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A study of methods for the purification and the removal of color from trinitrotoluene wash waters

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A STUDY OF METHODS FOR THE PURIFICATION AND THE REMOVAL OF COLOR FROM TRINITROTOLUENE WASH WATERS

BY

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A

THESIS

Submitted to the faculty of the

UNIVERSITY OF MISSOURI SCHOOL OF MINES AND METALLURGY

in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

Rolla, Missouri

1943

Approved by W. T. Schrenk.
Chairman of the Department of Chemical Engineering

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W. W.

Rolla, Missouri
May, 1943

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INTRODUCTION

Symmetrical trinitrotoluene is stable in the presence of moisture, but the nonsymmetrical trinitrotoluenes permit replacement of a nitro group with the formation of a nitrated cresol and nitrous acid[1]. Nitrated cresols form salts similar to the picrates. To avoid these nonsymmetrical trinitrotoluenes the Ordinance Department, U. S. A., requires that Grade I trinitrotoluene have a solidification point of at least 80.2°C.[2].

Numerous methods for purifying the crude trinitrotoluene and others for separating the nitrotoluenes have been suggested. The alpha trinitrotoluene may be separated by selective solution of the others and nitro derivatives in 180 proof alcohol[3], hot 100% sulfuric acid[4], carbon tetrachloride and alcohol[5], and dilute solutions of sodium sulfite[6]. The separation of the mononitrotoluenes is accomplished by distillation at reduced pressure followed by

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[1] Whitmore, Frank C. Organic chemistry. New York, D. Van Nostrand Co., Inc., 1937. p.734.

[2] Furman, N. H. (ed.) Scott's standard methods of analysis. 5th ed. New York., D. Van Nostrand Co., Inc., 1939. v II, p. 1681.

[3] Smith, G. Carlton. T N T, trinitrotoluenes and mono- and dinitrotoluenes their manufacture and properties. New York, D. Van Nostrand Co., Inc., 1918. pp. 53-54.

[4] Ibid. pp. 54-55.

[5] Ibid. pp. 55-56.

[6] Davis, Tenney L. The chemistry of powder and explosives. New York, John Wiley & Sons, Inc., 1941. v I, p. 145.

fractional crystallization[7].

The only satisfactory method known for producing Grade I trinitrotoluene is the sodium sulfite rinse. In this process, the crude trinitrotoluene is rinsed several times with boiling water and then with a five per cent solution of sodium sulfite[8] and followed by dilute acid rinses until the acid[9] washings are colorless.

The boiling water rinse has a definite yellow color and probably contains small amounts of many of the trinitrotoluenes, dinitrotoluenes, nitrated xylenes, trinitrobenzene, inorganic salts, sulfuric acid, and nitric acid and its reduction products.

The sodium sulfite treatment produces a deep red water probably containing an addition product of sodium sulfite and toluene[10], the majority of the nonsymmetrical trinitrotoluenes as dintrotoluene sodium sulfonates[11], an addition product with trinitrobenzene[12], oxidation products contained in crude trinitrotoluenes[13], the sodium sulfonate of trinitromethane[14], and lead salts[15]. It is to be noted, that the sodium sulfite does not react with the dinitro derivatives

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[7] Groggins, P. H. (ed.) Unit processes in organic synthesis. New York, McGraw Hill Co., Inc., 1938. p. 47.
[8] Davis, op. cit., p. 145.
[9] Smith, op. cit., p. 56.
[10] Muraour, M. H. Action du sulfite de soude sur quelques dèrivès trinitrès et sur le tetraintrométhane. Purification de la tolite. Bull. Soc. Chim. v 35, p. 373 (1924).
[11] Ibid. pp. 370-371.
[12] Ibid. p. 373.
[13] Ibid. p. 373.
[14] Ibid. pp. 371-372.
[15] Ibid. p. 373.

of benzene and toluene[16], nor does it react with trinitrometaxylene[17].

The yellow and red waters are produced in a ratio of one to three, and their combination produces approximately eight and eight-tenths pounds of water per pound of purified trinitrotoluene[18]. This combined water is of orange color.

A typical analysis of this waste reported by Schott and Ruchhoft[19] is given in Table 1.

TABLE 1

Properties of the Waste Water

Suspended solids	.03 p.p.t.[20]
Total solids	1.70 p.p.t.
Ash	.89 p.p.t.
Acidity	1.70 p.p.t.
Sulphates	.61 p.p.t.
Nitrate nitrogen	.03 p.p.t.
Oxygen ($K_2Cr_2O_7$)	.12 p.p.t.
B. O. D. (5 day)	0.0

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[16] Ibid. p. 373.
[17] Ibid. p. 374.
[18] Erickson, A. Private Conference.
[19] Trinitrotoluene wastes. Chem. & Met. Eng. v 50, no. 4, pp. 180-181 (1943)
[20] p.p.t. shall be used throughout this thesis to mean parts per thousand parts of waste water assuming a density of 1 unless otherwise stated.

The combined water is the influent to the waste disposal section. After neutralization with a fifty per cent solution of sodium hydroxide[21], the combined water is fed to the first effect of the quadruple effect evaporators. The concentrated liquor which shall be called thick liquor is a very deep red colored solution which might be mistaken for black on a casual examination. This contains approximately 35% solids[21a].

This thick liquor is stored until enough is available to warrant starting the incinerator and burning the waste. The ash is later diluted with condensate from the evaporators and discharged into the stream.

The waste sulfuric acid containing the oxides of nitrogen is passed countercurrently through hot flue gases to recover these oxides as a dilute nitric acid. The waste sulfuric acid is a syrupy liquid of dark brown color and specific gravity 1.61, and it presents a disposal problem.

The origin of the waste waters and the sulfuric acid waste are shown in Figure 1 with a present method of disposal of the waters.

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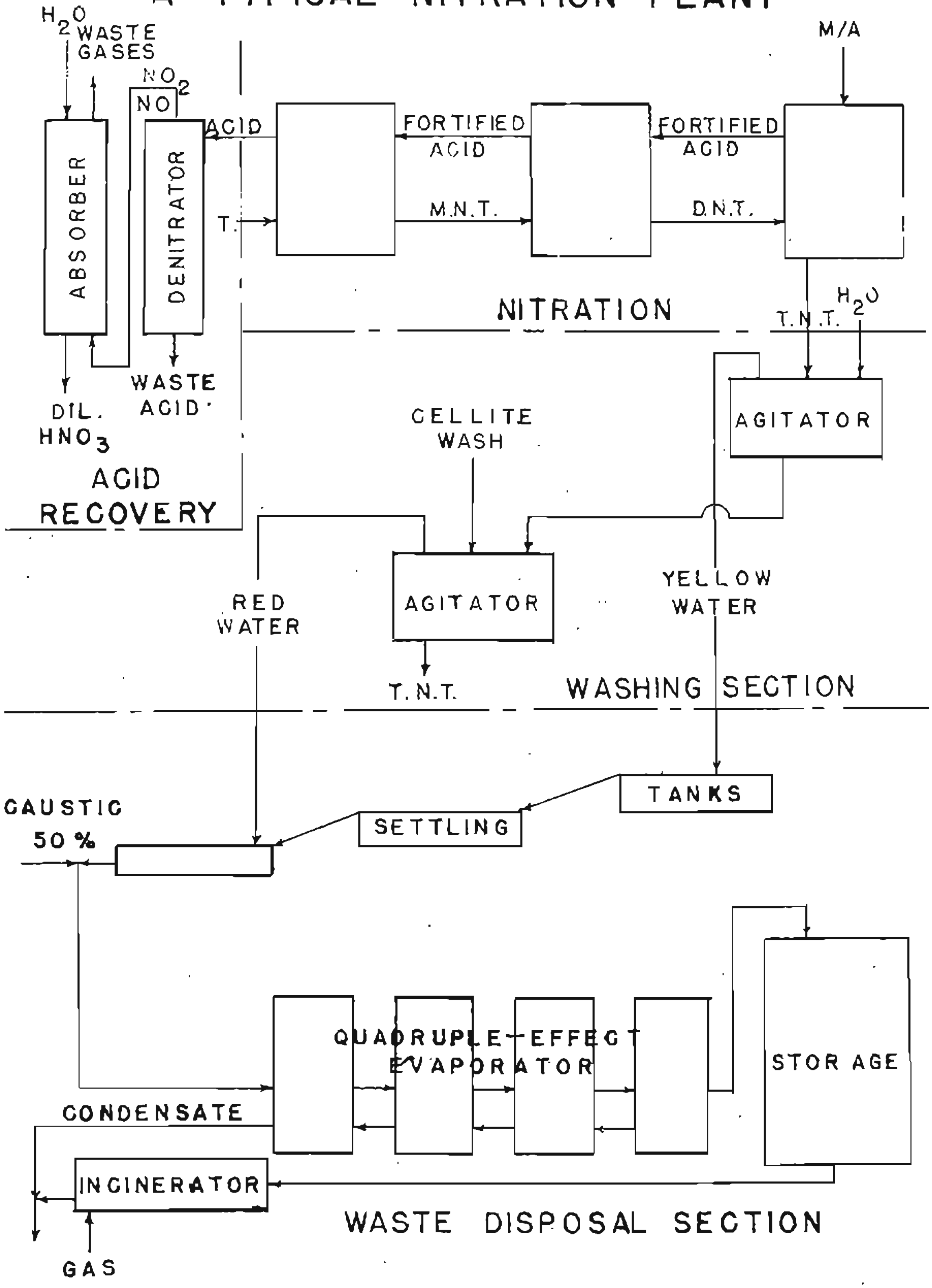
[21] Erickson, A. Private conference.
[21a] Ibid.

FIGURE 1
A TYPICAL NITRATION PLANT



The present method of disposing of the wash waters is an important part of the costs both in the original investment and operation. Evaporation is practiced only because no other satisfactory method of disposal is known.

Recovery of the dinitrotoluene sodium sulfonates in a more concentrated solution or as crystalline materials would permit the utilization of this nitro group nitrogen in the synthesis of N methylnitramine[22].

These are some of the reasons why this problem was selected as a research project.

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[22] Davis, op. cit., v I, p. 147

LITERATURE REVIEW

The literature pertaining to these wastes is well summarized in a recent article by F. W. Mohlman[23], Director of Laboratories for the Sanitary District of Chicago.

> ".....The waste waters are of two main types, one the acid or yellow water, and the other alkaline or red water. These liquors are odorless and have no B. O. D., but both, particularly the red waste, have intense colors which persist into high dilution. All usual methods of treatment, such as chemical precipitation, biological treatment and adsorption by activated charcoal are unsuccessful, and only chlorination, evaporation, or dilution remain as possible methods of disposal. Chlorination greatly reduces the color of the acid mixtures, but chlorine is hard to get now, even for munition works. This leaves only evaporation or dilution.
>
> "Evaporation was and is an expensive process, costing several thousand dollars per day, and requiring critical equipment such as quadruple-effect evaporators and kiln dryers, in addition to large amounts of caustic soda. In spite of this, facilities for evaporation were being installed at all TNT plants, without reference to the dilution capacity of the stream. ....
>
> "Investigations showed that the required dilutions could be determined, with the various river waters into which wastes were discharged, beyond which there would be no harm to water supplies from color and taste. Other requirements, such as freedom from toxicity to fish and human beings and freedom from acidity could be obtained at considerable lower dilutions than those necessary to eliminate color, ...With flows lower than this minimum, wastes must be stored and later discharged at higher stream flows." [24]

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[23] Industrial waste disposal. Chem. & Met. Eng. v 50, no. 2, p. 127 (1943).
[24] Ibid. pp. 128-129.

THE DETERMINATION OF COLOR BY BEER'S LAW

The application of Beer's Law may be tested by use of the colorimeter. The concentrations are inversely proportional to the depth of the liquids compared. The validity of this must be established for each system.

A Duboscq type colorimeter was used for all color determinations. Samples of the combined water were diluted to correspond to various percentages of the original water. The samples were compared with the water as received and the per cent calculated by Beer's Law.

Three series of these diluted samples were prepared; the first was prepared using boiled distilled water, the second was diluted with distilled water adjusted to a pH of 1.60 with nitric acid, and the third, with distilled water adjusted to a pH of 1.60 with sulfuric acid.

The results of these three series are tabulated in Tables 2, 3, and 4 and are graphically represented in Figures 2, 3, and 4.

TABLE 2

Comparison with Beer's Law of Samples without pH Adjustment

Per cent by dilution	Per cent by Beer's Law	pH
100.0	100	1.60
90.0	100	1.68
80.0	86	1.75
70.0	72	1.80
60.0	67	1.83
50.0	54	1.88
40.0	47	1.99
30.0	38	2.05
20.0	25	2.21
10.0	13	2.46
5.0	8	2.80
0.0	0	7.00

FIGURE 2

BEER'S LAW IN SOLUTIONS WITH VARYING PH

DATA FROM TABLE 2

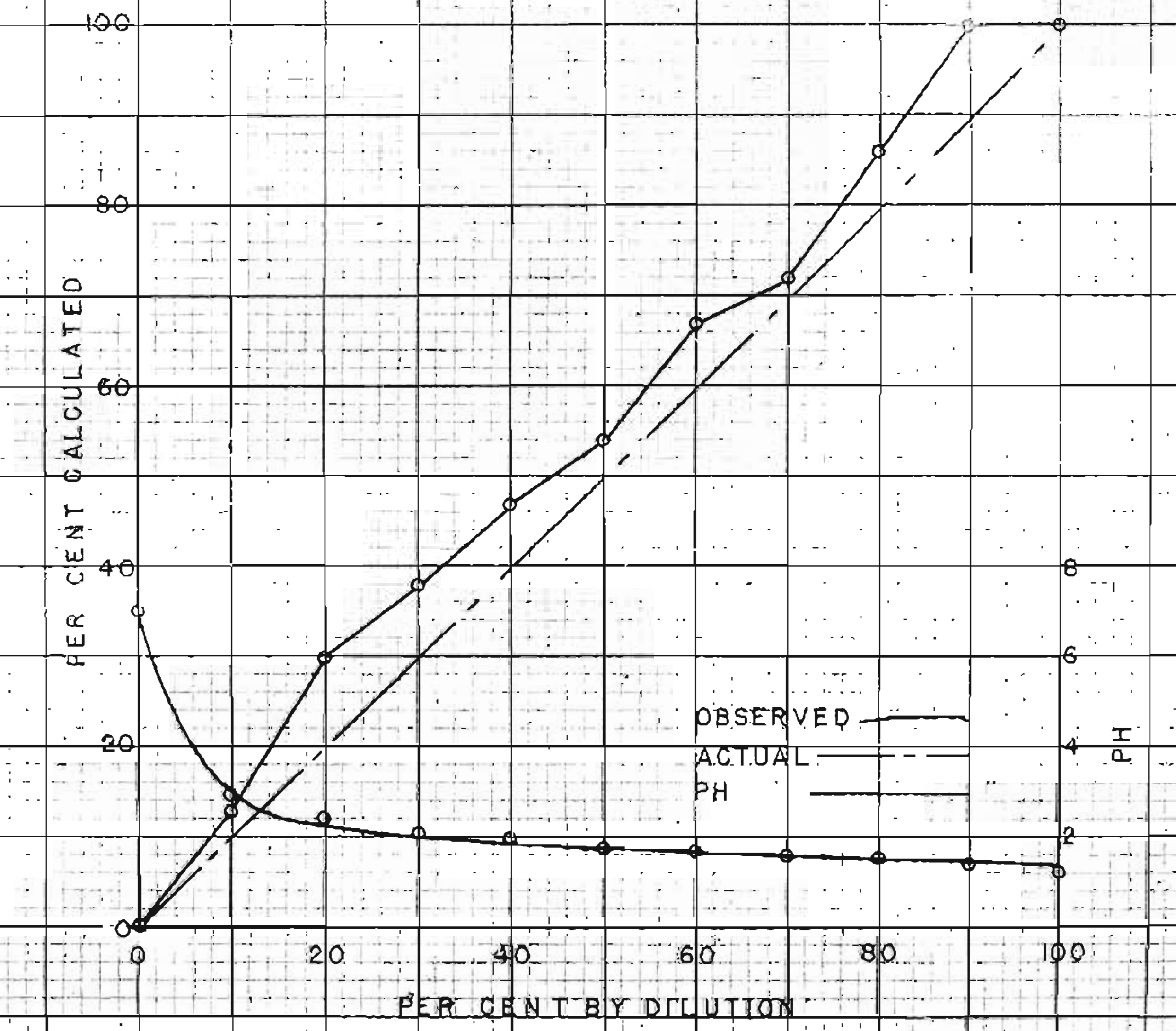


TABLE 3

Comparison with Beer's Law of Samples with pH Adjusted by Nitric Acid

Per cent by dilution	Per cent by Beer's Law	pH
100.0	100	1.60
90.0	85	
80.0	74	
70.0	66	1.57
60.0	60	
50.0	49	1.55
40.0	39	
30.0	28	1.58
20.0	18	
10.0	9	1.65
5.0	5	
1.0	1	1.55
0.0	0	1.60

FIGURE 3

BEER'S LAW IN SOLUTIONS OF FIXED PH BY NITRIC ACID — DATA FROM TABLE 3

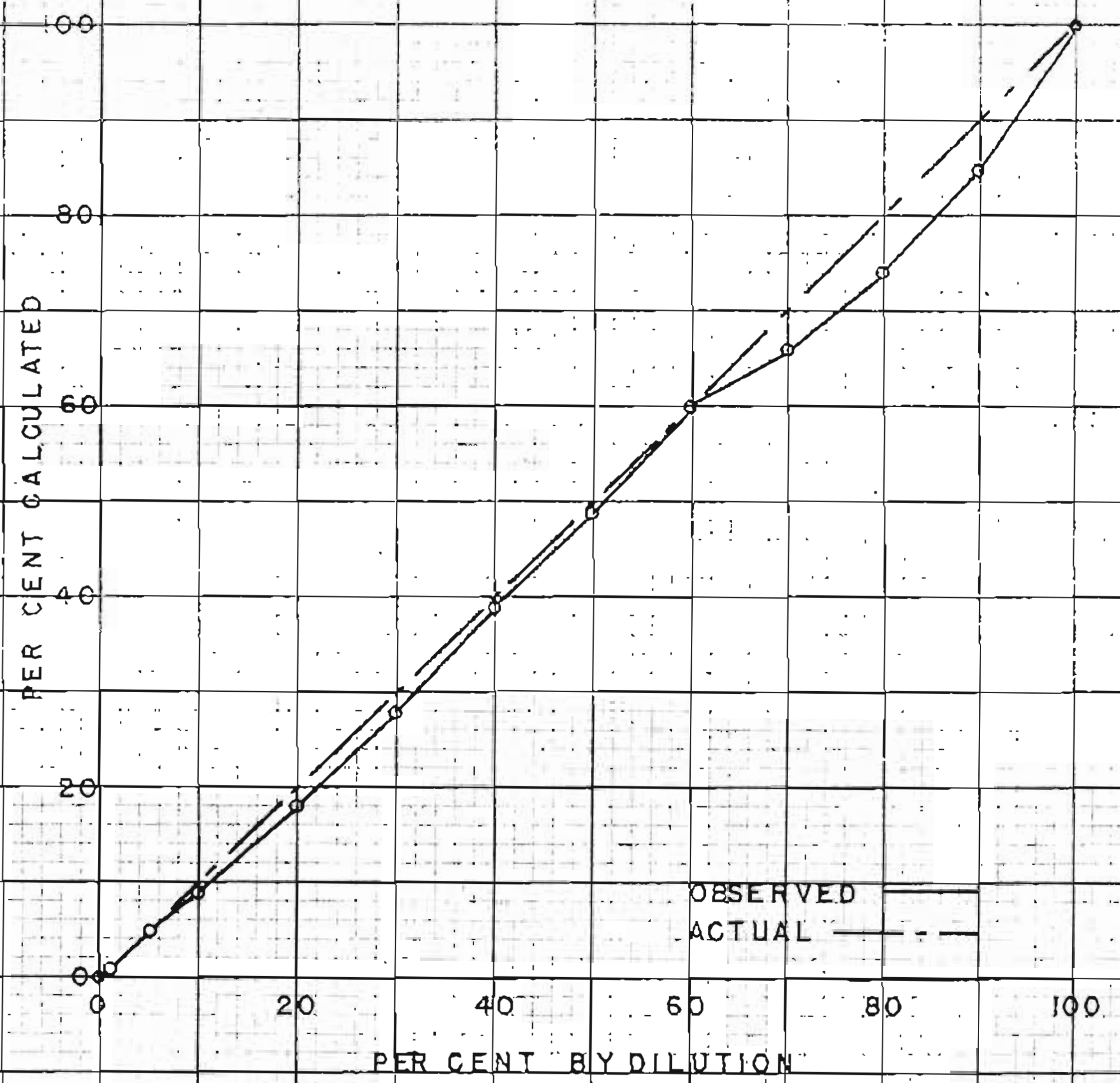


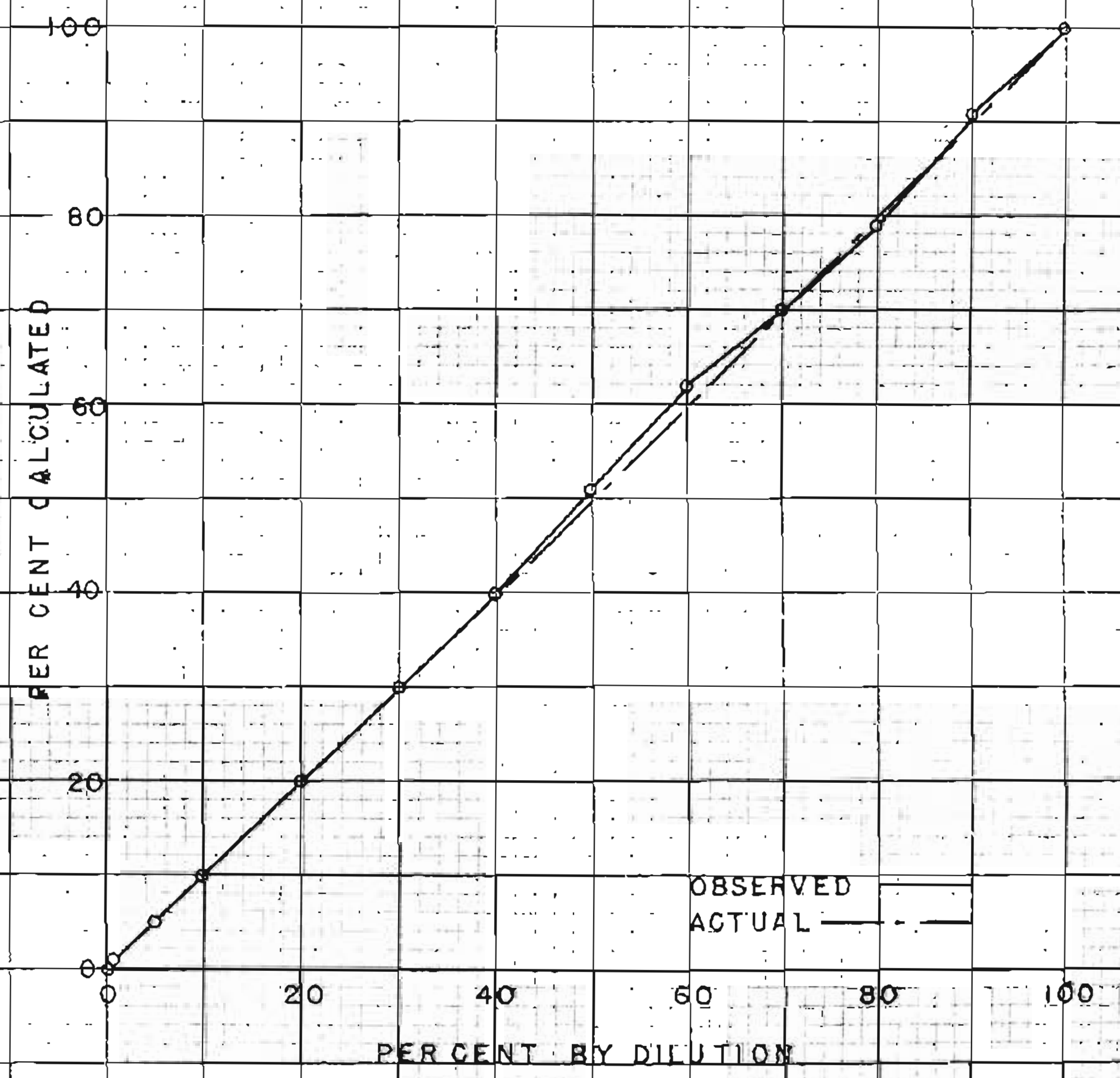
TABLE 4

Comparison with Beer's Law of Samples with pH Adjusted by Sulfuric Acid

Per cent by dilution	Per cent by Beer's Law	pH
100.0	100	1.62
90.0	91	1.62
80.0	79	1.62
70.0	70	1.64
60.0	62	1.62
50.0	51	1.63
40.0	40	1.62
30.0	30	1.62
20.0	20	1.63
10.0	10	1.63
5.0	5	1.65
1.0	1	1.65
0.5	0	1.62
0.0	0	1.63

FIGURE 4

BEER'S LAW IN SOLUTIONS OF FIXED PH BY SULFURIC ACID — DATA FROM TABLE 4



Results calculated using Beer's Law are highly inaccurate unless the pH of the solution is kept constant. This results from the dissolved compounds acting as indicators. Samples diluted with a nitric acid solution of pH 1.60 show greater deviations than do those diluted with a sulfuric acid solution of the same pH.

The errors resulting from small variations in the pH were desired, and the following series of experiments were run to determine the errors. Samples were diluted with a sulfuric acid solution (pH 1.60) and divided into two portions. One 20 ml portion was treated with 10 drops of 1:3 sulfuric acid, and the other portion with 10 drops of 1:10 ammonia solution (Sp. G. 0.90). The drops were approximately 1/50 of a milliliter and should not have caused a volume error in excess of one per cent.

It was concluded that these deviations were of such magnitude that they might be neglected without serious effect on the results.

The results are tabulated in Table 5 and graphically represented in Figure 5.

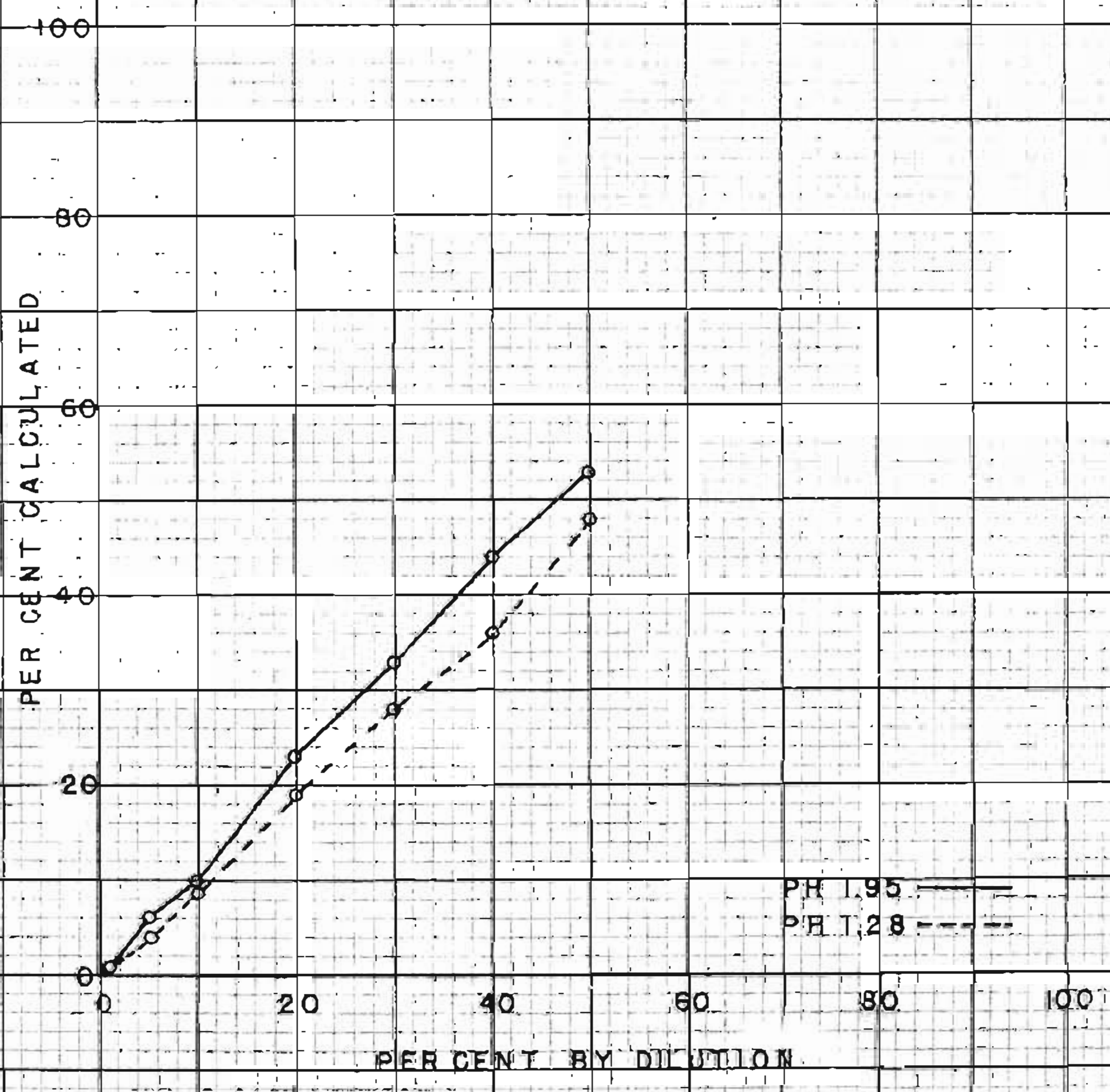
TABLE 5

Comparison with Beer's Law of Samples with Small Changes in pH

Per cent by dilution	Per cent by Beer's Law	pH
50.0	53	1.95
	48	1.28
40.0	44	1.95
	36	1.28
30.0	33	1.95
	28	1.28
20.0	23	1.95
	19	1.28
10.0	10	1.95
	9	1.28
5.0	6	1.95
	4	1.28
1.0	1	1.95
	1	1.28

FIGURE 5

EFFECT OF SMALL VARIATIONS IN PH ON THE APPLICATION OF BEER'S LAW FROM DATA IN TABLE 5



THE PH DETERMINATION

A Model 3F Coleman pH meter equipped with a glass electrode was used for all pH determinations.

As dry cell batteries of the original capacities were not available, radio batteries of equal voltages were substituted. No tendency for the standard cell adjustment to change more than 0.02 pH units was noted. This was checked several times during every series of readings.

The correction for temperature and asymmetrical potential was made with the buffer (pH 4.1) furnished for standardization. Readings are given to hundredths of a pH unit only for uniformity in the tables.

REAGENTS AND MATERIALS

Potassium Permanganate

A solution, containing 0.025 grams per milliliter of Mallinckrodt's Analytical Reagent Grade Potassium Permanganate, was prepared by direct weighing.

Sulfuric Acid

Unless otherwise specifically stated, all references to sulfuric acid shall be understood as the reagent grade of specific gravity 1.84 and containing 93.19 per cent sulfuric acid (Oil of Vitriol).

Activated Charcoals

The activated charcoals used throughout the research are the commercial varieties offered for sale by the various manufacturers.

The activated charcoals were screened to give an estimate of the surface area.

Standard Tyler Screens were used and the samples were sieved in the "Ro-Tap" for ten minutes. The samples used were 25 grams.

These results are tabulated in Tables 6 and 7 as per cent retained on each screen being calculated on total recovered.

TABLE 6

Screen Analyses of the Activated Charcoals

	Plus		Screen Sizes				Minus
No.	32	42	65	100	150	200	200
			Per Cent Retained				
1	0.0	0.0	0.6	1.0	3.0	7.6	87.5
2	0.0	0.0	0.0	0.0	0.8	17.2	82.0
3	0.4	0.3	0.6	1.3	4.0	16.8	76.5
4	0.0	0.0	0.0	0.0	0.0	8.4	91.6
5	0.0	0.1	7.3	11.8	14.8	16.2	49.0
6	0.0	0.0	0.1	2.6	8.2	13.6	74.5
7	0.1	0.1	2.7	5.2	9.4	13.0	69.4
8	1.6	2.8	11.1	12.0	14.2	12.3	46.0
9	0.0	0.0	0.0	0.1	5.0	11.0	83.0
10	0.0	0.0	1.1	1.9	3.1	4.9	89.0
11	0.1	0.1	3.6	3.6	7.6	13.5	71.5
12	42.3	10.3	35.5	9.6	0.9	0.8	0.7
13	0.0	0.0	0.0	1.0	3.1	7.4	88.5
14	0.0	0.1	1.4	1.4	2.0	3.3	92.0
15	0.0	0.0	0.9	3.9	12.7	27.0	55.4

KEY

1	Harsaw Cliff Char
2	Dow's Cliffchar Fine
3	Dow's Cliffchar Coarse
4	Burrell Cocoanut Pulverized
5	Mallinckrodt Decolorizing Carbon
6	Nuchar C-190 N
7	Nuchar 000
8	Nuchar #2
9	Nuchar C-115 N
10	Darco G-60
11	Darco S-51
12	Dicalite Kyrite
13	Dicalite M-23
14	Daigger's Bone Charcoal
15	Daigger's Decolorizing Carbon

TABLE 7

Screen Analyses of the Activated Charcoals

	Screen Sizes						
No.	6	8	12	20	28	32	42
	Per Cent Retained						
1	0.0	0.0	26.8	52.0	17.8	1.1	2.1(1)
2	35.2	49.8	13.0	7.0	1.0		
3	0.0	13.7	58.5	27.7	0.0		
4	3.0	47.3	41.4	8.2	0.0		
5	19.4	36.4	39.7	0.8	0.4	3.2	

KEY

1	Dow's Cliffchar 10x30
2	Dow's Cliffchar 4x10
3	Burrell Cocoanut 6-14
4	Burrell Activated Charcoal 6-14
5	Sargent Carbon Super Silcher

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(1) The last figure represents minus the previous screen, i.e., 2.1% is -32.

PRELIMINARY EXPERIMENTS

Insoluble Salts of the Colored Compounds

An insoluble double decomposition product resulting from the colored compounds and an inorganic salt was sought. The following salts were used: aluminum nitrate, ammonium nitrate, antiomony sulfate, barium chloride[25], bismuth sulfate, cadmium nitrate, calcium nitrate, chromic nitrate, chromous acetate, cobaltous nitrate, cupric acetate, ferric chloride, ferrous ammonium sulfate, lead nitrate, lithium chloride, magnesium chloride, manganous sulfate, mercuric chloride, mercurous nitrate, nickelous chloride, sodium chloride, stannic chloride, stannous chloride, strontium chloride, and zinc acetate. No decrease in color was observed.

Absorption with Flocculent Precipitates

Aluminum sulfate, ferric sulfate, and sodium aluminate did not noticeably decrease the color when used as coagulants.

Adsorption with Activated Charcoal

Activated charcoals made by several different concerns were tested. Although the different activated charcoals did show differences in adsorptive capacity, they did not act selectively. All the results indicated this method as a possible one for removing the color.

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[25] Muraour, op. cit., p. 370, reports an insoluble barium salt.

Chemical Oxidation

Combined water samples resulting from a partial adsorption were easily decolorized on heating with bromine water or with prolonged potassium permanganate treatment. The use of potassium permanganate followed by charcoal did not compare favorably with the use of charcoal first. Combined water samples as received were not completely decolorized by potassium permanganate in acid solution or bromine water under the conditions of these tests.

Extraction of the Colored Compounds

Numerous organic liquids were tested as selective solvents for the colored compounds in combined water as received and acidified.

The acids, ethers, halides, ketones, hydrocarbons, and nitro substituted hydrocarbons showed no solvent properties. The alcohols and higher organic (iso) aliphatic esters showed solvent properties increasing with temperature and acidity of the water layer.

A continuous extraction of the type suggested by Marshall[26] was used for the complete extraction of yellow water and combined water acidified with waste acid.

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[26] Chem. News.. v 143, p. 235 (1931).

ACTIVATED CHARCOAL PROPERTIES

Procedure

Throughout the study of activated charcoals a uniform procedure was maintained as closely as possible. This procedure is given here and the minor variations shall be called to attention throughout the thesis. The activated charcoals were weighed with an accuracy of 0.2 milligram and transferred to beakers. Samples of 25 ml size were acidified with 7.5 parts per thousand of sulfuric acid and added to the activated charcoals. These samples were stirred until completely wetted. Time was taken as zero when they were placed on the sand bath. During the one hour on the sand bath the samples were stirred every fifteen minutes.

At the end of the test, the samples were immediately filtered. The final volume was recorded and each was diluted to its original volume with distilled water.

The pH was determined by the glass electrode and the sample compared colorimetrically with a prepared standard.

Effect of Time

The only changes in the procedure were the initial heating of the water samples to sand bath temperature and the stirring every five minutes during the first half hour.

Thirty minutes appears sufficient time for the adsorption. Additional adsorption is probably the result of evaporation.

The results of these tests are tabulated in Table 8 and graphically represented in Figure 6.

TABLE 8

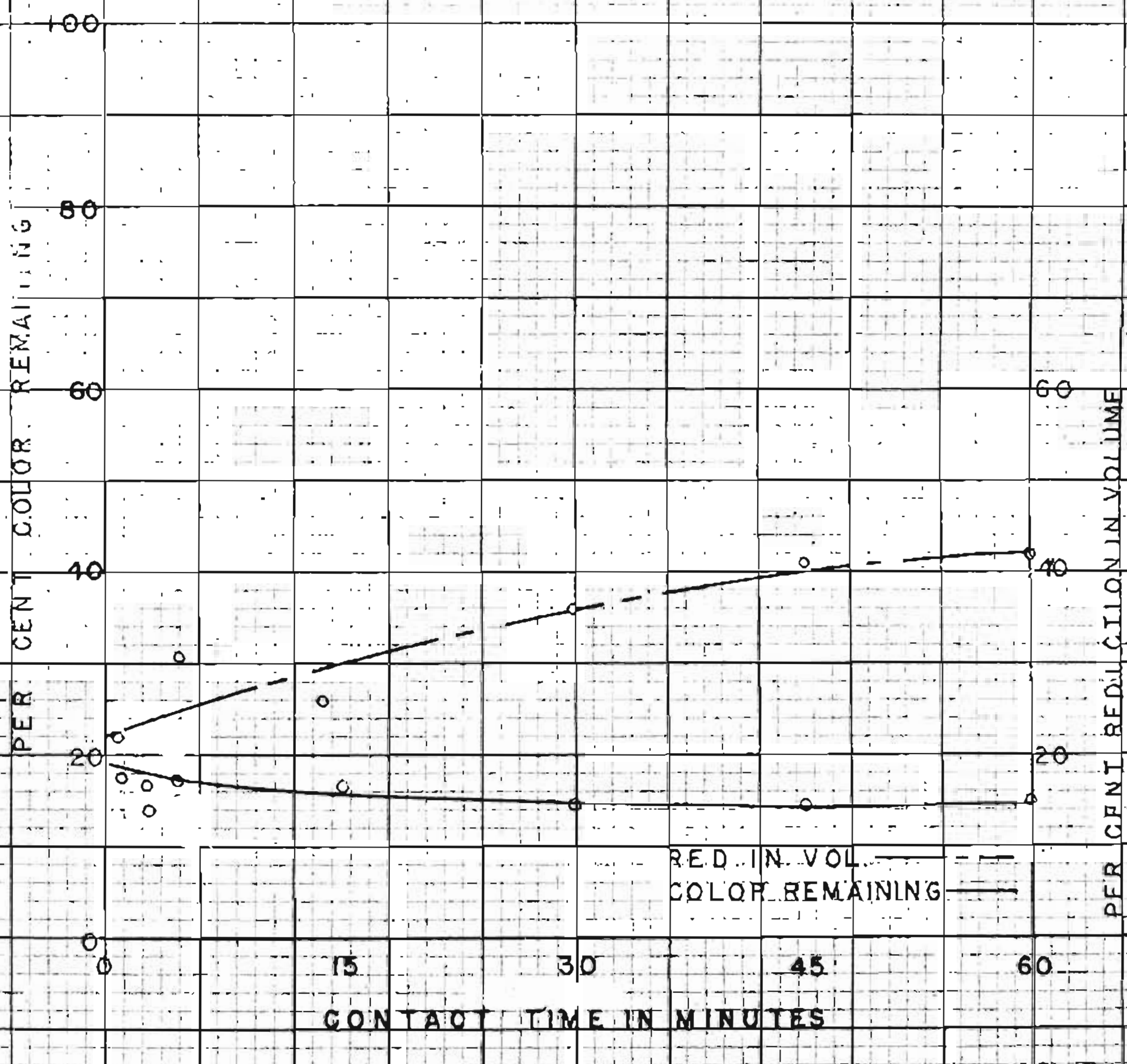
The Effect of Contact Time on Adsorption in Slightly Acidified Samples of Combined Water

Sample Number	Time	Per cent Reduction in Volume	Per cent Color	pH
1	1 min.	22	17.7	1.25
2	3 min.	14	16.6	1.35
3	5 min.	31	17.6	1.26
4	15 min.	26	16.7	1.32
5	30 min.	36	14.2	1.30
6	45 min.	41	14.5	1.25
7	60 min.	42	14.9	1.30

FIGURE 6

EFFECT OF CONTACT TIME ON ADSORPTION

DATA FROM TABLE 8



Effect of Temperature

One series of samples was treated at room temperature and a second series at sand bath temperature. The procedure agrees with the standard procedure.

The effect of temperature decreases with an increase of activated charcoal. The temperature, over the range investigated, aided adsorption, but these curves probably meet when an excess of charcoal is present.

The results of these tests are tabulated in Table 9 and graphically represented in Figure 7.

TABLE 9

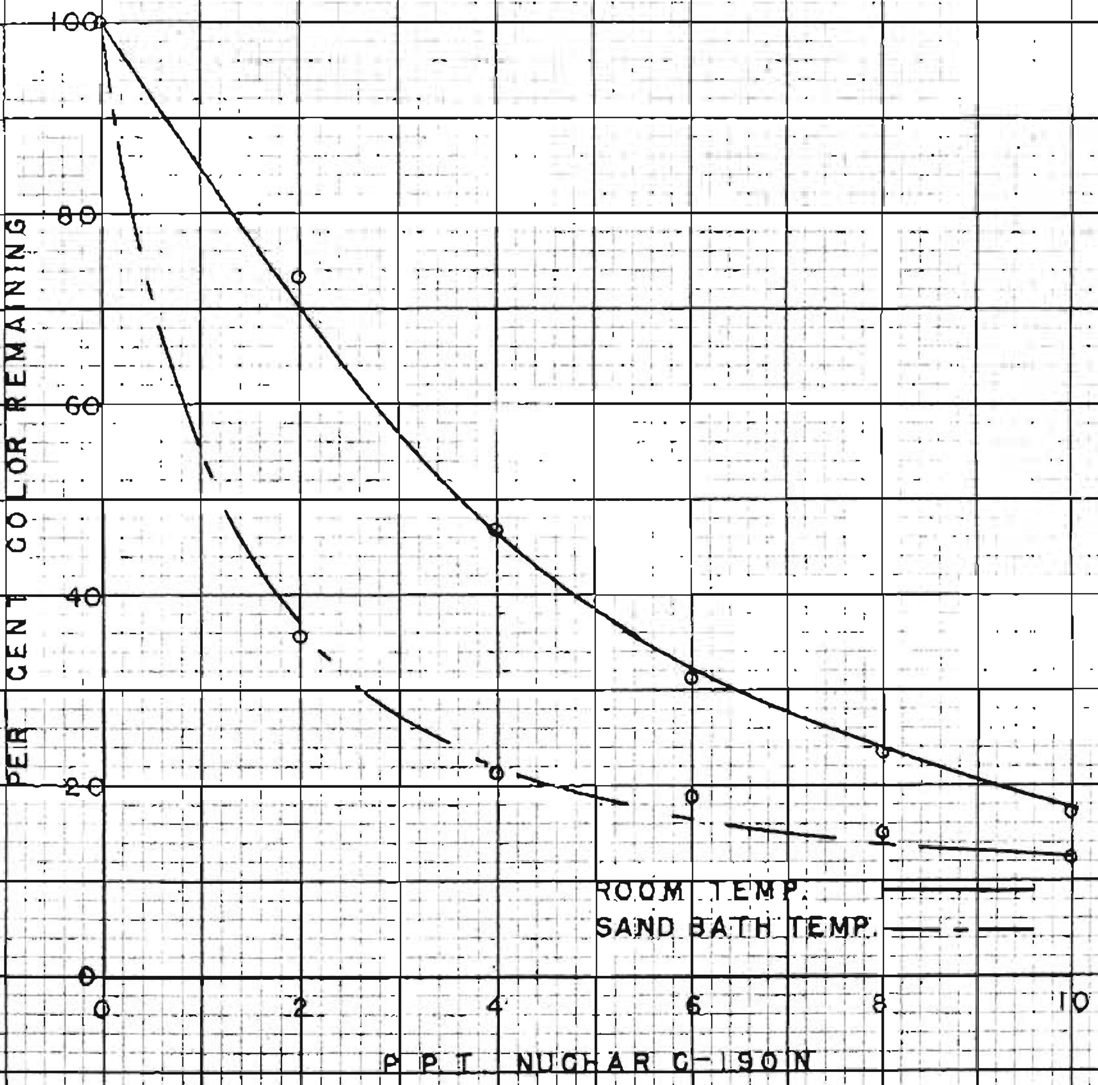
Effect of Temperature on Adsorption in Slightly Acidified Samples of Combined Water

Series Number	Temperature	Parts per Thousand of Nuchar C-190 N					
		2.	4.	6.	8.	10.	
1	Room	84.	88.	84.	82.	83.	F.V. %
		1.27	1.25	1.21	1.27	1.31	pH
		73.6	46.8	31.4	23.7	17.1	% Col.
2	Sand bath	81.	80.	81.	82.	82.	F.V. %
		1.11	1.09	1.06	1.23	1.28	pH
		35.7	21.6	18.8	15.2	12.5	% Col.

FIGURE 7

EFFECT OF TEMPERATURE ON ADSORPTION

DATA FROM TABLE 9



Effect of Agitation

One group consisting of two series was treated in all respects by the standard method. A second group was air stirred instead of hand stirred. The air was filtered through glass wool and each supply controlled by a screw clamp. One series from each was treated at sand bath temperature and the other series from each group at room temperature.

The air agitated samples show a general increase in adsorption. This increase is greater for the samples at room temperature than for the samples at sand bath temperature. Samples at the room temperature do not receive any agitation other than the periodic stirring; this stirring appears inadequate. Samples at the sand bath temperature are stirred by the bubbles during the treatment and the slight increase most likely results from the decrease in volume caused by evaporation. A slight temperature difference is to be expected as a result of the evaporation.

The results of these tests are tabulated in Table 10 and graphically represented in Figure 8.

TABLE 10

The Effect of Agitation on Adsorption in Slightly Acidified Samples of Combined Water Heated on the Sand Bath and at Room Temperature

Sand Bath

Series	Parts per Thousand of Nuchar C-190 N					
Number	4.	10.	20.	40.	60.	
3	61.	66.	55.	54.	49.	F.V. %
Air	1.30	1.24	1.38	1.45	1.52	pH
Agitated	22.2	11.0	6.0	1.2	Colorless	% Col.
					80. p.p.t.	
4	80.	82.	62.	57.	46.	F.V. %
Hand	1.09	1.28	1.32	1.38	1.55	pH
Stirred	21.6	12.5	7.3	1.1	Colorless	% Col.

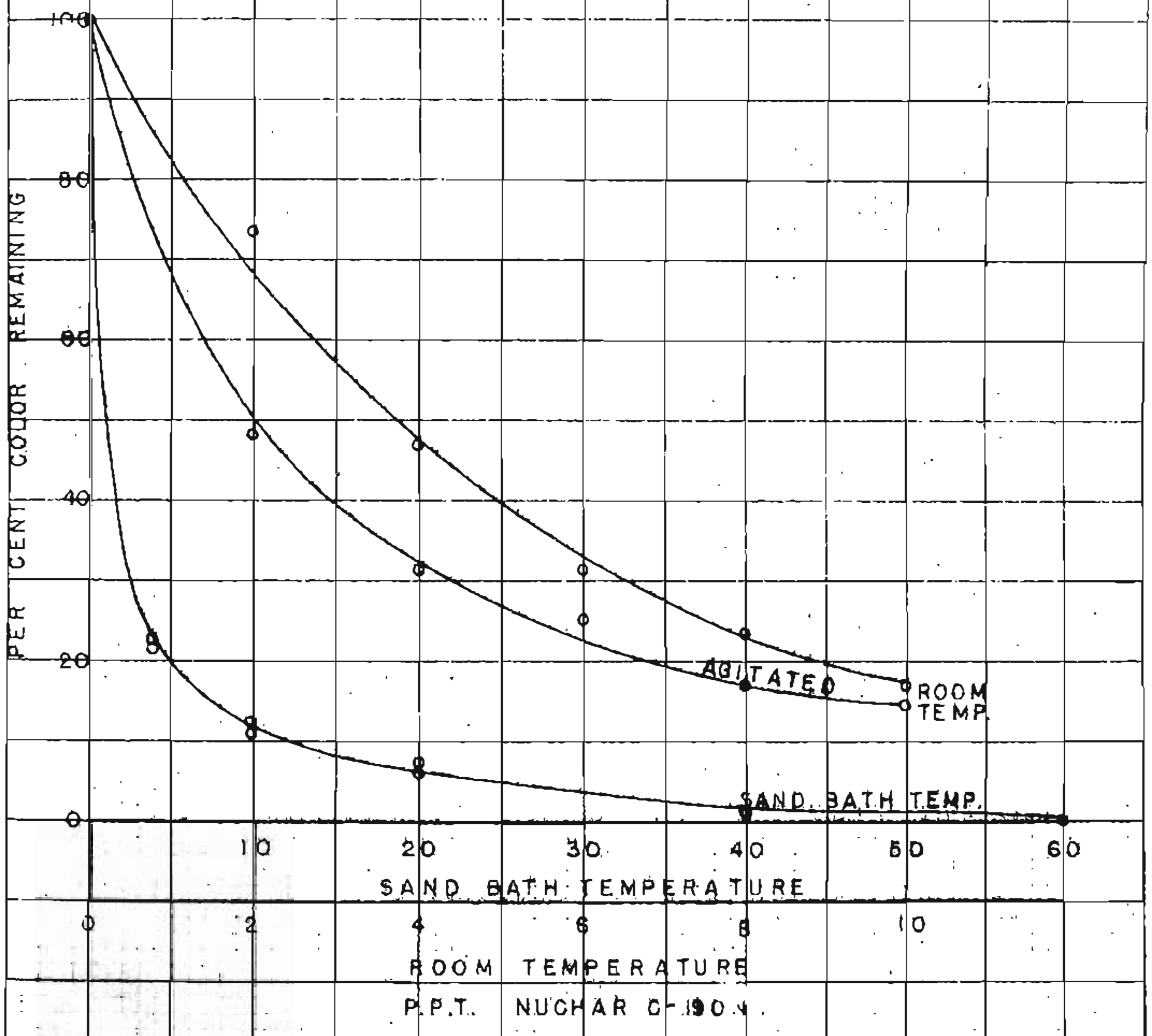
Room Temperature

	Parts per Thousand of Nuchar C-190 N					
	2.	4.	6.	8.	10.	
5	90.	90.	93.	88.	86.	F.V. %
Air	1.20	1.21	1.22	1.26	1.20	pH
Agitated	48.2	31.3	25.6	17.1	14.4	% Col.
1	84.	88.	84.	82.	83.	F.V. %
Hand	1.27	1.25	1.21	1.27	1.31	pH
Stirred	73.6	46.8	31.4	23.7	17.1	% Col.

FIGURE 8

EFFECT OF AGITATION ON ADSORPTION

DATA FROM TABLE 10



Effect of Acidification

All conditions of the experiments were maintained constant except the amount of sulfuric acid which was varied.

For any particular amount of activated charcoal, adding sulfuric acid reduces the per cent of color remaining in solution. Additions of more than 7.5 p.p.t. of sulfuric acid to the combined water shows only small increases in adsorption. The addition of sulfuric acid to the red water has a pronounced effect on adsorption, but this effect becomes smaller with increasing concentration.

Results for combined water with Nuchar C-190 N are shown in Table 11 and Figure 9. Results for red water using 4 p.p.t. of Nuchar C-115 N are shown in Table 12 and Figure 10.

TABLE 11

The Effect on Adsorption of Adding Sulfuric Acid to Samples of Combined Water Treated One Hour at the Sand Bath Temperature

Series Number	P.P.T. O.V.	Parts per Thousand of Nuchar C-190 N					
		2.	4.	6.	8.	10.	
6	0.0	82.	84.	82.	83.	82.	F.V. %
		1.72	1.69	1.70	1.66	1.68	pH
		46.3	30.0	22.0	15.0	14.7	% Col.
7	2.5	80.	80.	82.	78.	76.	F.V. %
		1.55	1.65	1.64	1.66	1.58	pH
		36.1	23.5	18.6	14.8	13.5	% Col.
8	7.5	81.	80.	81.	82.	82.	F.V. %
		1.11	1.09	1.06	1.23	1.28	pH
		35.7	21.6	18.8	15.2	12.5	% Col.
9	12.5	67.	66.	65.	64.	62.	F.V. %
		1.06	1.06	1.05	1.15	1.18	pH
		32.8	18.3	17.8	14.1	12.1	% Col.
10	25.0	86.	83.	79.	76.	76.	F.V. %
		0.90	0.91	0.96	0.89	0.88	pH
		33.6	21.0	18.5	14.0	13.4	% Col.
11	50.0	82.	81.	83.	77.	77.	F.V. %
		0.72	0.70	0.75	0.59	0.66	pH
		28.0	20.0	18.6	14.9	12.6	% Col.

FIGURE 9

EFFECT OF ACIDIFICATION WITH SULFURIC ACID ON ADSORPTION FROM COMBINED WATER

DATA FROM TABLE II

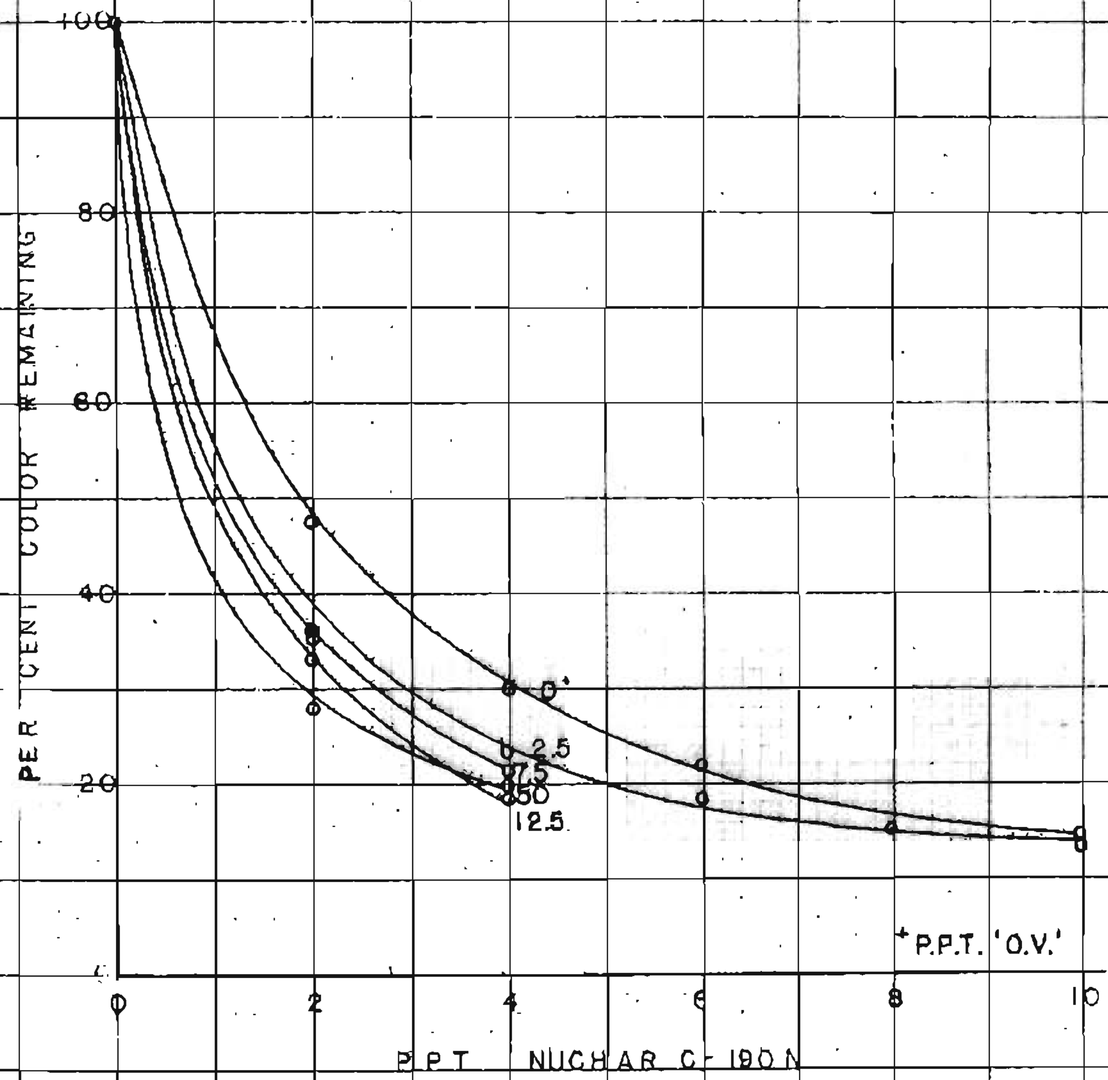


TABLE 12

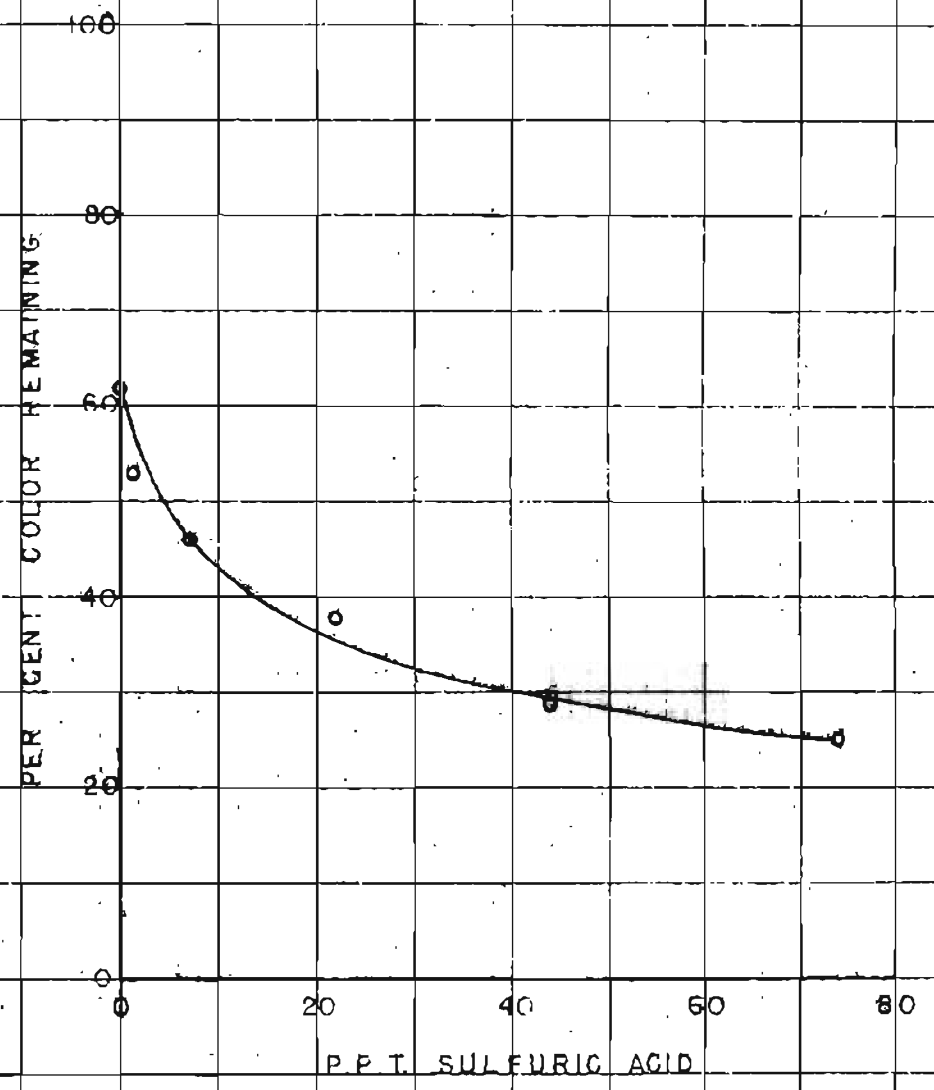
The Effect on Adsorption of Adding Sulfuric Acid to Samples of Red Water Treated One Hour on the Sand Bath

Series Number	4 Parts per Thousand Nuchar C-115 N			
11a	0.00	1.48	7.35	p.p.t.O.V.
	76.	75.	72.	F. V. %
	62.	53.	46.	% Color
11b	22.	44.	74.	p.p.t.O.V.
	72.	67.	80.	F. V. %
	38.	29.	25.	% Color

FIGURE 10

EFFECT OF ACIDIFICATION WITH SULFURIC ACID ON ADSORPTION FROM RED WATER

DATA FROM TABLE 12



ACTIVATED CHARCOAL TESTS

Selecting all conditions most favorable to color adsorption, and following the adopted procedure, all of the charcoals on hand were tested. Variable quantities of charcoal were used as follows: 4, 20, 40, 80, 120, and 160 p.p.t.

Nuchar C-190 N and C-115 N were studied in more detail and were used as reference charcoals.

These reference charcoals reduced the colors of the yellow water and the combined water to 1% of the original color and the water was essentially colorless. The red water must be reduced to 0.1% of the original to be colorless.

The red water requires more charcoal for decolorization per unit volume than does either of the other waters. The yellow water requires the least amount of charcoal per unit volume of solution. Data were obtained for the quantity of charcoal necessary for decolorization using a single treatment and for a countercurrent, double, and triple treatments. In each of these cases, the quantity of charcoal consumed for reducing the color to 1% of the original color was decreased.

The results of these tests are tabulated in Tables 13, 14, 15, 16, and 17. The data is also graphically presented on log-log plots in Figures 12, 13, 14, 15, and 16 on pages 48, 49, 50, 51, and 52.

TABLE 13

Results for Nuchar C-190 N in Combined Water Acidified with 7.5 Parts per Thousand of Sulfuric Acid

Series Number	Parts per Thousand of Charcoal						
	2.	4.	6.	8.	10.	20.	
8	81.	80.	81.	82.	82.	62.	F.V. %
	1.11	1.09	1.06	1.23	1.28	1.32	pH
	35.7	21.6	18.8	15.2	12.5	7.3	% Col.

	Parts per Thousand of Charcoal						
	24.	28.	32.	36.	40.	80.	
12	64.	64.	62.	59.	57.	46.	F.V. %
	1.30	1.36	1.38	1.43	1.38	1.55	pH
	5.3	4.8	4.1	2.9	1.1	Colorless	% Col.

TABLE 14

Results for Nuchar C-115 N in Combined Water Acidified with 36.7 Parts per Thousand of Sulfuric Acid

Series Number	Parts per Thousand of Charcoal 4.	20.	24.	28.	32.	36.	
12h	79.	69.	76.	69.	72.	72.	F.V. %
	1.21	1.34	1.26	1.29	1.29	1.24	pH
	28.	7.8	6.5	5.0	3.3	2.8	% Col.

	Parts per Thousand of Charcoal 40.	44.	48.	80.	
12i	56.	70.	65.	50.	F.V. %
	1.40	1.34	1.32	1.52	pH
	2.4	2.2	1.6	Colorless	% Col.

TABLE 15

Results for Nuchar C-115 N in Red Water Acidified with 36.7 Parts per Thousand of Sulfuric Acid

Series Number	Parts per Thousand of Charcoal					
	0.4	4.	12.	20.	28.	
12a	72.	77.	75.	74.	70.	F.V. %
	0.74	0.80	0.82	0.83	0.89	pH
	46.	26.	10.6	5.9	3.9	% Col.
	Parts per Thousand of Charcoal					
	36.	44.	52.	60.	68	
12b	63.	66.	60.	53.	58.	F.V. %
	0.91	0.92	0.91	0.96	0.95	pH
	2.5	1.6	1.3	0.85	0.67	% Col.
	Parts per Thousand of Charcoal					
		76.	84.	92.		
12c		56.	56.	49.		F.V. %
		0.95	0.96	1.01		pH
		0.49	0.38	0.14		% Col.

TABLE 16

Results for Nuchar C-115 N in Yellow Water

Not Acidified

Series Number	Parts per Thousand of Charcoal 0.2	0.4	0.8	2.0	2.8	
12d	84.	76.	85.	84.	84.	F.V. %
	0.94	0.91	0.87	0.82	0.91	pH
	79.	67.	60.	51.	35.	% Col.

	Parts per Thousand of Charcoal 3.6	4.0	6.0	6.8	8.0	
12e	84.	88.	85.	84.	85.	F.V. %
	0.95	0.86	0.95	0.88	0.91	pH
	28.	26.	16.2	8.3	5.9	% Col.

	Parts per Thousand of Charcoal 8.4	9.2	10.0	10.8	11.2	
12f	82.	81.	80.	77.	84.	F.V. %
	0.81	0.88	0.91	0.85	0.89	pH
	5.0	3.5	1.95	1.56	1.51	% Col.

	Parts per Thousand of Charcoal 11.6	12.0	20.0	
12g	83.	78.	74.	F.V. %
	0.90	0.92	0.95	pH
	1.26	0.60	Colorless	% Col.

TABLE 17

Results for Activated Charcoals other than the Reference Charcoals in Combined Water Acidified with 7.5 Parts per Thousand of Sulfuric Acid

Series Number	Parts per Thousand of Charcoal						
	4.	20.	40.	80.	120.	160.	
13 Dow's	68.	63.	71.	62.	56.	46.	F.V. %
Cliffchar	1.32	1.34	1.45	1.69	2.0	2.5	pH
R-Fine	40.	11.2	5.8	0.71	Colorless		% Col.
14 Dow's	74.	73.	63.	44.	47.	44.	F.V. %
Cliffchar	1.30	1.35	1.47	1.82	2.40	4.28	pH
R-Coarse	44.	12.5	7.0	0.60	0.67	1.3	% Col.
15 Dow's	79.	77.	64.	57.	40.	30.	F.V. %
Cliffchar	1.28	1.32	1.46	1.60	1.85	2.07	pH
10-30 mesh	82.	28.	9.1	3.1	0.79	0.76	% Col.
16 Dow's	76.	80.	66.	58.	50.	46.	F.V. %
Cliffchar	1.25	1.31	1.35	1.60	1.82	2.0	pH
4-10 mesh	83.0	55.	23.	6.7	2.2	1.2	% Col.
17 Nuchar	76.	70.	66.	38.	31.		F.V. %
000	1.22	1.36	1.40	1.70	1.90		pH
	30.	9.5	2.9	Colorless			% Col.
18 Nuchar	70.	63.	62.	50.	37.		F.V. %
#2	1.21	1.37	1.42	1.68	1.84		pH
	40.	11.3	5.7	0.42	Colorless		% Col.
19 Darco	63.	54.	63.	55.	47.		F.V. %
S-51	1.18	1.27	1.33	1.45	1.54		pH
	43.	15.1	7.8	2.8	Colorless		% Col.
20 Darco	65.	66.	62.	46.	39.		F.V. %
G-60	1.22	1.23	1.30	1.41	1.40		pH
	35.	10.5	5.3	Colorless			% Col.
21 Harsaw	67.	49.	66.	57.	47.	38.	F.V. %
Cliff Char	1.28	1.34	1.46	1.66	1.96	2.39	pH
	40.	11.6	6.6	0.92	Colorless		% Col.
22 Carbon,	60.	62.	51.	38.	28.	20.	F.V. %
Mallinckrodt	1.31	1.37	1.49	1.68	1.90	2.06	pH
Decolorizing	28.	8.8	2.9	0.43	Colorless		% Col.

TABLE 17 (Continued)

Results for Activated Charcoals other than the Reference Charcoals in Combined Water Acidified with 7.5 Parts per Thousand of Sulfuric Acid

Series Number	Parts per Thousand of Charcoal						
	4.	20.	40.	80.	120.	160.	
23 Burrell	66.	79.	62.	66.	51.	60.	F.V. %
Cocoanut	1.26	1.21	1.35	1.51	1.80	1.94	pH
6-14 mesh	96.	42.	7.6	0.54	Colorless		% Col.
24 Burrell	73.	71.	67.	66.	59.		F.V. %
Cocoanut	1.28	1.42	1.53	1.52	1.58		pH
Powdered	32.	8.1	1.9	1.0	0.1		% Col.
25 Burrell		70.	69.	66.	68.	64.	F.V. %
Act. Charcoal		1.32	1.37	1.55	1.65	1.85	pH
6-14 mesh		67.	23.	4.3	1.2	Colorless	% Col.
26 Daigger	68.	63.	70.	68.	63.		F.V. %
Bone	1.36	2.60[1]	3.55[1]	4.20[1]	4.53[1]		pH
Charcoal	79.	53.	54.	29.	24.		% Col.
27 Daigger	72.	60.	64.	48.	46.		F.V. %
Decolorizing	1.27	2.59[2]	1.34	1.06	1.60		pH
Carbon	46.	41.	7.9	1.1	Colorless		% Col.
28 Sargent		75.	70.	57.	73.	59.	F.V. %
Carbon Super		1.35	1.48	1.81	2.20[3]	2.62[3]	pH
Filcher		27.	15.9	4.8	2.8	0.92	% Col.
29 Dicalite	76.	76.	67.	69.	66.		F.V. %
Kyrite	1.26	1.26	1.26	1.35	1.22		pH
	92.	71.	46.	37.	30.		% Col.
30 Dicalite	76.	72.	68.	58.	45.		F.V. %
M-23	1.26	1.31	1.40	1.61	1.81		pH
	50.	14.4	9.2	0.98	Trace		% Col.

---

[1] Adjusted to a pH of 1.4 with H_2SO_4 for colar comparison.

[2] Adjusted to a pH of 1.3 with dilute H_2SO_4 for color comparison.

[3] Adjusted to a pH of 1.6 with dilute H_2SO_4 for color comparison.

A study of the adsorption data shows that they conform approximately to Freundlich's equation until about 7% of the original color remains, when it deviates sharply. This deviation indicates that less charcoal is required than is predicted by the equation. Checking determinations have substantiated these deviations.

MATHEMATICS OF ADSORPTION

Langmuir's Equation

A simple case of adsorption is cited in one of the physical chemistry texts[27]. The original derivation of this equation was for gases being adsorbed on a plane surface having identical elementary spaces capable of adsorbing only one molecule[28]. The equation is given in a slightly modified form for solutions.

If the variables and constants be represented by the following symbols:

x be the per cent of the original color removed per unit weight of adsorbent

y be the per cent of the original color remaining

a and b be constants

then at equilibrium the following relationship constitutes Langmuir's equation.

$$x = y/(a \quad by) \qquad (1)$$

This hyperbolic equation can be arranged to a linear form if the reciprocals of 'x' and 'y' be plotted.

$$a/y \quad b = 1/x \qquad (2)$$

The widespread use of this equation necessitates a graphical representation of at least one set of data with it. This is presented in Figure 11.

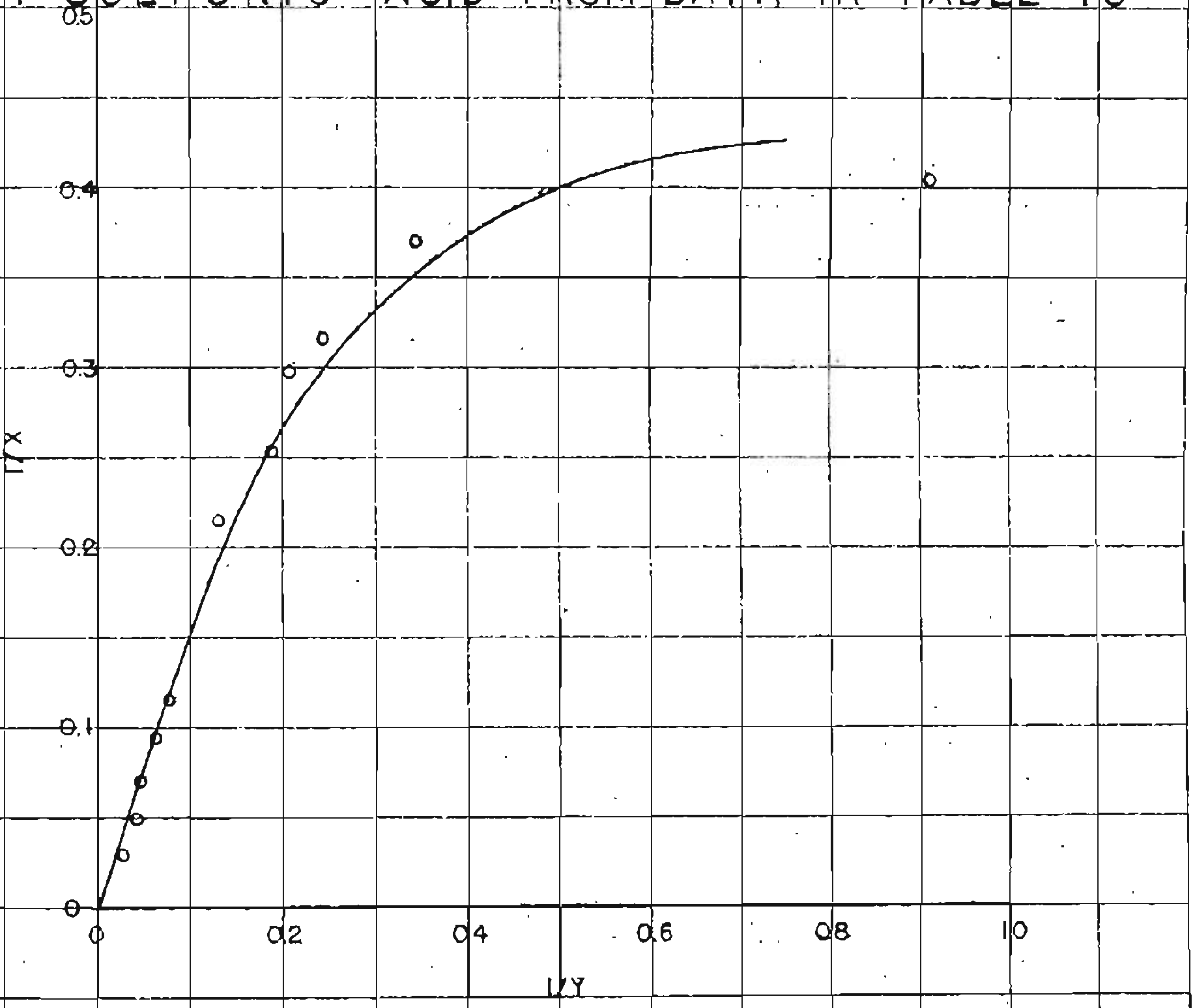
---

[27] Getman, Frederic H, and Farrington Daniels. Outlines of theoretic chemistry. 6th ed. New York, John Wiley & Sons, Inc., 1937. p. 223-224.

[28] Langmuir, Irving. The adsorption of gases on plane surfaces. J. Amer. Chem. Soc. v 40, pp. 1368-1371 (1918).

FIGURE 11

LANGMUIR'S EQUATION FOR NUCHAR C-190 N IN COMBINED WATER ACIDIFIED WITH 7.5 P.P.T. OF SULFURIC ACID FROM DATA IN TABLE 13



The graph shows a marked deviation from this equation as would be expected.

Freundlich's Equation for a One Stage Treatment

A purely empirical[29] relationship exists between the amount adsorbed per gram of adsorbent and the residual color. If the amount adsorbed be represented by 'X', the amount of the adsorbent as 'M', and the remaining color by 'C', the following relationship holds with a reasonable accuracy.

$$X/M = KC^{1/N} \quad (30) \qquad (3)$$

'K' and '1/N' are constants; the former may have any value but the latter usually lies between 0.1 and 0.7(31). The value of the exponent increases with temperature and approaches a value of 1 (32). Freundlich shows several systems which do not conform to the equation in his article, but these were for gaseous adsorption.

This equation lends itself to graphical representation on log-log paper. The logarithmic form is:

$$\log(X/M) = \log K + 1/N \log C \qquad (4)$$

This form results in a straight line if the '$\log(X/M)$' be plotted against '$\log C$' on ordinary graph paper or if 'X/M' be plotted against 'C' on log-log paper.

The tests on activated charcoal have been graphically represented in Figures 12, 13, 14, 15, and 16.

---

[29] Freundlich, H. (Paul Mahler, Trans.) Jerome Alexander, ed. Colloid chemistry. New York, Chemical Catalog Co., Inc., v I, p. 575, (1926).
[30] Ibid., p. 575.
[31] Ibid. p. 575.
[32] Ibid. p. 576.

FIGURE 12

ADSORPTION ISOTHERM FOR NUCHAR C-190N IN COMBINED WATER ACIDIFIED WITH 7.5 P.P.T. OF SULFURIC ACID FROM DATA IN TABLE 13

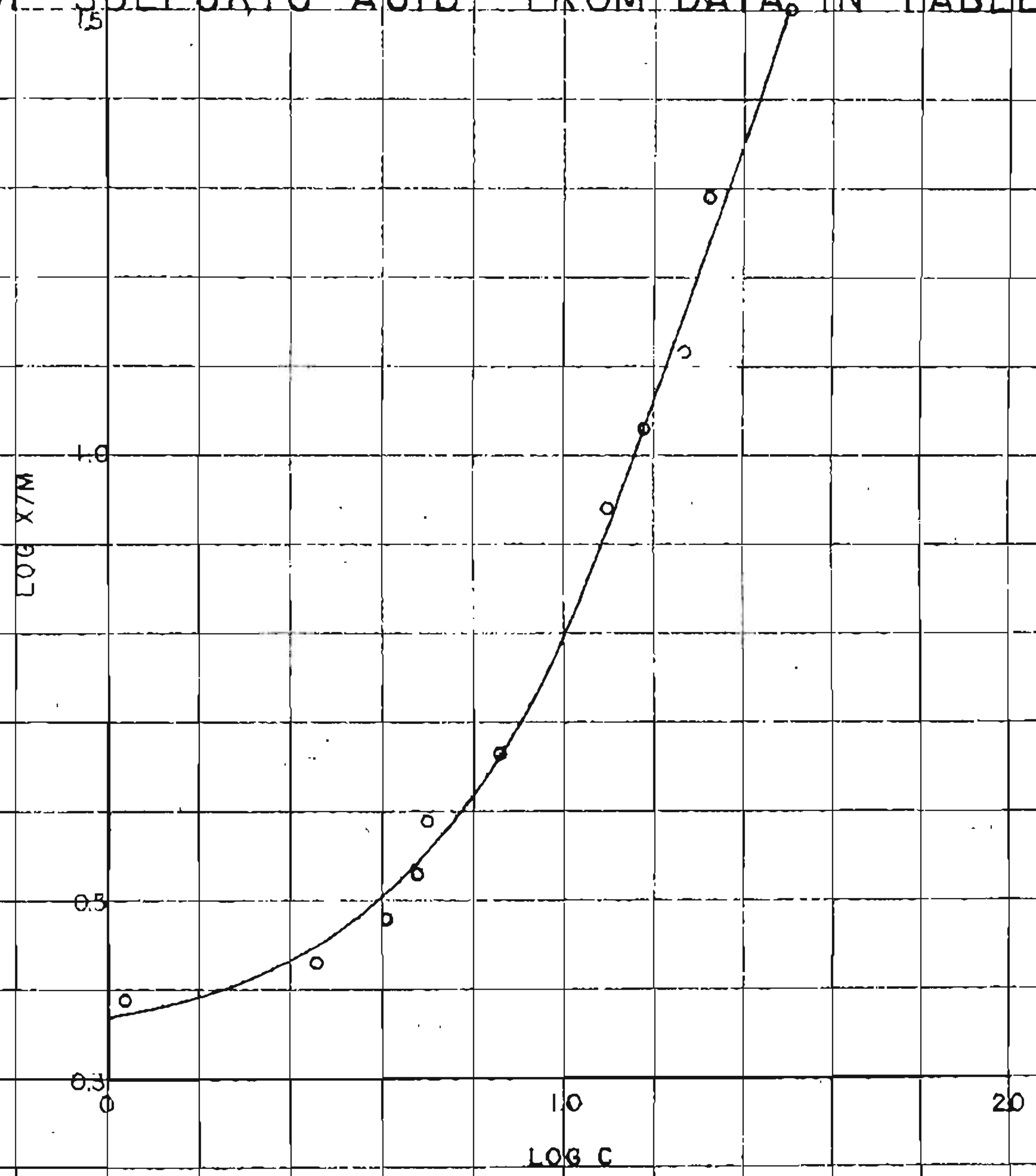


FIGURE 13

COMPARISON OF ADSORPTION ISOTHERMS FOR NUCHAR C-115 N IN COMBINED, RED, AND YELLOW WATERS

FROM DATA IN TABLES 14, 15, AND 16

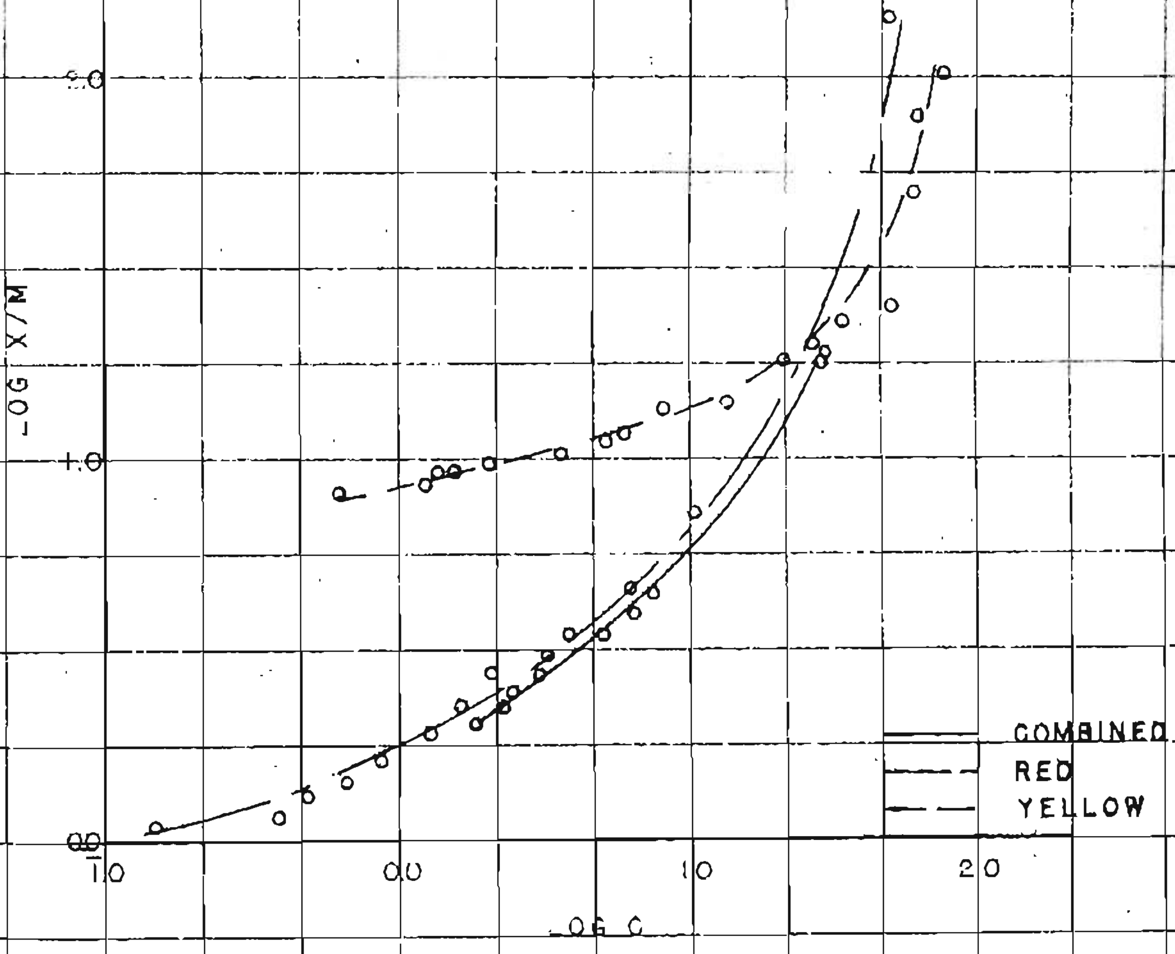


FIGURE 14

ADSORPTION ISOTHERMS FOR VARIOUS ACTIVATED CHARCOALS IN COMBINED WATER ACIDIFIED WITH 7.5 P.P.T. OF SULFURIC ACID FROM DATA IN TABLE 17

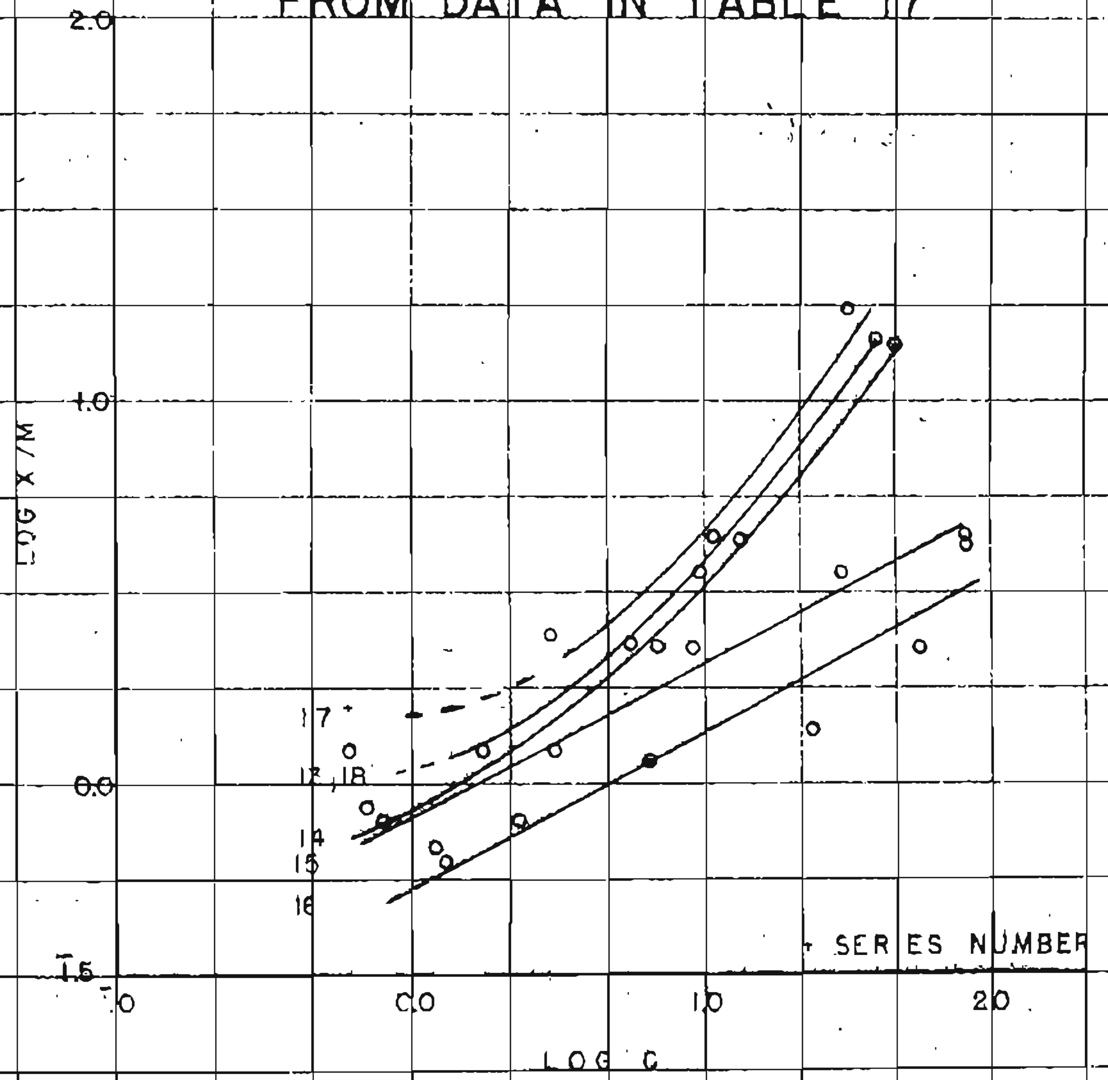


FIGURE 15

ADSORPTION ISOTHERMS FOR VARIOUS ACTIVATED CHARCOALS IN COMBINED WATER ACIDIFIED WITH 7.5 P.P.T. OF SULFURIC ACID FROM DATA IN TABLE 17

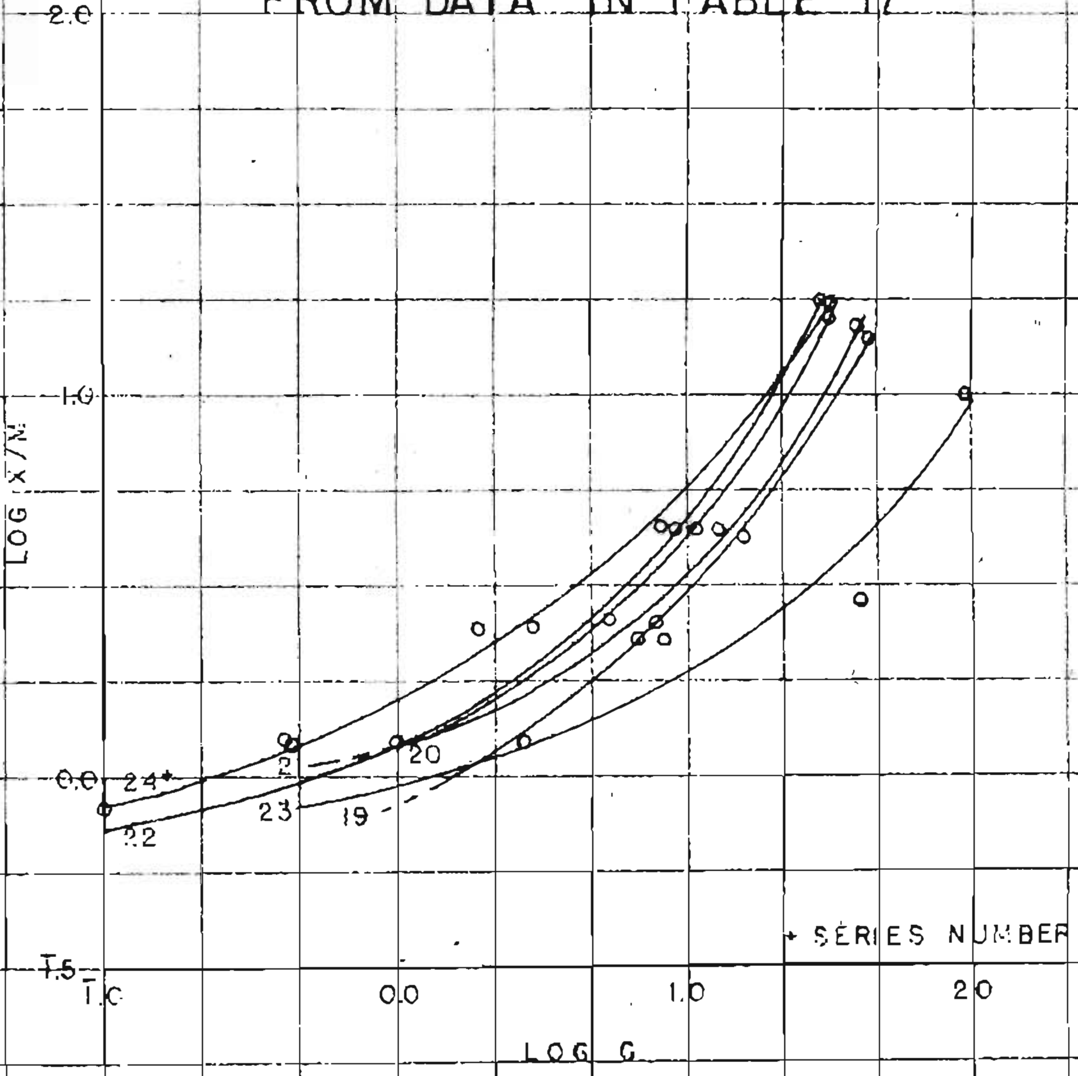
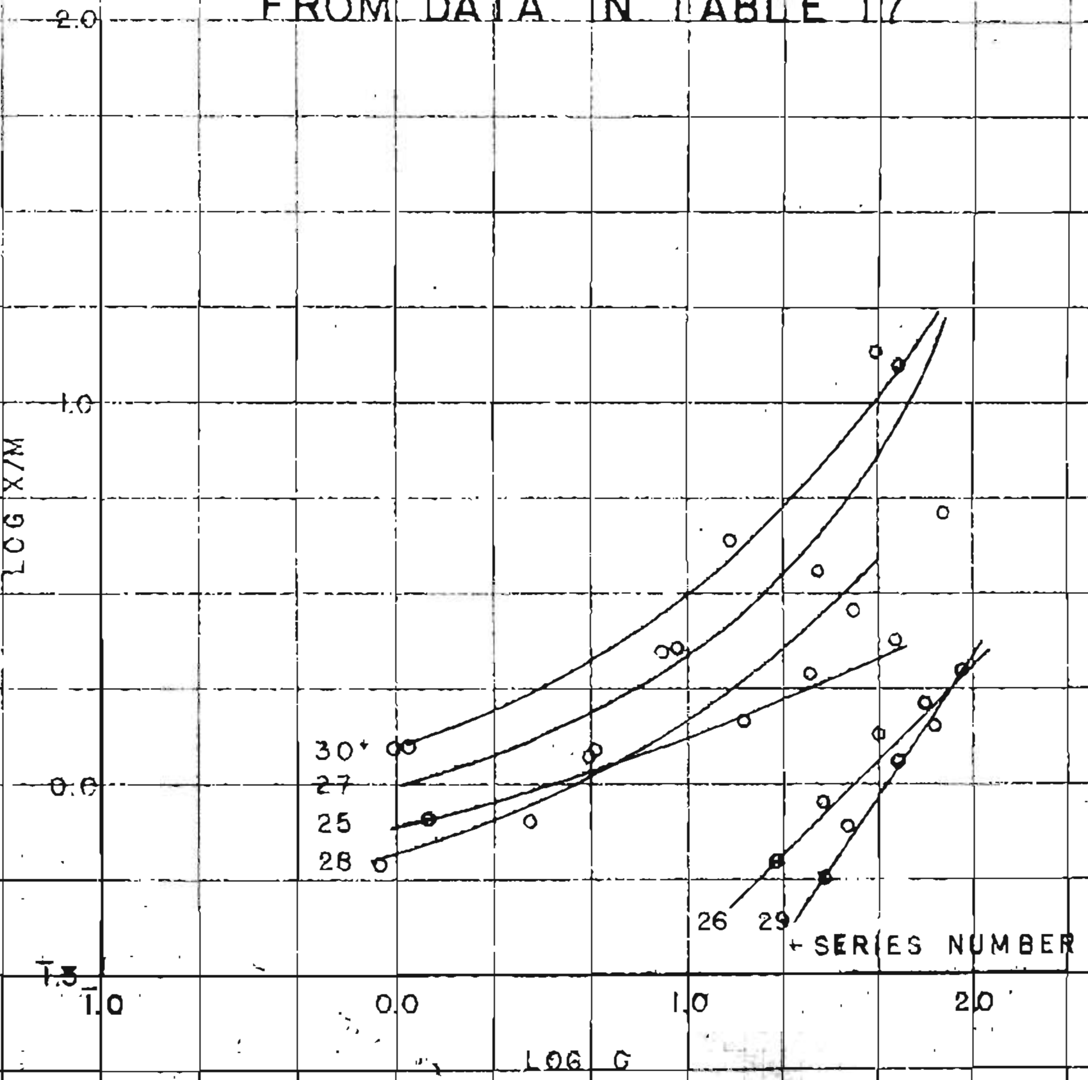


FIGURE 16

ADSORPTION ISOTHERMS FOR VARIOUS ACTIVATED CHARCOALS IN COMBINED WATER ACIDIFIED WITH 7.5 P PT OF SULFURIC ACID FROM DATA IN TABLE 17



Calculations for the One Stage Treatment

After sufficient data are plotted to establish the validity of the equation, the slope, '1/N', may be calculated and the intercept 'K' found. The logarithmic equation lends itself to calculation with logarithms.

$$\log M = \log X - \log K - 1/N \log C \qquad (5)$$

A log-log slide rule accomplishes the same result and permits calculation in the following form.

$$M = X/(KC^{1/N}) \qquad (6)$$

Graphical Solution of the One Stage Treatment

The Darco Corporation has copyrighted the "Darcograph"[33] which solves the logarithmic equation graphically. A sketch of this solution is given in Figure 17. This consists of log-log graph paper with a reference line in reality the logarithim of 'X' or the logarithim of '(100 - C)'. The data is plotted by use of a moveable scale with the same logarithmic modulus. The remaining color is the abscissa scale and the carbon doseage plotted down from the reference curve with the scale. Once the adsorption isotherm is established, the residual color is located and the difference

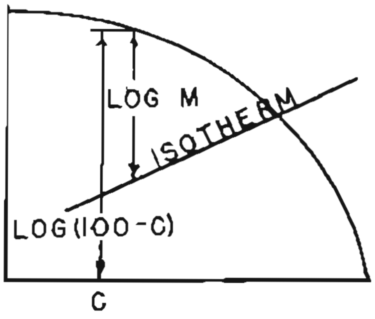


Figure 17

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[33] Darco Corporation, 60 East 42nd Street, New York, New York.

between the reference curve and the adsorption isotherm is read with the scale; this value is the carbon doseage.

Nomograph for the One Stage Treatment

A nomograph was located in the literature for the solution of the Freundlich equation for the group 'MK'[34]. This nomograph did not permit calculations to a residual color of one per cent, or a complete solution for the doseage.

This nomograph has been extended to calculate per cent color remaining to one per cent and to solve for the doseage.

The nomograph type required a separation of variables to give a function of the type

$$f_1(u) + f_2(v) \cdot f_3(w) = f_4(w).^{(35)} \qquad (7)$$

If the original equation be transformed by substitution of '(1 - C)' for 'X', rearrangeing and taking logarithms, the following equation results.

$$\log KM + 1/N \log C = \log (1 - C_f) \qquad (8)$$

The moduli for these scales were selected as 3 inches for the '1/N' uniform scale on the left side and as 3 inches for the 'KM' logarithmic scale on the right side. The curve of 'C' intermediate between these scales is the result of calculating several values of 'KM' for assumed values of '1/N' and 'C'.

The extension of this nomograph to calculate 'M' is a rather simple operation. A nomograph consisting of three

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[34] Sanders, Marshall T. Calculations for decolorizing carbons. J. Ind. Eng. Chem. v 15, p. 786 (1923).
[35] Lipka, Joseph. Graphical and mechanical compution. New York, John Wiley & Sons, Inc., 1918. p. 106.

vertical and parallel scales will solve the function

$$f_1(u) + f_2(v) = f_3(w)^{(36)} \qquad (9)$$

This form of the solution is started with the logarithmic 'KM' scale.

$$\log K + \log M = \log KM \qquad (10)$$

A selection of modulus for the 'K' scale of 3 inches results in the 'M' scale with a modulus of 1½ inches and the location of the 'M' scale with distances to the others in the ratio of 'KM' and 'K' moduli.

A nomograph was constructed using these relationships and is shown in Figure 18.

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[36] Ibid. p. 45.

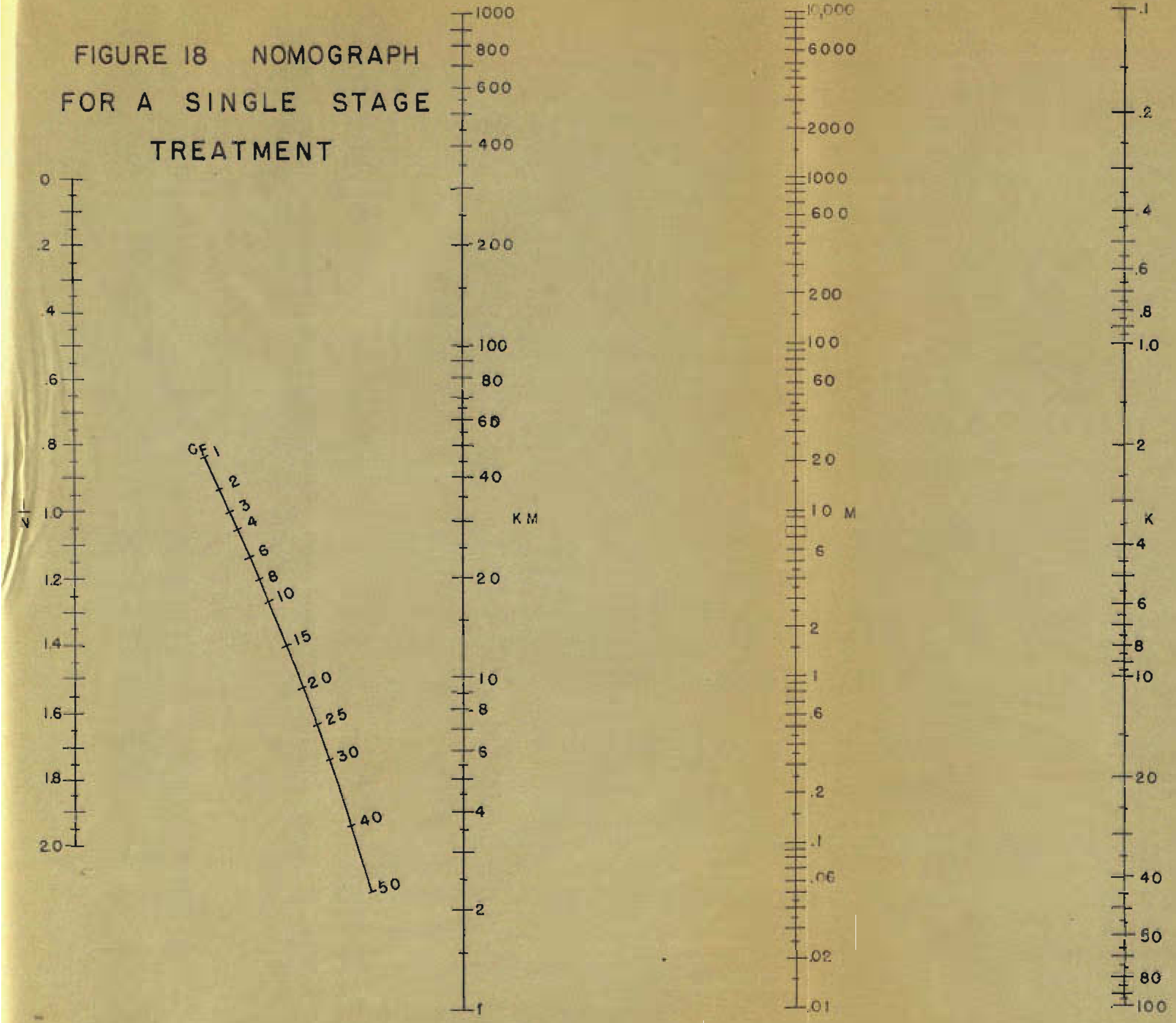

FIGURE 18 NOMOGRAPH FOR A SINGLE STAGE TREATMENT

Freundlich's Equation for a Two Stage Treatment

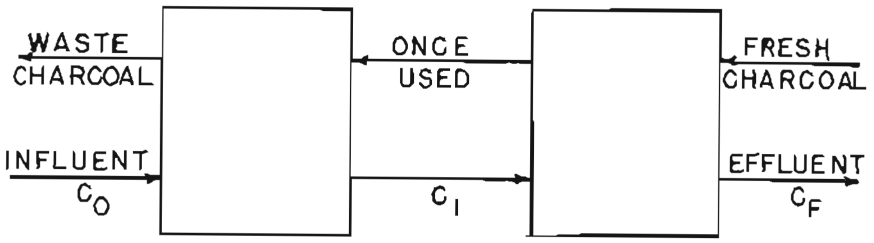

Figure 19, Countercurrent Treatment Flow Sheet

Freundlich's equation may be applied twice to a two stage process where

M_1, M_2 are the respective carbon doseages for a one and a two stage treatment

C_o is the influent color, usually called 100%

C_1, C_f are the respective per cents after the first and second treatment

$$(C_o - C_f)/M_2 = KC_1^{1/N} \qquad (11)$$

$$(C_1 - C_f)/M_2 = KC_f^{1/N} \qquad (12)$$

and by proportion[37]

$$(C_1 - C_f)/(C_o - C_f) = C_f^{1/N} / C_1^{1/N} \qquad (13)$$

A second derivation allows a relation of one stage treatment to the two stage treatment. Writing the one stage treatment equation in terms of the two stage symbols

$$(C_o - C_f)/M_1 = KC_f^{1/N} \qquad (14)$$

---

[37] Sanders, op. cit., v 20, p. 792, 1928.

The combination of equations (11), (12), and (14) yields an equation relating colors to the charcoal doseages.

$$(C_1 - C_f)/(C_o - C_f) = M_2/M_1 = C_f^{1/N}/C_1^{1/N} \quad (38) \qquad (15)$$

Calculations for the Two Stage Treatment

The value of the intermediate color concentration may be calculated by trial and error and the carbon doseage calculated with a knowledge of the single stage doseage[39].

After the intermediate color concentration has been found, the two stage doseage will be the single stage doseage to produce the intermediate color. This permits the use of any of the previous single stage calculations.

Graphical Solution of the Two Stage Process

A graph of per cent of the single carbon doseage required for the two step plotted against the slope of '1/N' for various values of 'C_f' may be calculated from equation (15). The Darco Corporation used this method for calculating the two stage doseage with a graph of per cent on a uniform scale and 1/N on a scale very closely approximated by a logarithmic scale. The final color concentration may be easily interpolated between the almost parrallel constant effluent curves.

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[38] Ibid. v 20, p. 792.
[39] Ibid. v 20, pp. 792-793.

A second graphical process for calculating the intermediate color concentrations is somewhat similar to a stripping tower design[40]. See Figure 20 for a graphical diagram. Equations (11) and (12) may be rewritten and solved for M_2K

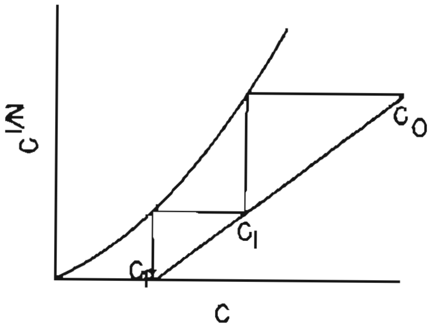

Figure 20

$$(C_o - C_f)/C_1^{1/N} = M_2K \qquad (16)$$

$$(C_1 - C_f)/C_f^{1/N} = M_2K \qquad (17)$$

These equations may be equated and a third equality results by subtraction of these two.

$$(C_o - C_f)/C_1^{1/N} = (C_1 - C_f)/C_f^{1/N}$$

$$= (C_o - C_1)/(C_1^{1/N} - C_f^{1/N}) \qquad (18)$$

These conditions are met by the similar triangles formed by the stepwise construction. This may be applied to any number of countercurrent adsorptions if the Freundlich equation applies to the entire range.

In use, one locates 'C_f' at the base and assumes a line terminating at 'C_o'. If it takes exactly two steps, the intermediate color is read and the ratio of activated charcoal calculated by equation (15) or any other which it is desired to use. If this requires more or less steps to produce the desired result, a new assumption must be made until the desired color removal is produced by the desired number of stages.

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[40] Ibid. v 20, pp. 792-793.

Another graphical method similar to this one is discussed under the non-ideal cases, but may be used in the ideal cases just as easily.

A Nomograph for the Two Stage Treatment

The solution for the intermediate color requires either a trial and error process or graphical methods and may be solved by a nomograph for the ratio 'C_2/C_1'. This nomograph was located in the literature but did not include one per cent[41].

A separation of the variables was necessary to include one per cent. The following separation became apparent only after a trigonometric substitution and several rearrangements.

$$1 = (C_2(C_1/C_2 - 1)/(C_o - C_2))(C_1/C_2)^{1/N} \tag{19}$$

$$1 = (C_2/(C_o - C_2))((C_1/C_2) - 1)(C_1/C_2)^{1/N} \tag{20}$$

$$\log 1 = 0 = \log(C_2/(C_o - C_2)) + \log((C_1/C_2) - 1) + 1/N \log(C_1/C_2) \tag{21}$$

$$0 = (\log(C_2/(C_o - C_2))/(\log C_1/C_2)) + (\log((C_1/C_2) - 1)/\log(C_1/C_2)) + 1/N \tag{22}$$

$$0 = (f_1(C_o/C_2))(f_2(C_1/C_2)) + f_3(C_1/C_2) + f_4(1/N) \tag{23}$$

This equation is of the form given in equation (7), and is solved by a nomograph of a type similar to the previous one.

The modulus of the uniform '$1/N$' scale was selected as 3 inches and the modulus for the non-uniform scale 'log $C_2/(C_o - C_2)$ was selected as 2.3 inches and calculated.

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[41] Ibid. v 20, p. 793.

Repeated calculations for the same 'C_2/C_1' ratio produced the curved center scale by use of the method of intersections. This nomograph is a part of Figure 21.

A second nomograph very easily solves the carbon doseage if the single treatment doseage and desired color of the effluent are known.

For this nomograph, the equation (15) is written as follows:

$$M_2/M_1 = (C_1 - C_2)/(C_o - C_2) \qquad (24)$$

This equation is adaptable to a square chart whose type equation is

$$f_1(u)/f_2(v) = f_3(w)/f_4(q) \qquad (25)$$[42]

The rearrangement of the equation serves better to show the scale required in terms of the known conditions.

$$M_2/M_1 = ((C_1/C_2) - 1)/((C_o/C_2) - 1) \qquad (26)$$

$$M_2/M_1 = ((1 - C_2/C_1)/(C_2/C_1))((C_2/C_o)/(1 - C_2/C_o)) \qquad (27)$$

The latter equation may be represented in mathematical notation by

$$f_1(M_2)/f_2(M_1) = f_3(C_2/C_1)/f_4(C_2/C_o) \qquad (28)$$

The moduli were selected as follows: M_1 is 8 inches; M_2, 40 inches; C_2/C_1, 0.4 inches; and C_2/C_o, 0.08 inches. This nomograph is included in Figure 21.

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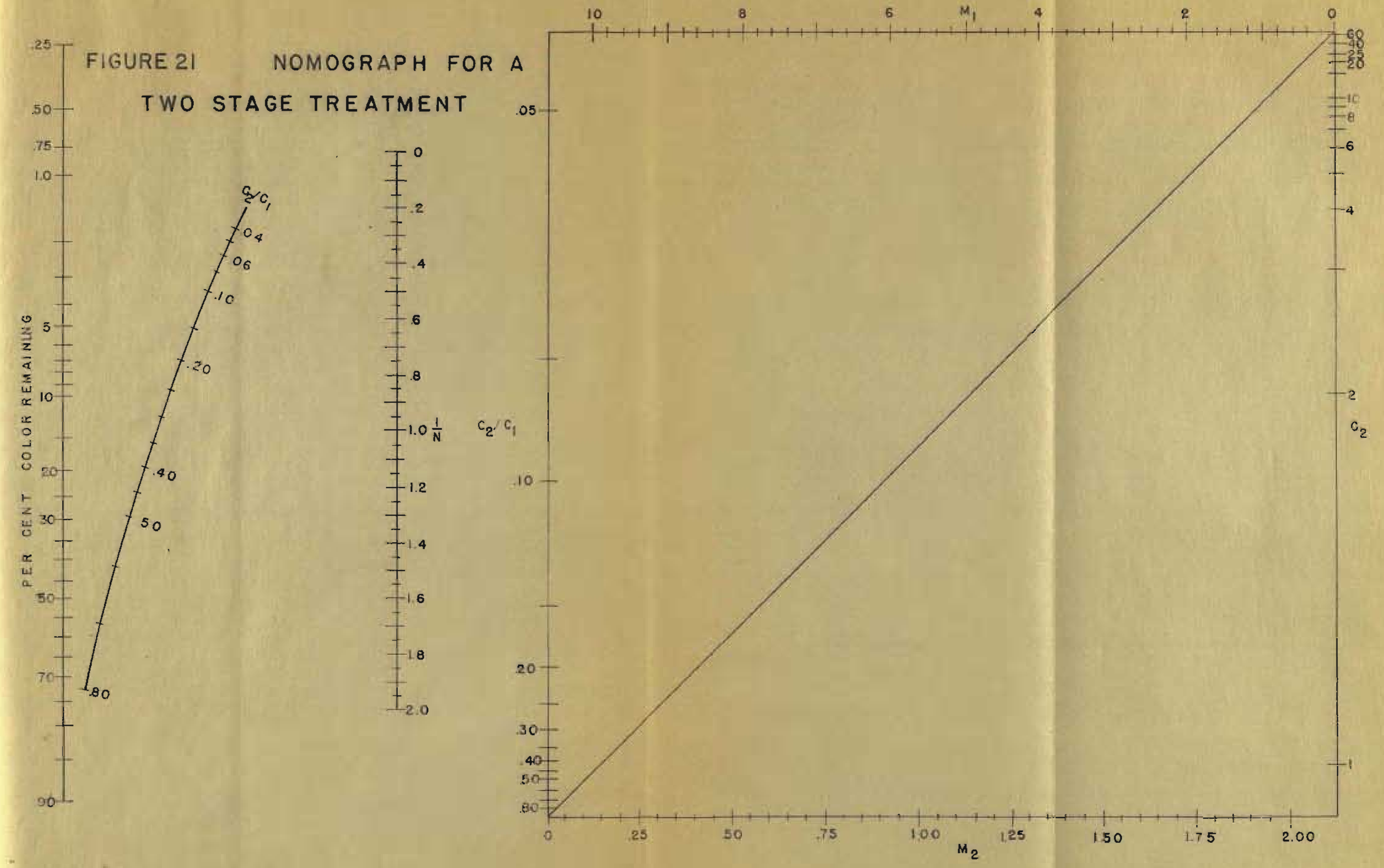
[42] Lipka, op. cit., pp. 68-69.

FIGURE 21 NOMOGRAPH FOR A TWO STAGE TREATMENT



An Outline for the Nomographic Solutions

The one stage treatment requires the values of 'K' and '1/N' be obtained from the laboratory data. The nomograph, Figure 18, is solved by aligning '1/N' with 'C_f' and locating with these 'KM_1'; rotating about 'KM_1' to align with 'K' gives 'M_1' for this process directly.

The two stage treatment requires a solution of the one stage only to find the carbon doseage.

The two stage nomograph is solved by aligning '1/N' with 'C_2' and reading the ratio 'C_2/C_1'; this ratio is carried to the square chart and aligned with 'C_2' and the intersection with the diagonal locates the center of rotation for finding 'M_2' by connecting with 'M_1'. If only per cent of single stage doseage is desired 'M_1' may be chosen as 10.

When the Freundlich Equation does not Apply

Cases were noted in the literature where an insufficient number of points were plotted to test the adsorption isotherm for extremely low and extremely high concentrations[43].

All activated charcoals tested on these waste waters deviated from Freundlich's equation when the color remaining was below 5%. In every case less activated charcoal than the adsorption isotherm indicates is required. Figures 12, 13, 14, 15, and 16 show these deviations.

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[43] Stratton, G. W., and D. F. Winkler. Ind. Eng. Chem. v 34, p. 605 (1942)

A Graphical Solution for any Number of Stages to Which the Freundlich Equation Applies in its Differential Form

Under ordinary usage the Freundlich equation has two constants; 'K', the intercept, and '1/N', the slope. This integrated equation applies only if the data be linear on a log-log graph. However, in cases like the present one, it becomes necessary to calculate a multiple stage treatment which cannot be calculated exactly by any of the previous methods. There are no methods recorded in the literature, to the author's knowledge, which apply when the adsorption isotherm does not hold.

The following method devised owes its origin to two sources: the equation developed by Sanders[44] and his method, and the several stage adsorption with fresh charcoal in each stage briefly covered by Walker, Lewis, McAdams, and Gilliland[45], both being for ideal cases where the Freundlich equation is assumed to apply.

If the original data be plotted as 'log X/M' against 'log C' and it be non-linear, the adsorption isotherm may be applied at any point by using the tangent and the intercept of the tangent; these being '1/N' and 'K' respectively for that point.

The equations corresponding to the two stage process may be written as are equations (11) and (12); the added

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[44] Sanders, op. cit., v 20, pp. 792-793.
[45] Principles of chemical engineering. New York, McGraw Hill Book Co., Inc., 1937. p. 510.

subscripts refer to the point at which a tangent was used.

$$(C_o - C_f)/M_2 = K_1C_1^{1/N_1} \qquad (29)$$

$$(C_1 - C_f)/M_2 = K_fC_f^{1/N_f} \qquad (30)$$

These may be solved for 'M_2' and a third equality be found by substraction.

$$(C_o - C_f)/K_1C_1^{1/N_1} = (C_1 - C_f)/K_fC_f^{1/N_f}$$

$$= (C_o - C_1)/(K_1C_1^{1/N_1} - K_fC_f^{1/N_f}) \qquad (31)$$

If two axes are selected at right angles and the values of 'C' plotted vertically, the values of '$KC^{1/N}$', evaluated by tangents at the various values of 'C', may be plotted horizontally; the result may be called an equilibrium curve. An operating line may be constructed from 'C_2' on the vertical axis through any point to the right of the axis intersecting a horizontal line through 'C_o' providing the angle is greater than the one which is tangent to the equilibrium curve. Steps may be constructed by proceeding horizontally to the equilibrium curve then vertically to the operating line; these steps are repeated until the line 'C_o' is intersected. When the operating line is so chosen that the second vertical line meets the operating and 'C_o' lines at their intersection, by similar triangles equation (32) may be established. See Figure 22.

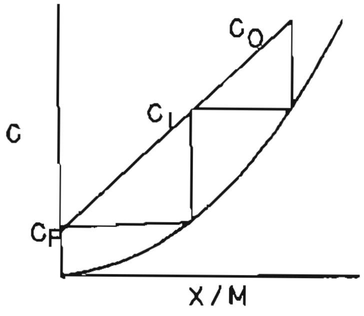

Figure 22

$$\begin{aligned}(C_o - C_1)/(K_1C_1{}^{1/N_1} - K_fC_f{}^{1/N_f}) \\ = (C_1 - C_f)/(K_fC_f{}^{1/N_f}) \\ = (C_o - C_f)/K_1C_1{}^{1/N_1} \qquad (32)\end{aligned}$$

These are the relationships shown in equation (31). It is to be remembered these were solved for 'M_2' and equated; therefore, the slope of this line is 'M_2' [46]. The values of '$K_cC_c{}^{1/N_c}$' were evaluated by tangents at the various points, but these tangents are adsorption isotherms at these points and are equal to 'X/M'. Hence, by plotting the laboratory data as 'X/M' against 'C' on ordinary graph paper, one may solve for the countercurrent stepwise activated charcoal doseage by using a number of steps equal to the number of stages. All of these solutions become rapid trial and error solutions except the single stage and infinite stage treatments which are definite solutions. The ratio of charcoal doseages are shown by the slopes. The data for Nuchar C-190 N and C-115 N have been plotted in this manner in Figures 23, 24, 25, and 26.

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[46] An exactly analogous solution may be proved mathematically by a material balance.

FIGURE 23 FROM DATA IN TABLE 13
GRAPHICAL CALCULATIONS FOR NUCHAR C-190 N IN COMBINED WATER

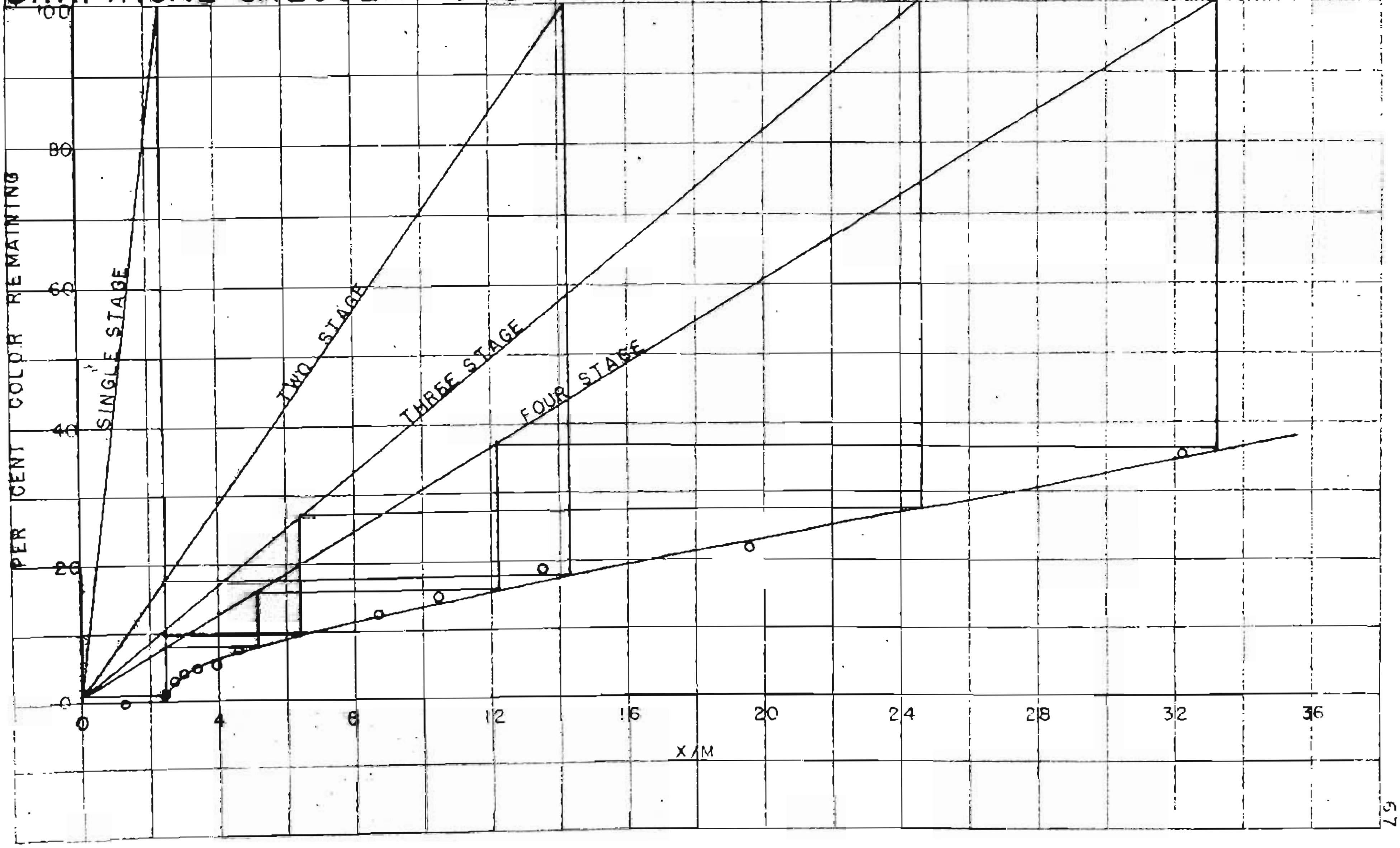


FIGURE 24 FROM DATA IN TABLE 14
GRAPHICAL CALCULATIONS FOR NUCHAR C-115 N IN COMBINED WATER

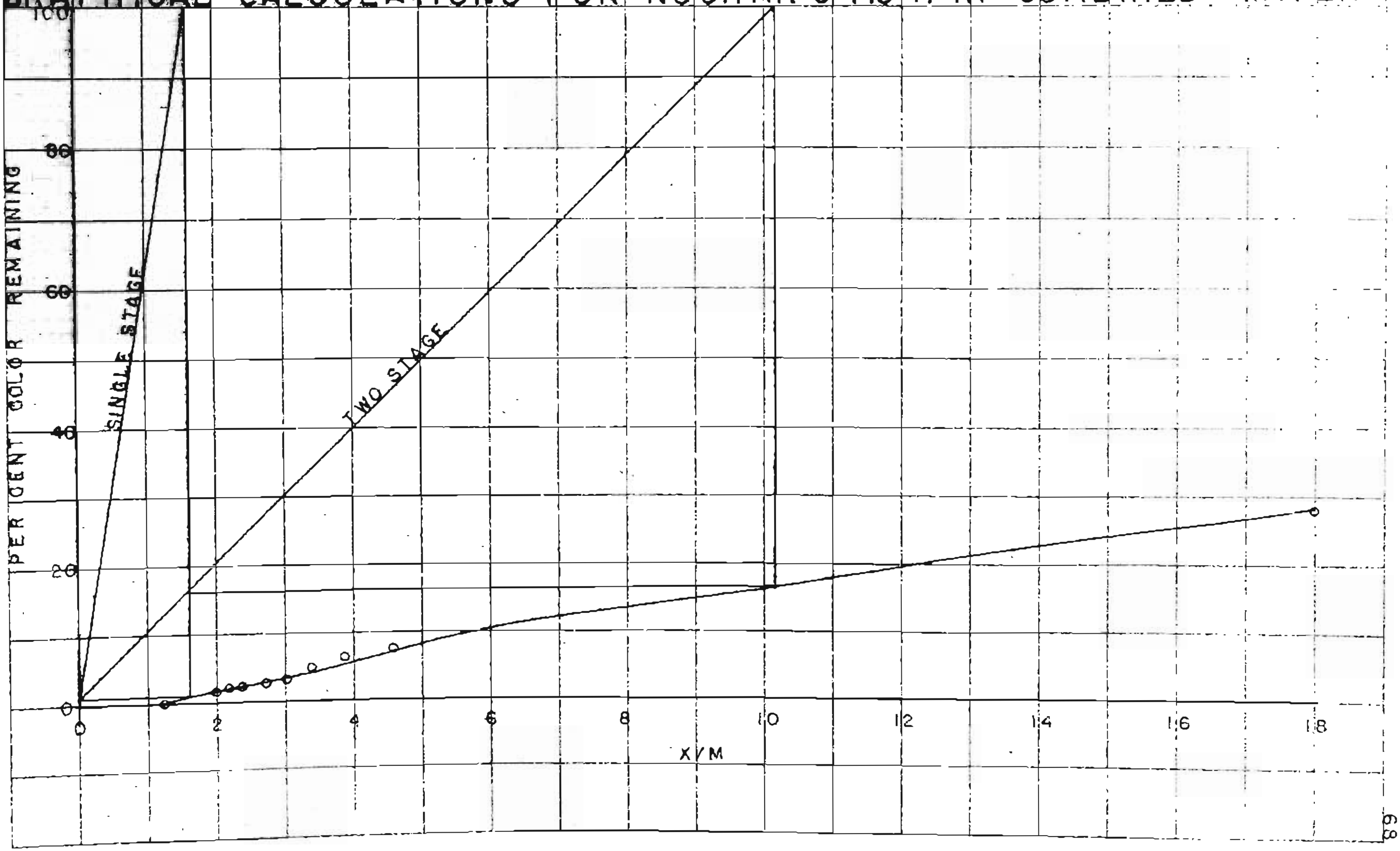


FIGURE 25 FROM DATA IN TABLE 15

GRAPHICAL CALCULATIONS FOR NUCHAR C-115 N IN RED WATER

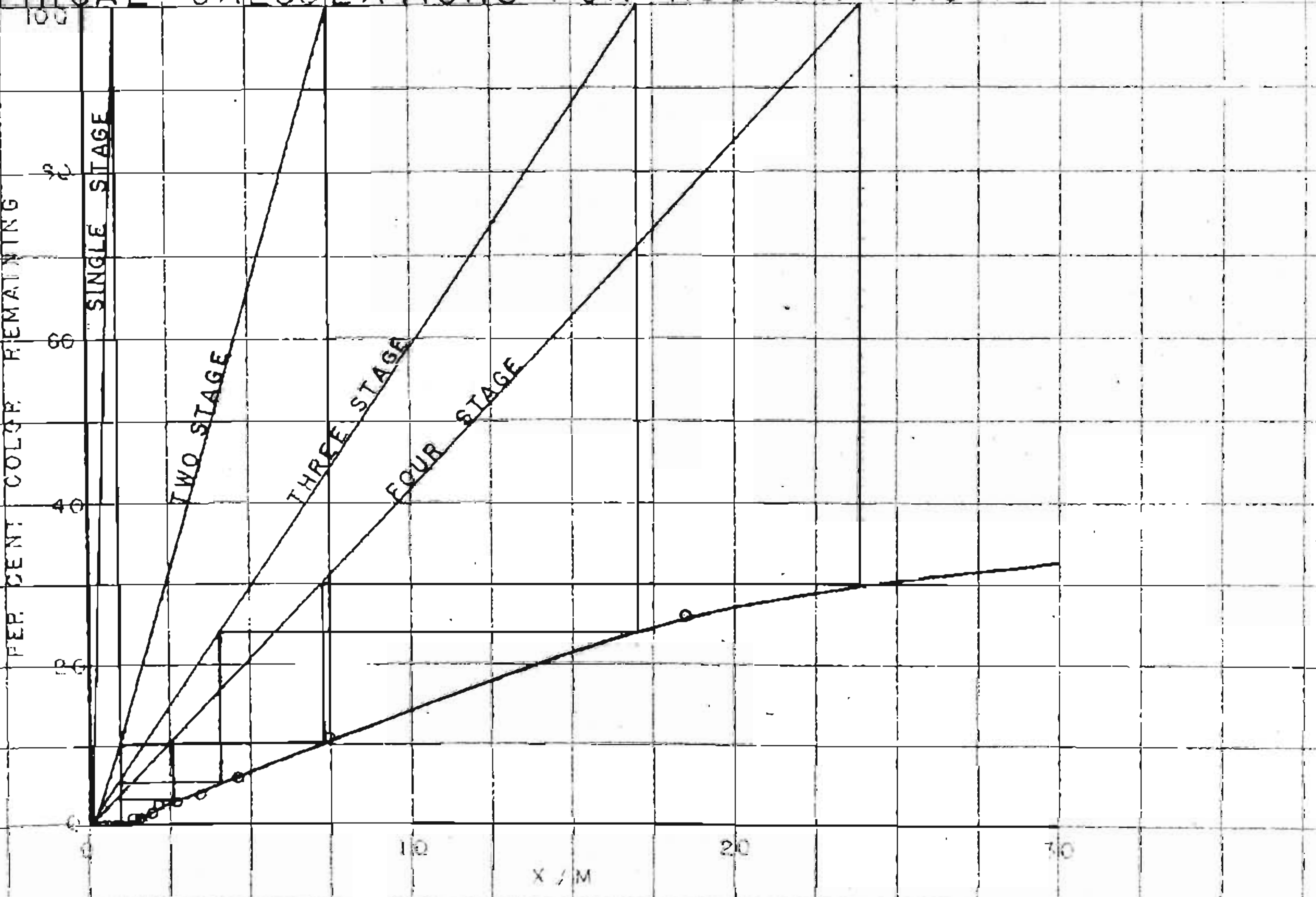
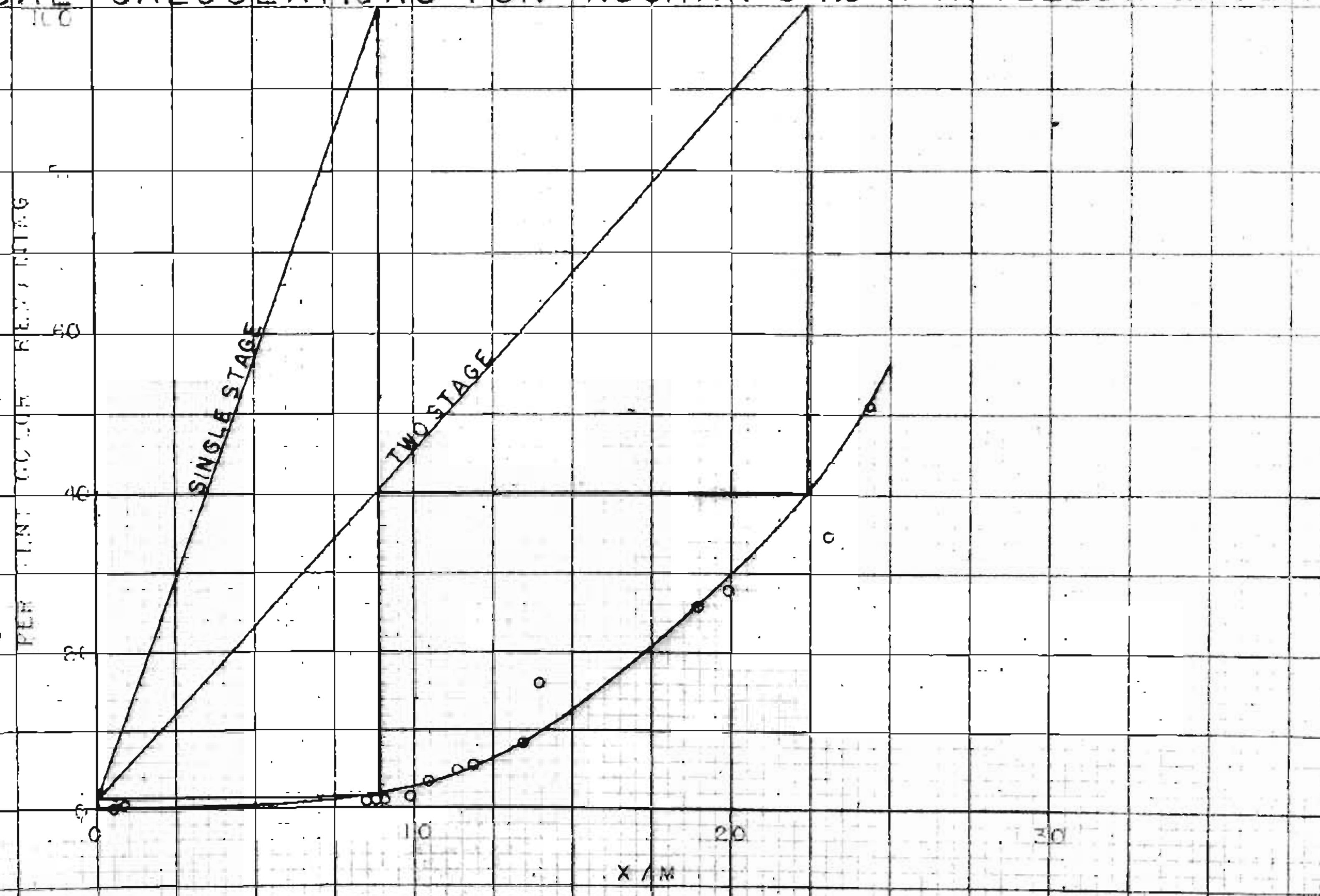


FIGURE 26 FROM DATA IN TABLE 16
GRAPHICAL CALCULATIONS FOR NUCHAR C-115 N IN YELLOW WATER



CALCULATED ADSORPTION TREATMENTS

Every single stage case may be calculated by using the adsorption isotherm as a tangent to the curve at the desired final color. These need not be tangents if they intersect the desired point and are considered to be of zero slope.

Tables show the calculated values for the various treatments. The results for the Nuchar's were calculated graphically in Figures 23, 24, 25, and 26. Results for the two stage treatments for the others were calculated by the adsorption isotherm. However, no data supports a linear isotherm for Kyrite and Bone Charcoal to 1%.

Nuchar C-190 N appears to have a slight advantage over the other charcoals tested.

Calculations show it would be more economical to treat the combined water than to treat the yellow and red water separately, but it is noted that the combined water has a higher acid concentration.

The advantage in treating combined water persists to the two stage treatments but becomes less significant.

All activated charcoal calculations are tabulated in Tables 18 and 19.

TABLE 18

Amounts of the Various Charcoals Required to Reduce the Remaining Color to 1% of the Original in a Single Treatment

Charcoal	Water	p.p.t.
Nuchar C-115 N	Red	124.
Nuchar C-115 N	Yellow	10.8
Nuchar C-115 N	Combined	60.3
Nuchar C-190 N	"	44.0
Dow's Cliffchar Fine	"	80.0
Dow's Cliffchar Coarse	"	84.0
Dow's Cliffchar 10x30	"	132.
Dow's Cliffchar 4x10	"	196.
Nuchar 000	"	64.0
Nuchar #2	"	80.0
Darco S-51	"	108.
Darco G-60	"	80.0
Harsaw's Cliff Char	"	84.0
Mallinckrodt Decolorizing	"	64.0
Burrell Cocoanut 6x14	"	66.0
Burrell Cocoanut Powdered	"	60.0
Burrell Activated 6x14	"	128.
Daigger's Bone Charcoal	"	4900.
Daigger's Decolorizing	"	100.
Sargent's Filcher	"	160.
Dicalite's Kyrite	"	2540.
Dicalite's M-23	"	84.0

TABLE 19

Amounts of the Various Activated Charcoals Required to Reduce the Remaining Color to 1% of the Original by Countercurrent Treatments

Charcoal	Water	p.p.t. of Charcoal Single Stage	Two Stage	Three Stage	Four Stage
Nuchar C-115 N	Red	124.	13.3	5.9	4.2
Nuchar C-115 N	Yellow	10.8	4.3		
Nuchar C-115 N	Combined	60.3	10.4		
Nuchar C-190 N	"	44.0	6.6	4.0	2.9
Dow's Cliffchar 10x30	"	132.	36.4		
Dow's Cliffchar 4x10	"	196.	64.0		
Daigger's Bone Charcoal	"	4900.	1600.		
Dicalite's Kyrite	"	2540.	320.		

ACTIVATED CHARCOAL--POTASSIUM PERMANGANATE TREATMENTS ON COMBINED WATER

Each of the series numbered 6, 7, 8, 9, 10, and 11 refers to 40 separate samples. This permitted almost uniform temperature and avoided any change in heating arrangement. The eight samples consisting of a vertical series were combined, thoroughly mixed and then an aliquot portion was withdrawn and diluted to its original volume. The color and pH of these samples were determined after dilution to the original volume.

After the analysis of the composite solution, it was divided into eight equal portions and a definite number of milliliters of a potassium permanganate solution containing 0.025 g per ml were added. The samples were stirred and placed on the sand bath at zero time. Each was stirred every fifteen minutes and at the end of one hour removed and filtered. After the final volume, each was diluted to the original volume (25 ml), and the pH and color determined as before. This process was repeated until all the data listed in each table was obtained.

The results of the charcoal-potassium permanganate treatment are summarized in six tables as follows: Table 20 is a continuation of series 6 from Table 11; Table 21, of series 7; Table 22, of series 8; Table 23, of series 9; Table 24, of series 10; and Table 25, of series 11. These results are graphically represented in Figures 27, 28, 29, 30, 31, and 32.

TABLE 20

Effect of Potassium Permanganate on Combined Water Samples Not Acidified Previously Treated with Nuchar C-190 N

p.p.t. $KMnO_4$	Parts per Thousand of Activated Charcoal					
	2.	4.	6.	8.	10.	
0	82.	84.	82.	83.	82.	F.V. %
	1.72	1.69	1.70	1.66	1.68	pH
	46.	30.	22.	15.0	14.7	% Col.
1	73.	58.	74.	68.	67.	F.V. %
	1.95	1.90	2.00	2.10	2.05	pH
	33.	26.	20.8	17.5	13.0	% Col.
2	73.	74.	78.	76.	73.	F.V. %
	2.01	2.02	2.00	2.10	2.09	pH
	19.3	13.7	10.8	7.9	6.25	% Col.
3	80.	80.	74.	79.	76.	F.V. %
	2.05	2.03	2.03	2.06	2.09	pH
	14.2	9.0	6.6	3.6	2.71	% Col.
4	83.	84.	78.	82.	82.	F.V. %
	2.11	2.10	2.08	2.11	2.14	pH
	10.6	6.8	3.4	2.2	1.8	% Col.
5	83.	86.	77.	78.	80.	F.V. %
	2.13	2.06	2.10	2.12	2.19	pH
	8.0	3.8	2.4	1.6	1.2	% Col.
6	83.	88.	85.	87.	89.	F.V. %
	2.15	2.12	2.14	2.21	2.24	pH
	4.8	2.5	1.7	1.1	1.1	% Col.
7	94.	89.	91.	70.	89.	F.V. %
	2.19	2.20	2.20	2.25	2.29	pH
	3.7	1.9	1.2	0.80	0.74	% Col.

FIGURE 27

EFFECT OF POTASSIUM PERMANGANATE ON COMBINED WATER NOT ACIDIFIED PREVIOUSLY TREATED WITH NUCHAR C-190N DATA FROM TABLE 20

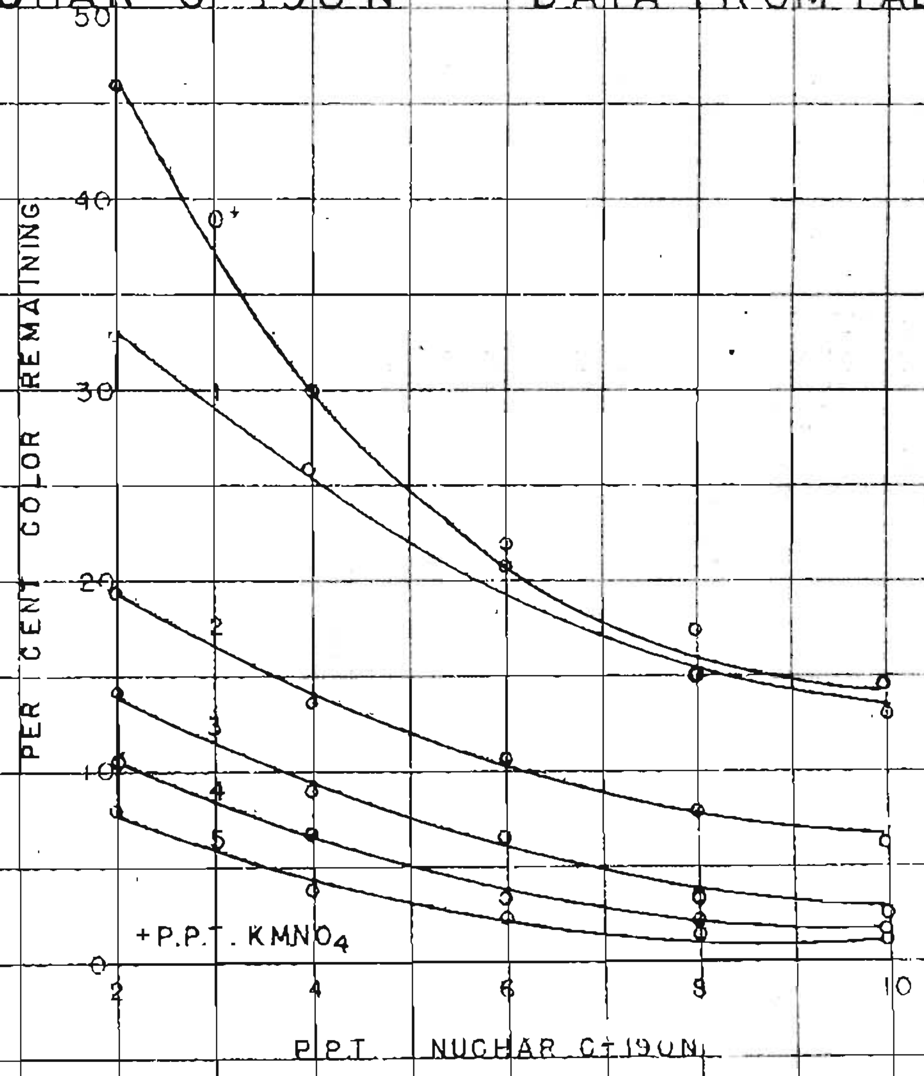


TABLE 21

Effect of Potassium Permanganate on Combined Water Samples Acidified with 2.5 Parts per Thousand of Sulfuric Acid Previously Treated with Nuchar C-190 N

p.p.t. $KMnO_4$	Parts per Thousand of Activated Charcoal					
	2.	4.	6.	8.	10.	
0	80.	80.	82.	78.	76.	F.V. %
	1.55	1.65	1.64	1.66	1.58	pH
	36.	23.5	18.6	14.8	13.5	% Col.
1	72.	70.	74.	70.	64.	F.V. %
	1.52	1.50	1.51	1.60	1.61	pH
	24.	19.2	17.8	13.9	9.8	% Col.
2	77.	77.	76.	71.	67.	F.V. %
	1.55	1.51	1.61	1.72	1.63	pH
	16.8	10.8	8.9	5.9	5.3	% Col.
3	82.	85.	75.	78.	73.	F.V. %
	1.61	1.58	1.72	1.61	1.69	pH
	14.4	6.8	5.4	3.7	2.8	% Col.
4	85.	79.	79.	74.	76.	F.V. %
	1.60	1.61	1.74	1.70	1.69	pH
	9.2	5.7	3.5	2.2	2.1	% Col.
5	77.	85.	82.	75.	78.	F.V. %
	1.64	1.59	1.73	1.72	1.70	pH
	7.2	3.4	2.5	1.4	1.2	% Col.
6	82.	88.	82.	82.	82.	F.V. %
	1.65	1.62	1.70	1.75	1.70	pH
	6.0	2.8	1.7	1.3	0.86	% Col.
7	92.	96.	88.	88.	87.	F.V. %
	1.68	1.65	1.75	1.75	1.80	pH
	4.7	2.1	1.4	0.94	0.72	% Col.

FIGURE 28

EFFECT OF POTASSIUM PERMANGANATE ON COMBINED WATER ACIDIFIED WITH 2.5 P.P.T. OF SULFURIC ACID-PREVIOUSLY TREATED WITH NUCHAR C-190N FROM DATA IN TABLE 21

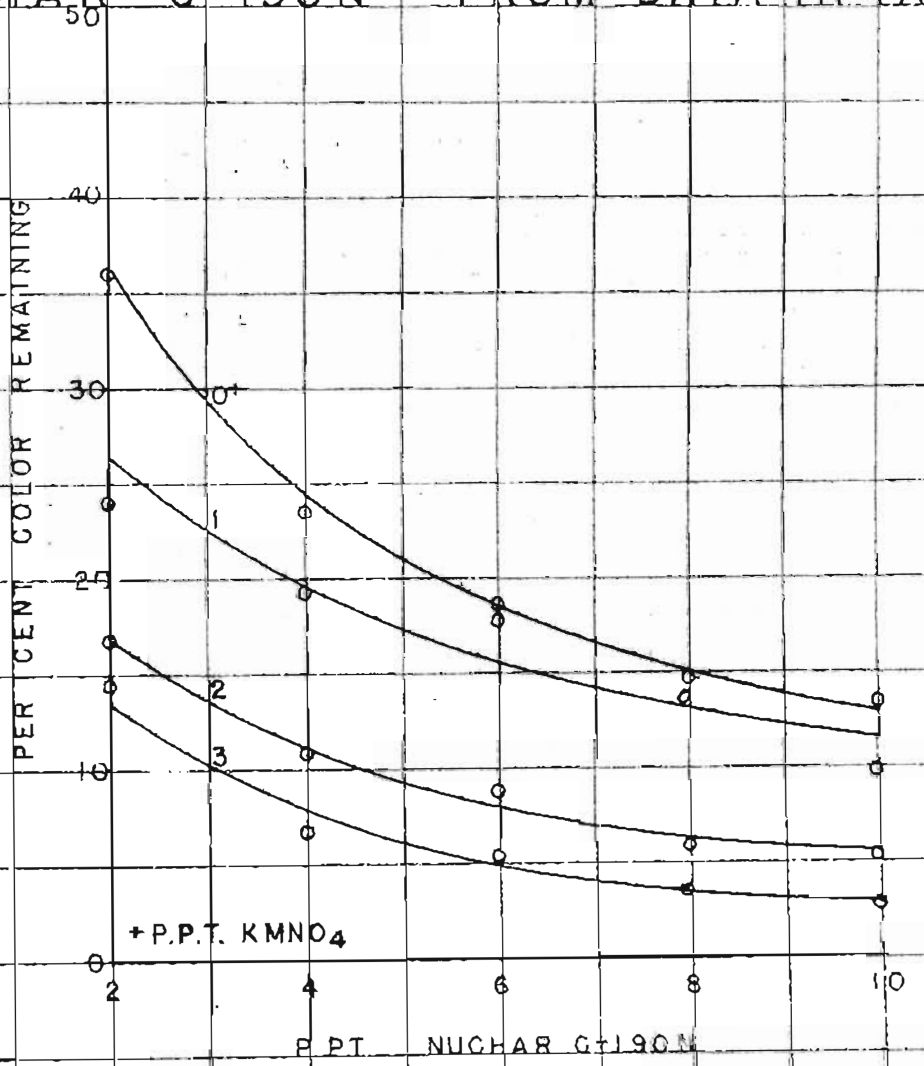


TABLE 22

Effect of Potassium Permanganate on Combined Water Samples Acidified with 7.5 Parts per Thousand of Sulfuric Acid Previously Treated with Nuchar C-190 N

p.p.t.	Parts per Thousand of Activated Charcoal					
$KMnO_4$	2.	4.	6.	8.	10.	
0	81.	80.	81.	82.	82.	F.V. %
	1.11	1.09	1.06	1.23	1.28	pH
	35.7	21.6	18.8	15.2	12.5	% Col
1	70.	64.	64.	68.	65.	F.V. %
	1.22	1.23	1.31	1.27	1.29	pH
	18.7	16.8	11.3	10.6	7.9	% Col.
2	73.	71.	56.	75.	80.	F.V. %
	1.30	1.29	1.31	1.25	1.28	pH
	12.2	9.5	7.1	5.2	4.2	% Col.
3	78.	78.	82.	77.	76.	F.V. %
	1.32	1.28	1.30	1.31	1.30	pH
	10.2	6.6	4.5	3.1	2.2	% Col.
4	80.	76.	75.	71.	72.	F.V. %
	1.33	1.37	1.31	1.30	1.30	pH
	8.2	5.0	2.9	1.7	1.2	% Col.
5	74.	74.	77.	87.	84.	F.V. %
	1.42	1.37	1.33	1.37	1.33	pH
	5.4	3.4	1.8	1.4	0.83	% Col.
6	76.	80.	74.	81.	95.	F.V. %
	1.35	1.38	1.37	1.34	1.37	pH
	4.6	2.2	1.1	0.98	0.75	% Col.
7	81.	82.	89.	86.	91.	F.V. %
	1.39	1.39	1.32	1.36	1.35	pH
	4.0	1.6	0.90	0.60	0.60	% Col.

FIGURE 29

EFFECT OF POTASSIUM PERMANGANATE ON COMBINED WATER ACIDIFIED WITH 7.5 P.P.T. OF SULFURIC ACID PREVIOUSLY TREATED WITH NUCHAR C-190N FROM DATA IN TABLE 22

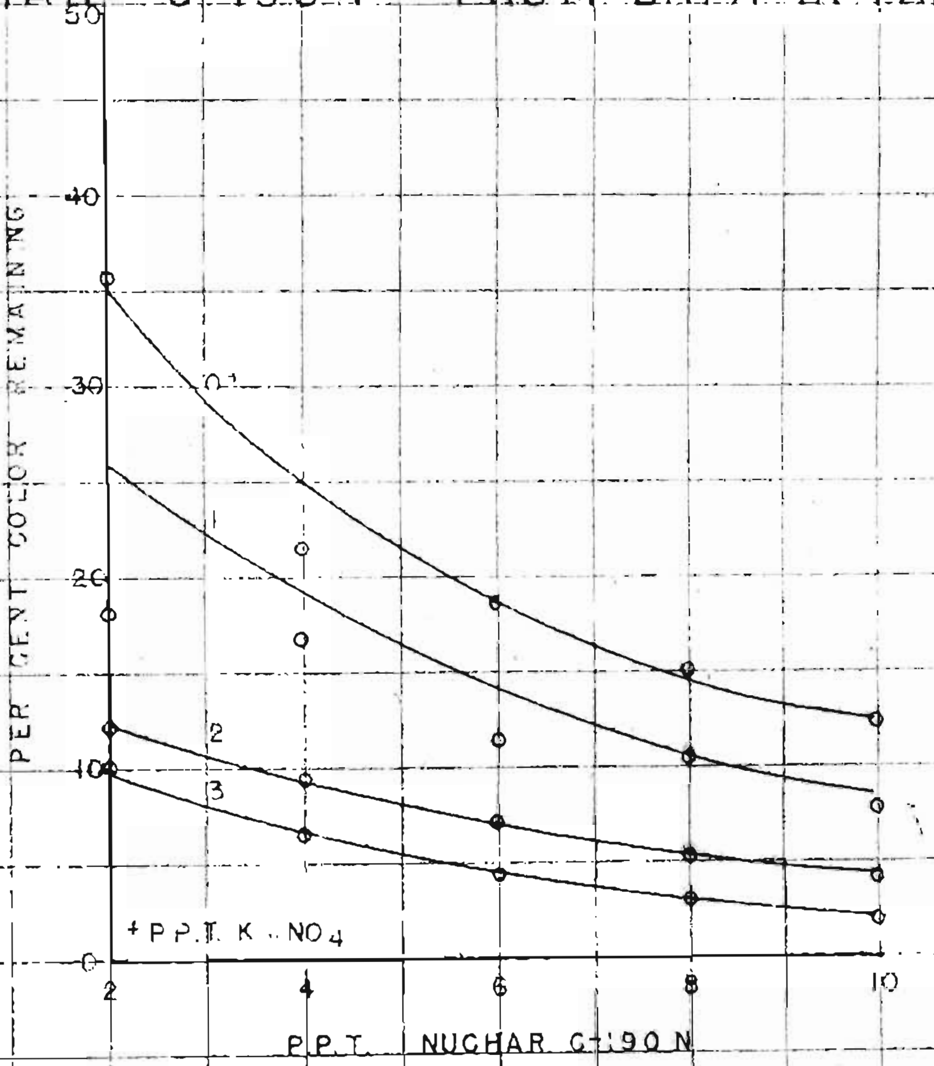


TABLE 23

Effect of Potassium Permanganate on Combined Water Samples Acidified with 12.5 Parts per Thousand of Sulfuric Acid Previously Treated with Nuchar C-190 N

p.p.t.	Parts per Thousand of Activated Charcoal					
KMnO$_4$	2.	4.	6.	8.	10.	
0	67.	66.	65.	64.	62.	F.V. %
	1.06	1.06	1.05	1.15	1.18	pH
	32.8	18.3	17.8	14.1	12.1	% Col.
1	52.	57.	40.	43.	45.	F.V. %
	1.21	1.40	1.30	1.27	1.30	pH
	19.0	12.1	9.1	7.0	4.8	% Col.
2	50.	59.	38.	52.	50.	F.V. %
	1.29	1.31	1.33	1.25	1.25	pH
	12.0	8.4	5.4	3.4	2.7	% Col.
3	58.	64.	54.	58.	54.	F.V. %
	1.31	1.31	1.22	1.31	1.36	pH
	8.5	5.9	2.9	2.0	1.0	% Col.
4	58.	72.	53.	50.	44.	F.V. %
	1.44	1.40	1.35	1.35	1.36	pH
	6.4	3.3	1.9	1.0	0.70	% Col.
5	60.	67.	59.	59.	54.	F.V. %
	1.38	1.38	1.40	1.33	1.39	pH
	4.8	2.3	1.0	0.76	0.52	% Col.
6	53.	68.	60.	59.	56.	F.V. %
	1.39	1.31	1.43	1.50	1.35	pH
	3.1	1.7	0.68	0.50	0.45	% Col.
7	65.	72.	58.	72.	58.	F.V. %
	1.45	1.30	1.34	1.40	1.35	pH
	2.6	1.1	0.62	0.37	0.22	% Col.

FIGURE 30

EFFECT OF POTASSIUM PERMANGANATE ON COMBINED WATER ACIDIFIED WITH 12.5 P.P.T. OF SULFURIC ACID PREVIOUSLY TREATED WITH NUCHAR C-190 N FROM DATA IN TABLE 23

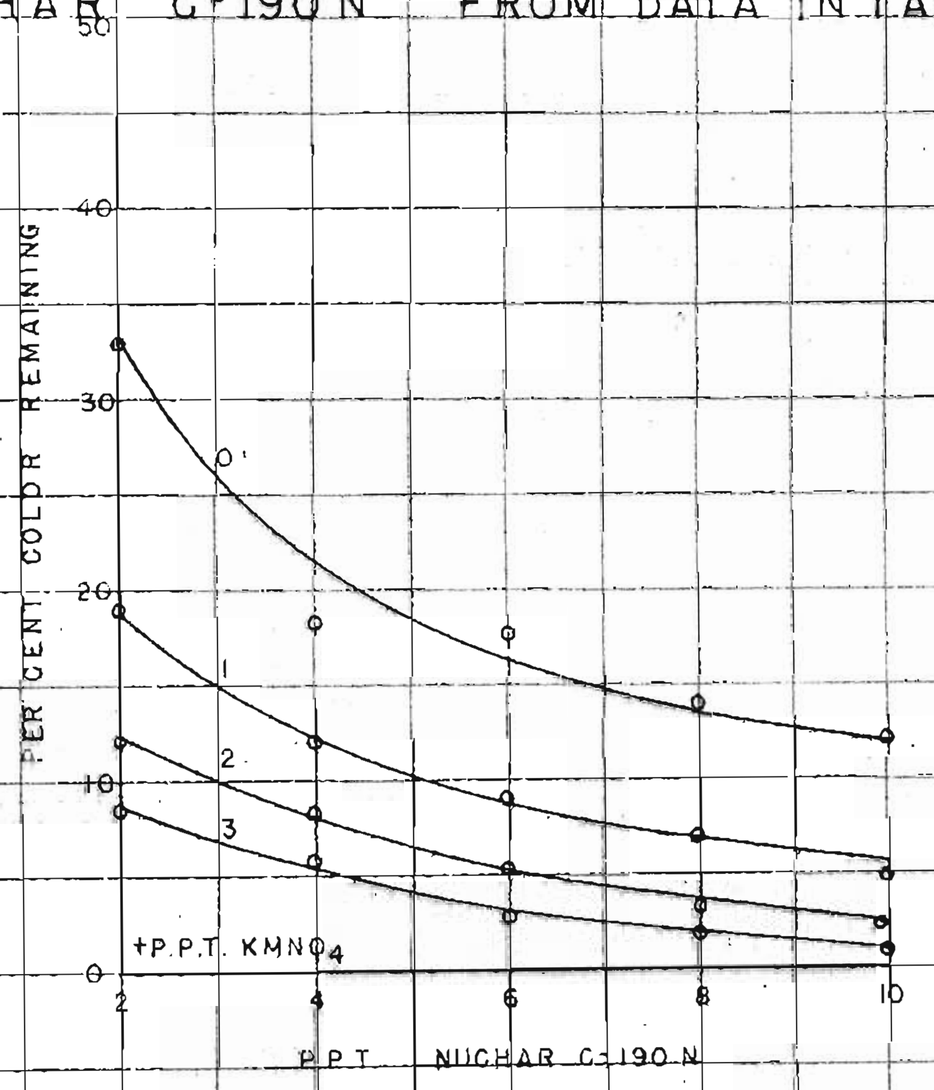


TABLE 24

Effect of Potassium Permanganate on Combined Water Samples Acidified with 25 Parts per Thousand of Sulfuric Acid Previously Treated with Nuchar C-190 N

p.p.t. $KMnO_4$	Parts per Thousand of Activated Charcoal					
	2.	4.	6.	8.	10.	
0	86.	83.	79.	76.	76.	F.V. %
	0.90	0.91	0.96	0.89	0.88	pH
	33.6	21.	18.5	14.0	13.4	% Col.
1	66.	52.	58.	58.	56.	F.V. %
	0.89	0.80	0.81	0.91	0.90	pH
	18.0	10.3	7.9	5.6	5.2	% Col.
2	54.	58.	68.	64.	62.	F.V. %
	0.94	0.86	0.80	0.90	0.94	pH
	8.9	5.8	5.3	4.1	3.1	% Col.
3	76.	69.	65.	69.		F.V. %
	0.85	0.86	0.85	0.82		pH
	8.6	5.1	3.2	2.0		% Col.
4	85.	73.	68.			F.V. %
	0.80	1.01	0.85			pH
	7.3	3.4	2.3			% Col.
5	85.	76.				F.V. %
	0.80	0.82				pH
	5.4	2.6				% Col.
6	81.	82.				F.V. %
	0.89	0.86				pH
	3.7	1.5				% Col.
7	85.					F.V. %
	0.88					pH
	2.7					% Col.

FIGURE 31

EFFECT OF POTASSIUM PERMANGANATE ON COMBINED WATER ACIDIFIED WITH 25 P.P.T. OF SULFURIC ACID PREVIOUSLY TREATED WITH NUCHAR C-190 N FROM DATA IN TABLE 24

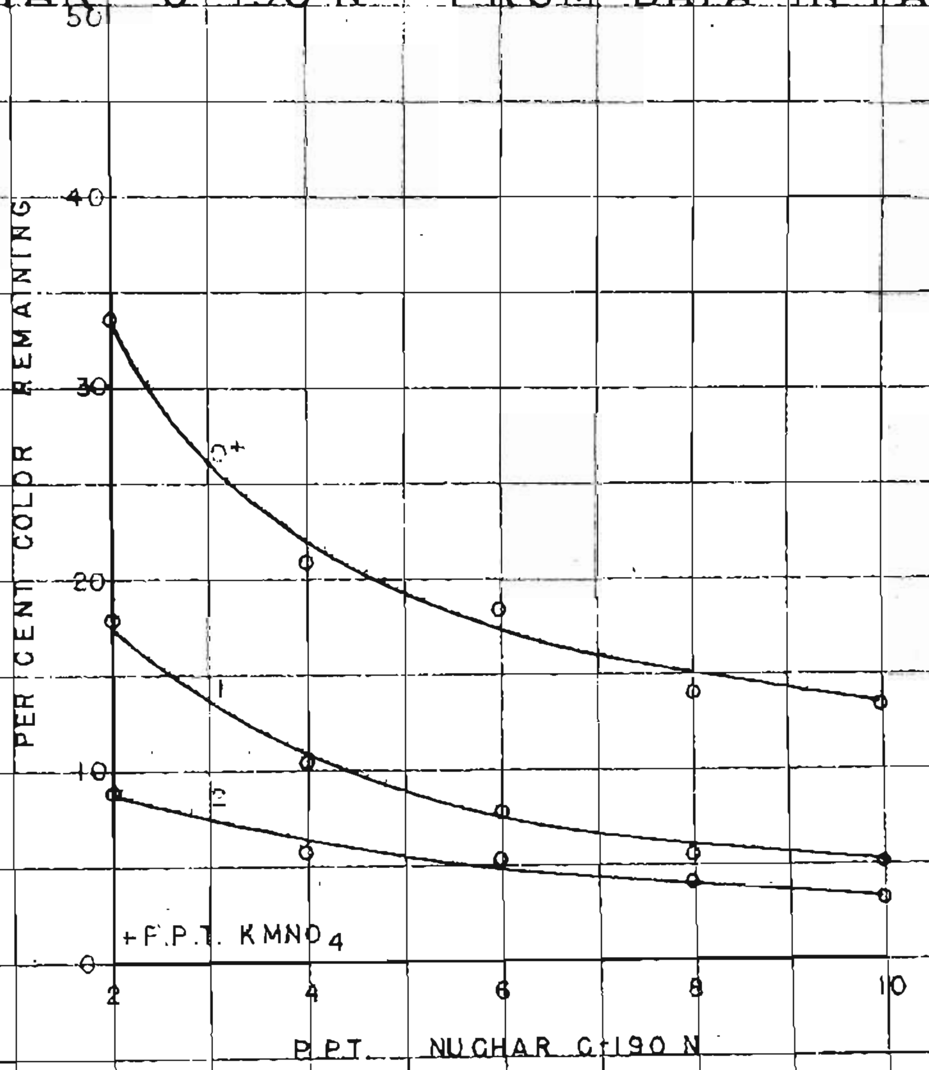


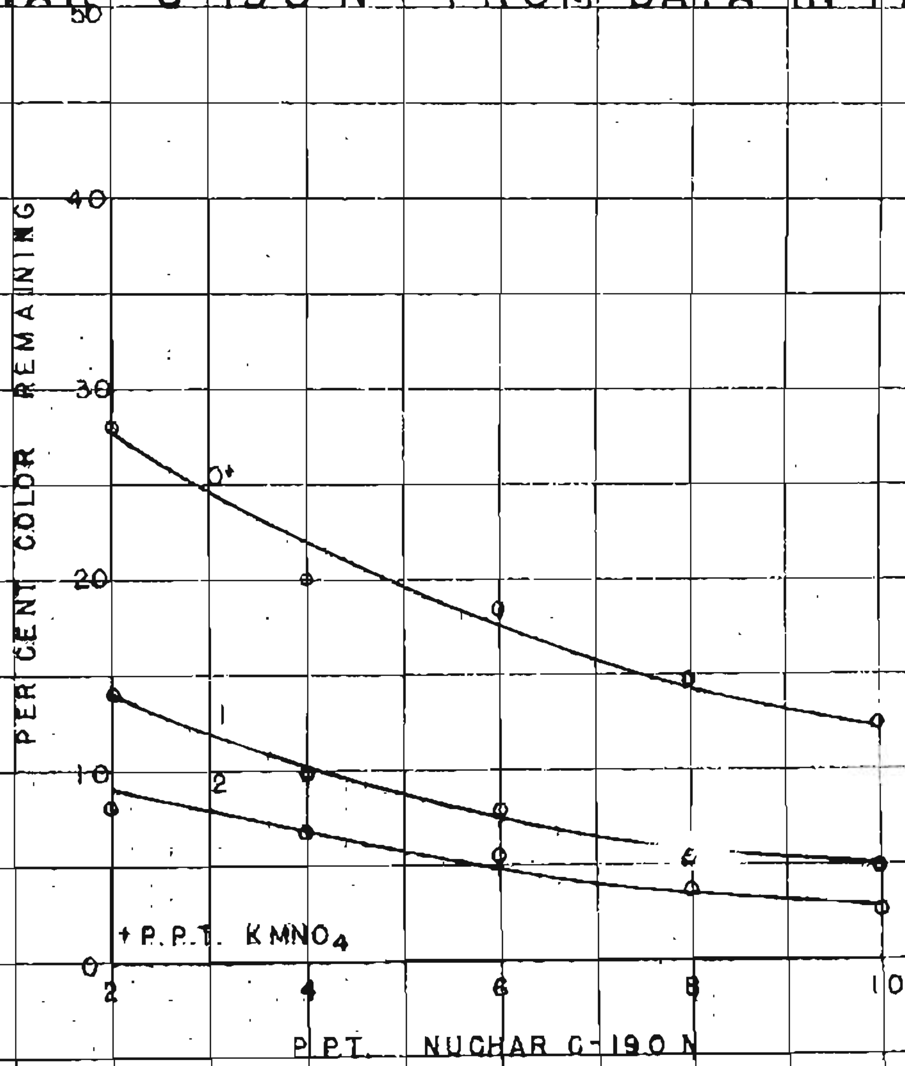
TABLE 25

Effect of Potassium Permanganate on Combined Water Samples Acidified with 50 Parts per Thousand of Sulfuric Acid Previously Treated with Nuchar C-190 N

p.p.t. $KMnO_4$	Parts per Thousand of Activated Charcoal					
	2.	4.	6.	8.	10.	
0	82.	80.	83.	77.	77.	F.V. %
	0.72	0.70	0.75	0.59	0.66	pH
	28.	20.	18.6	14.9	12.6	% Col.
1	69.	66.	66.	58.	62.	F.V. %
	0.70	0.66	0.68	0.70	0.59	pH
	14.0	9.9	8.0	5.5	5.0	% Col.
2	67.	70.	75.	67.	71.	F.V. %
	0.70	0.66	0.83	0.79	0.70	pH
	8.1	6.8	5.6	3.8	2.8	% Col.
3	76.	76.	70.	73.		F.V. %
	0.68	0.70	0.75	0.56		pH
	7.6	4.7	3.4	2.2		% Col.
4	83.	77.	78.			F.V. %
	0.67	0.68	0.62			pH
	5.5	3.3	2.9			% Col.
5	85.	84.				F.V. %
	0.70	0.72				pH
	4.6	2.2				% Col.
6	84.	84.				F.V. %
	0.78	0.80				pH
	3.3	1.5				% Col.
7	79.					F.V. %
	0.65					pH
	2.2					% Col.

FIGURE 32

EFFECT OF POTASSIUM PERMANGANATE ON COMBINED WATER ACIDIFIED WITH 50 P.P.T. OF SULFURIC ACID PREVIOUSLY TREATED WITH NUCHAR C-190 N FROM DATA IN TABLE 25



The color destroyed by the permanganate may be due to oxidation of the side chain of toluene base compounds or by destruction of the ring structure. Both conclusions may be used to explain decolorization. Dinitro derivatives should be oxidized to benzoic acid derivatives. If the oxidation product is toxic, this treatment accomplishes only decolorization, and adsorption or dilution must be relied upon to produce a water suitable for discharge into streams.

The addition of sulfuric acid to the sample increases the amount of adsorption by charcoal as well as the amount of color destroyed by potassium permanganate. A minimum of 7.5 p.p.t. of acid is required for efficient use of the charcoal. Slightly better results for the combined treatment with charcoal and permanganate resulted when 12.5 p.p.t. of acid were added. Some adsorption and oxidation were noted when no acid was added as is indicated in the tables and graphs.

RECOVERY OF ACTIVATED CHARCOAL

A brief study was made of methods for recovery of both the adsorbed color and the charcoal used in these experiments. The used charcoal was treated with a concentrated solution of sodium hydroxide in an attempt to free the adsorbed materials. Colored compounds were removed from the charcoal by this process but only in solutions more dilute than the original. Alkaline isoamyl alcohol was tried as a solvent with slightly better but indifferent results.

Time did not permit the removal of the color by steam or heat or the combined effect of steam and heat. It is desireable that these studies be made on the used charcoals.

EXTRACTION TESTS

A large number of tests were made for the extraction of this water by essentially immiscible solvents in which the colored compounds showed a greater solubility than in water. Isoamyl alcohol, isobutyl alcohol, and fusel oil showed promise. Isoamyl alcohol was selected for exhaustive tests because of its commercial availability and relationship to fusel oil.

Samples of 50 ml of combined water with various amounts of sulfuric acid were treated with different volumes of isoamyl alcohol. The mixing was performed with a spiral stirrer which cleared the sample tubes by approximately one quarter inch on all radii. The samples were stirred at 1000 r.p.m. for ten minutes with the stirrer rotating in a direction tending to lift the water layer into the alcohol layer. Separation was accomplished by the use of a separatory funnel. The standards were a part of the large amounts of water prepared for the samples and were later saturated with isoamyl alcohol by adding it dropwise and shaking in a separatory funnel until the first appearance of a second phase. This extraction procedure was repeated a second and a third time in some cases, for an approximation of multiple contact extraction.

It was found that on the addition of 12.5 p.p.t. of sulfuric acid to the red water that sulfur dioxide was liberated and that a yellow foam-like substance appears; this organic compound which separates is soluble in carbon-tetrachloride, chloroform, carbon disulfide, benzaldhyde, isoamyl and isobutyl alcohols but not in ethylene dibromide.

The addition of sulfuric acid favors the extraction of the combined water; the effect of this addition is very evident in the first extraction until more than 62.5 p.p.t. of sulfuric acid has been added; further additions are without any appreciable effect, though the second raffinate of combined water shows improvement up to and including 375 p.p.t. of sulfuric acid.

The additional volumes of extractant appear beneficial in the first extraction of combined water, but the raffinates from the second extraction show very small benefits in changing from 50 to 100 v.p.h. of isoamyl alcohol.

The extraction of the yellow water without acidification offers no problem. Almost any desired raffinate can be achieved by either of two methods; the increased use of solvent or by repeated extractions.

The extraction process may be stopped at any concentration of color and the remaining color adsorbed by charcoal. The large amount of sulfuric acid would not interfere, but rather aid adsorption.

The results of extraction of the combined water with varying amounts of sulfuric acid by isoamyl alcohol are tabulated in Table 26 and graphically in Figures 33 and 34.

Red water strongly acidified with sulfuric acid shows the extraction characteristics tabulated in Table 27 and are shown by a graph in Figure 35.

Extraction data for the yellow water as received with isoamyl alcohol are tabulated in Table 28 and are shown graphically in Figure 36.

TABLE 26

The Effects of Concentrated Sulfuric Acid and Varying Amounts of Isoamyl Alcohol on the Extraction of Combined Water

Series Number	p.p.t. H_2SO_4	Extraction	v.p.h.(1) Isoamyl Alcohol			
			20.	50.	100.	
32	12.5	1st				F.V. %
			1.08	1.28	1.13	pH
			86.	68.	64.	% Col.
		2nd	86.	82.	70.	F.V. %
			1.11	1.09	1.09	pH
			66.	54.	53.	% Col.
33	37.5	1st				F.V. %
			0.70	0.70	0.78	pH
			50.	50.	45.	% Col.
		2nd	84.	80.	65.	F.V. %
			0.69	0.88	0.66	pH
			44.	36.	32.	% Col.
34	62.5	1st				F.V. %
			0.62	0.61	0.61	pH
			41.	31.	25.	% Col.
		2nd	84.	78.	74.	F.V. %
			0.65	0.60	0.50	pH
			23.	16.2	12.4	% Col.
35	125.0	1st	99.	95.	90.	F.V. %
			-3.45	-3.41	-3.40	pH
			51.	35.	25.	% Col.
		2nd	95.	87.	78.	F.V. %
			-3.50	-3.44	-3.56	pH
			28.	16.7	12.9	% Col.
36	375.0	1st	109.	106.	97.	F.V. %
			-4.00	-3.98	-3.95	pH
			39.	31.	22.	% Col.
		2nd	104.	97.	81.	F.V. %
			-4.09	-4.10	-4.07	pH
			11.6	7.0	4.5	% Col.
37	625.0	1st	121.	106.	98.	F.V. %
			-4.15	-4.30	-4.30	pH
			40.	34.	26.	% Col.
		2nd	111.	91.	71.	F.V. %
			-4.27	-4.38	-4.23	pH
			16.7	7.7	8.9	% Col.

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(1) Volumes of Alcohol per hundred volumes of Water.

FIGURE 33

EXTRACTION TESTS OF COMBINED WATER
ACIDIFIED WITH SULFURIC ACID
FROM DATA IN TABLE 26

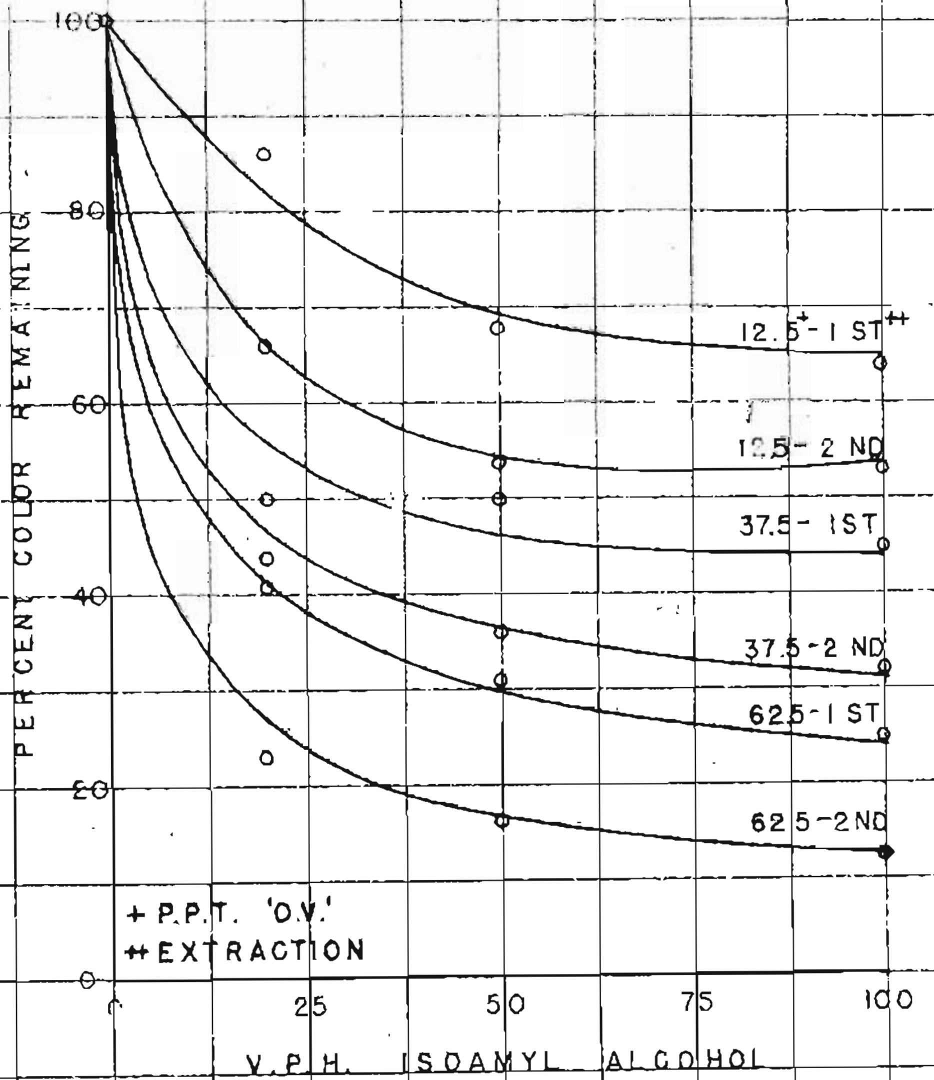


FIGURE 34

EXTRACTION TESTS OF COMBINED WATER
ACIDIFIED WITH SULFURIC ACID
FROM DATA IN TABLE 26

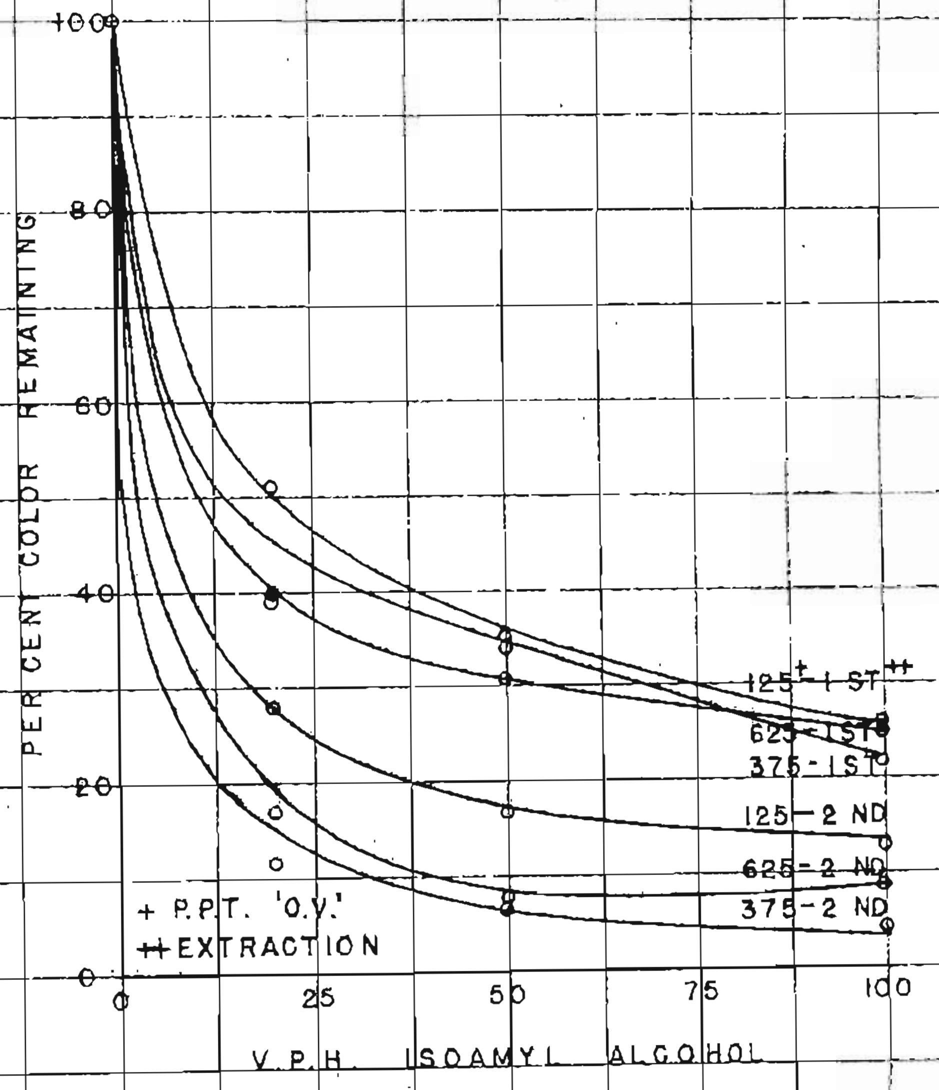


TABLE 27

The Effect of Varying Amounts of Isoamyl Alcohol Used in the Extraction of Red Water Acidified with 375 parts per Thousand of Sulfuric Acid

Series Number	Extraction	Vols. per Hundred of Isoamyl Alcohol						
		20.	60.	100.	140.	200.	300.	
38	1st	93.	85.	78.	74.	67.	50.	F.V. %
		-4.20	-4.00	-4.14	-4.10	-4.12	-4.16	pH
		87.	63.	55.	45.	38.	32.	% Col.
	2nd	86.	80.	64.	55.	48.		F.V. %
		-4.04	-4.03	-4.07	-4.00	-3.95		pH
		11.2	5.8	3.7	3.4	3.4		% Col.
	3rd	79.	71.	46.				F.V. %
								pH
		5.5	3.0	3.0				% Col.

FIGURE 35

EXTRACTION TESTS OF RED WATER ACIDIFIED WITH 375 P.P.T. OF SULFURIC ACID

FROM DATA IN TABLE 27

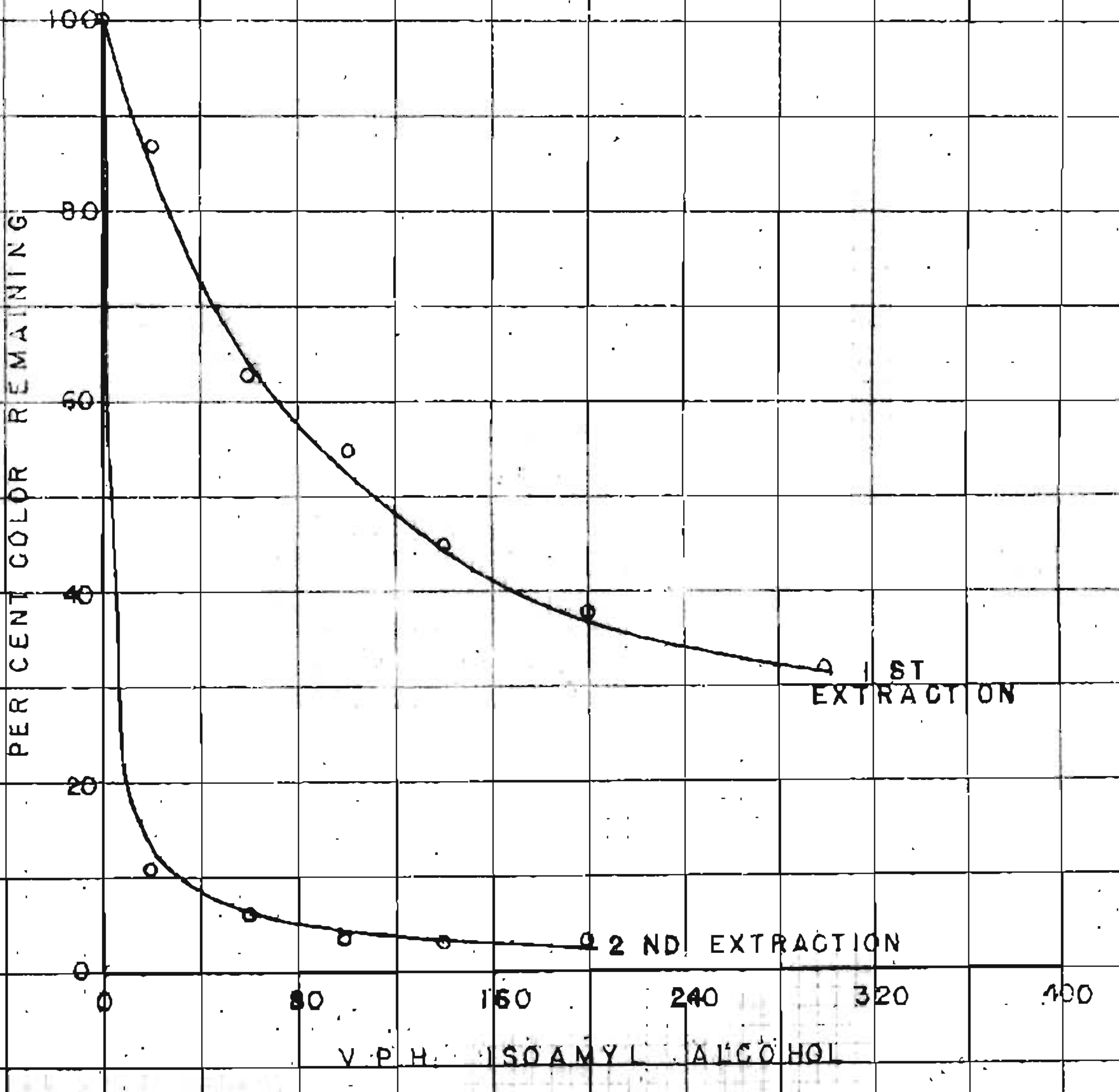


TABLE 28

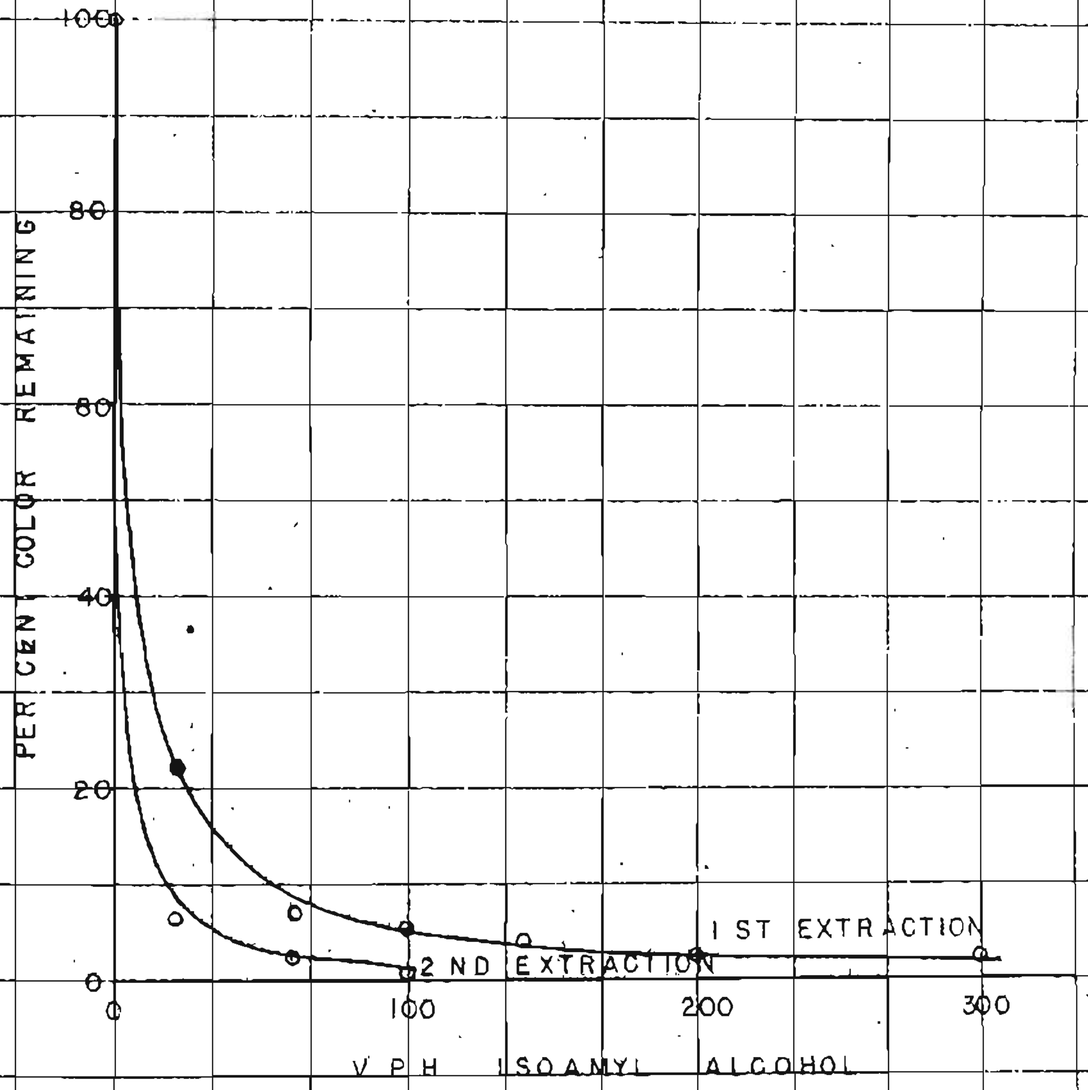
The Effect of Varying Amounts of Isoamyl Alcohol used in the Extraction of Yellow Water as Received

Series Number	Extraction	Vols. per Hundred of Isoamyl Alcohol						
		20.	60.	100.	140.	200.	300.	
39	1st	94.	94.	92.	81.	76.	61.	F.V. %
		0.62	0.75	0.86	0.89	0.90	0.90	pH
		22.2	7.1	5.5	4.1	2.4	2.6	% Col.
	2nd	89.	93.	75.				F.V. %
		1.00	0.90	0.93				pH
		6.5	2.3	0.95				% Col.

FIGURE 36

EXTRACTION TESTS OF YELLOW WATER AS RECEIVED

FROM DATA IN TABLE 28



REPRESENTATION OF EXTRACTION EQUILIBRIUM

Nernst's Distribution Law

The distribution law applies only to systems of complete immiscibility and then only as a limiting case. The solute concentration in phase one is proportional to the solute concentration in phase two.

Isoamyl alcohol has a slight solubility in water and the presence of hydrochloric acid tends to make the two miscible, but sulfuric acid does not exhibit such a marked effect on the solubility of isoamyl alcohol in water.

The data shown in the extraction section do not agree with the ideal distribution law as applied to a double contact extraction.

Graphical Representation

If a basis of 100% be selected in some definite weight of solvent, it becomes possible to calculate the per cent extracted per gram of solvent, provided the extracting weight of the solvent is that used in treating the arbitrarily assumed weight of water. An approximate relationship by volume may be used provided the amount of solute involved is small enough to cause a negligible change in volume. This may be extended to a system of very slight solubilities if the extracting solvent is saturated with the raffinate solvent and the raffinate solvent is saturated with the extracting solvent.

ISOAMYL ALCOHOL--WASTE WATERS

DISTRIBUTION RATIO

Throughout this distribution study every per cent has been calculated to per cent per milliliter of saturated solvent. The alcohol was saturated with distilled water and the waste water was saturated with alcohol. These conditions are those usually encountered in countercurrent extraction with reflux.

The samples of red and combined water were acidified with 37.4 parts per thousand of sulfuric acid and then saturated with alcohol. The yellow product which separated on acidification of the red water redissolved when the water was saturated with alcohol.

The samples of waste water were introduced into 50 ml oil sample bottles and the alcohol was added. After securely closing the mouths of the bottles with corks, the bottles were taped to a four blade propellor.

The samples were rotated at approximately 50 r.p.m.; this speed permits the liquids to thoroughly mix. After twenty minutes of agitation, the samples were removed and the extract and raffinate were separated. The raffinate was compared colorimetrically with a sample which was saturated with alcohol by a similar agitation process.

All of these waters can be extracted if acidified; the red water is the most difficult, the yellow water the easiest, and the combined water intermediate between the red and yellow waters. Any water may be extracted more easily if sulfuric acid is added.

The equilibrium curve for yellow water and isoamyl alcohol shows a very surprising "hump" which is further substantiated by the previous extractions.

The results of these distribution tests are tabulated and graphically represented as follows: combined water in Table 29, and Figure 37; red water in Table 30 and Figure 38; and yellow water in Table 31, and Figure 39.

TABLE 29

Distribution Equilibrium Data for Isoamyl Alcohol and Combined Water Acidified with 36.8 Parts per Thousand of Sulfuric Acid

Sample Number	Alcohol v.p.h.	Final Color
25E	0.2	88.3
26E	0.8	77.0
27E	1.2	73.3
28E	1.6	69.8
29E	2.0	69.0
30E	2.8	64.4
31E	4.0	62.5
32E	8.0	54.4
33E	20.0	48.2
34E	28.0	43.6
35E	40.0	38.0
36E	60.0	32.5
37E	100.0	30.0(1)
38E	100.0	30.1(2)
39E	100.0	29.8
40E	150.0	26.4
41E	400.0	16.5

---

(1) This sample was run for ten minutes in the stirrers previously used.

(2) This is the same sample run for thirty minutes.

FIGURE 37

COLOR DISTRIBUTION CHART FOR ISOAMYL ALCOHOL AND COMBINED WATER ACIDIFIED WITH 36.8 P.P.T. OF SULFURIC ACID FROM DATA IN TABLE 29

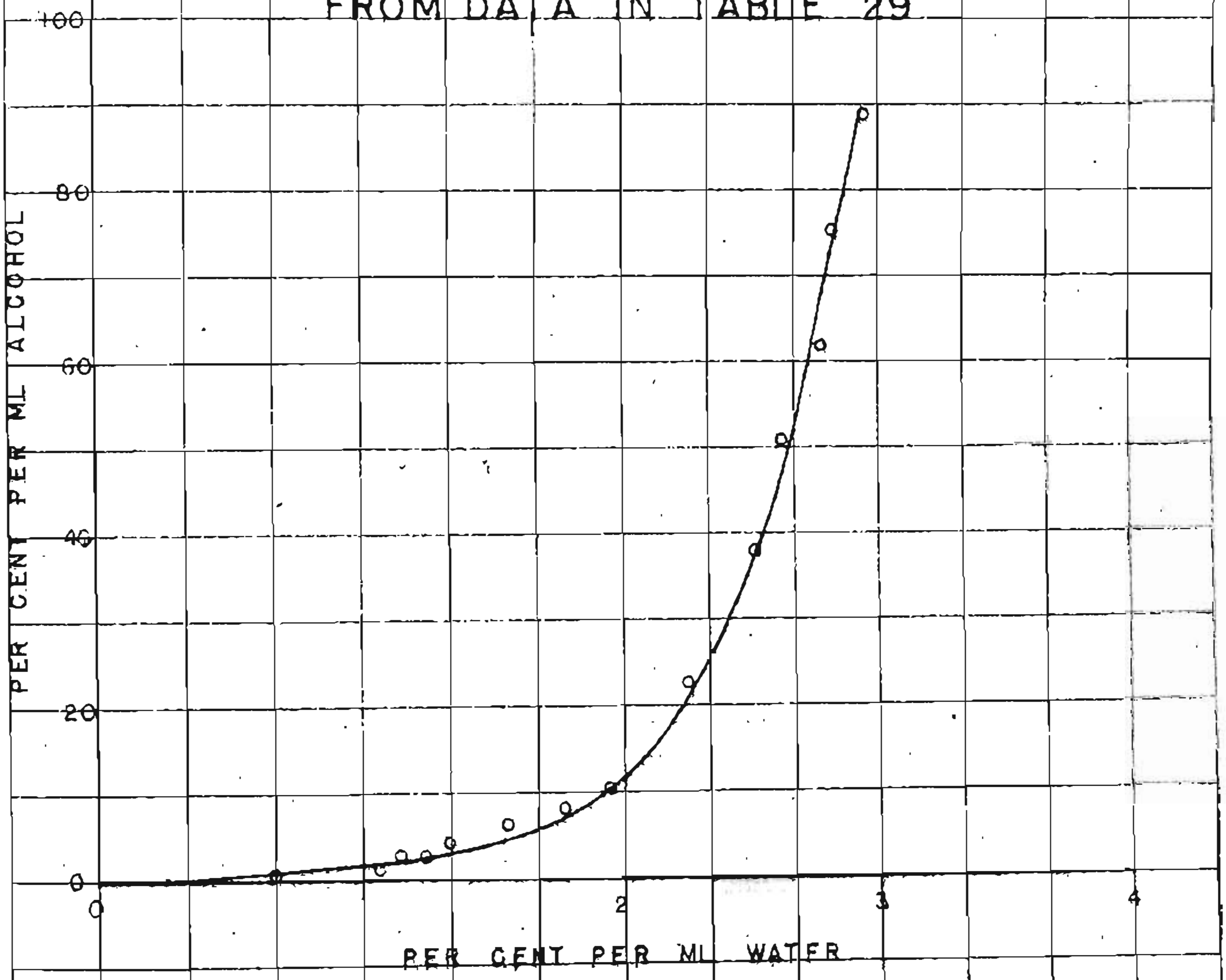


TABLE 30

Distribution Equilibrium Data for Isoamyl Alcohol and Red Water Acidified with 36.8 Parts per Thousand of Sulfuric Acid

Sample Number	Alcohol v.p.h.	Final Color
1E	0.2	98.6
2E	0.6	88.1
3E	1.0	84.8
4E	1.8	85.2
5E	3.4	83.8
6E	19.4	74.6
7E	59.4	62.4
8E	200.	43.7
9E	400.	38.6
10E	500.	35.1
11E	1500.	30.0

FIGURE 38

COLOR DISTRIBUTION CHART FOR ISOAMYL ALCOHOL AND RED WATER ACIDIFIED WITH 36.8 P.P.T. OF SULFURIC ACID FROM DATA IN TABLE 30

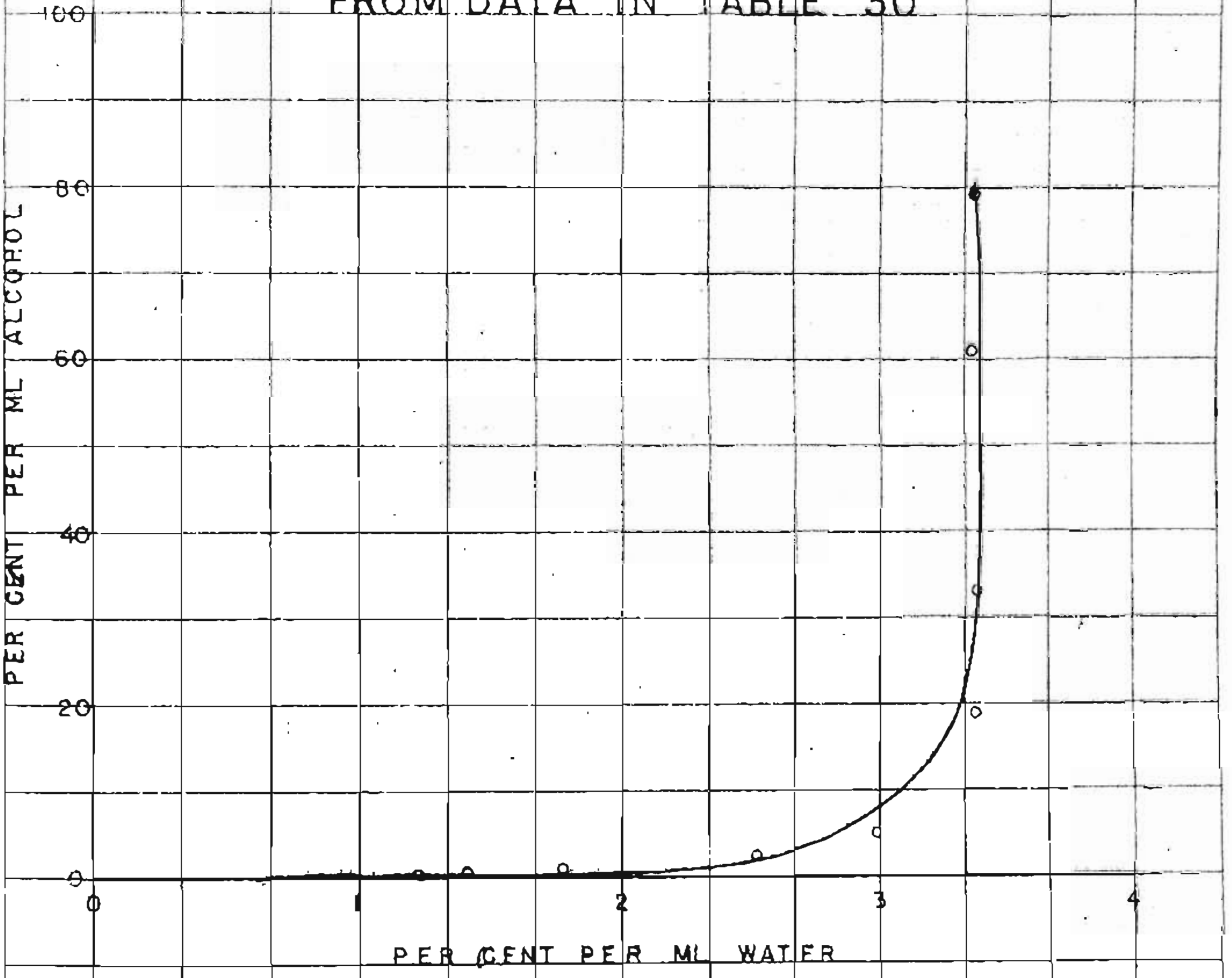


TABLE 31

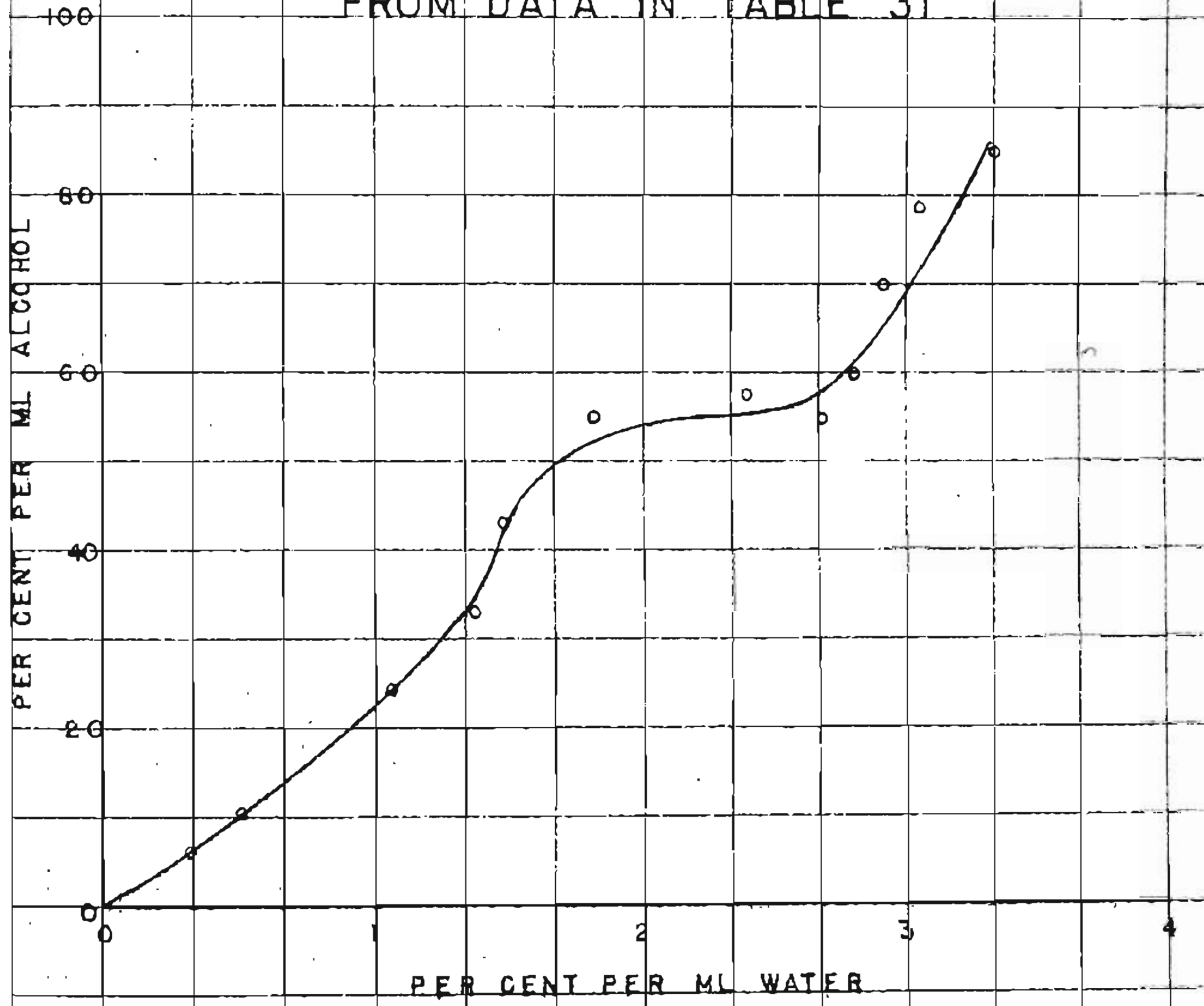
Distribution Equilibrium Data for Isoamyl Alcohol and Yellow Water as Received

Sample Number	Alcohol v.p.h.	Final Color
12E	0.3	86.
13E	0.8	83.
14E	1.2	76.
15E	1.6	72.
16E	2.0	70.
17E	2.4	67.
18E	2.8	60.
19E	4.0	45.
20E	6.0	36.
21E	8.0	34.
22E	12.0	26.
23E	28.0	12.5
24E	60.0	7.6

FIGURE 39

COLOR DISTRIBUTION CHART FOR ISOAMYL ALCOHOL AND YELLOW WATER AS RECEIVED

FROM DATA IN TABLE 31



EXTRACTION CALCULATIONS

The ratio of volumes of saturated alcohol to water to obtain any desired color by countercurrent extraction may be found from the slope of the line connecting the original concentration-extract point with the intersection of the desired raffinate-fresh solvent point. This is a slight modification of the Evan's method[47].

Solvent extraction may be used to reduce the color to any desired point, and the remainder of the color adsorbed by activated charcoal. The equilibrium conditions may be changed by the amount of acid used.

Figure 40 is a graphical design to remove seventy-five per cent of the colored bodies in three equilibrium contacts. The slope of the line shows that 0.21 gallons of alcohol saturated with water would be required to treat one gallon of water saturated with alcohol and acidified with 37.4 parts per thousand of sulfuric acid.

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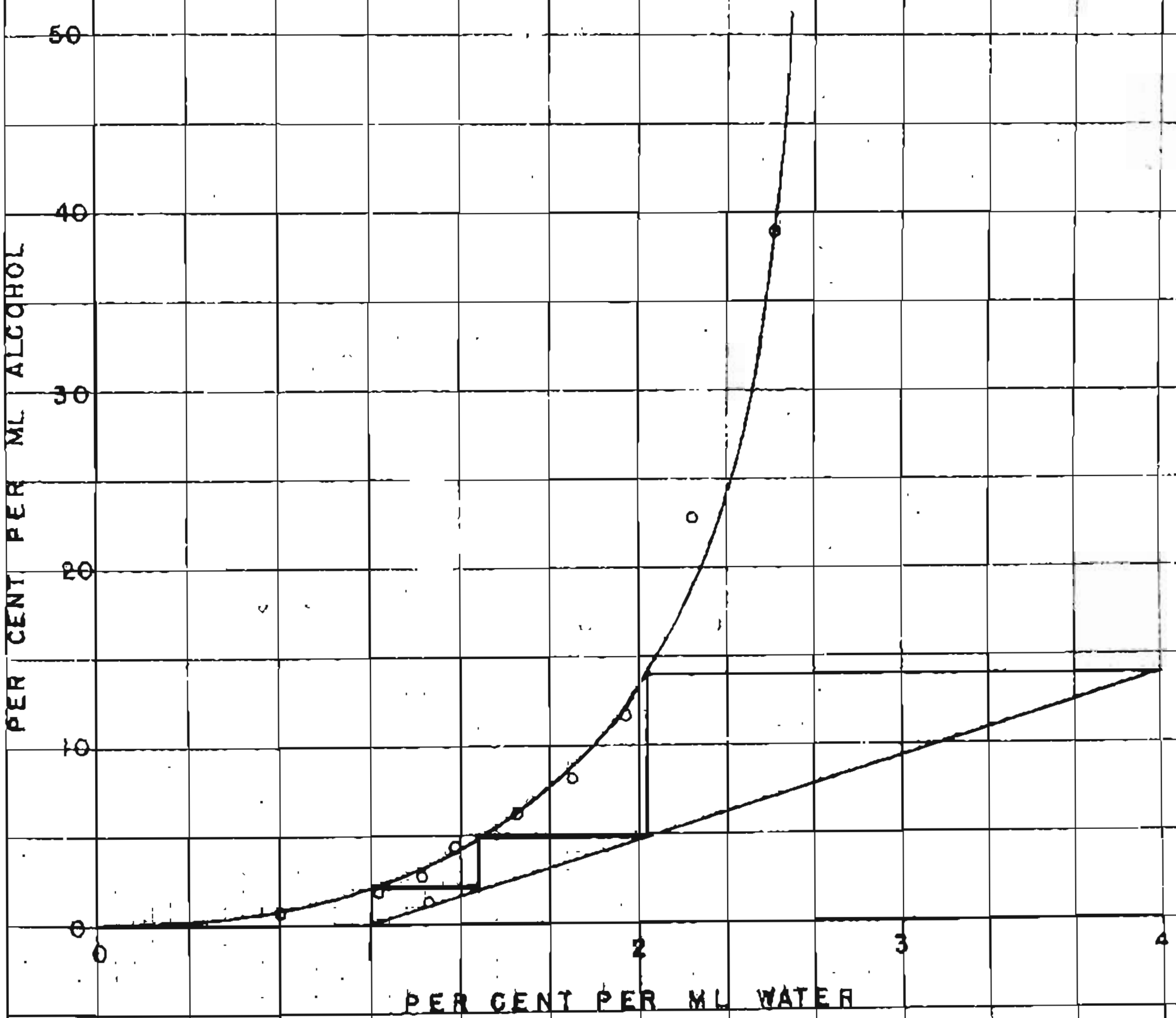
[47] Perry, John B. Chemical engineer's handbook. 2nd ed. New York, McGraw Hill Book Co., Inc., 1941. p. 1243.

FIGURE 40

DESIGN FOR AN IDEAL THREE STAGE COUNTERCURRENT EXTRACTION FROM DATA IN TABLE 29



EXTRACTION WITH ISOAMYL ALCOHOL--ACTIVATED CHARCOAL TESTS

The samples of combined water listed in Table 26 were divided into 10 ml portions and three of these portions were treated with Nuchar C-115 N. The amount required was calculated from Figure 24. One portion was treated with ten per cent less than the required, a second with the required, and the third with ten per cent more.

Six 10 ml graduated cylinders were selected with about the same depth for the 10 ml graduation. Standards were prepared with 1.0, 0.75, 0.50, 0.25, and 0.00 per cent of the original color. The treated water was diluted to 10 ml and compared with these standards.

All of these adsorption tests are tabulated in Table 32 with a summary of the extraction data. More complete extraction data may be found in Table 26.

TABLE 32

Adsorption with Activated Charcoal of the Isoamyl Alcohol Raffinates

Series Number	v.p.h. Alcohol	F.V. %		-10%	Calc'd	10%	
33	20	84	0.0	16.	18.	20.	p.p.t.
			44.	0.5	0.5	0.5	% Col.
	50	80	0.0	13.	14.	15.	p.p.t.
			36.	0.5	0.25	0.25	% Col.
	100	65	0.0	9.	10.	11.	p.p.t.
			32.	0.25	0.25	0.0	% Col.
35	20	95	0.0	11.	13.	14.	p.p.t.
			28.	0.5	0.25	0.25	% Col.
	50	87	0.0	6.	7.	8.	p.p.t.
			16.7	0.25	0.25	0.25	% Col.
	100	78	0.0	4.	5.	6.	p.p.t.
			12.9	0.25	0.25	0.25	% Col.
37	20	111	0.0	8.	9.	10.	p.p.t.
			16.7	1.0	0.5	0.25	% Col.
	50	91	0.0	3.6	3.8	4.2	p.p.t.
			7.7	0.75	0.5	0.75	% Col.
	100	71	0.0	2.4	2.6	2.8	p.p.t.
			8.9	1.0	0.5	1.0	% Col.

POTASSIUM PERMANGANATE--ISOAMYL ALCOHOL TESTS ON COMBINED WATER

A study was made of decolorizing the waters by first oxidizing a part of the color by varying amounts of potassium permanganate and then removing additional color by solvent extraction. In this series, 50 ml samples were acidified with sulfuric acid and then treated with 5, 10, and 15 ml of the standard potassium permanganate solution. They were thoroughly mixed, placed on the sand bath for one hour, and stirred at fifteen minute intervals. The samples were filtered, evaporated on the sand bath to the original volume (50 ml) and the pH and color determined.

These samples were extracted with isoamyl alcohol and the raffinates tested as in the previous extraction series. No water was added to the raffinates to bring them back to their original volumes, but the color and pH were taken at the final volume.

The addition of sulfuric acid slightly increased the amount of color destroyed by the potassium permanganate. The addition of sulfuric acid increases the quantity of color removed by the isoamyl alcohol when used alone or following a potassium permanganate treatment. The graph readily shows the most desirable volume of solvent that should be used in treating a given volume of combined water.

The results of these combined treatments are summarized in Tables 33, 34, and 35, and graphically in Figures 41, 42, and 43.

The results of potassium permanganate without any extraction are shown graphically in Figure 44.

TABLE 33

The Effects of Varying Amounts of Potassium Permanganate and Isoamyl Alcohol on Combined Water Acidified with 12.5 Parts per Thousand of Sulfuric Acid

Series Number	p.p.t. $KMnO_4$	Extraction	v.p.h. Isoamyl Alcohol				
			0.	20.	50.	100.	
32	0	1st					F.V. %
			1.04	1.08	1.28	1.13	pH
			100.	86.	68.	64.	% Col.
		2nd		86.	82.	70.	F.V. %
				1.11	1.09	1.09	pH
				66.	54.	53.	% Col.
40	2.5	1st					F.V. %
			1.11	1.10	1.20	1.18	pH
			33.	23.	19.9	16.9	% Col.
		2nd		82.	83.	76.	F.V. %
				1.13	1.15	1.16	pH
				15.8	16.2	14.4	% Col.
41	5.0	1st					F.V. %
			1.10	1.20	1.19	1.17	pH
			12.7	9.4	7.6	5.9	% Col.
		2nd		87.	82.	72.	F.V. %
				1.11	1.16	1.21	pH
				7.5	5.4	3.8	% Col.
42	7.5	1st					F.V. %
			1.13	1.20	1.23	1.20	pH
			9.5	6.8	5.0	4.3	% Col.
		2nd		87.	76.	70.	F.V. %
				1.20	1.21	1.22	pH
				3.6	3.6	2.0	% Col.

FIGURE 41

RESULTS OF A POTASSIUM PERMANGANATE-ISOAMYL ALCOHOL TREATMENT ON COMBINED WATER ACIDIFIED WITH 12.5 P.P.T. OF SULFURIC ACID FROM DATA IN TABLE 33

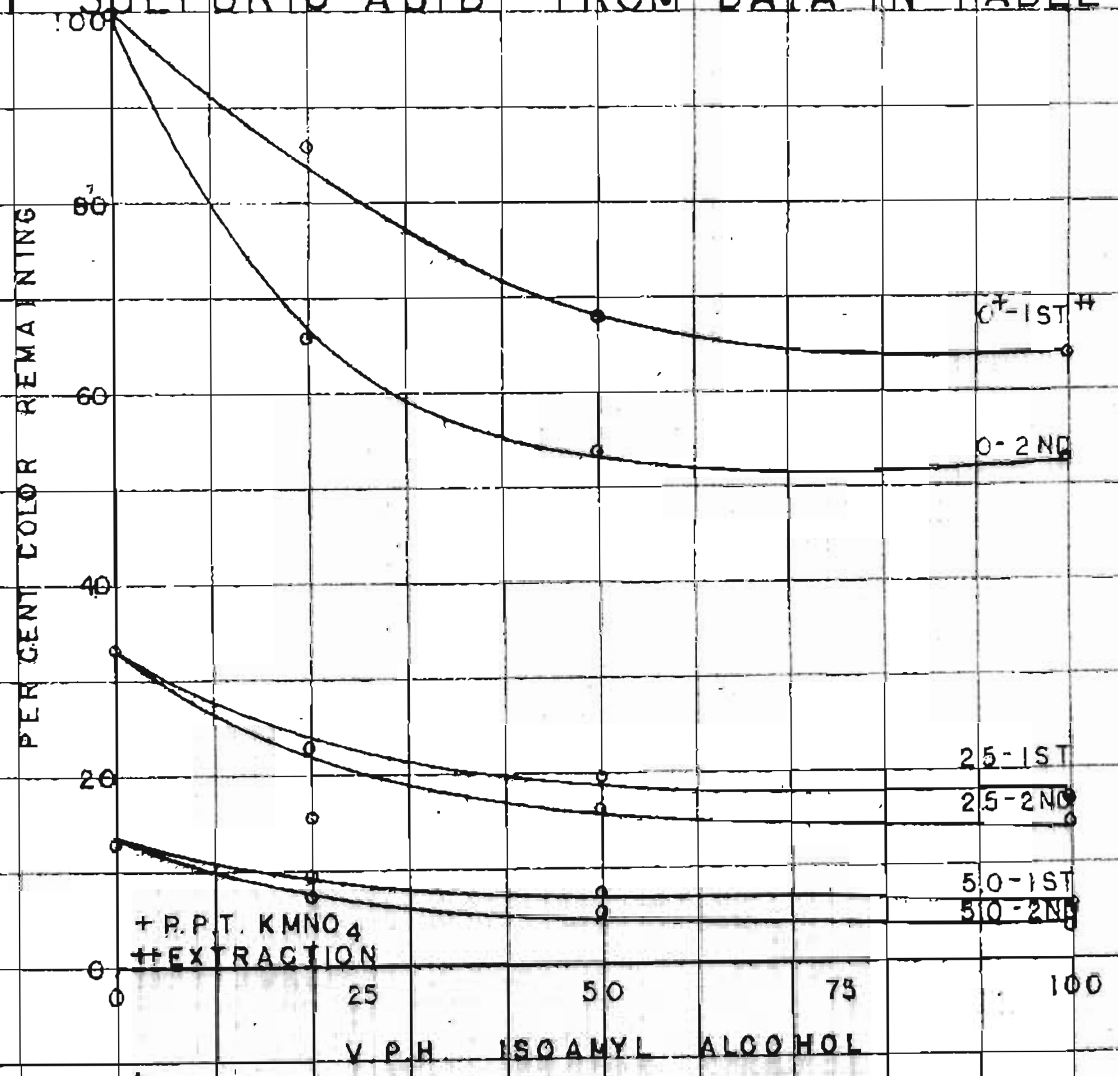


TABLE 34

The Effects of Varying Amounts of Potassium Permanganate and Isoamyl Alcohol on Combined Water Acidified with 37.5 Parts per Thousand of Sulfuric Acid

Series Number	p.p.t. $KMnO_4$	Extraction	v.p.h. Isoamyl Alcohol				
			0.	20.	50.	100.	
33	0	1st					F.V. %
			0.76	0.70	0.70	0.78	pH
			100.	50.	50.	45.	% Col.
		2nd		84.	80.	65.	F.V. %
				0.69	0.88	0.66	pH
				44.	36.	32.	% Col.
43	2.5	1st					F.V. %
			0.81	0.75	0.81	0.81	pH
			29.	17.3	13.0	11.5	% Col.
		2nd		85.	86.	74.	F.V. %
				0.65	0.82	0.72	pH
				13.0	9.9	6.7	% Col.
44	5.0	1st					F.V. %
			0.60	0.91	0.83	0.79	pH
			13.2	9.5	5.2	4.4	% Col.
		2nd		87.	82.	70.	F.V. %
				0.75	0.81	0.70	pH
				4.9	3.1	2.0	% Col.
45	7.5	1st					F.V. %
			0.81	0.83	0.83	0.91	pH
			8.3	5.4	3.2	2.8	% Col.
		2nd		81.	79.	68.	F.V. %
				0.77	0.70	0.84	pH
				2.8	1.3	1.5	% Col.

FIGURE 42

RESULTS OF A POTASSIUM PERMANGANATE ISOAMYL ALCOHOL TREATMENT ON COMBINED WATER ACIDIFIED WITH 37.5 P.P.T. OF SULFURIC ACID FROM DATA IN TABLE 34

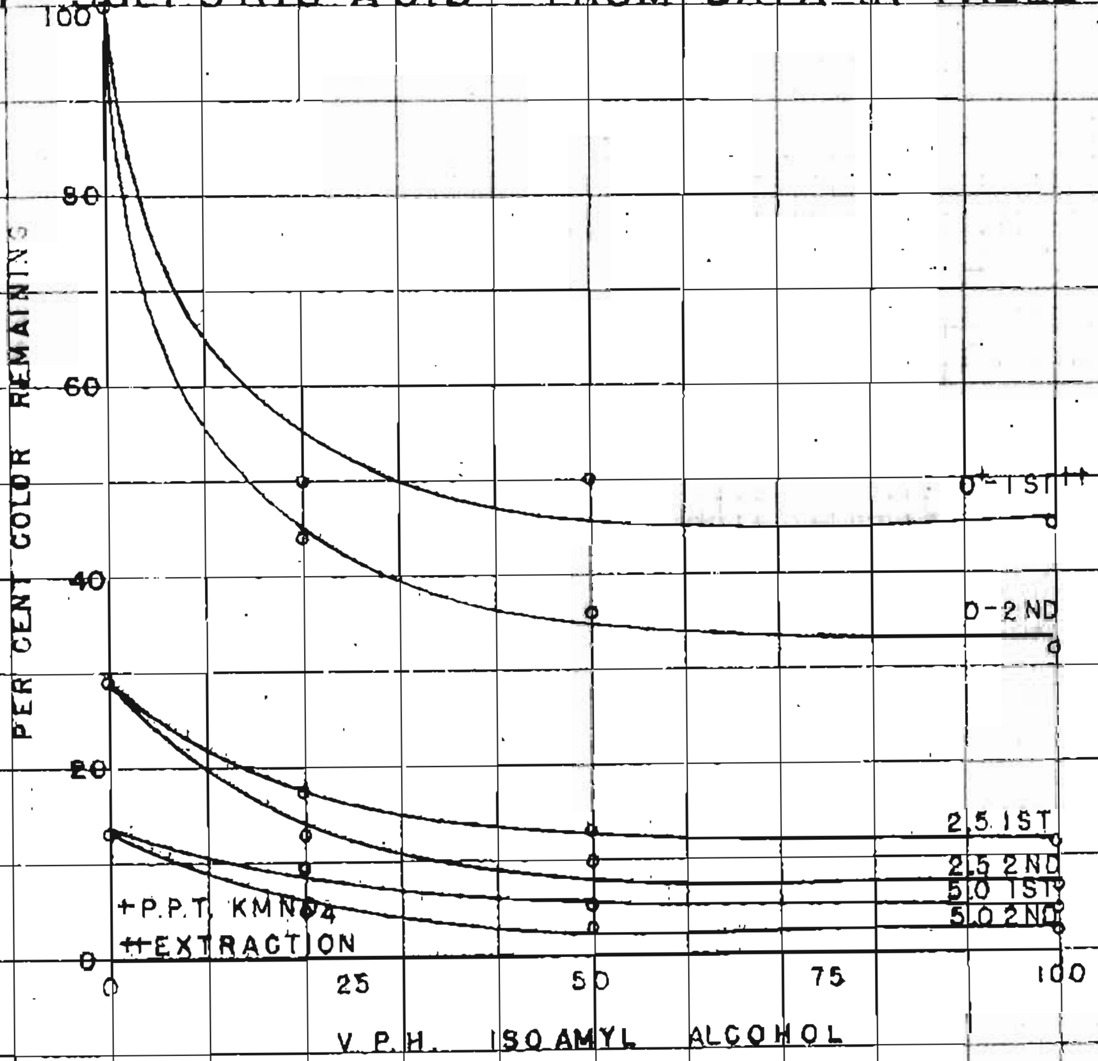


TABLE 35

The Effects of Varying Amounts of Potassium Permanganate and Isoamyl Alcohol on Combined Water Acidified with 62.5 Parts per Thousand of Sulfuric Acid

Series Number	p.p.t. $KMnO_4$	Extraction	v.p.h. Isoamyl Alcohol				
			0.	20.	50.	100.	
34	0.	1st					F.V. %
			0.52	0.62	0.61	0.61	pH
			100.	41.	31.	25.	% Col.
		2nd		84.	78.	74.	F.V. %
				0.65	0.60	0.50	pH
				23.	16.2	12.4	% Col.
46	2.5	1st					F.V. %
			0.50	0.59	0.62	0.50	pH
			31.	11.6	8.8	6.9	% Col.
		2nd		88.	84.	69.	F.V. %
				0.51	0.55	0.61	pH
				6.2	4.6	4.4	% Col.
47	5.0	1st					F.V. %
			0.49	0.69	0.69	0.61	pH
			10.8	5.0	3.4	3.5	% Col.
		2nd		90.	80.	67.	F.V. %
				0.62	0.68	0.53	pH
				2.1	1.4	0.73	% Col.
48	7.5	1st					F.V. %
			0.53	0.71	0.69	0.56	pH
			5.9	1.9	1.0	0.82	% Col.
		2nd		87.	80.	56.	F.V. %
				0.51	0.60	0.55	pH
				1.3	0.82	0.13	% Col.

FIGURE 43

RESULTS OF A POTASSIUM PERMANGANATE ISOAMYL ALCOHOL TREATMENT OF COMBINED WATER ACIDIFIED WITH 62.5 P.P.T. OF SULFURIC ACID FROM DATA IN TABLE 35

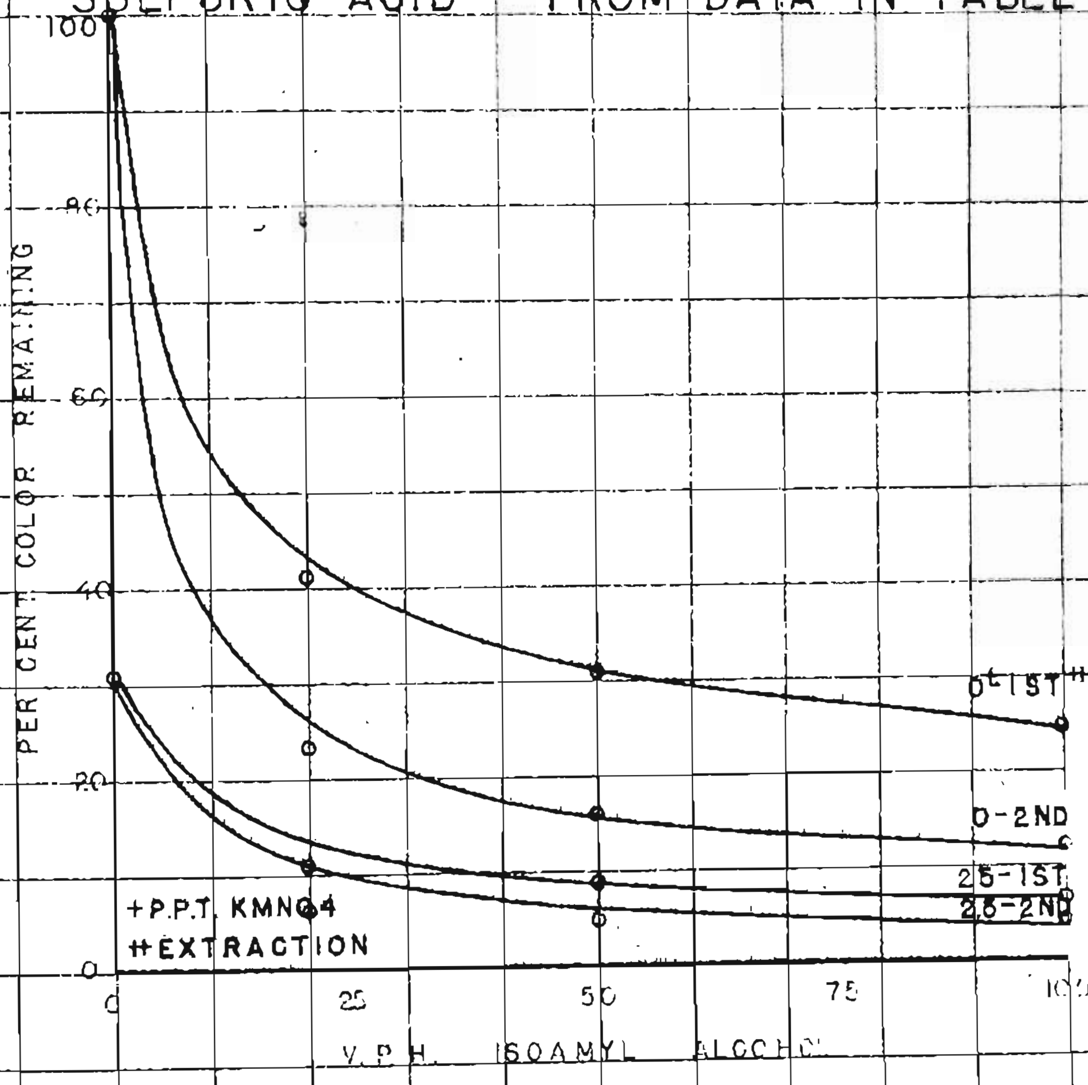
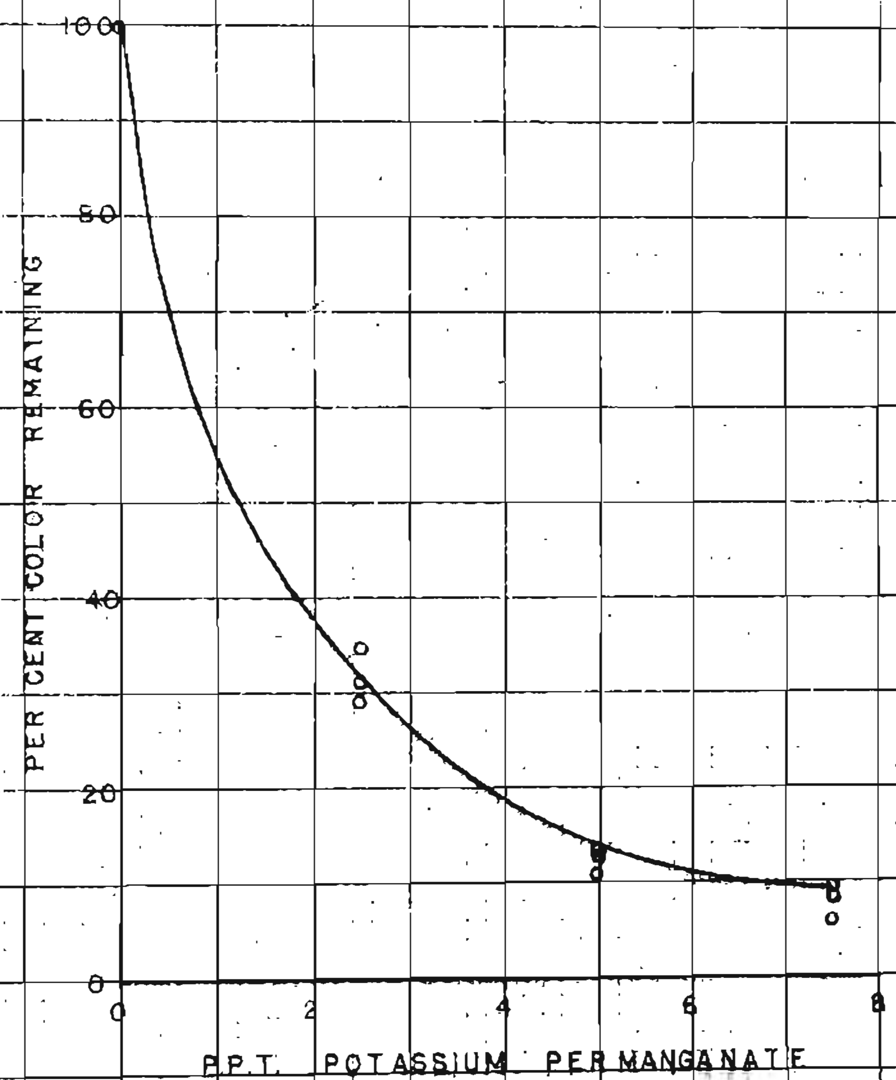


FIGURE 44

EFFECT OF ACIDIFICATION ON POTASSIUM PERMANGANATE TREATMENT

FROM DATA IN TABLES 33, 34, AND 35



RECOVERY OF ISOAMYL ALCOHOL

Isoamyl alcohol is a relatively expensive solvent and its use in a solvent extraction process requires that it be recovered and used repeatedly. A series of experiments were performed to study the recovery of the solvent.

The isoamyl alcohol extract from the red and combined water was subjected to distillation. The distillate was essentially isoamyl alcohol provided the distillation was not carried to a point where sulfuric acid acted as a dehydrating agent forming unsaturated hydrocarbons. Amylene was identified as one of the unsaturated decomposition products.

The effect of sulfuric acid was entirely removed when it was neutralized with an excess of sodium bicarbonate. Distillations proceeded smoothly and 80% of the alcohol was recovered. The addition of sodium bicarbonate to the extract produced an insoluble precipitate which did not in any way interfere with the distillation. The residue from alkaline distillation was always completely soluble in water whereas the oily material remaining from distilling highly acid extracts was entirely immiscible with water.

The distillate from the yellow water extract was slightly yellow in color, indicating an incomplete separation. This would indicate the necessity of neutralizing the yellow extract before recovering the solvent.

Attempts to remove the color from the alcohol by an alkaline water solution were unsuccessful. A highly colored water solution was obtained.

Treatment of extracts with solid potassium hydroxide precipitated an insoluble mass, but the extract retained its yellow color.

SUGGESTED TREATMENT

A study of the laboratory results would indicate that activated charcoal adsorption offers a satisfactory method of decolorizing the combined water which method should be economical and result in a tremendous saving in the cost of plant installation.

A two stage countercurrent adsorption system would probably be the most desirable and the following suggestions are made regarding plant construction.

A series of wood treating tanks of desirable capacity may either be set into the ground or on the surface and connected suitably for countercurrent treatment. The adsorption should be carried on at an elevated temperature with mixing; these conditions may be accomplished by the use of live steam for about one-half hour.

It will be preferable to treat the combined water after it has been acidified with waste acid, decolorized by activated charcoal, equivalent to at least 7.5 p.p.t. of sulfuric acid (Sp. G. 1.84).

Nuchar C-190 N is recommended for the combined water treatment and the application of 6.6 p.p.t. of this charcoal will produce an effluent with 99% of the color removed. Much less activated charcoal is required to produce an effluent in which 75% or less of the color is removed. A three stage countercurrent system may be designed which will consume only 4.0 p.p.t. of the same activated charcoal.

CONCLUSIONS

The waste waters from a trinitrotoluene plant may have most of the color removed by:

1. Potassium permanganate
2. Potassium permanganate and extraction
3. Extraction
4. Extraction and adsorption
5. Adsorption and potassium permanganate
6. Adsorption

Hydrous oxides were ineffective in removing the colors from the waste waters.

Solvent extraction satisfactorily separates most of the colored compounds with ease. A more comprehensive research program should be made on this phase of the study, i.e., utility and identification of the extracted compounds, the effect of temperature, the use of higher alcohols, etc.

The color may be removed by a single, two, three, or four stage countercurrent adsorption. The presence of sulfuric acid and slightly elevated temperature (80-90°C.) increase the efficiency of the activated charcoal. Equilibrium is established at these elevated temperatures in thirty minutes.

A three or two stage countercurrent treatment with activated charcoal offers a possible economic removal of color from these waste waters. A suggested three stage treatment with an activated carbon is included in the thesis. Smaller quantities of charcoal may be used to reduce the color to any point that is satisfactory for disposal by dilution with the available water.

The studies on adsorption by activated charcoal have been carried to a point where refinements may be discovered by pilot plant operations.

Further studies on phases of the adsorption are recommended and needed particularly with respect to the recovery of the spent charcoal and its disposal.

SUMMARY

A large number of investigations have been made to remove the color from waste wash waters from a trinitrotoluene plant. These investigations have involved the use of chemical reatents, sorption by hydrous oxides, adsorption by activated charcoals, and solvent extraction.

None of the many coagulants producing hydrous oxides materially reduce the color contained in the combined water by the methods used.

Potassium permanganate under certain conditions materially reduces the color. In no case, was a colorless water obtained from combined water when permanganate was used alone.

The per cent color remaining after oxidation with various quantities of permanganate was reduced by solvent extraction. Using isoamyl alcohol as the solvent, the color was reduced in some instances to one per cent of the original color.

All of the waste waters were treated with immiscible solvents in attempting to remove the color. Isoamyl alcohol, isobutyl alcohol, and fusel oil were tested. The extraction with isoamyl alcohol was studied intensively and equilibrium diagrams were determined. The addition of sulfuric acid increased the amount of coloring matter removed. More color was removed when the pH of the solution was below two. It is possible though not economically feasible to reduce the color to one percent of the original by sol-

vent extraction. Continuous as well as batch extraction processes were tested and solvent recovery was studied.

Partial extraction with immiscible solvents followed by activated charcoal adsorption were used sucessfully in reducing the color to one per cent of the original in the combined water.

A dual treatment of the combined waste water with activated charcoal followed by oxidation with potassium permanganate reduced the color to one per cent of the original. The residual color may be reduced to below one per cent or to some greater value.

Adsorption by activated charcoal gave the most promising results. Twenty activated charcoals were studied, and the two most promising were studied intensively. Adsorptions were most satisfactory from a sulfuric acid medium. The addition of 7.5 p.p.t. of concentrated sulfuric acid gave a medium for very satisfactory extraction though increased amounts tended to enhance adsorption. Adsorption by activated charcoal is increased by an increase in temperature. The adsorption was complete at sand bath temperatures in less than thirty minutes. Most of the activated charcoals used produced an essentially colorless water when sufficient quantities were used. A single stage treatment for removing the color in combined water to one per cent of the original color is apparently not economical.

A two and three stage countercurrent treatment reduces the quantity of activated charcoal used to such a point where it may be economically feasible. Much less activated charcoal is required if a residual color above one per cent is permissible.

A graphical calculation for the quantity of activated charcoal required for reducing the color to any residual content has been presented.

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