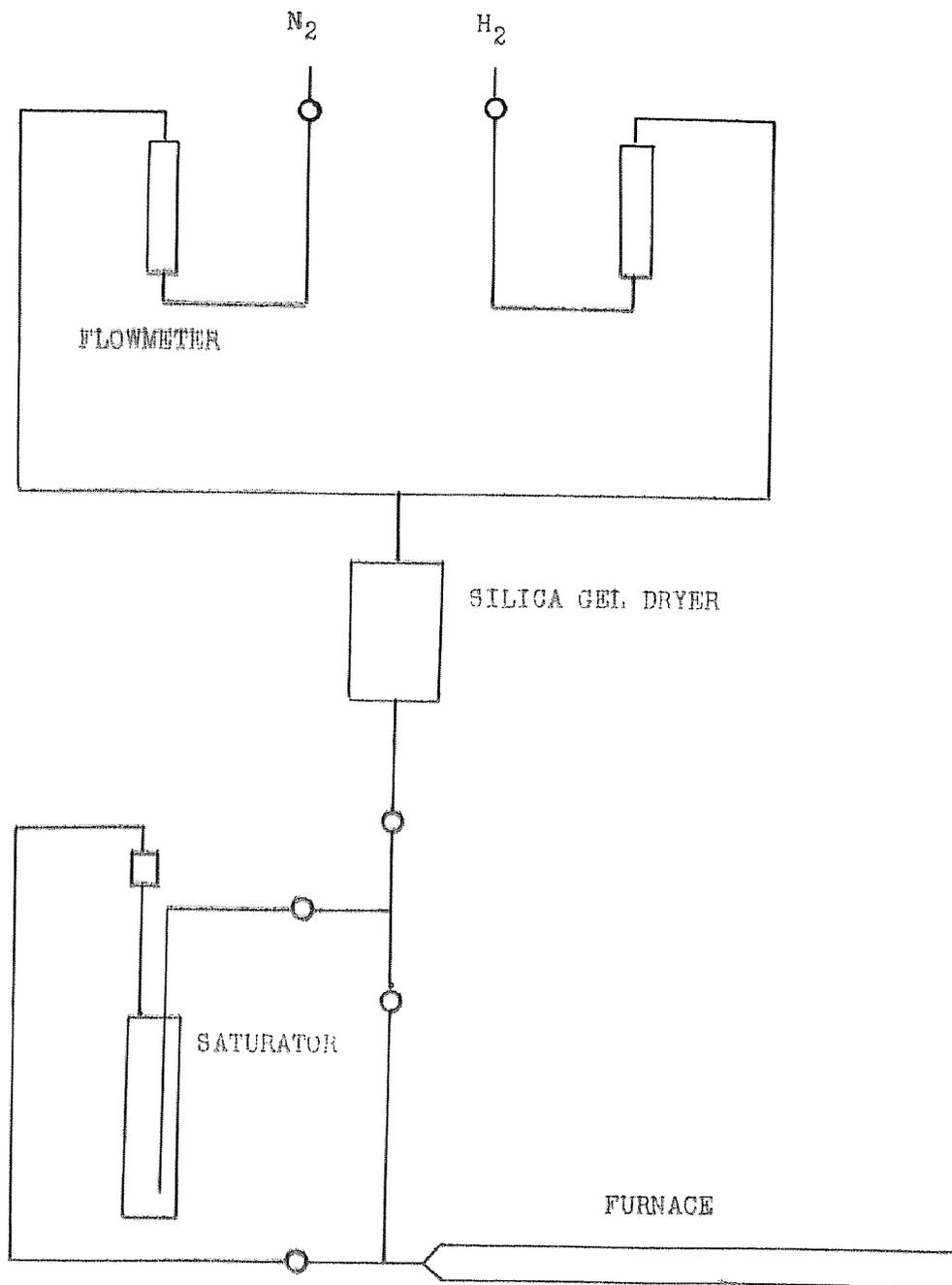


FIGURE I

PLAN OF THE HEAT TREATING EQUIPMENT

FLOBAR HEATING ELEMENTS

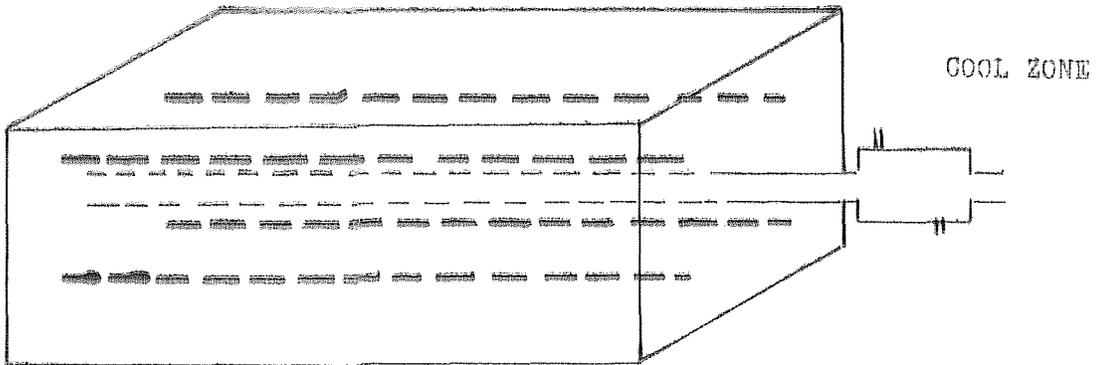


FIGURE II

BURRELL FURNACE

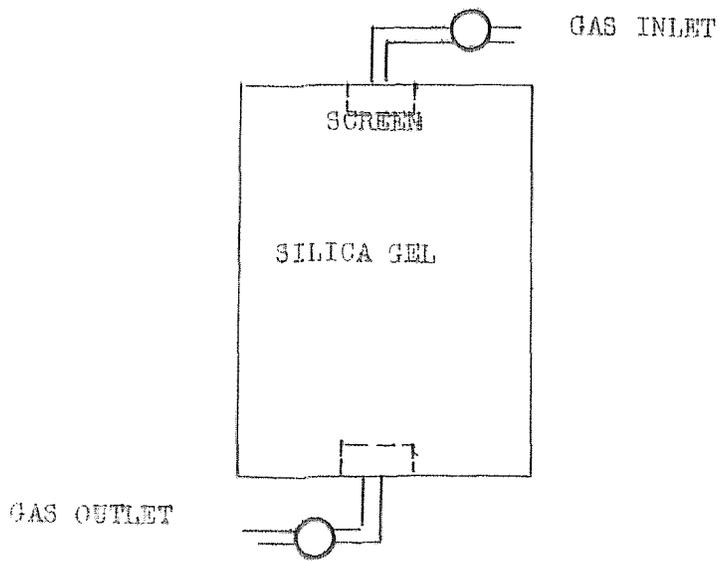


FIGURE III

GAS DRYER

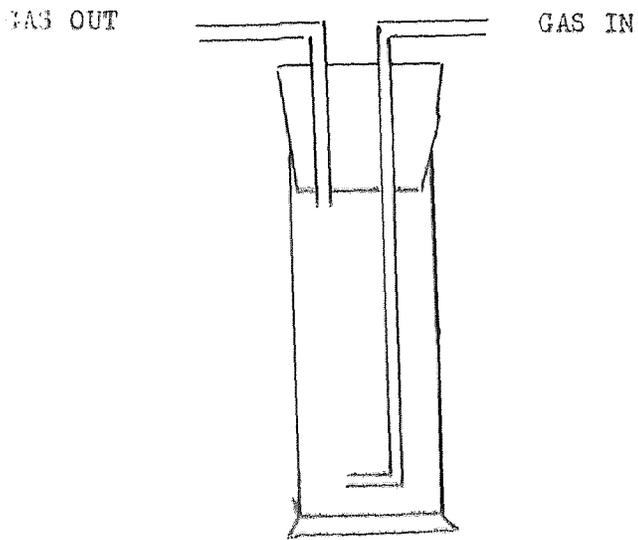


FIGURE IV
BUBBLER

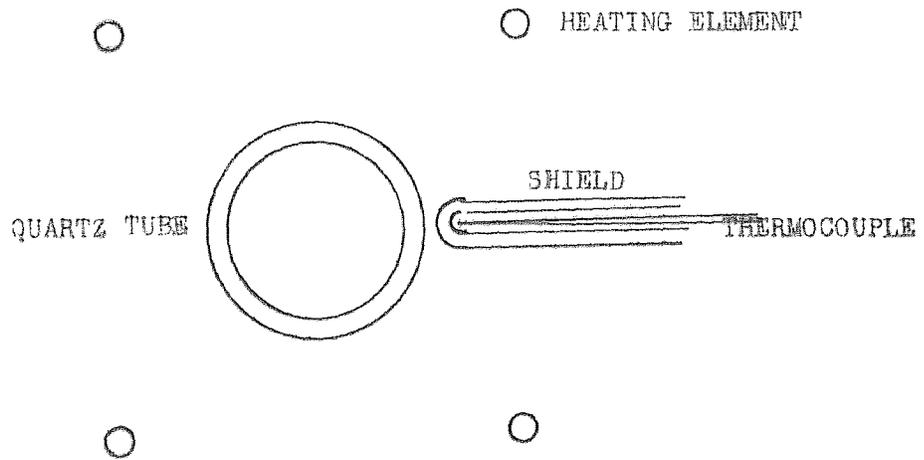


FIGURE V
THERMOCOUPLE SENSING ELEMENT

The procedure for activating a sample in hydrogen is as follows: The perlite in a ceramic boat is placed in the quartz tube approximately four inches from the mouth. The system is then flushed with nitrogen for fifteen minutes to remove traces of air. The system is then switched from nitrogen to hydrogen. The hydrogen is ignited as it passes from the mouth of the tube thus eliminating the possibility of an explosion due to accumulations of gas. The boat containing the perlite is then pushed into the hot zone of the tube. At the end of the treatment the boat is pulled back into the cool zone and allowed to stand for fifteen minutes, the system is then switched to nitrogen and the sample removed.

Vacuum Activation. This treatment was carried out in a vacuum system employing a mechanical pump and an oil diffusion pump.

(Figure VI). The perlite was suspended in a nickel boat in a glass lung. Heating was done by radio frequency coupling. It was impossible to measure temperature as the excellent insulating properties of the perlite caused the outside of the boat to become very hot while the inside was cool. After several tries this difficulty was overcome to some extent by placing short nickel rods in the boat with the perlite to conduct the heat. The system was pumped slowly down to 0.06 microns pressure and then heated gently. At first large volumes of gas were released and the pressure increased rapidly, heating was then discontinued until the pressure had again fallen. This procedure was repeated until the pressure did not increase on heating indicating the absence of gas. The sample was then maintained at a temperature below a red heat for several minutes and then cooled in vacuum. The pressure of the system was measured with a Pirani gauge (Figure VII).

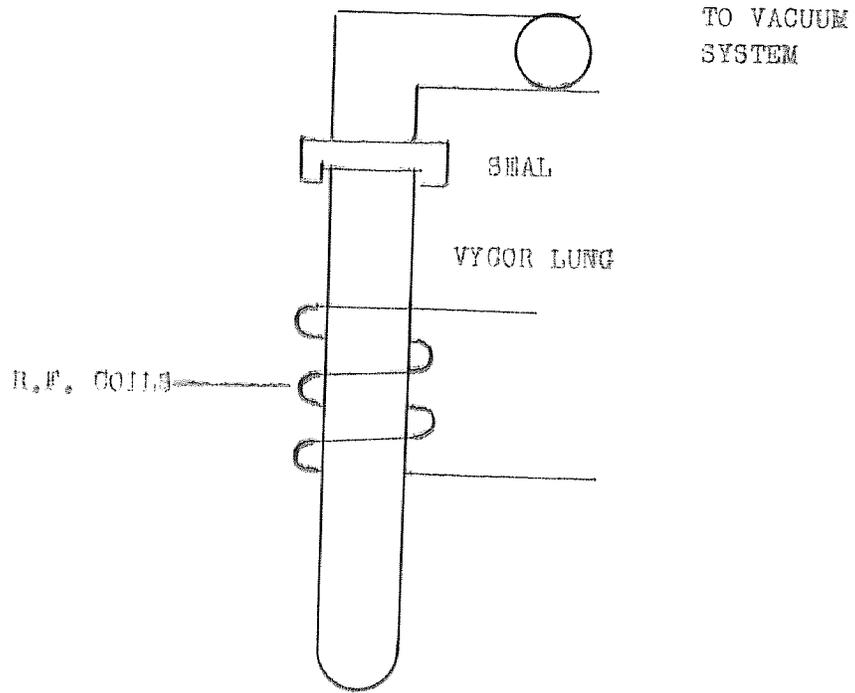


FIGURE VI
VACUUM LUNG

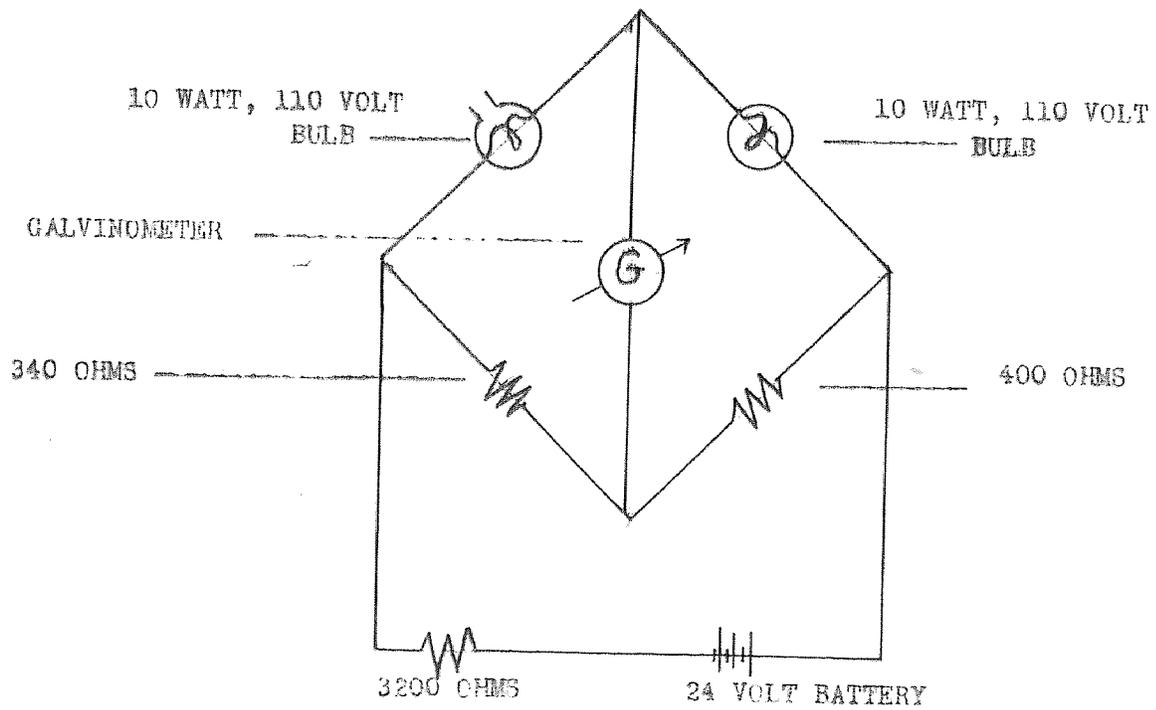


FIGURE VII
PIRANI GAUGE

Hydrogen Peroxide Activation. Samples of washed perlite were boiled for thirty minutes in a 10 percent solution of hydrogen peroxide. This treatment has been found to have a certain cleaning effect on glass and in certain cases to etch the surface (16). After boiling the samples were washed with low conductivity deionized water and oven dried at 105 degrees Centigrade.

Sulfuric Acid Activation. Samples of washed perlite were boiled for 10 minutes in ten percent sulfuric acid. The samples were then washed with low conductivity deionized water and oven dried at 105 degrees Centigrade.

Sodium Hydroxide Activation. A method described by Rayouk and Salem (17) was also tried. A freshly oxidized sample of perlite was treated with a dilute caustic solution for twenty minutes. The results did not seem particularly encouraging and hence the experiment was discontinued. This method is based on the fact that glass is etched by dilute caustic solutions.

EVALUATION

A preliminary evaluation of the activation treatments was made using a column packed with perlite. The column was 13 centimeters high and 0.90 centimeters in diameter. A 0.01 gram per liter solution of methylene blue was applied drop by drop at the top of the column from a burette. The fluid leaving the bottom of the column was checked visually against distilled water on a white background, the first drop of blue being noted. The results of these tests may be seen in Table IV.

ACTIVATION TREATMENTS USED

TABLE IV

HEAT TREATMENTS

<u>TEMPERATURE °C</u>	<u>TIME MINUTES</u>	<u>ATMOSPHERE</u>	<u>COOLING</u>	<u>CC TO FIRST DROP OF BLUE *</u>
350°	135	air	slow	17.1
600°	30	air	slow in 50% Relative Humidity	16.5
600°	30	air	slow in 0% Relative Humidity	12.5
300°	30	N ₂	slow in 0% Relative Humidity	9
300°	30	N ₂	fast in 0% Relative Humidity	9.5
300°	30	dry H ₂	slow in 0% Relative Humidity	10
600°	30	dry H ₂	slow in 0% Relative Humidity	12
500°	45	wet H ₂	slow in 0% Relative Humidity	12
400°	30	air	slow in 50% Relative Humidity	18
400°	-	vacuum	-	-

CHEMICAL TREATMENTS

30 min. boil in 10% H ₂ O ₂	water wash	10
10 min. boil in 30% H ₂ SO ₄	water wash	low
20 min. boil in 10% NaOH	water wash	low

* average of five readings.

An examination of Table IV leads one to conclude that the air baked samples show the greatest adsorption of methylene blue. Treatments at comparable temperatures in nitrogen and hydrogen were not as effective leading me to conclude that oxidizing conditions are necessary for this activation. Also, it is shown that oxidizing conditions at low temperatures, as is the case in boiling hydrogen peroxide, are also not effective. Hence, it may be concluded that both high temperatures and oxidizing conditions are necessary for effective activation of perlite.

METHYLENE BLUE ADSORPTION

The adsorption of methylene blue from aqueous solutions is one of the standard tests used to determine the adsorption power of various materials. The tests employed here are a variation on the methods used by many investigators.

A Beckman model B Spectrophotometer was used to measure the concentration of the methylene blue solutions before and after adsorption. All solutions were measured in standard one centimeter cells with deionized water as the standard. All measurements were made at 25 degrees Centigrade.

In calibrating the spectro'photometer transmittance measurements were taken at intervals between 3,500 and 10,000 Angstroms for a 1×10^{-3} grams per liter solution of methylene blue. A plot of wavelength versus transmittance showed a minimum in the region between 5500 and 7000 Angstroms (See Figure VII). Each of the standard solutions to be used in the adsorption studies were then calibrated in this region. (See Figure VIII)

This plot confirmed the fact that a true minimum occurred at 650-660 millimicrons and that this minimum held over the concentration range of interest. A plot was then made of absorbence versus concentration as in figure IX. Percent absorbence is the log to the base ten of the reciprocal of the percent transmittance. This plot, being a straight line, served as a calibration for all later work on methylene blue.

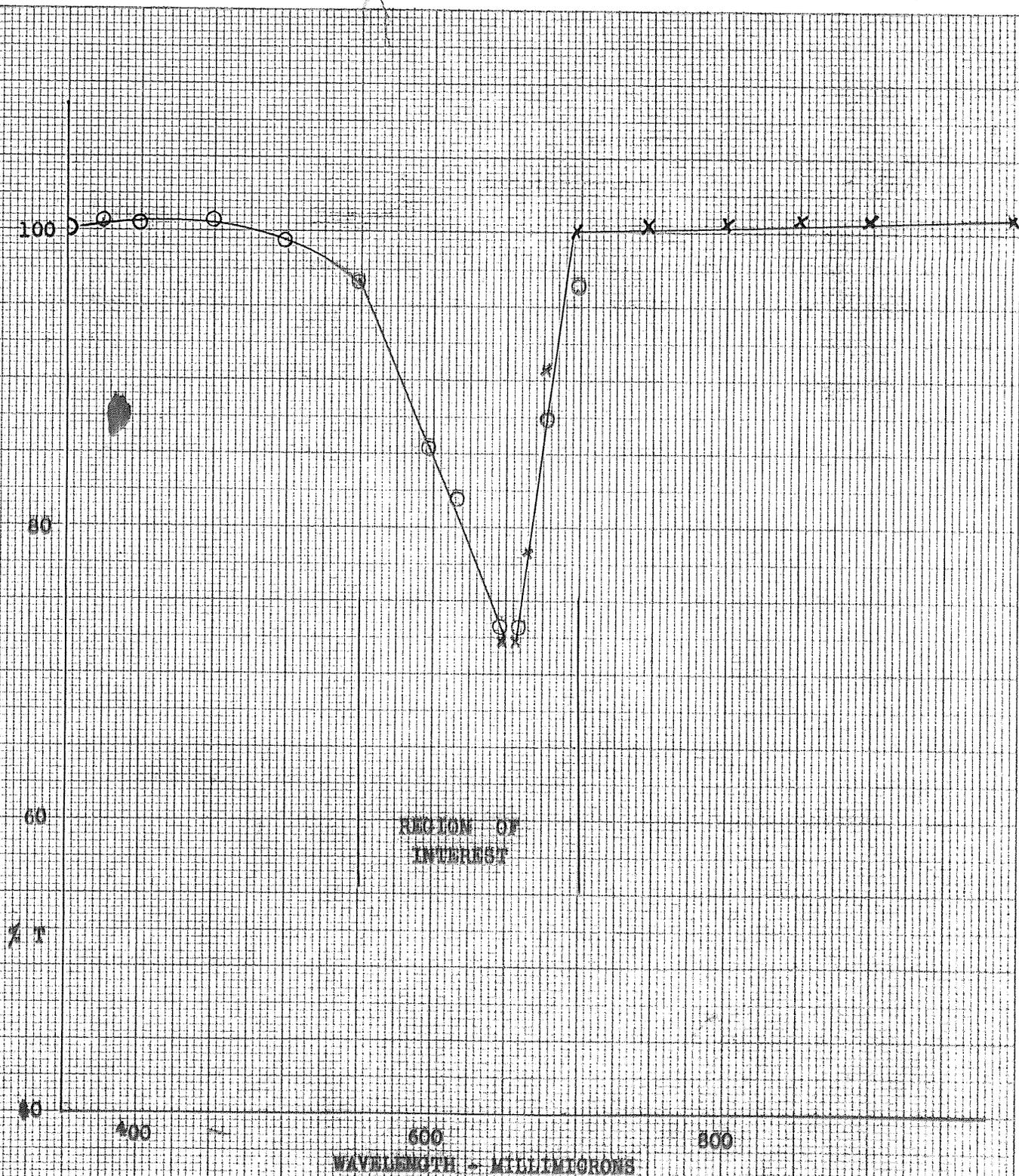


FIGURE VII
PLOT OF WAVELENGTH VERSUS PERCENT TRANSMITTANCE FOR 1×10^{-3} GRAMS PER LITER METHYLENE BLUE, BECKMAN MODEL B SPECTROPHOTOMETER.

100

80

60

40

20

0

WAVELENGTH MILLIMICRONS

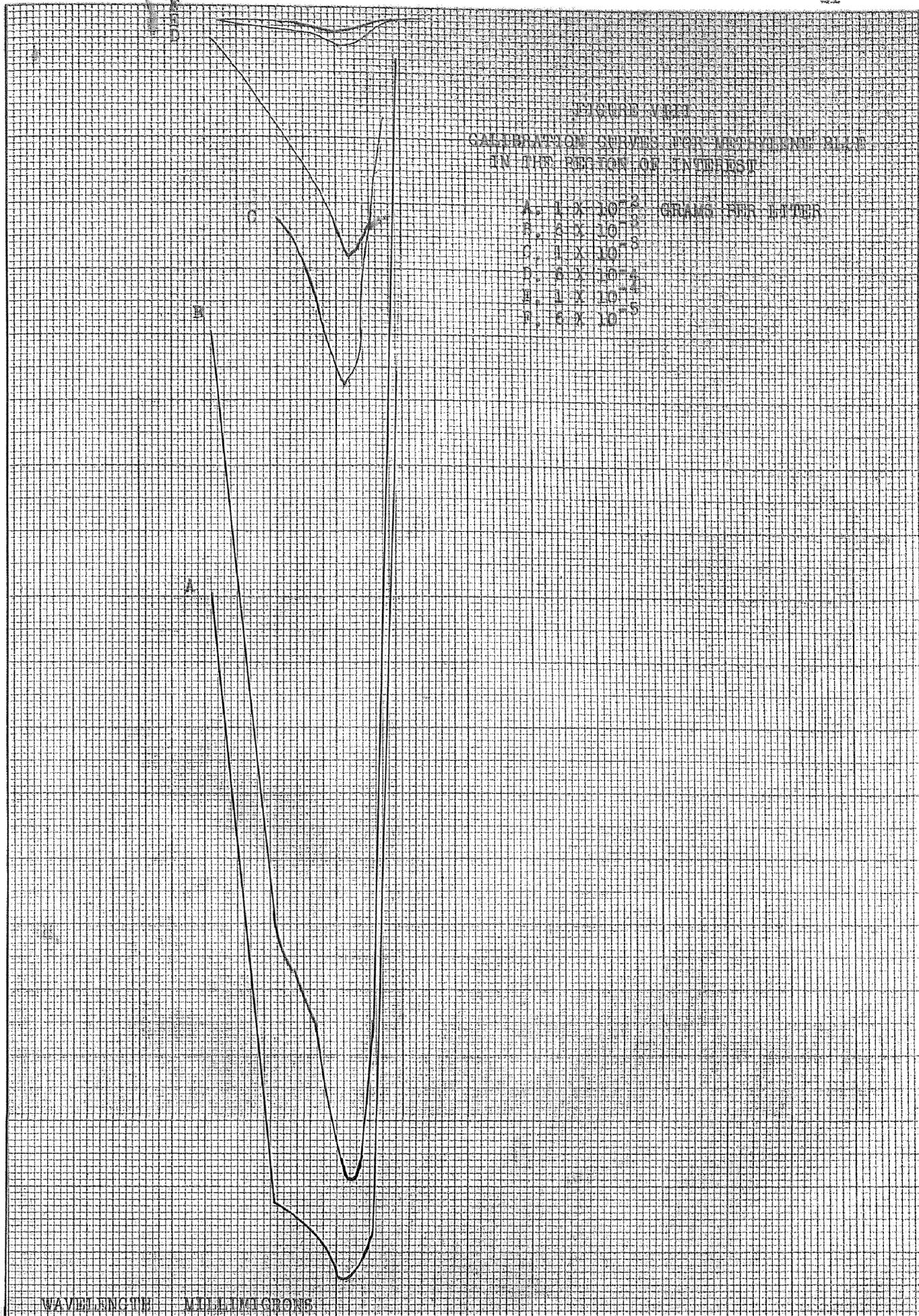
400

600

800

FIGURE 1000
CALIBRATION CURVES FOR METHYLENE BLUE
IN THE REGION OF INTEREST

- A. 1×10^{-2} GRAMS PER LITER
- B. 3×10^{-3}
- C. 1×10^{-3}
- D. 3×10^{-4}
- E. 1×10^{-4}
- F. 3×10^{-5}



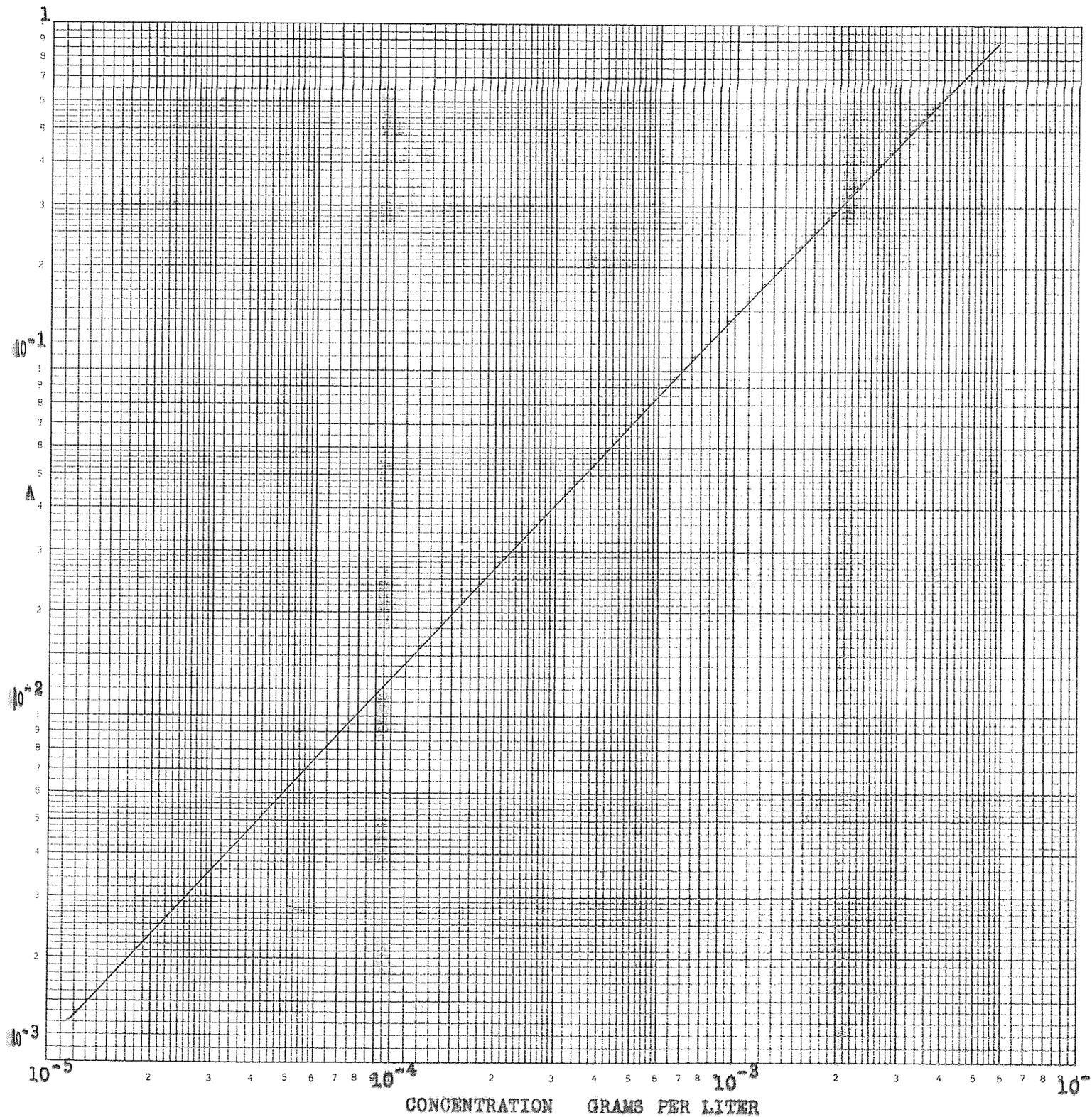


FIGURE IX
CALIBRATION CURVE FOR METHYLENE BLUE AT 665 MILLIMICRONS, BECKMAN MODEL B SPECTRO-
PHOTOMETER, RED PHOTOCCELL, ONE CENTIMETER CELLS.

In the study of the adsorption of methylene blue by perlite six methylene blue solutions were used, 1×10^{-2} , 6×10^{-3} , 1×10^{-3} , 6×10^{-4} , 1×10^{-4} , and 6×10^{-5} grams per liter. A ~~500~~ 1 milligram sample of the perlite to be studied was placed in fifty milliliters of solution. The solution was gently agitated every three minutes for one hour. Temperature was maintained at 25 degrees Centigrade. pH varied from 6.8 to 7.0. The perlite was then filtered out using a small funnel with a small wad of glass wool in the stem. Glass wool was used as in blank runs it showed negligible pickup of the dye while filter paper showed a large pickup. The concentration of the filtrate was then measured using a Beckman Model B spectrophotometer and one centimeter cells.

A study was made of the adsorption properties of six perlites. Activation treatments for these samples are described in the section on activation. All adsorptions were carried out as outlined in the preceding paragraph.

The data has been correlated using the Freundlich equation

$$\frac{x}{m} = k C_f^{1/N}$$

$$\text{of } \log \frac{x}{m} = \log k + \frac{1}{N} \log C_f$$

Where x is the grams methylene blue adsorbed

m is the grams of perlite

C_f is the equilibrium concentration
in grams per 100 milliliters

k and N are constants

C_i is the initial concentration of the solution in grams
per 100 milliliters.

As can be seen by examining the isotherms (Figures X thru XV) no startling changes in the adsorptive properties were brought about, but some differences were noted. If one examines the slope of the isotherm and adsorptive capacity of the sample, these changes are most apparent.

TABLE V

<u>TYPE OF ACTIVATION</u>	<u>Slope</u>	<u>$\frac{x}{m}$ at $C_f = 10 \times 10^{-4}$</u>
As received	2.05	0.75
12 hr. 400°C oxidation	1.65	90
24 hr. 400°C oxidation	1.37	80
Heated 0.06 microns	1.60	14
H ₂ O ₂ boiled	0.982	35
H ₂ O ₂ treatment + 12 hr. 400°C oxidation	1.098	20

From the figures for x/m at a specified equilibrium concentration it seems apparent that the use of oxidation at 400°C as an activating treatment is the most effective, while other treatments are not so effective. In all cases, the values of x/m at the apparent saturation are between 400 and 500 $\times 10^{-4}$ grams per gram, but the values of C at which this saturation is reached vary widely from 35 $\times 10^{-4}$ grams/100 cc for 12 hour oxidized samples to 210 $\times 10^{-4}$ grams/100 cc for perlite in the as received condition. It seems logical that since the saturation values of x/m are almost the same in all cases, that the surface area of the perlite has not been changed to any degree. A possible explanation of the differences in the equilibrium concentrations at which equilibrium is reached may be that some of these surfaces were cleaner

than others. In the as received condition we have a large number of foreign molecules sorbed on the surface. It seems possible that the activating procedures used here were actually methods of desorbing or more likely destroying by oxidation these materials. Then for each type of activation the dye had to compete with these contaminating substances. Of course, several conditions are necessary for this to be true. The foreign substances must be lightly held, and the affinity of the surface for the dye must be stronger than that for the contaminants. It is possible that this phenomenon may be represented by an equation presented by Ockrent. (18)

$$\frac{\frac{(\bar{x})}{(\bar{m})_1}}{\frac{(\bar{x})}{(\bar{m})_2}} = \frac{K_2 C_1}{K_1 C_2}$$

This equation apparently holds to some extent in several cases.

TABLE VI

AS RECEIVED PERLITE - METHYLENE BLUE

G_1 gm (10^{-6}) 100 cc	G_2 gm (10^{-6}) 100 cc	Milliliters Methylene blue	Grams Perlite	$\frac{x}{m}$ gm (10^{-6}) gm Perlite
1000	600.0	50	0.5	400
600	180.0			420
100	77.0			23
60	78			
10	13			
6	8.7			
1000	700			300
600	220			380
100	60			40
60	42			18
10	5			5
6				
1000	600			400
600	212			388
100	64			36
60	47			13
10	5			5
6				

Aver- age				
1000	633			367
600	204			396
100	67			33
60	44.5			15.5
10	5			5
6	-			-

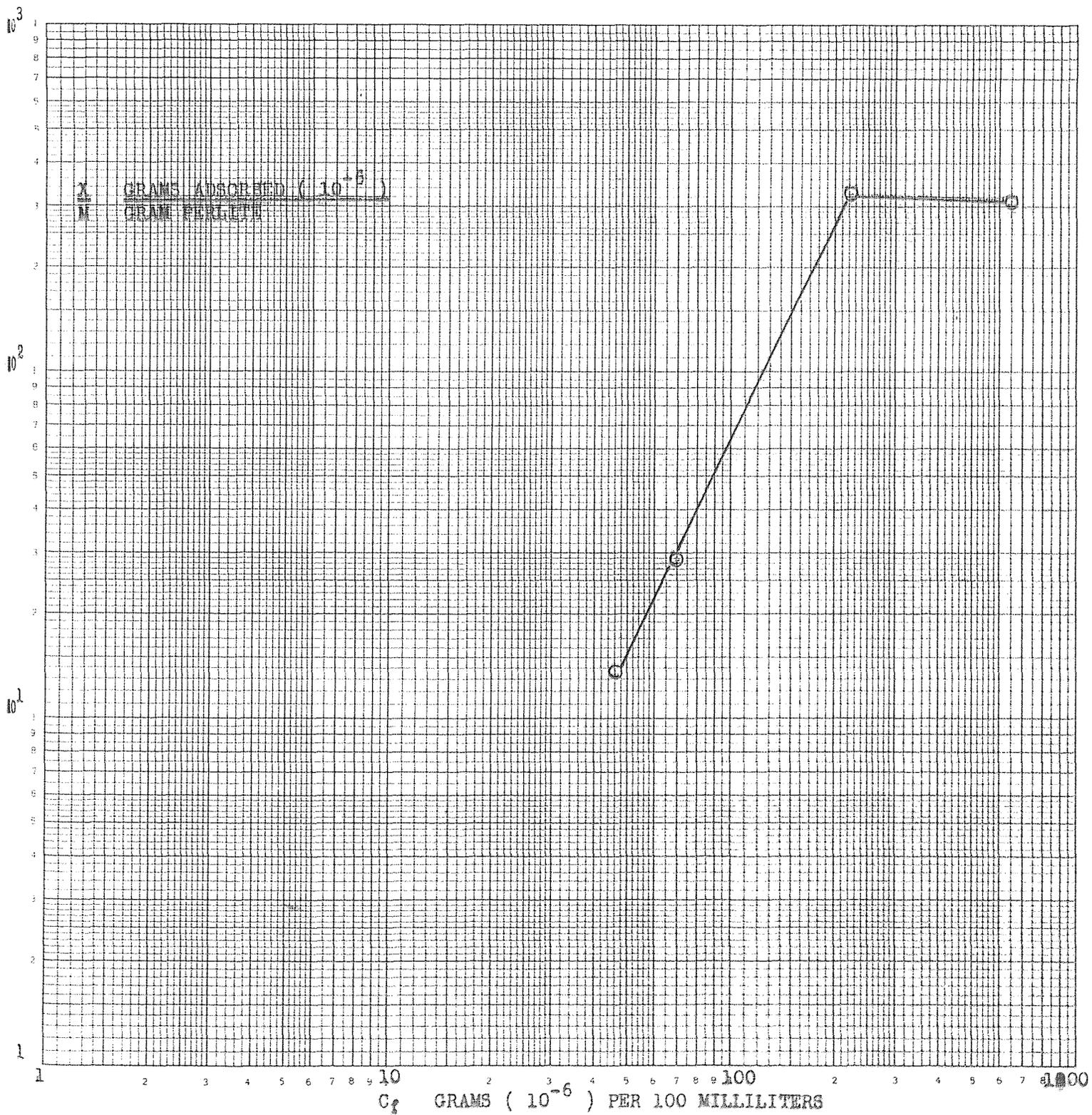


FIGURE X
 ADSORPTION OF METHYLENE BLUE BY PERLITE IN THE AS RECEIVED CONDITION AT 25°C.,

TABLE VII

400°C OXIDIZED PERLITE - METHYLENE BLUE

C_i gm (10^{-6}) 100 cc	C_f gm (10^{-6}) 100 cc	Milliliters Methylene Blue	Grams Perelite	$\frac{C_i - C_f}{m}$ gm (10^{-6}) gm Perlite
1000	500	50	0.5	500
600	82			518
100	10			90
60	7.7			52.3
10	0			10
6	0			6
1000	500			500
600	100			500
100	9.0			91
60	12			48
10	2.5			7.5
6	0			
1000	500			500
600	70			530
100	9.5			90.5
60	6.0			54
10	2			8
6				
** ***** **				
Average				
1000	500			500
600	84			516
100	9.5			90.5
60	8.57			51.43
10	2.25			7.75
6	-			

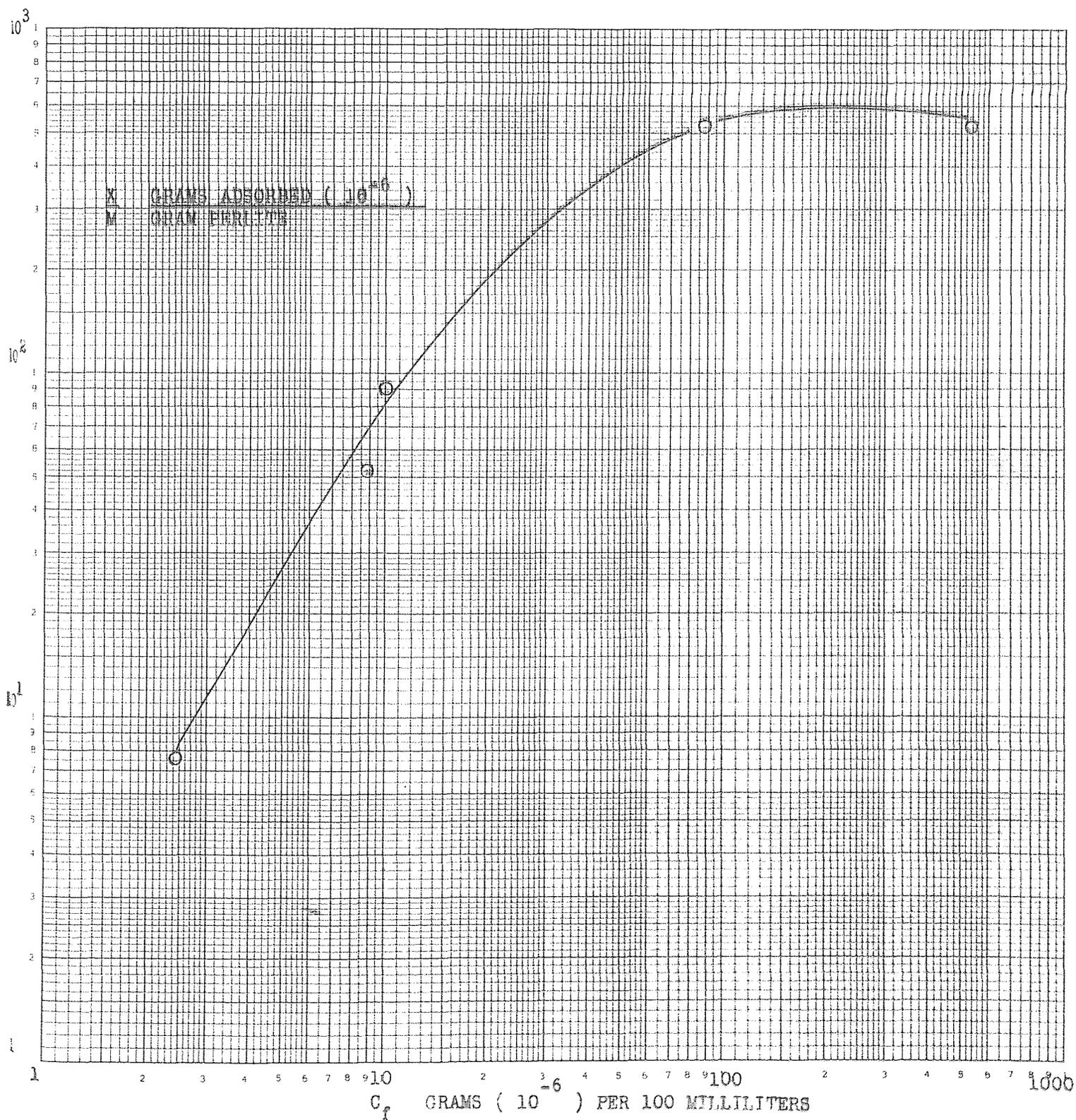


FIGURE XI
 ADSORPTION OF METHYLENE BLUE BY PERLITE HEATED IN AIR AT 400°C FOR 12 HOURS

TABLE VIII

24 HOUR 400°C OXIDIZED PERLITE-METHYLENE BLUE

<u>Cl</u> <u>gm (10⁻⁶)</u> 100 cc	<u>CF</u> <u>gm (10⁻⁶)</u> 100 cc	Milliliters Methylene Blue	Grams Perlite	$\frac{x}{m}$ <u>gm (10⁻⁶)</u> gm Perlite
--	--	----------------------------------	------------------	--

1000	600	50	0.5	400
600	145			455
100	20			80
60	16			44
10	8.5			1.5
6	6.2			0

1000	600			400
600	100			500
100	18			82
60	7.5			52.5
10	0			-
6				

1000	600			400
600	110			490
100	14.5			85.5
60	12.5			47.5
10	2.0			7.0

Aver-				
age 1000	600			400
600	118.3			481.7
100	17.5			82.5
60	12			48
10	3.5			6.5
6				

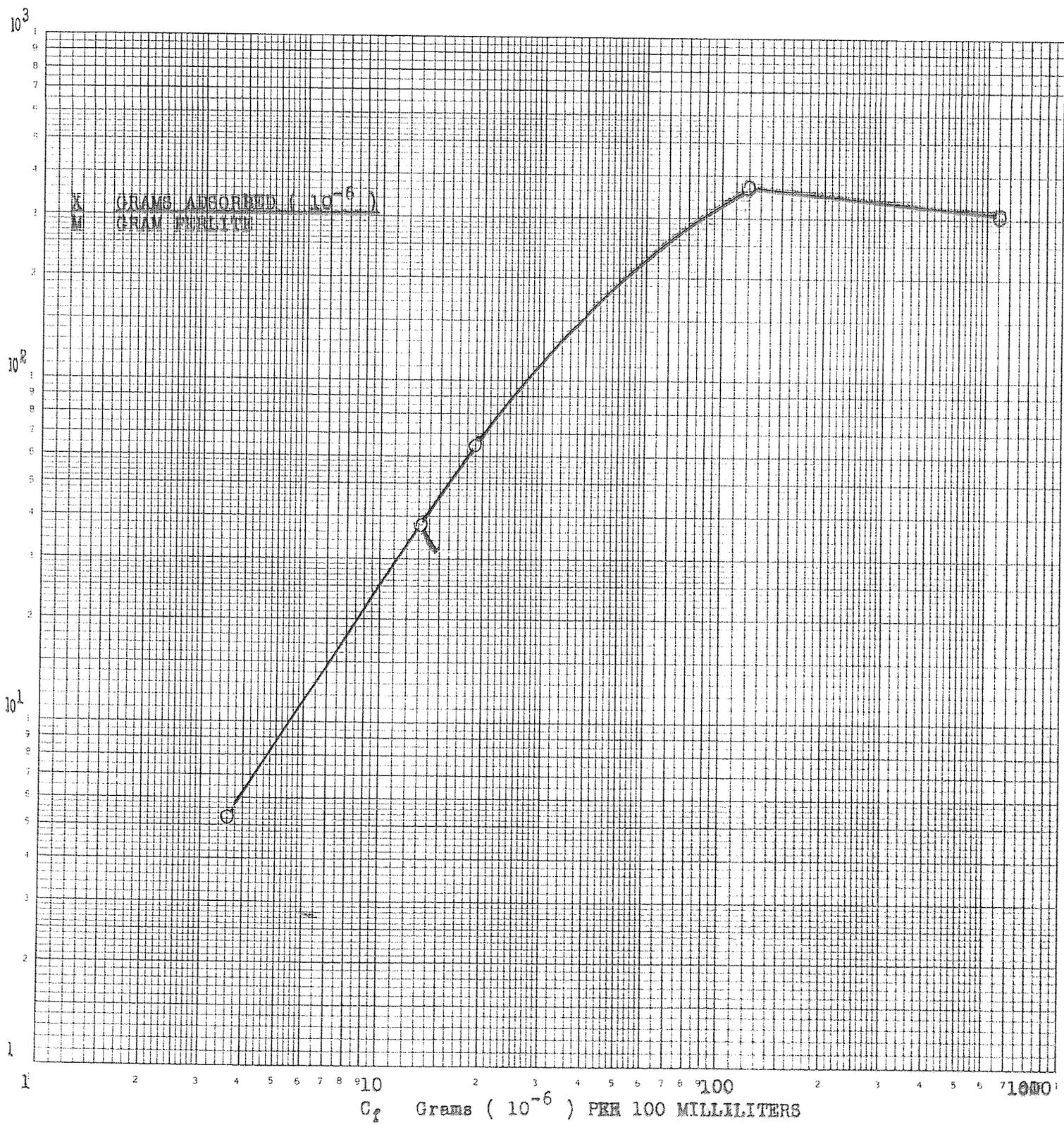


FIGURE XII
 ADSORPTION OF METHYLENE BLUE BY PERLITE ACTIVATED AT 400°C. FOR 24 HOURS.

TABLE IX

VACUUM HEATED PERLITE - METHYLENE BLUE

<u>C1</u> <u>gm (10⁻⁶)</u> 100 cc	<u>Cf</u> <u>gm (10⁻⁶)</u> 100 cc	Milliliters Methylene Blue	Grams Perlite	<u>$\frac{x}{m}$</u> <u>gm (10⁻⁶)</u> gm Perlite
1000	500	50	0.5	500
600	87			513
100	28			72
60	22			38
10	18			
6	22			
1000	550			450
600	92			508
100	25			75
60	18			42
10	5			5
6	2			4
1000	500			500
600	100			500
100	34			64
60	26			34
10	5			5
6	-			-
* * * * *				
Aver- age				
1000	516.3			483.7
600	93			507
100	29			71
60	22			38
10	5			5
6				-

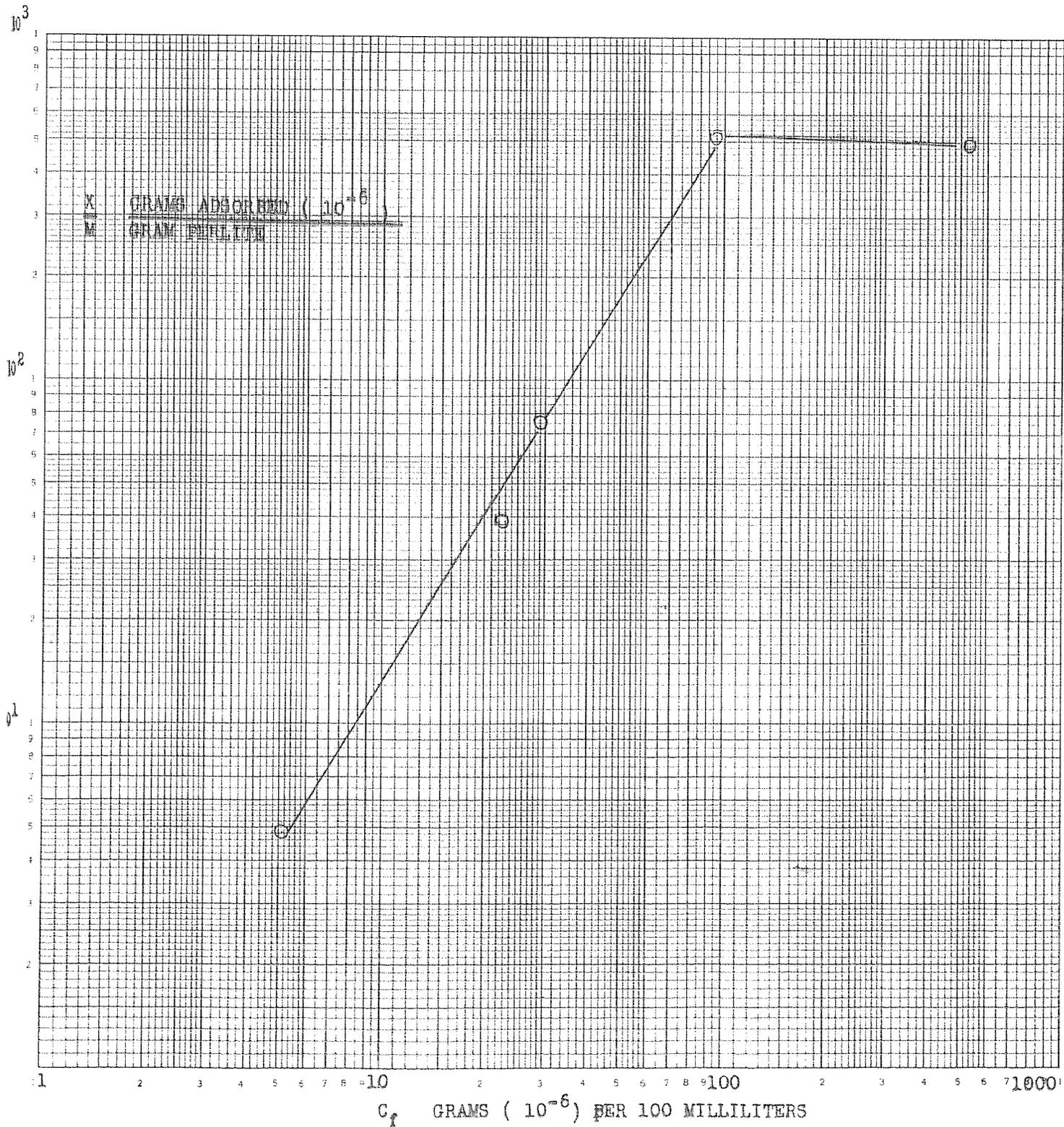


FIGURE XIII
 ADSORPTION OF METHYLENE BLUE BY PERLITE HEATED IN VACUUM.

TABLE X

H₂O₂ BOIL PERLITE - METHYLENE BLUE

<u>Ci</u> <u>gm (10⁻⁶)</u> 100 cc	<u>Cf</u> <u>gm (10⁻⁶)</u> 100 cc	Milliliters Methylene Blue	Grams Perlite	<u>$\frac{C_i}{C_f}$</u> <u>gm (10⁻⁶)</u> gm Perlite
1000	580	50	0.5	420
600	130			470
100	45			57
60	2.7			33
10	2.6			7.4
6	0			6
1000	500			500
600	150			450
100	35			65
60	21			39
10	1.7			8.3
6				
1000	600			400
600	100			500
100	40.5			60
60	16			44
10	5.5			4.5
6				

Aver-				
age 1000	560			440
600	126.6			473.4
100	38.3			61.7
60	21.3			38.7
10	3.27			6.73
6				

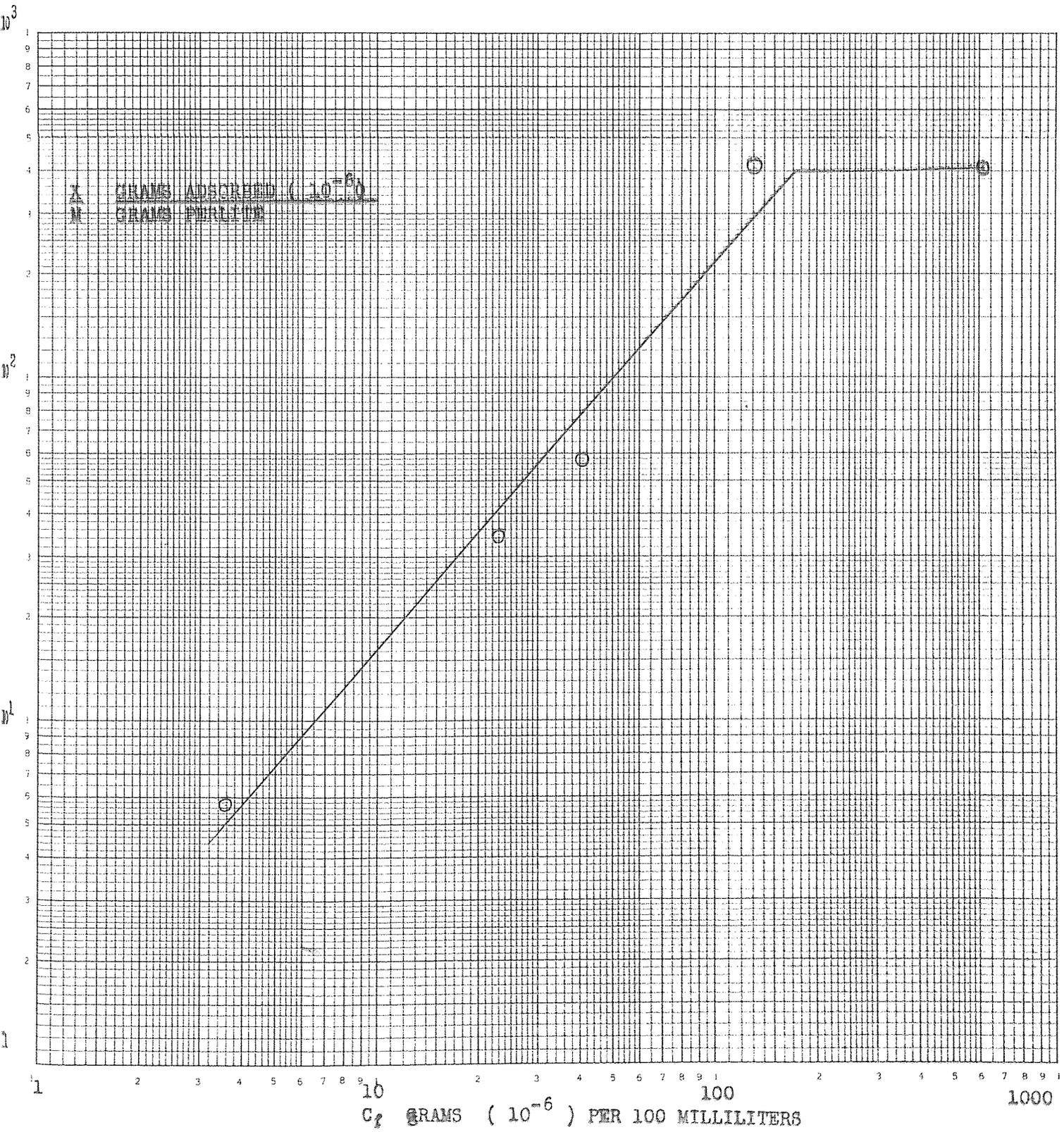


FIGURE XIV
 ADSORPTION OF METHYLENE BLUE BY PERLITE BOILED IN HYDROGEN PEROXIDE

TABLE XI

H₂O₂ -- 400°C OXIDATION PERLITE - METHYLENE BLUE

$\frac{C_i}{100 \text{ cc}}$ gm (10 ⁻⁶)	$\frac{C_f}{100 \text{ cc}}$ gm (10 ⁻⁶)	Milliliters Methylene Blue	Grams Perlite	$\frac{x}{m}$ gm (10 ⁻⁶) gm Perlite
1000	600	50	0.5	400
600	160			440
100	24			76
60	11			49
10	16			-
6	-			0
1000	600			400
600	130			470
100	20			80
60	16			44
10	-			
6	-			
1000	500			500
600	150			450
100	18			82
60	10.5			49.5
10	3			7
6				
* * * * *				
Aver- age				
1000	566			434
600	147			453
100	20.6			79.4
60	12.5			47.5
10	3			7
6				

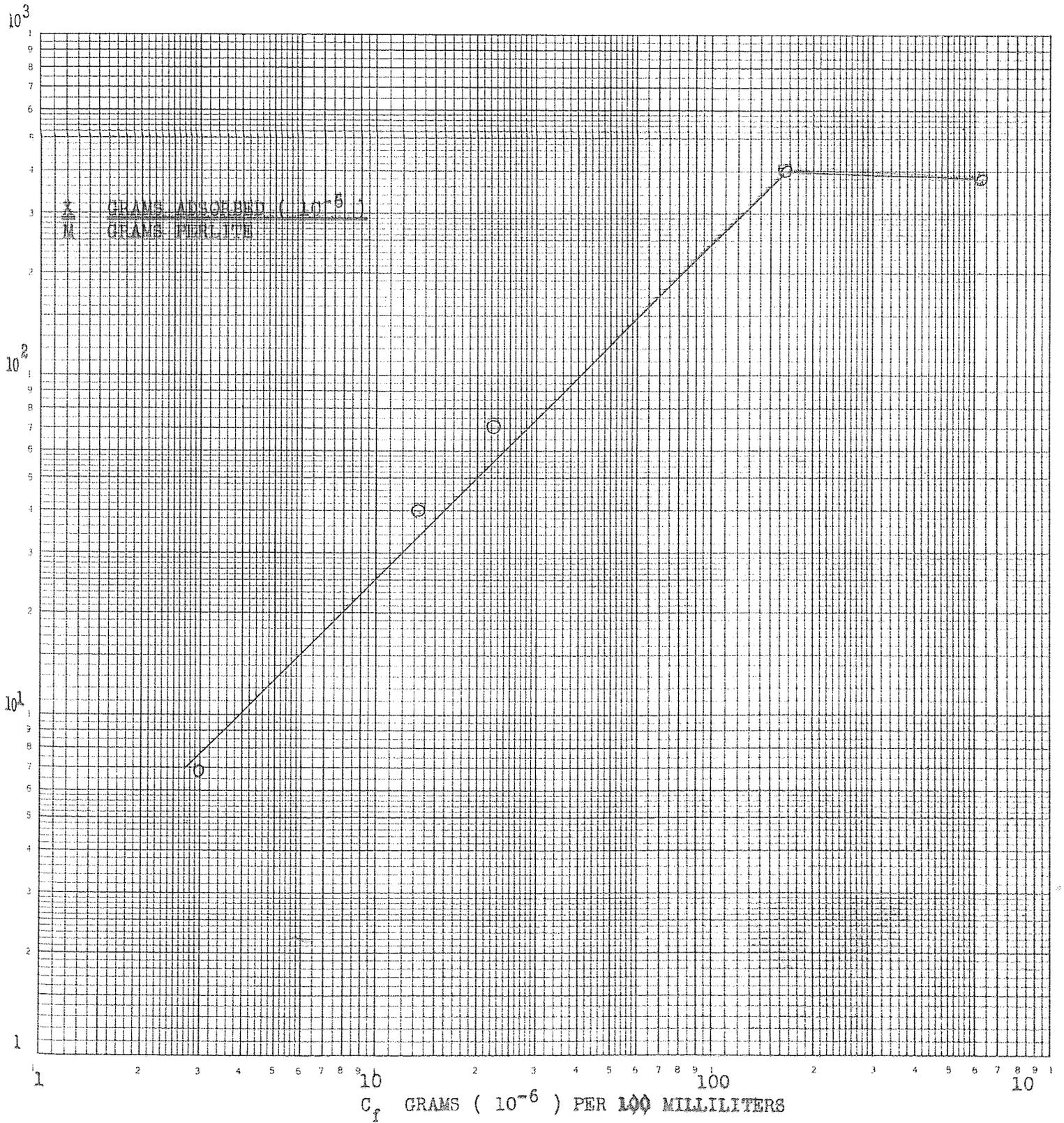


FIGURE XV
 ADSORPTION OF METHYLENE BLUE BY PERLITE BOILED IN HYDROGEN PEROXIDE FOLLOWED BY
 A4400°C. AIR BAKE.

EFFECT OF pH ON METHYLENE BLUE ADSORPTION

It was decided that the effect of pH in the adsorption of methylene blue by perlite would be of interest.

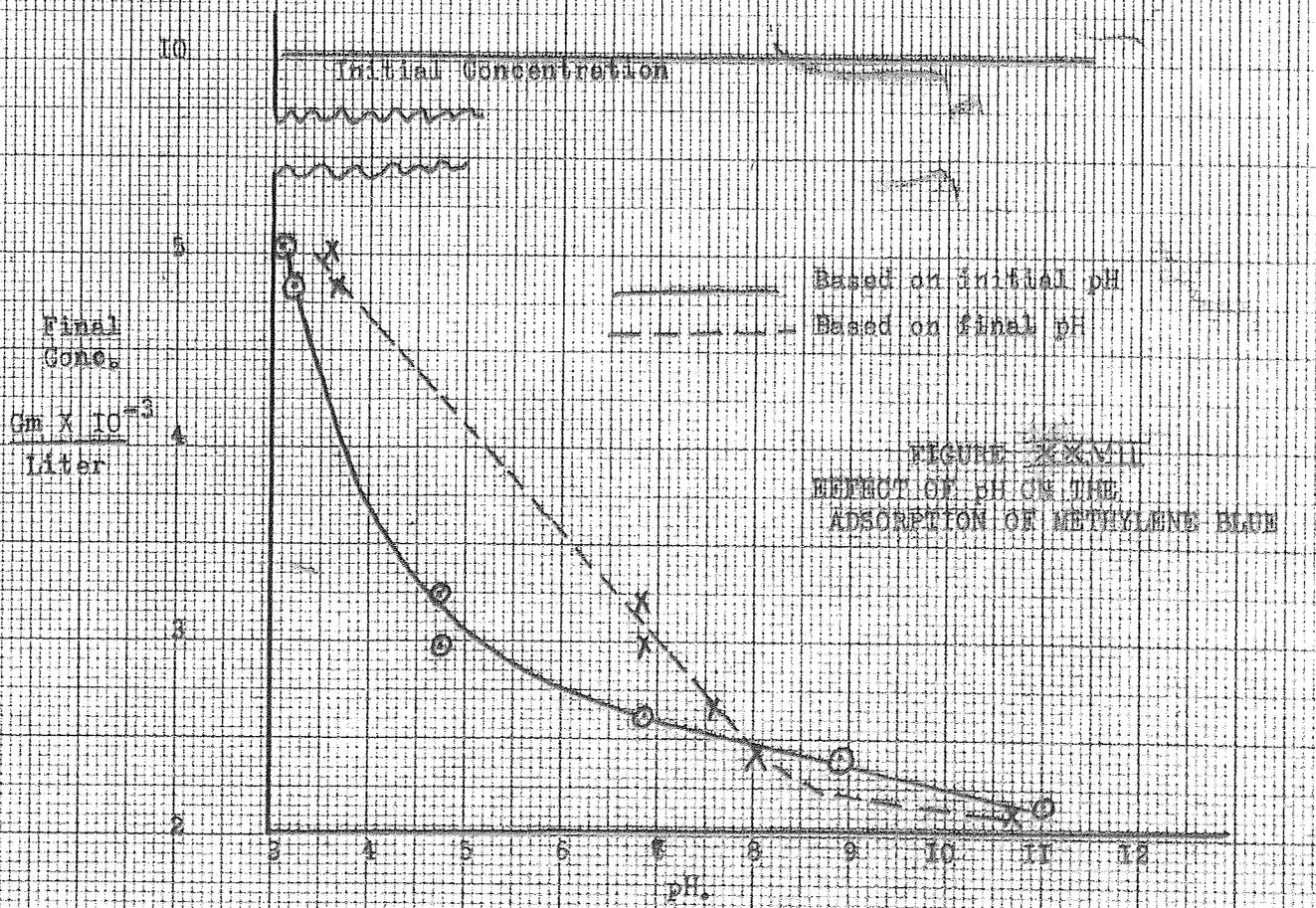
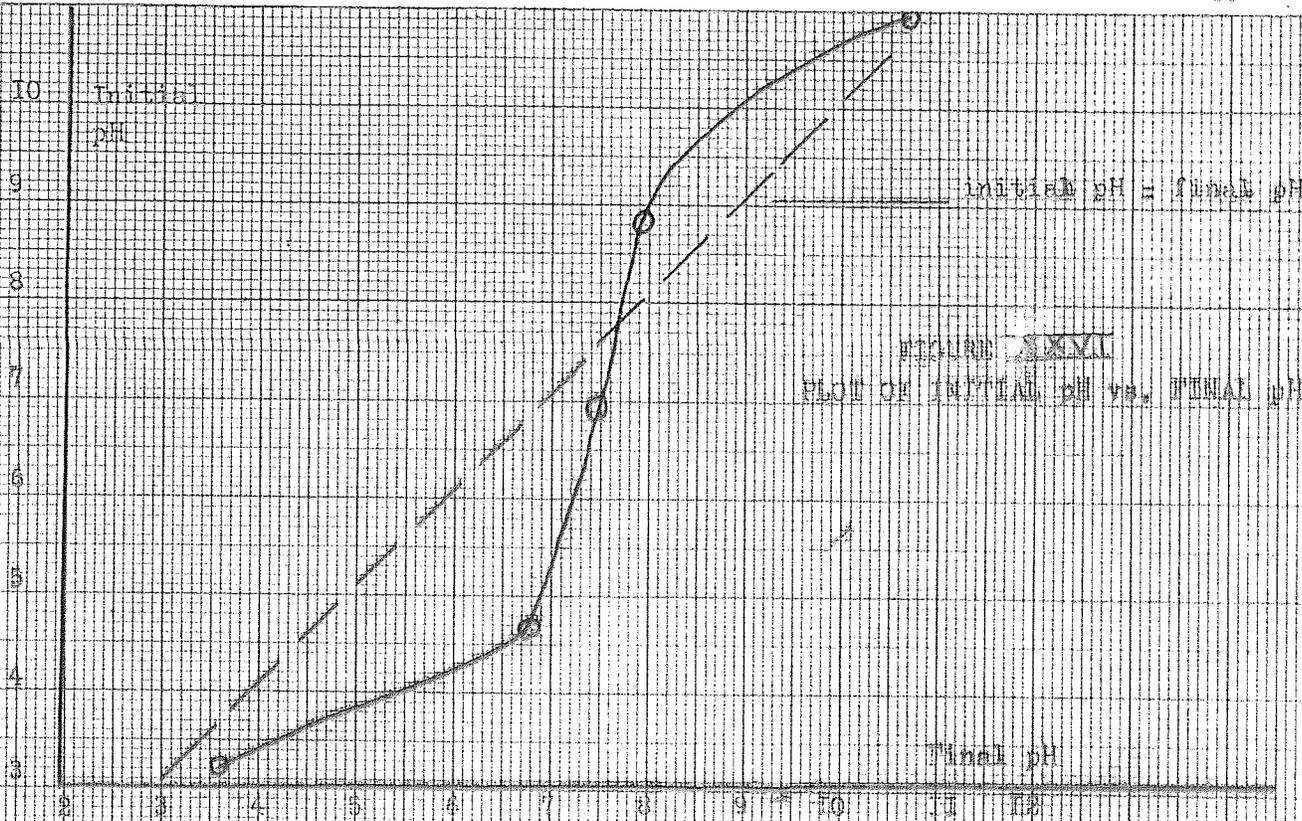
The perlite sample used for this experiment was one which previously had been treated with hydrogen peroxide as outlined in a previous section, the sample was then activated in air at 400 degrees Centigrade for two and one-half hours as in the section on activation.

Fifty milliliter samples of methylene blue (0.01 grams per liter) were used. The pH was adjusted with small portions of hydrochloric acid or sodium hydroxide. The amounts of acid or base added were small enough that no significant change in concentration was noted. The fifty milliliter samples were treated with one gram of perlite and agitated for thirty minutes at 25 degrees Centigrade. The final pH was then measured using a Beckman pH meter; all readings were taken at 25 degrees Centigrade. The final concentration of the solution was measured on the spectrophotometer.

TABLE XII

<u>Initial pH</u>	<u>Final pH</u>	<u>Final Concentration grams per liter</u>	<u>Methylene Blue Adsorbed grams per liter</u>
3.2	3.6	4.8×10^{-3}	5.2×10^{-3}
4.62	6.8	3.2×10^{-3}	6.8×10^{-3}
6.9	7.5	2.6×10^{-3}	7.4×10^{-3}
8.9	8.0	2.4×10^{-3}	7.6×10^{-3}
11.05	10.72	2.1×10^{-3}	7.9×10^{-3}

As was expected the methylene blue was adsorbed to a greater extent in the more basic solutions. It should be noted that while the maximum adsorption occurs at the higher pH values the final concentration at pH 11 was 2.1×10^{-3} grams /l representing the sorption of 79% of the original color. The value of pH 7 was only 74% of the original concentration while that at pH 3 was 52% of the original, hence the biggest change was between pH 7 and pH 3 which was 27% as against a change of 5__ between pH 7 and pH 11. This seems to justify the use of a pH of 7 for the work in methylene blue.



COTTON BLUE ADSORPTION

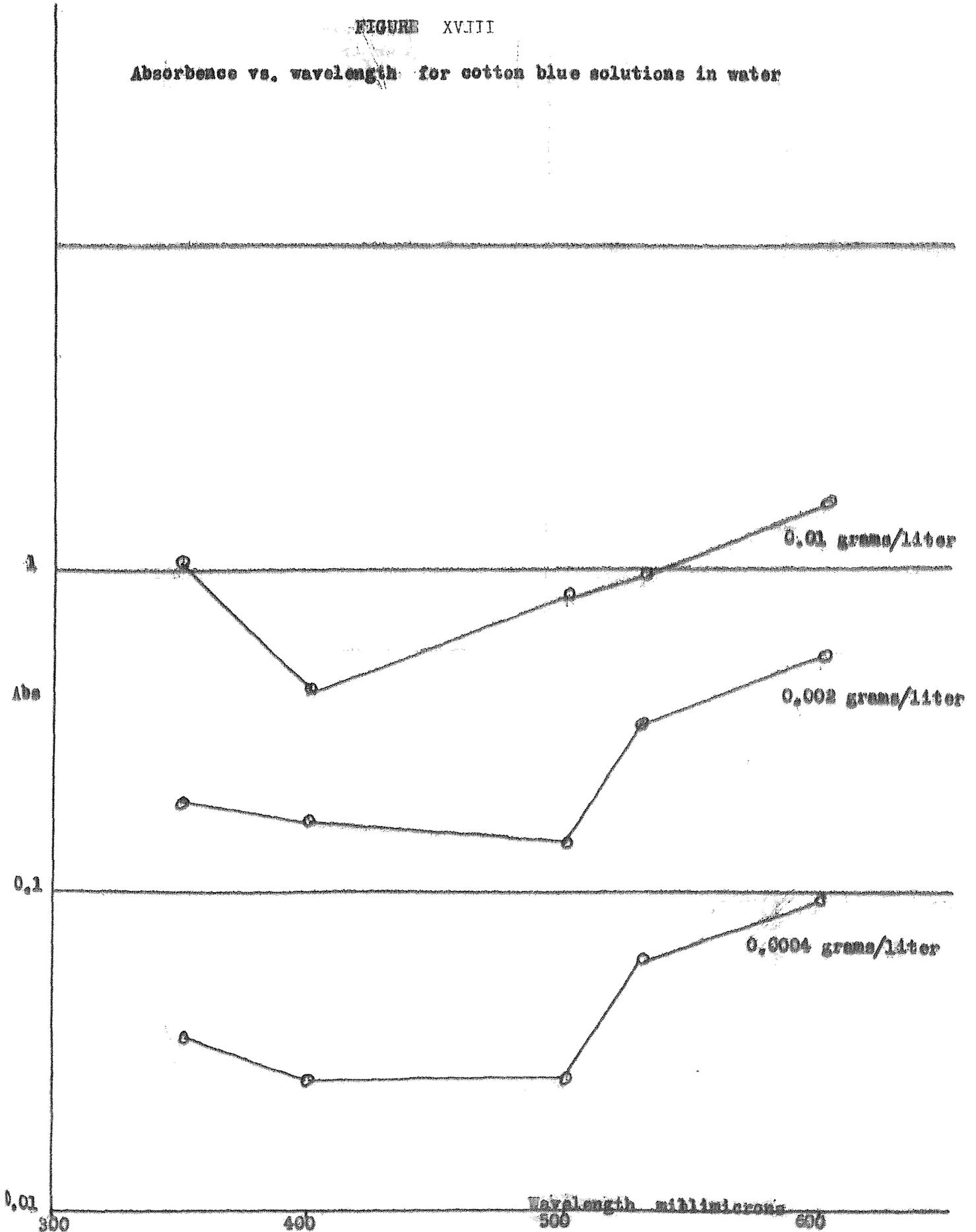
Adsorption measurements were made for the acid dye cotton blue on perlite. The concentrations of the solutions were measured using a Beckman Model B, Spectrophotometer. In calibrating this instrument three dye solutions were used, 0.01, 0.002, 0.0004 grams per liter. Absorbance measurements were made at 50 millimicron increments between 350 and 600 millimicrons. A maximum was found at 530 millimicrons (Figure XVIII). A calibration curve of absorbance versus concentration was then made at this wavelength for five dye concentrations (Figure XIX).

The procedure for the adsorption studies was as follows; to 50 milliliters portions of dye solution (Concentrations 0.01, 0.002, 0.0001 and 0.0004 grams per liter) 500 ~~g~~ mg 1 milligram portions of activated perlite were added. The solutions were agitated at 3 minute intervals for one hour at 25 degrees Centigrade. The perlite was then filtered from the dye solution and the concentration measured using the spectrophotometer. The dye solutions were maintained at pH 7. Four perlites were studied, as received, 400 degree Centigrade air baked, hydrogen peroxide boiled, and perlite heated at low pressures. The activation treatments given these samples is discussed in the section on activation. For each perlite studied three samples were tested at each of the concentrations shown above.

None of the samples studied showed a measurable adsorption. There seems to be some similarity here with certain charcoals which will adsorb dye but not acid dyes. (See section on activation and pretreatment.) However, in this case, an activation treatment was not found which would produce a perlite which would adsorb an acid dye.

FIGURE XVIII

Absorbance vs. wavelength for cotton blue solutions in water



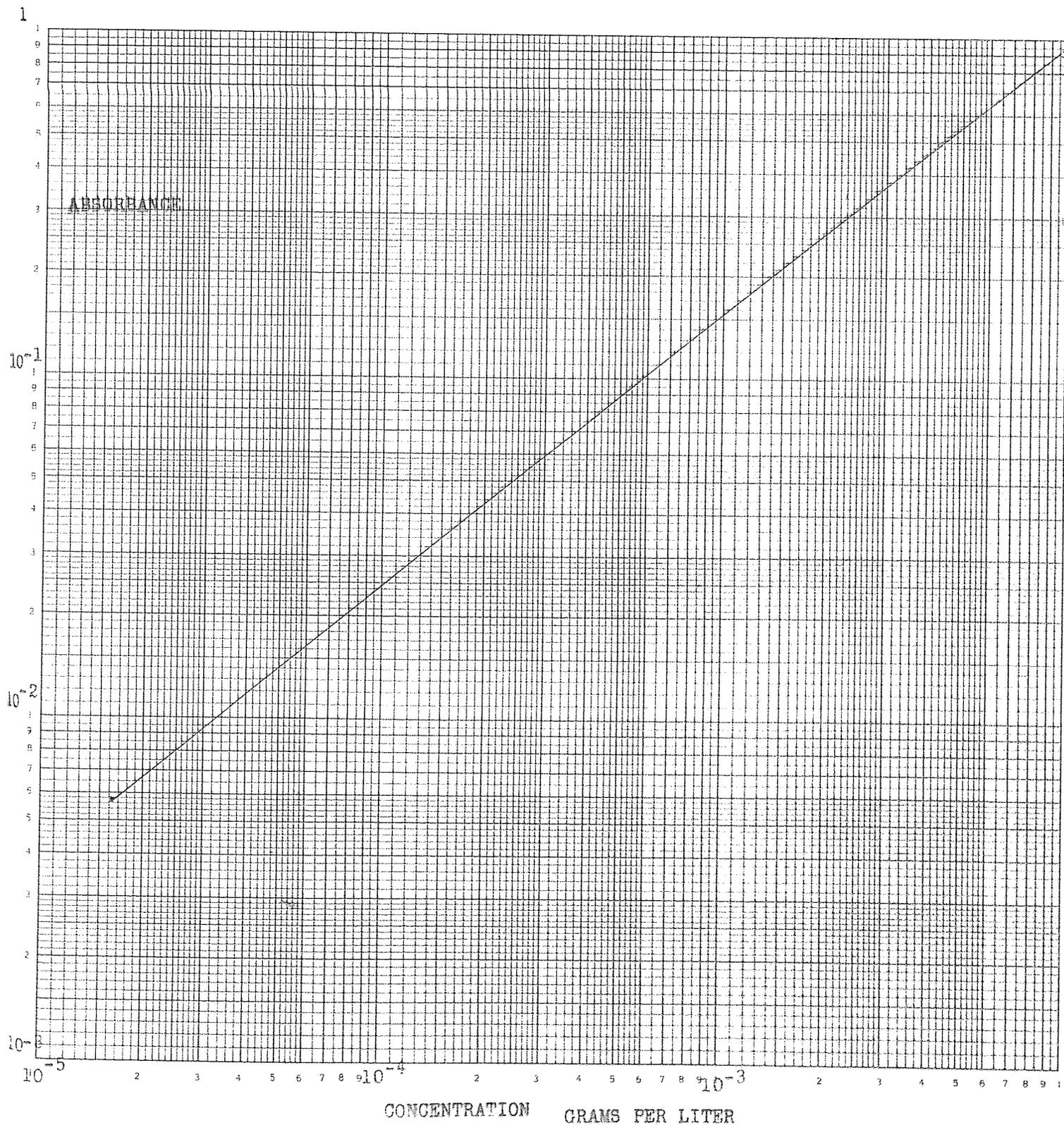


FIGURE XIX

CALIBRATION CURVE FOR MOTTION BLUE AT 25°C.. BECKMAN MODEL B SPECTROPHOTOMETER
ONE CENTIMETER CELLS.

IODINE IN METHYL ALCOHOL

In the case of adsorption of iodine from methyl alcohol solutions a spectrophotometric method of analysis was used employing a Beckman B, Spectrophotometer. Three solutions were used to calibrate the apparatus, 0.3675, 0.0734, 0.00734 grams per liter of I_2 . Absorbance measurements were taken for these samples between 3500 and 7500 Angstroms. The resulting plot (Figure XX) shows a maximum of 450 millimicrons. A plot of absorbance versus concentration was then made (Figure XXI) from this data.

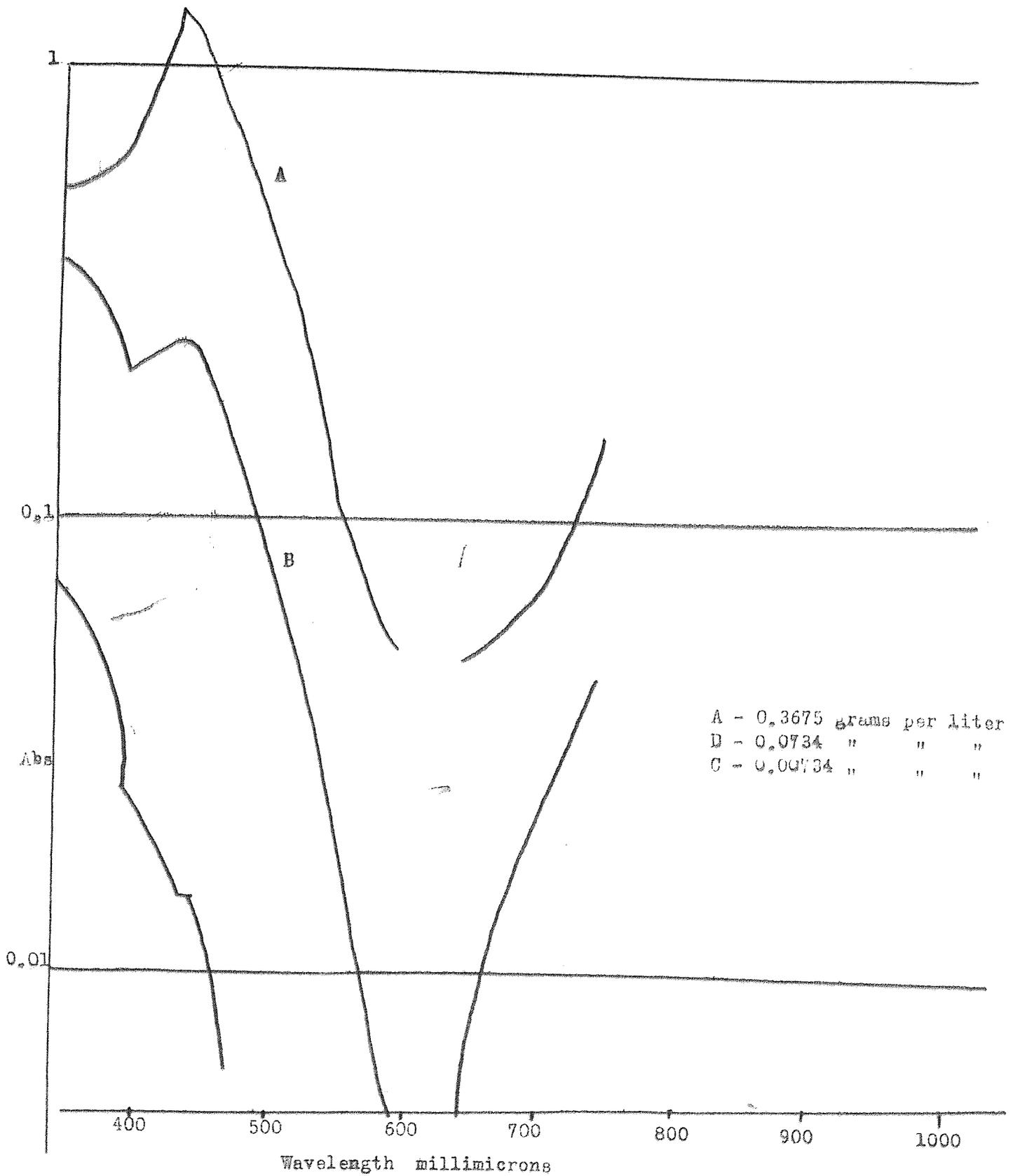
Adsorption was measured by placing 0.5 gram samples of perlite in 20 cc samples of the iodine solution. The solution was agitated every three minutes during the test. The temperature of the solution was 25 degrees Centigrade. After one hour the samples were filtered using a small funnel with a small wad of glass wool in the stem. The concentration of the filtered solution was then measured on the spectrophotometer and discarded. No attempt was made to control pH.

A crude rate determination was made using three 0.365 grams per liter samples and measuring the concentration at 0.5, 1.0 and 2.0 hours. There was a slight change in concentration between 0.5 and 1.0 hours but none between 1.0 and 2.0 hours so the adsorption may be considered to be essentially complete after one hour.

In the study of adsorption from methyl alcohol solutions two types of perlite were used, the first was oxidized in air at 400 degrees Centigrade and the second was used in the as received condition. As can be seen from the data and the adsorption isotherms the amount

FIGURE XX

Absorbance vs. wavelength for three solutions of iodine in methyl alcohol



adsorbed was rather small. A surprising development was that the perlite in the as received condition seemed to adsorb slightly more iodine than the oxidized samples.

TABLE XIII
ADSORPTION OF IODINE FROM METHYL ALCOHOL SOLUTIONS

PERLITE IN AS RECEIVED CONDITION

<u>Gi</u> <u>Grams</u> <u>Liter</u>	<u>Cf</u> <u>Grams</u> <u>Liter</u>	<u>Milliliters</u> <u>Solution</u>	<u>Grams</u> <u>Perlite</u>	$\frac{x}{m}$ <u>Grams (10⁻⁶)</u> <u>Gram Perlite</u>
.38	.34	20	0.5	16
.0734	.070	20	0.5	1.26
.017	.0065	20	0.5	4.8
.38	.35	20	0.5	12
.0734	.07	20	0.5	7.26
.017	.013	20	0.5	1.6
.38	.35	20	0.5	12
.0734	.072	20	0.5	6
.017	-	20	0.5	-

***** **

average

.38	1	13.3
.0734		4.84
.017		2.9

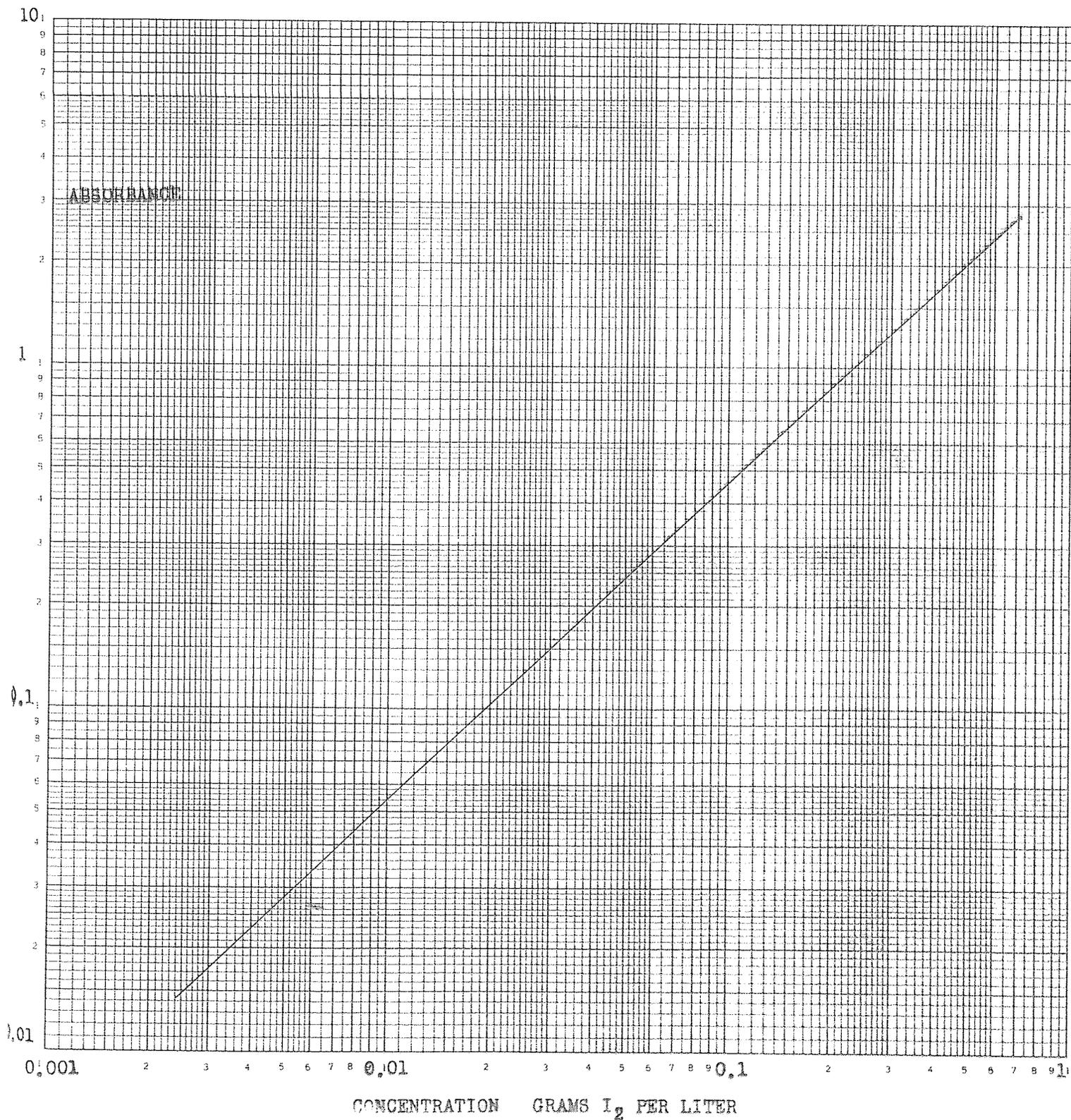


FIGURE XXI
CALIBRATION OF IODINE IN METHYL ALCOHOL, BECKMAN MODEL B SPECTROPHOTOMETER
ONE CENTIMETER CELLS.

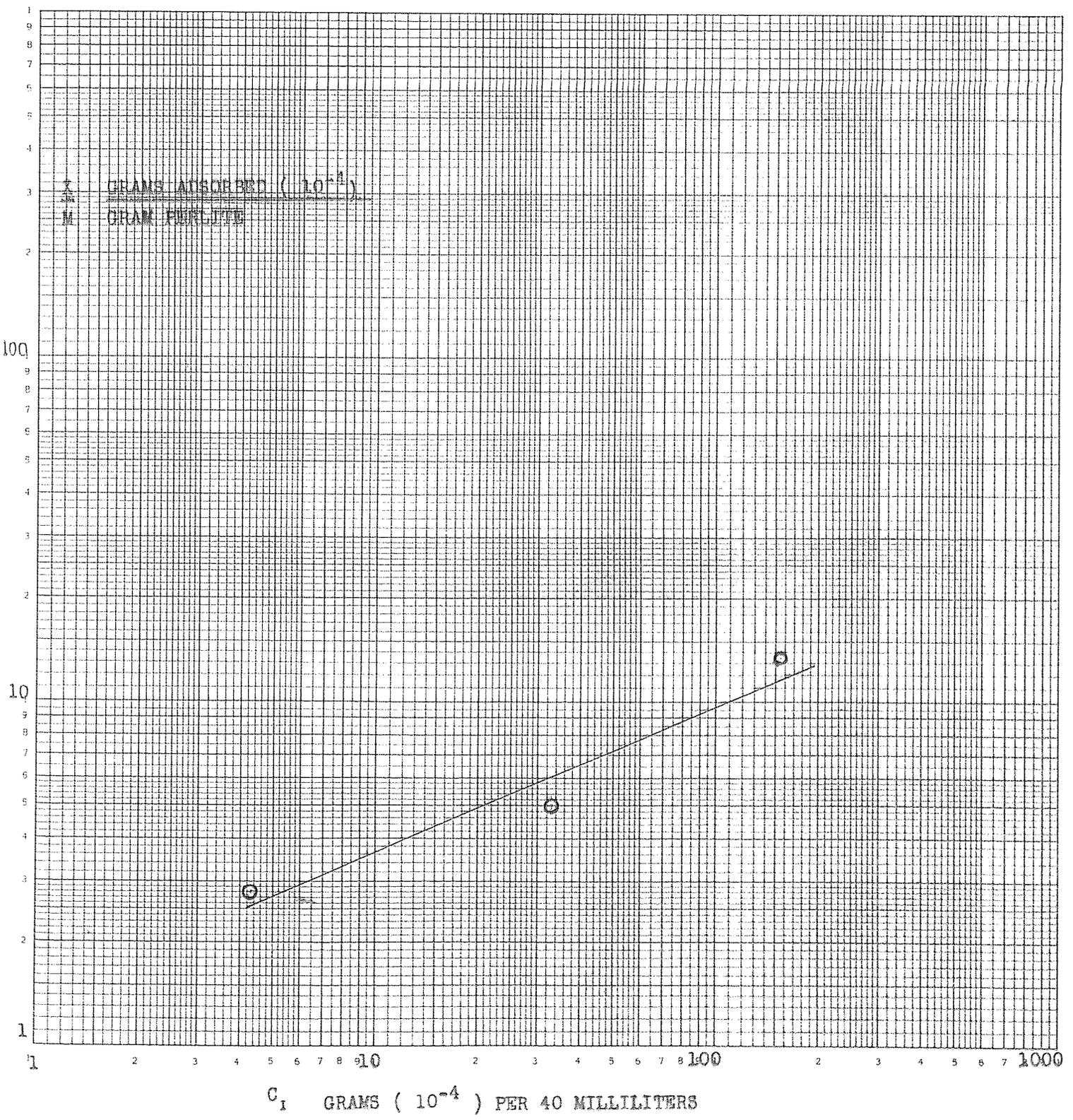


FIGURE XXIII
ADSORPTION OF IODINE FROM METHYL ALCOHOL SOLUTIONS BY PERLITE IN THE AS RECEIVED
CONDITION.

TABLE XIV
ADSORPTION OF IODINE FROM METHYL ALCOHOL SOLUTIONS
400° C OXIDIZED PERLITE

<u>Ci</u> <u>Grams</u> <u>Liter</u>	<u>Cf</u> <u>Grams</u> <u>Liter</u>	<u>Milliliters</u> <u>Solution</u>	<u>Grams</u> <u>Perlite</u>	<u>x/m</u> <u>Grams (10⁻⁶)</u> <u>Gram Perlite</u>
.38	.34	20	0.5	16
.0734	.070	20	0.5	1.26
.017	.0065	20	0.5	4.2
.38	.35	20	0.5	12
.0734	.07	20	0.5	7.26
.017	.013	20	0.5	1.6
.38	.35	20	0.5	12
.0734	.072	20	0.5	6
.017	-	20	0.5	-

average

.38	1	13.3
.0734		4.84
.017		2.9

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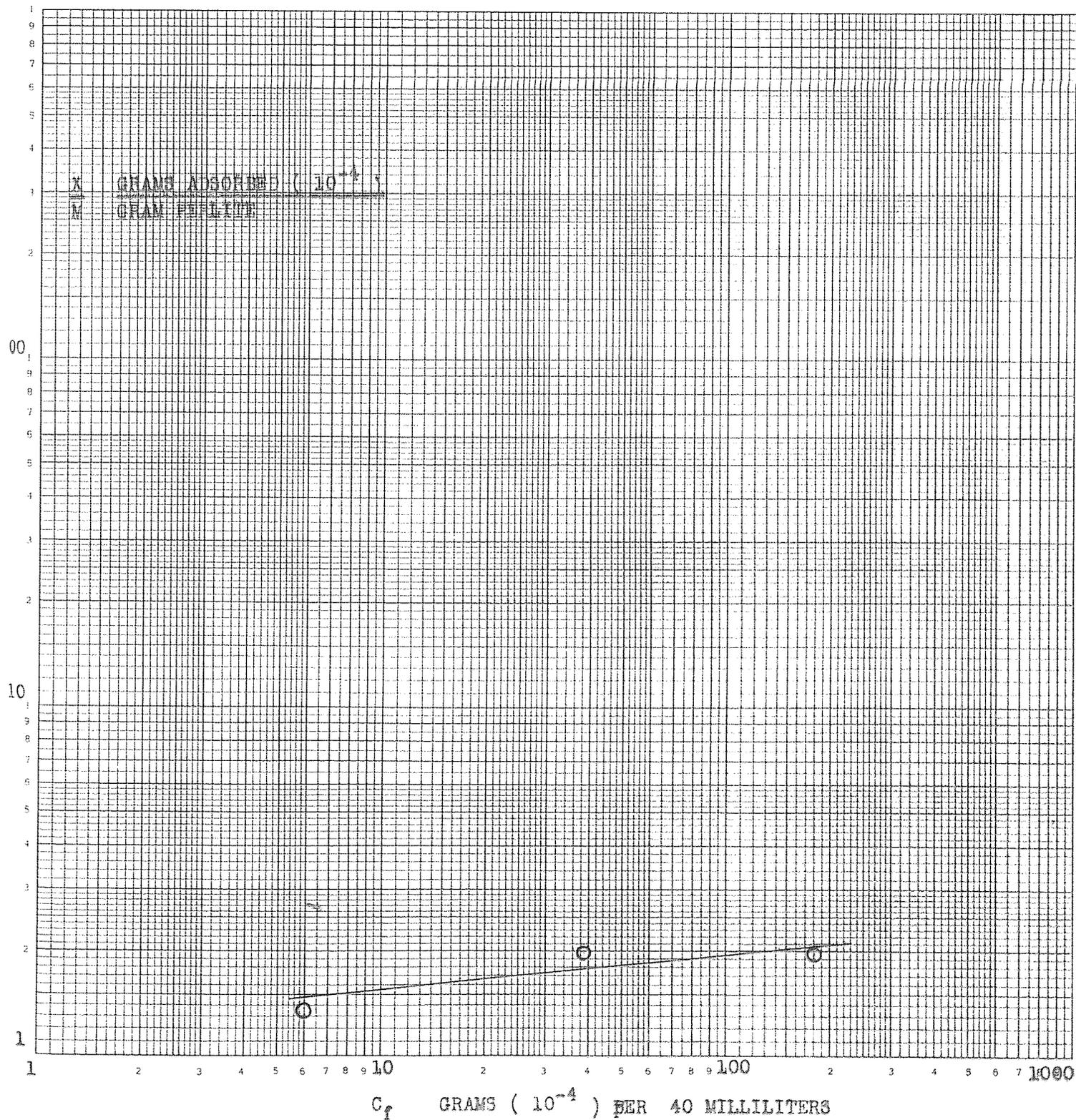


FIGURE XXIV.
 ADSORPTION OF IODINE FROM METHYL ALCOHOL BY PERLITE OXIDIZED IN AIR AT 400°C .

IODINE FROM AQUEOUS IODINE PLUS POTASSIUM IODIDE SOLUTION

Adsorption measurements were also carried out on aqueous solutions of iodine plus potassium iodide. The concentrations of solutions were obtained by standard analytical techniques. The perlite used was activated in air at 400 degrees Centigrade for 24 hours.

In this case, as in that of adsorption from methyl alcohol solutions, the amount adsorbed was so small in relation to the initial concentration of the solution that the experimental error in the analysis is of the same order of magnitude as the values for x/m . (See Table XIII). But, it seems safe to assume that some adsorption did occur and from the shape of the isotherms this adsorption was physical rather than chemical.

The effect of pH on the adsorption of iodine from aqueous solution of potassium iodide plus iodine was also studied. Two 50 milliliter portions of the solution were prepared, each contained 127 milligrams of iodine per 100 milliliters of solution. To the first was added 10 milliliters of 10 percent hydrochloric acid, while the second was not so treated. In each case the amount of iodine adsorbed per gram of oxidized perlite was 1.3 milligrams. This test was run at 25 degrees Centigrade, for one hour with sufficient agitation.

TABLE XV

ADSORPTION OF I₂ FROM I₂ - KI SOLUTIONS (OXIDIZED)

PERLITE HEATED IN VACUUM

Ci Milligrams I ₂ 100 Milliliters	Cf Milligrams I ₂ 100 Milliliters	x/m Milligrams I ₂ Gram Perlite	Milliliters Solution	Grams Perlite
144	144	0	100	1.0
92.7	91.5	1.2	100	1.0
14.55	14.01	9.54	100	1.0
9.15	9.00	0.15	100	1.0
8.15	7.90	0.25	100	1.0
127	-	1.295	50	1.0 (no acid added)
127	-	1.300	50	1.0 (10 cc of 10% HCL added)

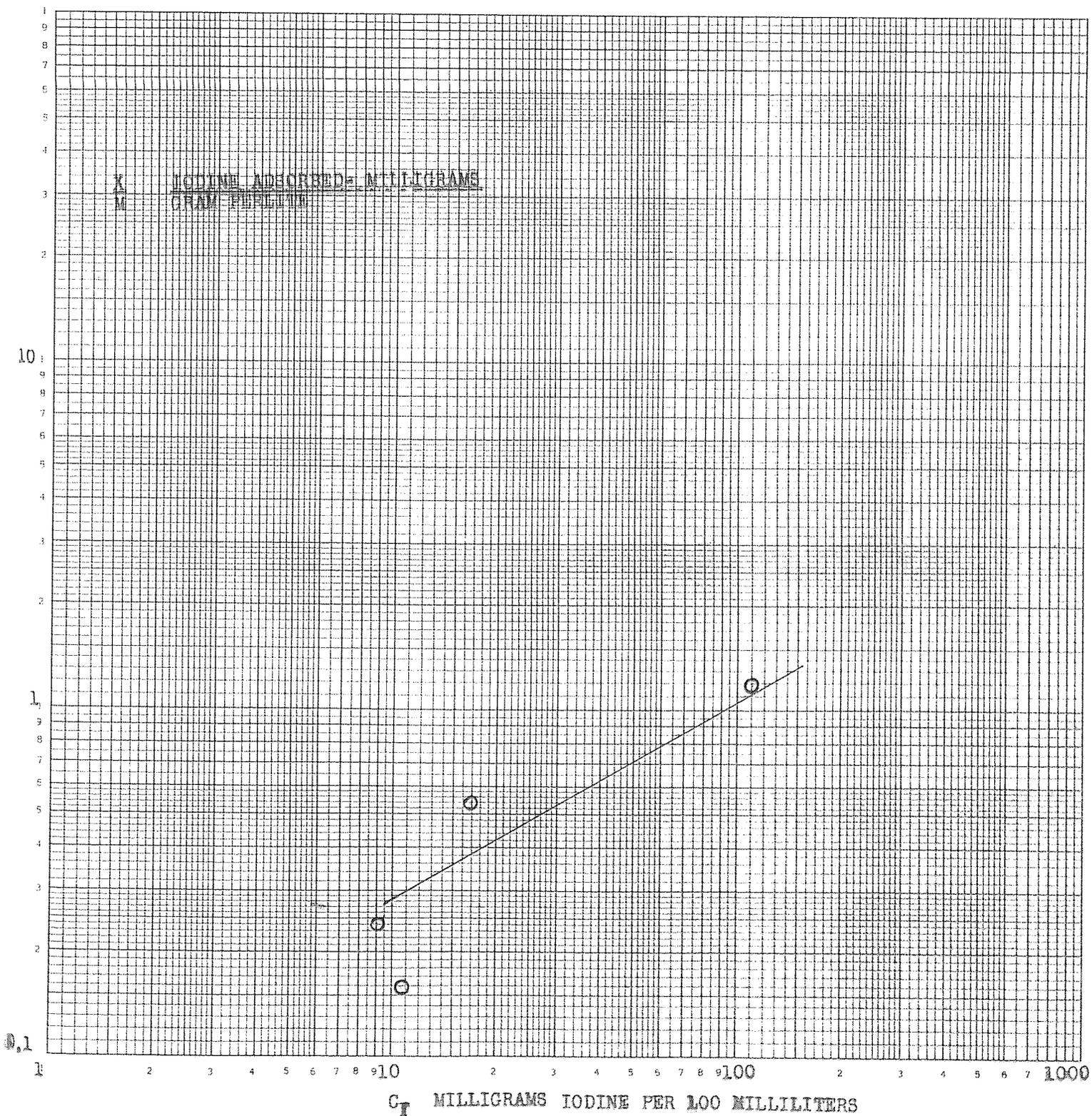


FIGURE XXII
 ADSORPTION OF IODINE FROM IODINE AND POTASSIUM IODIDE SOLUTIONS BY PERLITE HEATED
 IN VACUUM.

ADSORPTION OF ACETIC ACID

The adsorption of acetic acid by perlite was studied. In this study 100 milliliter portions of the acid were treated with 500 milligram lots of perlite oxidized at 400 degrees Centigrade in air for 24 hours. The temperature of the solution was 25 degrees Centigrade. Each sample was agitated every three minutes for one hour. The perlite was then filtered out and the acid titrated. The concentration of acetic acid in the various solutions was found by titration with a standard sodium hydroxide solution. The adsorption seems rather low, as may be seen by the table below. Each reading is the average of three samples at a particular concentration.

TABLE XVI

<u>Solution No.</u>	<u>Initial concentration grams acetic acid for 100 cc</u>	<u>x/m grams acetic acid removed per gram perlite</u>
A.	2.76	.0082
B	1.38	.0104
C	0.69	0
D	0.345	.0064
E	0.173	.0014

There seems to be a scattering of the data here and actually a better analytical method should have been used. But since the values of x/m were so small it was decided that the determination of the exact amount of acetic acid adsorbed would not add greatly to our knowledge. However, one receives the impression on examining the data that a maximum is reached at an equilibrium concentration of about 1.4 grams acetic acid per 100 cubic centimeters of solutions, the value of x/m at this point is approximately 0.01 grams acetic acid per gram perlite. Values of

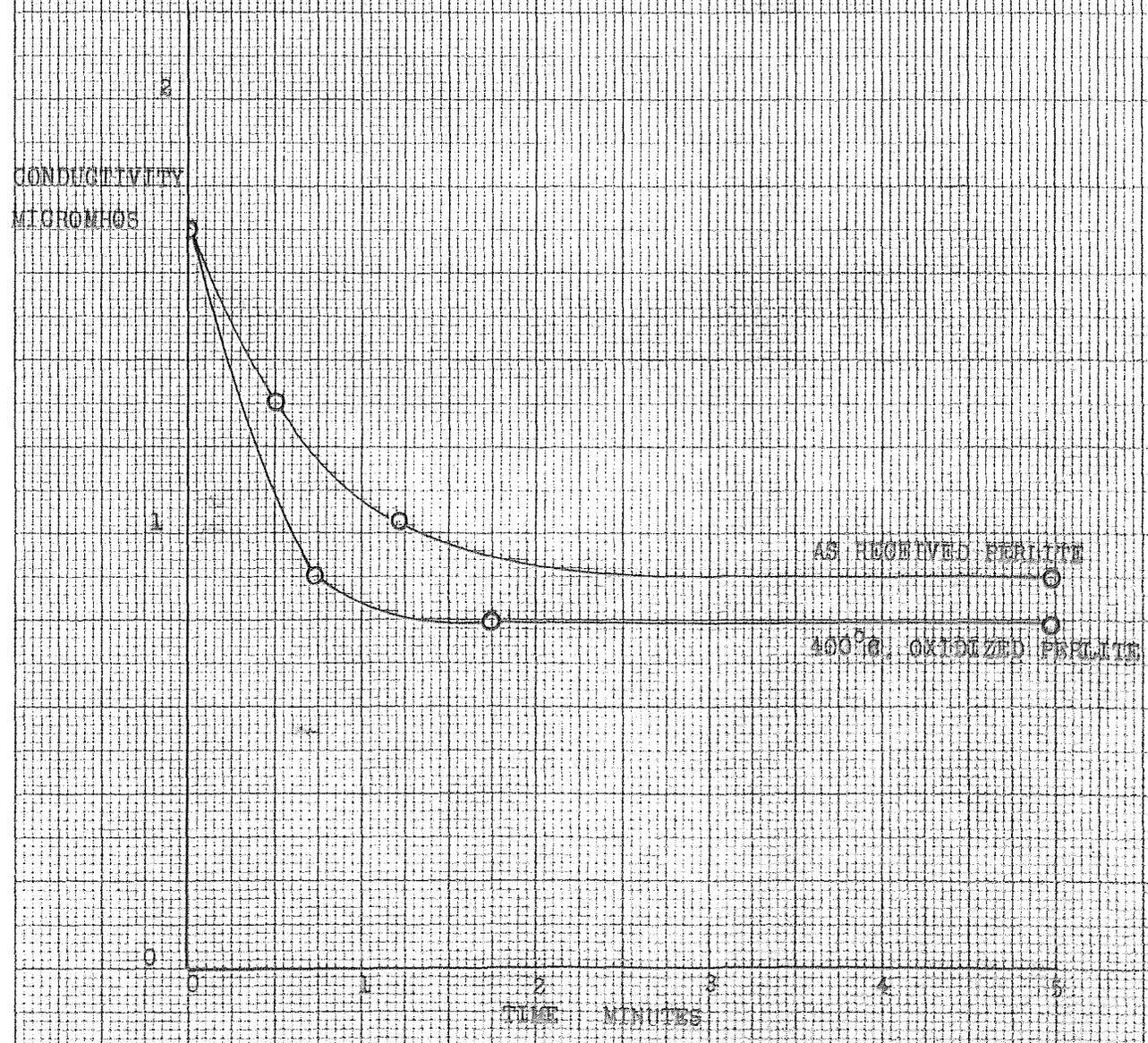
x/m of 0.24 grams/gram have been reported for animal charcoal (19) and 0.9 grams/gram on sugar charcoal (20).

A rate determination was made for the adsorption of acetic acid from a 0.0862 grams per liter solution by perlite in the as received condition, and perlite treated in air at 400 degrees Centigrade for one hour.

A conductivity cell was introduced into a beaker containing 100 milliliters of the acid, and a conductivity measurement was made. One gram of perlite was added and the solution stirred vigorously. Conductivity measurements were made at frequent intervals until equilibrium had been reached. The runs were made at 25 degrees Centigrade.

Examination of Figure XXV suggests that equilibrium is reached in approximately two minutes.

FIGURE XXV
RATE OF ADSORPTION OF ACETIC ACID ON PERLITE



SURFACE AREA

Several conclusions may be drawn as to the surface area of perlite. Information from the Perlite Institute has been received to the effect that 1.25 cubic centimeters of nitrogen are adsorbed per gram of perlite. A fairly simple calculation leads one to believe that the specific surface of perlite is 5.47×10^4 centimeters squared per gram.

This calculation based on information received from the Perlite Institute shows that perlite has a surface area far below that of other more common adsorbents listed below:

TABLE XVII

<u>Adsorbent</u>	<u>Surface area per gram-cm²</u>	<u>How Measured</u>	<u>Reference</u>
zinc oxide	8.8×10^4	N ₂ adsorption	21
zinc oxide	7.3×10^4	gas permeability	21
Titanium dioxide	1.4×10^4	heat of wetting	22
Acetylene black	6.4×10^5	N ₂ adsorption	21
Activated charcoal	7.7×10^6	N ₂ adsorption	23
Sugar Charcoal	6.6×10^6	heat of wetting	24
Silica gel.	4.1×10^6	heat conductivity	25
Cotton	2.2×10^6	gas adsorption	26

An approximation of the surface area may be made using the method of Paneth and Radu (27). They computed the effective area of a methylene blue molecule assuming it to be a cube. This area was $54A^2$

per molecule. By assuming a saturation value of 5×10^{-4} grams of methylene blue per gram of perlite in the preceding section, we may calculate a specific surface area of $4.78 \times 10^3 \text{ cm}^2$ per gram of perlite. This figure is approximately one order of magnitude lower than that obtained by nitrogen adsorption. One item is of interest, however. Paneth and Radu measured the surface area of sugar charcoal by this method and found that their values were in error by 97 percent, while on perlite the error was about 91%.

Using the method reported by Smith and Hurley (28) where the area occupied by an acetic acid molecule is assumed to be 20.5 square Angstroms, a specific area of 20.5×10^4 may be calculated using the data reported in a previous section. This figure is approximately four times that reported by the Perlite Institute.

CONCLUSIONS

An evaluation of perlite as an adsorbent has been made. Several conclusions may be drawn from the data.

Oxidation at 400 degrees Centigrade appears to be the optimum activation treatment of those treatments which were evaluated. Heat treatment in inert or reducing atmospheres or in vacuum were not promising. Attempts to clean the surface or to increase the surface area by chemical treatments were also not effectual.

The adsorption of methylene blue from aqueous solutions was studied. It was found that perlite oxidized at 400 degrees Centigrade was the most effective activation for adsorption of this material. It was also disclosed that regardless of the method of activation the surface of the perlite seems to be saturated on adsorption of 40 to 50 milligrams of the dye per gram of adsorbent.

The adsorption of acetic acid from aqueous solutions showed that a maximum adsorption of 15 millimoles of acid per gram of adsorbent was the best that could be achieved.

The study of the adsorption of the acid dye cotton blue from aqueous solutions showed that adsorption if any was extremely low for perlite activated in several ways.

Iodine was adsorbed from both aqueous and methyl alcohol solutions. A maximum value of 1.33 milligrams of iodine per gram of perlite was achieved in alcohol. With aqueous solutions adsorption was approximately one milligram of iodine per gram of perlite.

The surface area of perlite was calculated an area of $4.78 \times 10^{+3}$ CM^2 per gram is reported for methylene blue adsorption. This is about one order of magnitude below the area reported by the Perlite Institute.

It is the considered opinion of the author that the material perlite will be of little use as an adsorbent unless some method can be found to increase its surface area.

COMPARISON OF ADSORPTIVE POWER OF
PERLITE AND ACTIVATED CARBON

<u>Material Adsorbed</u>	<u>Equilibrium Concentration</u>	<u>Carbon π/m</u>	<u>Perlite π/m</u>
Methylene Blue	.032 gm/l	0.268 gm/gm	0.6×10^{-5} gm/gm
I ₂ (Aqueous Soln.)	.127 g/l	0.65 gm/gm	0.4×10^{-5} gm/gm
Acetic Acid	30 gm/l	1.8 gm/gm	0.82×10^{-2} gm/gm

The above table gives a brief comparison of the adsorptive powers of perlite and activated charcoal. It should be obvious from this data that the adsorptive capacity of perlite is several orders of magnitude below that of carbon.

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