# Treatment of wastewater from torpedo refueling facilities

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# TREATMENT OF WASTEWATER FROM TORPEDO REFUELING FACILITIES

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## INTRODUCTION

As a result of refueling torpedoes after practice firing or on a regular fuel-replacement basis, two disposal problems are presented. That of unused fuel that has been replaced, and that of wastewater from the refueling area which inevitably contains small concentrations of the major fuel components. This report addresses possible solutions to the latter, although on the basis of the results, solutions are also recommended for disposal of the unused fuel. Time constraints dictated that only Otto Fuel II be considered in this study. It is believed, however, that similar results would be obtained for the other major fuel type currently in use, NOSET Fuel A, which contains a propellant chemically similar to that in Otto Fuel.

Otto Fuel II itself consists of 75% propylene glycol dinitrate (PGDN) as propellant, 24% di-n-butyl sebacate as a stabilizer and 1% 2-nitrodiphenylamine as an inhibitor. Previous results have indicated that solutions resulting from contact of the fuel with water are toxic to microorganisms and other life forms. PGDN also has well documented physiological effects, similar to its homologue, glycerol trinitrate (also known as nitroglycerin). This has necessitated the implementation of special precautionary procedures for personnel in fuel production and utilization facilities.

The purpose of this project was to (1) determine biodegradability and possible toxic effects of the dilute fuel waste stream on organisms commonly found in domestic waste treatment plants; and (2) if toxic, devise an acceptable treatment procedure.

## MATERIALS AND METHODS

### Preparation of Aqueous Fuel Solutions

Aqueous solutions of Otto Fuel II were prepared by stirring 100 ml deionized water with 100 ml fuel for 24 hours. Concentrations of the 3 fuel components (PGDN, 2-NDPA, and di-n-butyl sebacate) were measured directly via gas chromatography after extraction into benzene using a glass column (4' x 1/8") with 3% SE 30 on 80/100 mesh acid-washed DMCS chromasorb W. Saturated aqueous solutions ranging from 2,400 mg/l up to 2,800 mg/l Otto Fuel were obtained. It should be noted that in reporting levels of "Otto Fuel" in solution, the concentration of PGDN is often given because of its high solubility relative to the other compounds in the fuel (di-n-butyl sebacate and 2-NDPA). As long as solutions were prepared below the melting point of 2-NDPA (75°C), its presence in aqueous dilutions was very low, relative to the amount of PGDN present (1%). 2-NDPA is also non-toxic and has been found to support mixed culture growth when present as the only carbon source. The third component, di-n-butyl sebacate

is very insoluble and does not appear in chromatograms of benzene extractions of aqueous fuel dilutions.

## Biodegradability and Toxicity

Biodegradability and toxicity are somewhat qualitative parameters and may be determined in a number of ways. The method utilized in the present research was ~~a modification of~~ the Hach manometric Biochemical Oxygen Demand ~~test~~ apparatus (Kessick, 1976). Known quantities of aqueous Otto fuel ranging from 10-500 mg/l were placed in 300 ml BOD bottles with 5 ml acclimated bacteria and the necessary nutrients. Biodegradability was assessed by measuring $O_2$ uptake in conjunction with initial-final determinations of Otto fuel concentration. An acclimated bacterial population was produced by feeding 50 mg aqueous Otto fuel plus 1 gram soy broth daily to an aerated, 5 liter aerated reactor containing clarified municipal sewage. In the BOD bottle test, lack of $O_2$ uptake plus a negligible amount of breakdown indicate that the substance is non-biodegradable.

To test for toxicity, 10 to 50 mg/l quantities of aqueous Otto fuel were added to 300 ml BOD bottles containing 5 ml acclimated seed, nutrients, and 300 mg/l glucose. One bottle contained only seed, nutrients and glucose to provide a measurement of uninhibited bacterial activity. In such a comparison, decreasing $O_2$ uptake with increasing fuel concentration would indicate toxicity. (See Fig. 1)

## Assessment of Non-Biological Treatment Techniques

With knowledge of certain physical properties of the nitrate ester, PGDN, two non-biological treatment methods appeared most promising. The first was carbon adsorption, the success of which would rely on the high adsorbability of PGDN. The second technique explored was base hydrolysis, a reaction well known for nitrate esters, in which a strong base would hydrolize PGDN to its corresponding alcohol, propylene glycol, and nitrate. This treatment is especially attractive in that propylene glycol is biodegradable (Sax, 1968); therefore, breakdown products of such a reaction could be treated by conventional biological processes.

In the laboratory scale assessment of the feasibility of carbon adsorption, PGDN removal efficiencies were measured as Total Organic Carbon by the Beckman Carbon Analyzer. Since PGDN is 22% carbon, conversion to actual PGDN concentration from TOC is straightforward. Two types of experiments were carried out. Batch tests involved the addition of 30 mg/l concentrations of PGDN as TOC to 500 ml stirred vessels containing 2, 4, and 6 grams (30x50) mesh Pittsburgh activated carbon. Equilibrium concentrations were then measured to determine

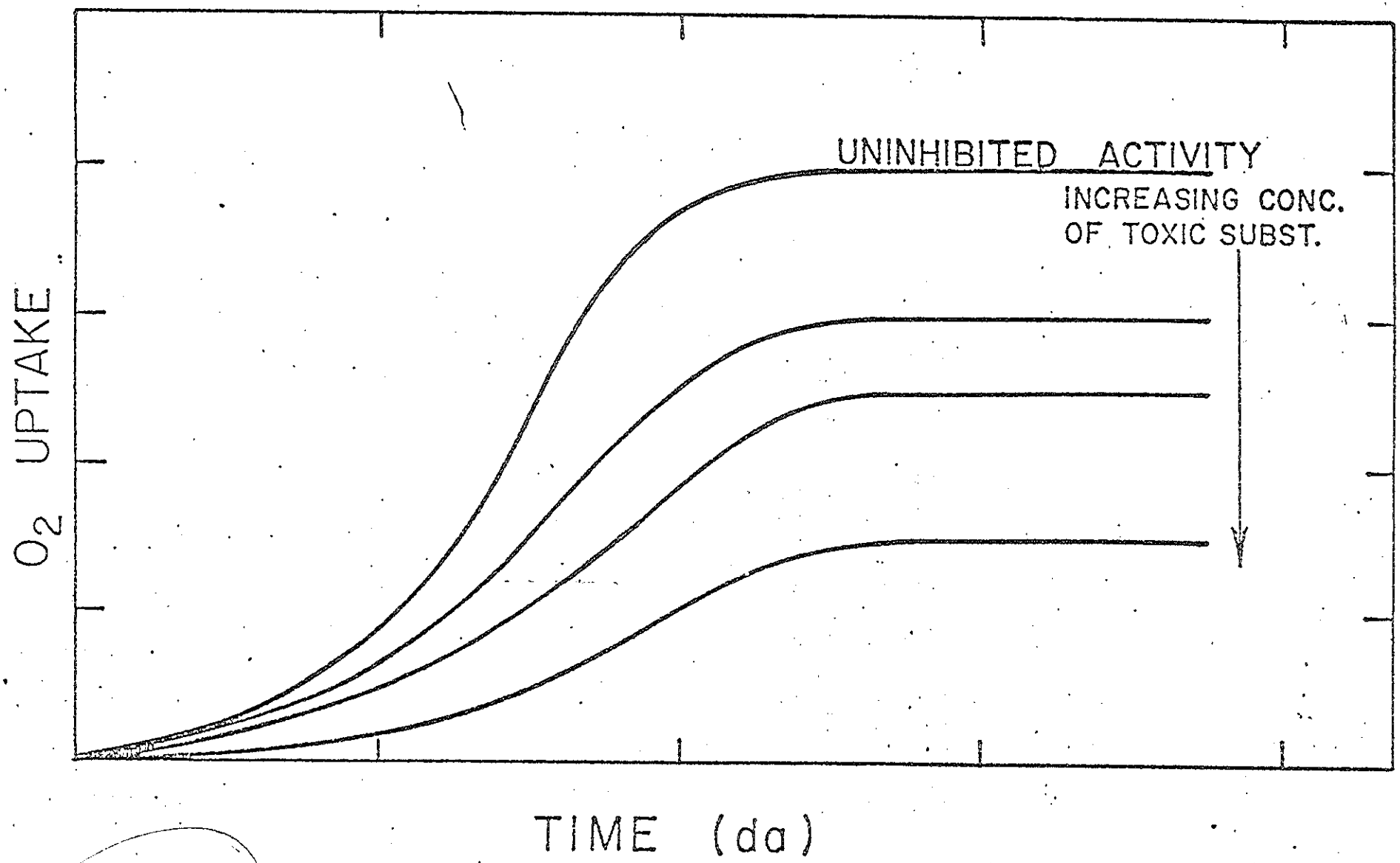


Figure 1. Hypothetical Biochemical Oxygen Demand Progressions.

removal efficiencies in terms of mg PGDN adsorbed/gm carbon. With this data, a batch isotherm was constructed according to the Freundlich model to evaluate adsorptive capacity of the carbon. The shape of a Freundlich isotherm line can indicate the suitability of different treatment schemes. A flat line shows that adsorption is relatively constant for increasing concentrations of adsorbate, and hence, amenable to batch treatment. A steep slope shows increased efficiency of adsorption with increasing concentration of adsorbate, which is appropriate for packed-bed column operation.

The second type of adsorption experiment utilized a packed carbon column to establish a breakthrough curve, which in addition to the batch isotherm, is necessary in the design of full-scale column reactors. Four liters of a dilute solution of aqueous Otto fuel was pumped at a rate of 8 ml/min through a 3 cm glass column packed with 0.8 g 30x50 mesh carbon. Effluent samples were taken with time until saturation was observed. A plot of $C/C_o$ vs. volume treated gave the break-through curve from which the efficiency of the operation was evaluated.

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## RESULTS

### Biodegradability/Toxicity

No measureable breakdown occurred and no oxygen was consumed after 5 days, in BOD bottle tests in which aqueous solutions of Otto fuel were used as the sole substrate, at all concentrations. (See Table 1). Therefore, the fuel was considered to be non-biodegradable and possibly toxic.

In the specific test for toxicity, in which a comparison is made with uninhibited bacterial activity on pure glucose, it was found that oxygen uptake decreased as the fuel concentration was increased (See Fig. 2). Therefore, the tests indicate that the fuel is not only non-biodegradable, but toxic to bacterial growth, and, hence, not amenable in its unaltered state to conventional sewage treatment.

### Base Hydrolysis

In base hydrolysis tests, 4 mg/l solutions of Otto fuel were reacted with base in a 500 ml stirred vessel and decrease in concentration with time was followed by GC. The first trial used the most inexpensive commercially available base, $Ca(OH)_2$, or lime. The PGDN solution was saturated with lime, and a pH of 10.8 was maintained by occasional addition of more lime (See Table 2). As can be seen from the table, removal was only 59% after 4 hours, which was not considered sufficient to insure safe disposal. A second trial utilized a stronger base, NaOH (0.1 M). With

TABLE 1 - BIODEGRADABILITY DATA FOR OTTO FUEL

| True Conc. | Determined Concentration (mg/l) Initial | Final (after 5 days) |
|---|---|---|
| 10 | 9.1 | 8.9 |
| 20 | 21.1 | 20.1 |
| 30 | 29 | 28 |
| 50 | 46 | 43 |
| 100 | 94 | 96 |
| 200 | 201 | 177 |
| 300 | 300 | 300 |
| 500 | 489 | 496 |

TABLE 2 - $Ca(OH)_2$ HYDROLYSIS OF OTTO FUEL

| Time | pH | Conc. PGDN (mg/l) |
|---|---|---|
| 0:00 | 10.8 | 4.0 |
| 0:15 | " | 2.1 |
| 0:30 | " | 2.1 |
| 0:45 | " | 2.1 |
| 1:00 | " | 1.6 |
| 1:15 | " | " |
| 1:30 | " | " |
| 1:45 | " | " |
| 2:00 | " | " |
| 4:00 | " | " |

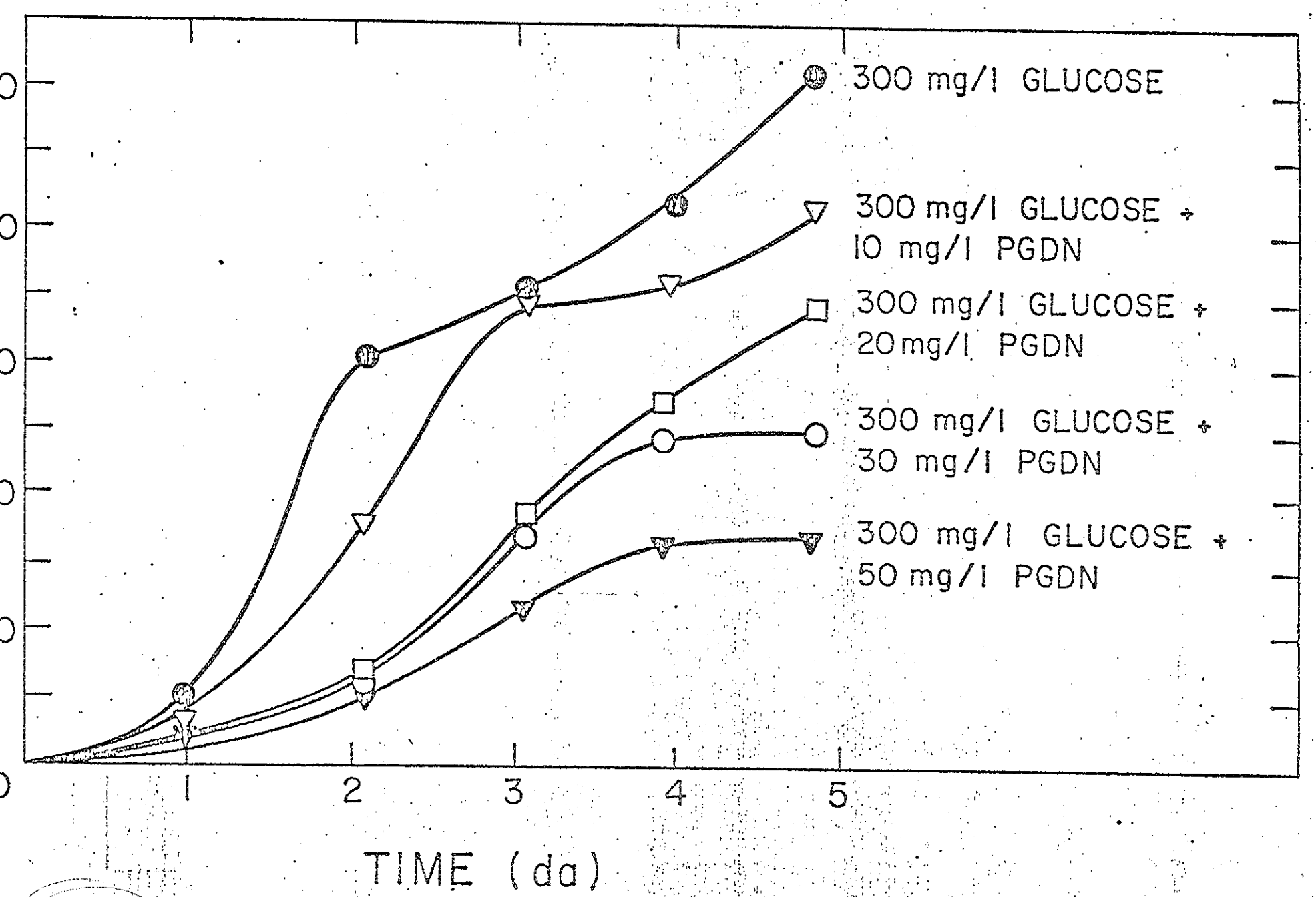


Figure 2. Actual BOD Curves for Glucose - PGDN Mixtures.

other conditions identical to the lime experiment, all the PGDN had been hydrolyzed to the biodegradable alcohol, propylene glycol, in 15 minutes. Corresponding to this conversion was a drop in pH from 13.2 to 11.2.

Carbon Adsorption

In the carbon adsorption batch tests, solutions of Otto fuel in the 100-200 mg/l range were reduced to 10-20 mg/l (see Table 3 and Fig. 3). The table indicates that with similar waste stream concentrations and carbon mass utilized, approximately 90% removal can be expected. In the column tests, 3900 ml of a 110 mg/l PGDN solution were treated before exhaustion of the column. Approximately 88% removal resulted up until breakthrough (see Table 4 and Fig. 4). Considering the size of the column utilized (3 cm in length) the results indicate a good potential for adsorption of dilute PGDN waste streams by activated carbon with a breakthrough capacity of 145 mg/g at a loading of approximately 3 gpm/ft$^2$. A larger column would undoubtedly produce a more regular curve from which design parameters could be calculated.

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Since carbon adsorption treatment would probably produce an effluent containing approximately 10% of the influent PGDN concentration, it was considered worthwhile to investigate as an additional step, the removal capability of biological mass cultures in the 10mg/l PGDN range. While toxic to some extent to the mass culture, it was found that about 55% removal occurred in 5 hours due to adsorption and entrapment in the microbial floc (see Table 5). Therefore, biological treatment would be able to aid in removal if, for example, a 100 mg/l PGDN waste stream was reduced to 10 mg/l PGDN by carbon adsorption, then was fed to an activated sludge unit to reduce the PGDN concentration to 4-5 mg/l.

## CONCLUSIONS

The success of combined base hydrolysis and carbon adsorption techniques suggests economical and effective package treatment plants which could process both concentrated and dilute streams of torpedo fuel for disposal into sewage systems. Such a treatment scheme is depicted in Fig. 5. From storage drums, concentrated fuel is fed into a stirred tank reactor containing enough NaOH to maintain a pH greater than 11.0. Since the hydrolysis reaction goes to completion independent of PGDN concentration, only temperature increase and possible foaming would have to be controlled to convert concentrated fuel into biodegradable components (see Fig. 6). Foam production is expected from the reaction of di-n-butyl sebacate to form the soap-like compound, sodium sebacate. The reaction

TABLE 3

~~TYPICAL~~ CARBON ADSORPTION

BATCH DATA

| | Weight Activated Carbon (g) in 500ml Solution | | |
|---|---|---|---|
| | 2 | 4 | 6 |
| PGDN as Carbon (Initial) mg/l | 30 | 30 | 30 |
| PGDN as Carbon (Equilibrium) mg/l | 14.6 | 8 | 3 |
| PGDN (Equilibrium) mg/l | 66.4 | 36.7 | 13.7 |
| Total Carbon Adsorbed (mg/l) | 15.4 | 22.0 | 27.0 |
| Total Carbon Adsorbed (mg/g Activated Carbon) | 3.85 | 2.75 | 2.25 |
| PGDN Adsorbed (mg/g Activated Carbon) | 17.5 | 12.5 | 10.2 |

Fig 3.

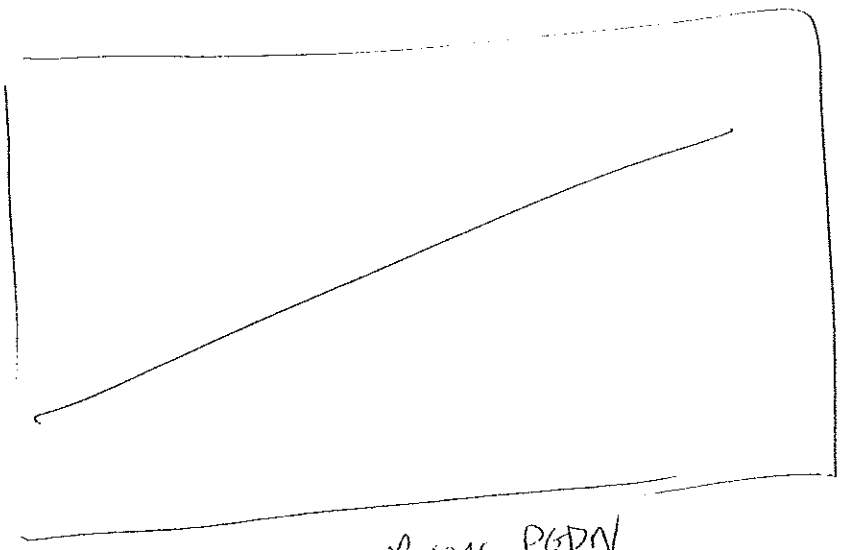


TABLE 4

ADSORPTION OF PGDN IN A CARBON COLUMN

| PGDN (mg/l as TOC) | Vol. treated (ml) | $C/C_o$ |
|---|---|---|
| 2.8 | 0 | .12 |
| 3.0 | 500 | .17 |
| 4.1 | 925 | .25 |
| 6.0 | 1275 | .40 |
| 9.7 | 1625 | .47 |
| 11.3 | 1725 | .51 |
| 12.2 | 1925 | .55 |
| 13.2 | 2275 | .63 |
| 15.1 | 2490 | .67 |
| 16.1 | 2650 | .71 |
| 17.0 | 2825 | .76 |
| 18.2 | 2925 | .80 |
| 19.2 | 3250 | .90 |
| 21.6 | 3625 | .95 |
| 24.0 | 3900 | 1.0 |

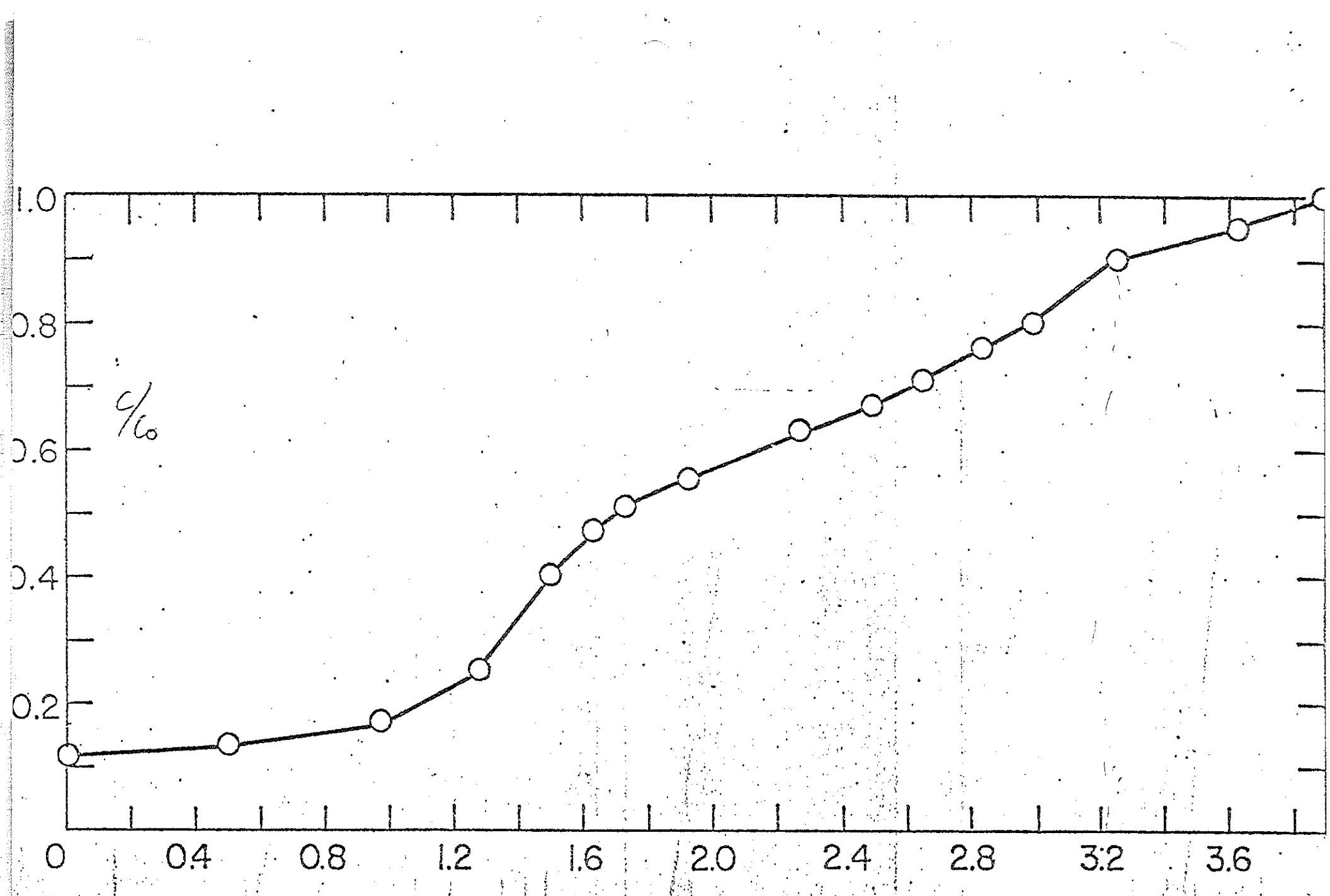



Figure 4. Results of Carbon Column Experiments.

TABLE 5

MASS CULTURE DIE AWAY STUDY

10 mg PGDN added to 1.0 l settled sewage effluent fed 24 hours previously with 1 g soy broth

| TIME (hrs) | PGDN CONCENTRATION (mg/l) Filtered floc | Centrifuged floc |
|---|---|---|
| 0 | 9.8 | 9.9 |
| 0 | 10.0 | 9.9 |
| 0.5 | 8.6 | 8.9 |
| 1.0 | 7.2 | 7.3 |
| 2.0 | 6.5 | 6.6 |
| 3.0 | 5.3 | 5.2 |
| 4.0 | 4.6 | 4.9 |
| 5.0 | 4.3 | 4.7 |

S.S. Initial - 376 mg/l

S.S. Final - 387 mg/l

55% Removal (Avg.)

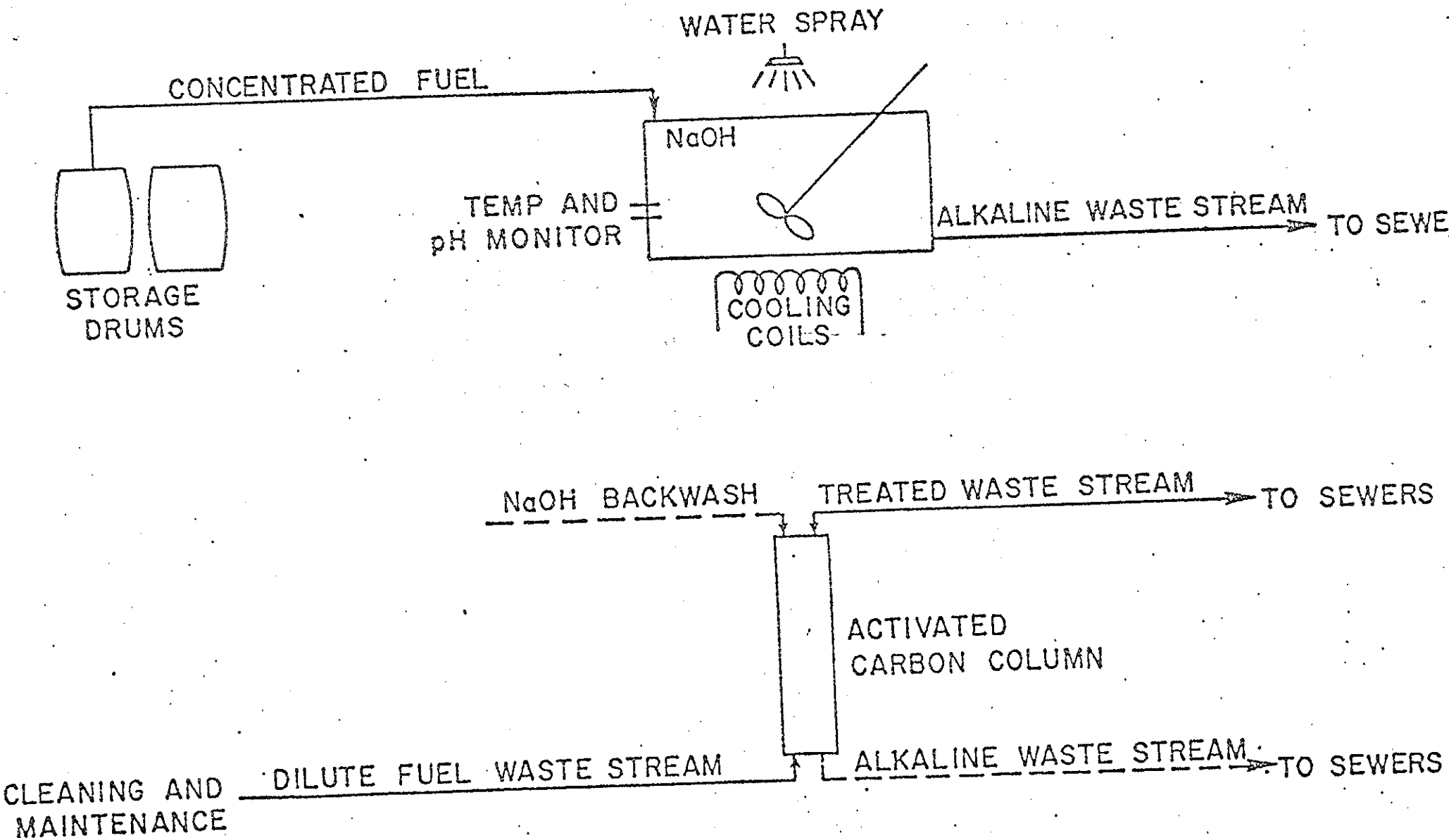
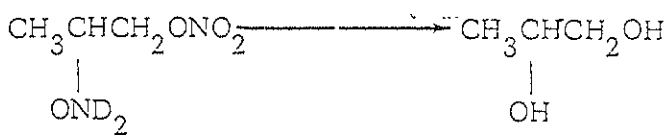
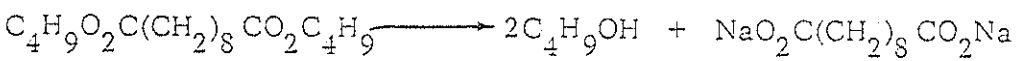



Figure 5. Recommended Treatment Scheme for OTTO FEUL II Wastes.

BREAKDOWN PRODUCTS OF BASE HYDROLYSIS



PGDN PROPYLENE GLYCOL



DI-N-BUTYL SEBACATE N-BUTANOL SODIUM SEBACATE

TRACE 2-NDPA UNREACTED

Fig 6.

should be designed for a holding time in excess of 15 minutes, to insure complete conversion. The alkaline waste stream from such a reactor could be fed without further treatment into sanitary sewers, which have high neutralizing capacity.

Any dilute streams that become available for disposal could be treated most economically by carbon adsorption on site. Waste streams in the 5-10 ppm range would be reduced by this treatment to less than 1 ppm, and should then be suitable for disposal into sanitary sewers. Even final effluents in the 10mg/l PGDN range could be further reduced by biosorption in an activated sludge system, as was demonstrated by the mass culture die-away studies (see Table 5). An added advantage of this system is the possibility of regenerating exhausted carbon by backwashing with the same strong base as is suggested in the concentrated fuel treatment. The carbon column would concentrate the PGDN into a small volume so that when backwashed, it would be converted most economically to propylene glycol and could also be fed into the sewers. As a final step in the research, this possibility of regeneration with NaOH was given some preliminary testing. Batch adsorption tests identical to those described were run again, except that upon reaching equilibrium, the carbon was removed, filtered and treated with an equal volume of a saturated NaOH solution. The resulting solution was analyzed both for carbon content and PGDN content. The carbon was then returned to the adsorption vessels and the same experiment was repeated, to determine the extent of regeneration. Table 6 and Fig. 7 indicate excellent regeneration of activated carbon by NaOH. Especially encouraging are the data on the regeneration supernatant which prove that most of the PGDN is desorbed by NaOH, and at the same time is converted to propylene glycol. Therefore, all effluent streams from the proposed treatment system, including the backwash stream, would be suitable for disposal into ordinary municipal sewers.

part of

In conclusion, then, it has been found that (1) aqueous streams of Otto fuel are non-biodegradable and toxic to bacterial activity in the concentration range of interest; and (2) non-biological treatment methods are available which will convert the toxic component, PGDN, into a biodegradable form; and (3) it may be possible to dispose of both dilute and concentrated waste streams, after the recommended treatment, into sanitary sewers. Before a full-scale system is developed, pilot-scale tests are necessary to confirm these results.

ANALYSIS OF REGENERATION SUPERNATANT

| CARBON (G) | 2 | 4 | 6 |
|---|---|---|---|
| PGDN (MG/L) | 0 | 0 | 0 |
| TOC (PROPYLENE GLYCOL) (MG/L) | 15 | 31 | 40 |

part of table 6

Fig 6.

Isotherms