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INDUSTRIAL WASTE TREATMENT USING ADSORPTION-OXIDATION PROCESS.(U)
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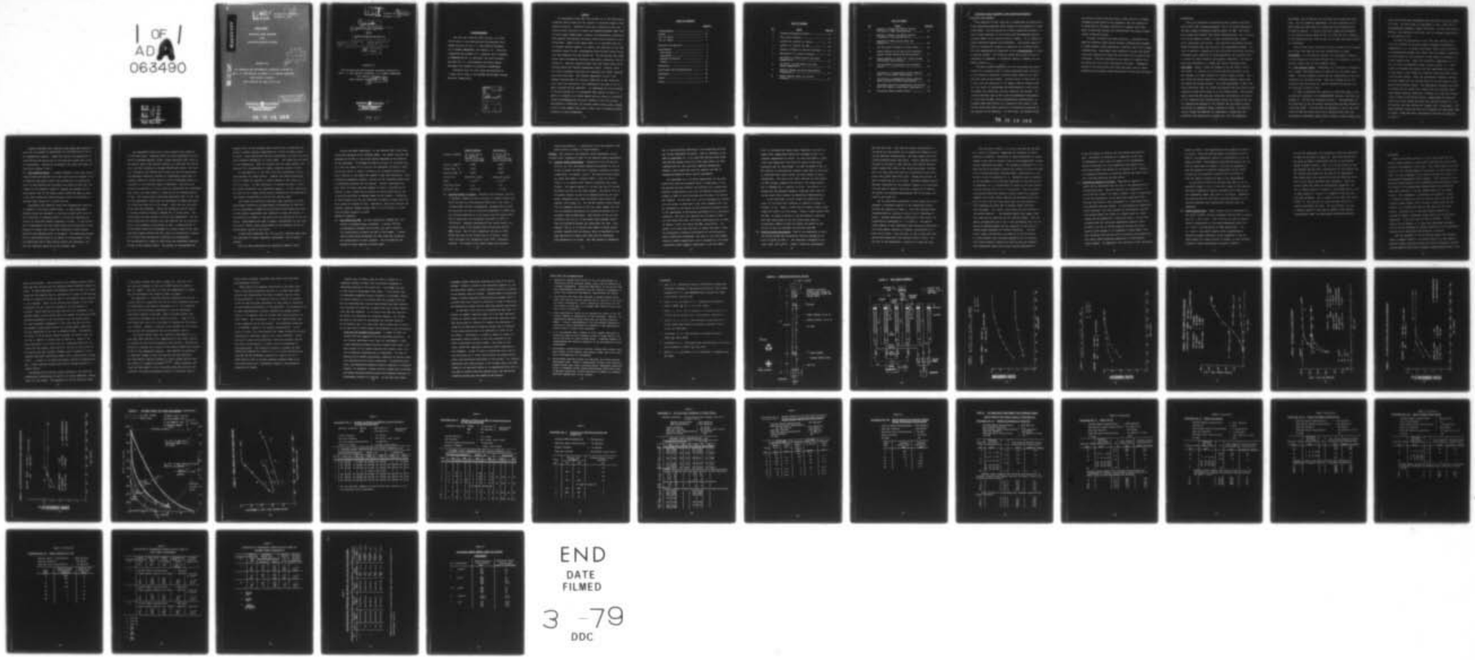

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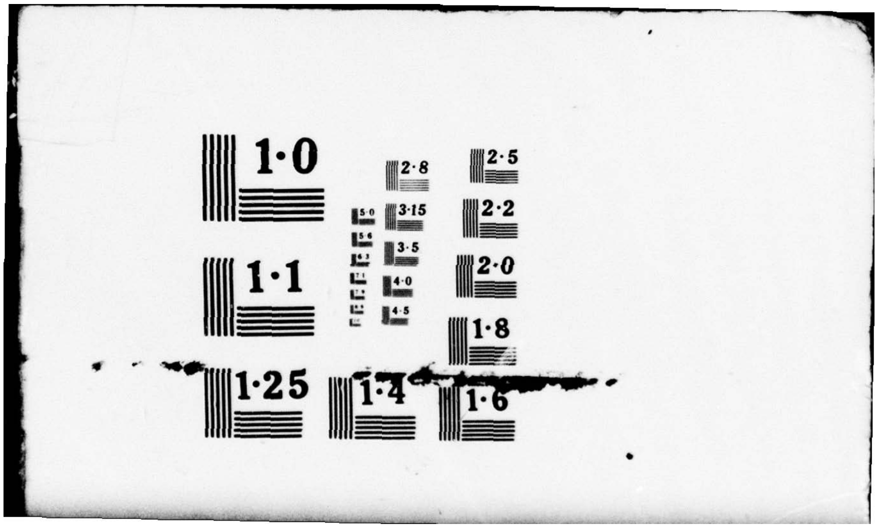
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FINAL REPORT

INDUSTRIAL WASTE TREATMENT
USING
ADSORPTION-OXIDATION PROCESS

PREPARED FOR

THE PETROLEUM AND ENVIRONMENTAL TECHNOLOGY DIVISION OF
THE U. S. ARMY MOBILITY EQUIPMENT R & D COMMAND (MERADCOM)
FORT BELVOIR, VIRGINIA
UNDER CONTRACT NO. DAAK 70-77-C-303

GENERAL ELECTRIC
**Re-entry & Environmental
Systems Division**

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⑨ FINAL REPORT,

⑥

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USING
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⑩ Dr. K. K. Jain

Prepared for

The Petroleum and Environmental Technology Division of
The U. S. Army Mobility Equipment R & D Command (MERADCOM)
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GENERAL ELECTRIC
Re-entry & Environmental Systems Division
3198 Chestnut St., Philadelphia, Pa. 19101

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Laboratory work for this study was performed by J. Lazur and R. Ross of the GE-RESD and GE-Space Systems Division, respectively.

SUMMARY

An experimental study has been carried out on the adsorption-oxidation (A/O) process for the removal of dissolved organics from aqueous solutions. Laboratory tests were conducted on pure and binary mixture solutions of phenol and dimethylformamide (DMF) and an actual waste sample under a variety of experimental conditions. Both granular and powdered activated carbon were evaluated in the A/O process. Based on the phenol data, it is concluded that the A/O process removes organics at a faster rate than any of the other processes tested in this investigation which include carbon adsorption and ozonation with and without UV. The A/O process also shows better ozone utilization efficiency than direct ozonation, with or without UV. Data are presented which show that ozone reacts with adsorbed phenol and thereby regenerates carbon. However, after the initial oxidation reactions are completed, the carbon regeneration rate slows down. The slowdown apparently is due to the changed reactions and the reaction conditions on the carbon surface, which are expected to vary depending on the type of the organic material and the adsorbent. To understand the full potential of the A/O process, it is recommended that removal of other organics be studied in a similar manner and more effort be directed toward investigating the reaction chemistry of the A/O process. Development of additional A/O process schemes which permit intimat contact of the organic with ozone, carbon, and UV radiation simultaneously is also recommended.

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ABSTRACT

INDUSTRIAL WASTE TREATMENT USING ADSORPTION-OXIDATION

OBJECTIVE AND APPROACH

The objective of this study was to demonstrate the application of the adsorption-oxidation (A/O) process to the treatment of industrial wastes. The A/O process is a novel, proprietary process currently being developed by the Re-entry and Environmental Systems Division (RESD) of the General Electric Company. It is designed to remove dissolved organics from wastewater. The process concept is based on removing the organics by adsorption on a suitable adsorbent and regenerating the adsorbent in-situ simultaneously by using a chemical oxidant. The oxidation scheme may include the use of catalysts, UV radiation, or ultrasonic energy to enhance the oxidation reaction.

ABSTRACT

The basic concept feasibility for the A/O process was demonstrated in a previous study[1] in which experiments were conducted on the removal of munitions chemicals using carbon as the adsorbent and ozone as the oxidant. Another result of that study was to show that the reactivity of an organic chemical towards ozone is a key factor in determining the effectiveness of the process; the higher the reactivity, the more effective the process. For certain chemicals such as RDX (cyclo-trimethylene-trinitramine, or cyclonite) and HMX (cyclo-tetramethylene-tetranitramine, or octogen) which have little or no reactivity with ozone, it was further shown that their reactivity is dramatically enhanced in the presence of UV radiation, In this study, the primary effort

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was directed toward combining carbon, ozone, and UV in a single treatment process based on the hypothesis that the presence of UV would lead to increased reactivity of organics with ozone which in turn will increase the effectiveness and range of application of the A/O process.

In order to achieve the above objective, a laboratory program was conducted using various process configurations designed to bring together carbon adsorption, ozonation, and UV in a single treatment step. Experiments were conducted on actual and synthesized waste samples and using both semi-batch and continuous flow conditions. Data were obtained on the removal of organics from the waste and on the ozone utilization efficiency. Comparative studies of the A/O process with other processes such as carbon adsorption and ozonation (with and without UV) were also performed.

EXPERIMENTAL

Tests were performed on synthesized waste samples containing phenol and/or DMF (dimethylformamide) and on an actual pharmaceutical waste sample containing primarily phenol and DMF. The actual waste sample was obtained from Pfizer Pharmaceuticals, Inc. in Puerto Rico and according to Pfizer, it also contained xylene, sulfate salts, phthalides, and acetone. Both granular and powdered carbons, Calgon Filtrasorb 300, were tested in the experimental program. In order to provide a comparison of the A/O process with other processes, experiments were conducted on carbon adsorption and ozonation with or without UV under identical experimental conditions. All experiments were performed in a column type reactor described below.

TEST SETUP: Figure 1 shows the design of the A/O reactor used in this study. It consists of a 33-inch long 49-mm ID Pyrex column and contains a UV lamp enclosed in a quartz tubing as shown. Fig. 1 also shows the method devised for contacting granular carbon with the liquid and the gas streams. For those experiments in which powdered carbon was used, the carbon was premixed with the liquid stream instead of using fixed layers as in the former method. The influent waste stream and the ozone gas stream are introduced at the bottom of the column and the treated mixture leaves the column at the top. For sampling and analyses of the effluent gas and liquid streams, the mixture is separated using a separatory funnel. An identical reactor design was employed for experiments on adsorption and ozonation, the latter with or without UV. For the adsorption experiments, the UV lamp was not activated and no ozone was introduced. For the ozonation experiments, an inert material such as glass beads was substituted for carbon and the UV radiation was utilized as desired. A total of six such columns were assembled in the overall setup as shown in Fig. 2 so that the A/O, ozonation, and the adsorption runs could be made at the same time under identical conditions.

Figure 2 also shows the details for each column for the measurement of gas flow rate and the ozone concentration in gases.

EXPERIMENTS: For description purposes, the experiments conducted in this program may be broadly divided into two categories; (a) with granular carbon, and (b) with powdered carbon.

(a) With Granular Carbon: Experiments were conducted on synthesize waste samples containing phenol and DMF and with the Pfizer waste sample. The main parameter varied was the concentration of the contaminant(s) in the waste stream. Data were obtained on the A/O, ozonation with and without UV, and the adsorption processes, and are reported in Tables 1 and 2.

In order to determine the reactivity of DMF with ozone, an experiment was conducted on a synthesized DMF solution, both with and without UV. The data are reported in Table 3. The importance of the reactivity to the A/O process effectiveness has been observed in a previous study[1]. From the data of experiments 1 and 2, the reactivity of DMF with ozone could not be assessed since under the experimental conditions, phenol which is known to react quickly with ozone, and carbon which decomposes ozone may have a priority demand for ozone. In other words, in experiments 1 and 2, ozone may be preferentially consumed by phenol and carbon. As seen from Table 3, DMF has a low reactivity with ozone, but it increases significantly in the presence of UV.

The data from experiments 1 and 2 show that reaction conditions were limited by the ozone supply and phenol concentration, respectively, i.e., in either case ozone, carbon, and UV could not be simultaneously brought into contact with the organic contaminant. The main reason for this situation is that phenol is extremely reactive towards ozone. Under such conditions, regeneration of carbon can only be accomplished using a series process, i.e., first carbon is saturated with phenol and then regenerated with ozone. An experiment of this design was conducted using the actual pharmaceutical waste sample. Under the experimental condition selected, the ozone supply was the limiting factor in the A/O system so that phenol would saturate carbon. The experimental procedure consisted of running the A/O column until steady state was achieved (under ozone-supply limiting conditions), flushing the column and rinsing carbon in-place with deionized water, regenerating the saturated carbon with ozone (being fed along with deionized water) for a certain period, and then feeding the original waste stream again. The liquid effluent stream was monitored throughout the experiment, data for which along with other experimental conditions are reported in Table 4.

Another experiment was conducted using oxygen gas instead of ozone for the purpose of determining its contribution and role in the regeneration process. Oxygen was used for the generation of ozone and was the carrier gas in the ozone gas stream used in all the experiments. Comparative performance for ozone and oxygen are depicted in Figures 3 and 4.

(b) With Powdered Carbon: A primary drawback of the above experimental scheme was analyzed to be that carbon was not exposed to UV. In addition, gas-liquid contact was considered to be inefficient since (1) gas bubbles which initially were small as they were just released by the diffuser tended to collapse and coalesce at the lamp support, and (2) the annular space around the lamp is small, ~8 mm, which caused the liquid and gas to move in the annulus as separate slugs instead of a uniform mixture.

Experiments with powdered carbon were designed and conducted in response to the above problem areas. In these experiments, powdered carbon was suspended in the waste stream itself with the twin objectives of exposing carbon to UV and also improving the contact of ozone with organics adsorbed on carbon. It was obvious that UV penetration into the liquid stream will deteriorate in the presence of carbon; this effect was minimized by active mixing caused by the bubbling action of the gases. The underlying assumption is that mixing caused by the gases is strong enough to move the liquid past the UV lamp surface rapidly and frequently, and that the reactions caused by UV are extremely fast.

All experiments except one in this category were conducted in semi-batch mode. Powdered carbon for these experiments was prepared by grinding granular carbon, Calgon Filtersorb 300, which is the same as used in the previous series, in a ball mill for several hours and then screening it through 140/220 mesh screen. The fraction retained in the 140/220 mesh screen was used for experiments. The experiment basically consisted of suspending a known mass of powdered carbon in a known volume of liquid containing a known concentration of the selected organic contaminant. The slurry was stirred for a period of 2-3 hours until an equilibrium was established. This slurry was then exposed to ozone and UV for varying periods of time. The column reactor described previously (Fig. 1) was used for the experiments except that the mechanisms of supporting granular carbon was taken out of the column. After the run, the entire slurry mass was withdrawn. Carbon was separated from the liquid by vacuum filtration through a Whatman No. 42 filter paper. Filtered carbon was then allowed to dry at room temperature. The air-dried carbon and the filtrate were then analyzed for the concentrations of the organics still present on each. A known portion of the air-dried carbon was resuspended in a known volume of the original waste sample solution and the slurry was stirred over a period of 2-3 hours until equilibrium conditions were established. The concentration of carbon in this slurry was maintained identical to that of the original slurry. The purpose of resuspending the exposed carbon in the original waste solution was to determine the extent of carbon capacity regenerated as a result of being exposed to O_3/UV. After equilibrium had been established, the slurry was filtered through a Whatman No. 42 filter paper. The carbon was air-dried at room temperature. Both the filtrate and the carbon samples were analyzed for concentrations of organic chemicals present in each.

In experiment no. 5, the feed slurry was continuously recirculated through the column reactor. Samples were taken periodically from the stream for analysis of phenol present on the carbon and in the free liquid. In this experiment, no attempt was made to filter the carbon and measure its regenerated capacity. In this experiment, an O_3/UV run at a lower initial phenol concentration corresponding to free phenol concentration in the A/O run was also made.

All except one semi-batch experiment were conducted on synthesized phenol solution at an approximate concentration of 1000 mg/l. For one experiment, a sample of actual waste (from Pfizer) was used. In this series, experiments were conducted to study the effects of concentration of carbon in the slurry, UV, and initial pH of the feed slurry. Measurements were made on phenol concentration in free solution and on carbon, ozone concentration in the influent and the effluent gases, and pH of the slurry.

A batch O_3/UV experiment (No. 11) was also conducted under iden cal conditions to obtain comparative performance data on phenol removed.

Data for these experiments are reported in Tables 5 and 6.

During semi-batch experiments, it was observed that liquid with carbon was entrained in the effluent gases. The carbon carryover was estimated at 15-20% of the initial amount depending on the duration of the experiment. No attempt was made to recover the entrained carbon since the impact of its loss on the experiment in terms of determining the effect of ozone on carbon is not considered significant. Only a portion of the carbon was needed to make this evaluation. From a practical standpoint however, recovery of the entrained carbon would be considered essential for the process. Another observation was that after the slurry had been exposed to ozone or ozone/UV for 20 minutes or more, carbon did not settle out easily which may be due to particle attrition or adsorbed gases on the surface. Filtration of these samples also did not take place as easily as those which had been exposed 10 minutes or less. Apparently, there were physical and probably chemical changes brought about in the structure of carbon upon prolonged exposure to ozone.

METHODS OF ANALYSIS:

(a) Free Phenol and DMF: For each experiment, samples were collected in stoppered glass containers. A Varian 3700 gas chromatograph, equipped with an HFID, was used to measure the concentration of phenol and DMF in each sample. A Varian CDS-111 data system integrated the peak areas and calculated the concentration of each component. The GC operating conditions for each compound are given below:

	Phenol Analysis	DMF Analysis
Column & Packing	10 ft SS; 20% by wt. Carbowax 20M-TPA on Chromosorb W 80/100 DMDS	10 ft SS; 20% by wt. Carbowax 20M-TPA on Chromosorb W 80/100 DMDS
Injector Temp. °C	250°C	200°C
Column Temp. °C	211°C	146°C
Detector Temp. °C	250°C	220°C
Carrier Gas	Helium 60 cc/min.	Helium 60 cc/min.
Range	1×10^{-11}	1×10^{-11}
Injection Volume	3 μl	2 μl
Retention Time	10.33 min.	7.1 min.

(b) Adsorbed Phenol on Carbon: Basically the procedure consisted of heating a sample of carbon secured in a quartz sample tube which was held in a CDS pyroprobe Model 120 in the inlet of a Perkin-Elmer 990 gas chromatograph equipped with an HFID. The pyroprobe coil had an indicated temperature of 800°C while the internal temperature in the quartz tube was around 500°C. The GC temperature was programmed from 80°C to 150°C at 16°C/minute. Organics desorbing off the carbon sample were separated using a 10% Carbowax 20M on Chromosorb 100/120 DMDS column. The GC inlet temperature was set at 200°C. Helium was used as the carrier gas at 30 cc/min. Areas under the peaks were integrated using a PEP 1 dedicated computer. The weight of the carbon sample was obtained using a microbalance. A calibration curve was prepared using known amounts of phenol on carbon samples.

RESULTS: The results of the granular carbon experiments are described first; followed by those of the powdered carbon experiments.

(a) Granular Carbon Experiments: Comparison of the A/O process with O_3, O_3 + UV, and carbon adsorption processes for the removals of phenol and DMF from a synthetic solution are shown, respectively, in Figures 5 and 6. The data for these figures are taken from Table 1 (Column B data). From the data in Table 1, it is obvious that reaction conditions were ozone-limited. For phenol removal, it is seen that the A/O process performed the best of the three schemes. The effect of UV on the phenol removal is seen to be marginal which is not altogether unexpected since ozone and phenol react easily and rapidly, even without UV. For the DMF removal, carbon adsorption is somewhat effective in the very early stages only and can be considered essentially an ineffective process due to extremely rapid breakthrough. Efficiencies of the A/O, the ozonation, and the O_3 + UV processes while somewhat better than the adsorption process are essentially the same. From Figures 5 and 6, it is obvious that phenol is being preferentially removed from the mixture, which is explained by the high reactivity of phenol with ozone and its relatively high adsorptivity on carbon. Poor DMF removal is apparently due to ozone-limiting conditions of the experiment and also due to poor adsorption on carbon. This is confirmed by the data of experiment no. 3 on a pure DMF solution which shows that DMF has limited reactivity with ozone alone, but when combined with UV, the reactivity improves severalfold. However, since carbon has very low capacity for DMF, no adsorption-oxidation effect can be anticipated.

For experiment no. 4 in which regeneration of the spent carbon with ozone was attempted after a steady-state in the A/O process had been achieved (as indicated by a steady-state effluent concentration), the ratio of effluent concentration (phenol or DMF) in the A/O process and the ozone + UV process was computed. If the ratio is 1, the two processes are identical; the extent of departure of the ratio downward from 1 may be considered as the extent of the adsorption-oxidation effect or the improvement in the process performance due to adsorption-oxidation. The ratio was computed from the data in Table 4 for both before and after the carbon regeneration and is shown in Figures 7 and 8 for phenol and DMF, respectively. For phenol, it is seen that the ratio is always less than 1 which is interpreted as superior performance for the A/O process. Under steady-state conditions, the ratio is ~0.9 with virgin carbon or before regeneration; and it decreases to ~0.8 after regeneration which suggests improvement in the A/O effect.

Prior to achieving the steady-state conditions, the ratio is higher after regeneration which most probably is due to incomplete regeneration of carbon. As seen from Table 4, spent carbon was regenerated with ozone for about an hour which apparently was not long enough. For DMF, as shown in Fig. 8, the behavior is qualitatively similar except that no A/O effect is indicated with virgin carbon, the ratio being 1.0 before regeneration. The drop in the ratio observed for both phenol and DMF strongly suggests that nature of the carbon surface may be changing due to exposure to ozone. In addition to reacting with the adsorbed organics, ozone may react with the carbon itself which affects its adsorption characteristics.

In one experiment in which oxygen was substituted for ozone, it was found that oxidation of organics by oxygen is minimal, if any. Figure 3 shows data for phenol removal using oxygen and ozone in an A/O system. Figure 4 shows similar data for DMF. As shown in Figure 4, low DMF removal is achieved even when using ozone in the A/O system since there is preferential demand of ozone for phenol and carbon so that little, if any, is available for reaction with DMF.

(b) Powdered Carbon Experiments: Data on one experiment in which the liquid stream was continuously recycled through the reactor is given in Table 5. The experiment consisted of two runs, O_3/UV, and O_3/UV/C. Figure 9 shows the experimental data for both runs. Note that the phenol concentration in the stream for the O_3/UV/C run is computed by adding the free and the adsorbed concentrations. The data clearly show that O_3/UV/C performs better than O_3/UV. Another important result conveyed by the data is that both the free and the adsorbed phenol compete for ozone in the contacting scheme. Furthermore, the ozone data show that its utilization is more efficient with O_3/UV/C than with O_3/UV. Taking into account ~30 mg/l of ozone lost due to UV alone (estimate obtained experimentally using water as the influent stream), it is calculated from the data in Figure 9 that over a period of 75 minutes, the O_3/UV/C run consumed approximately 60% of the ozone consumed in the O_3/UV run.

For the semi-batch experiments in this series which were designed to determine capacity of the regenerated carbon, the data are reported in Table 6. Note that adsorbed phenol concentrations are reported in terms of mg of phenol/gm of carbon. Nominal experimental conditions for this series are represented by experiment no. 6 in Table 6. The exposed carbon samples in this experiment were allowed to equilibrate with fresh phenol solution of original concentration for 2 hours and 24 hours. From the data, it can be seen that equilibrium has essentially been achieved within 2 hours. For the rest of the experiments, a period of 2 hours was used.

From the data in Table 6, it can be seen that the pH drops as a result of ozonation, suggesting the formation of acidic products of reaction. The extent of phenol adsorption on virgin carbon is also seen to depend on pH; as the pH approaches extreme values, adsorption decreases. For example, in experiment no. 8 in which the pH of the phenol solution was raised to ~ 12 by the addition of sodium hydroxide, adsorbed phenol concentration is only 15-20% of that in experiment no. 6. Obviously, such a condition is not desirable for an efficient adsorption or the A/O process. In experiment no. 9, concentration of carbon in the feed suspension was reduced from 3.34 to 1.34 gms/liter. The free phenol concentration data from samples in which carbon was suspended suggests that little carbon capacity was generated which probably is due to the fact that ozone feed rate was lowered in this experiment by about 50% to minimize carbon carryover with the gases. As a result, free phenol was still present in the reacted mixture. The adsorbed phenol data suggest that some ozone may be reacting with the adsorbed phenol. This apparent contradiction may be due to the possibility that the oxidation of adsorbed phenol was not completed to the extent of making carbon available for further adsorption. In other words, phenol concentration on carbon at 20 and 30 minutes of ozone exposure time decreased apparently due to reaction with ozone; however, products of reaction were not desorbed and consequently there was no extra capacity generated at

20 and 30 minutes as shown by the free phenol concentration data. The effect of UV, based on a comparison of the data of experiments 6 and 7, does not appear to be overwhelming which at first does not seem surprising since phenol reacts with ozone readily and rapidly in the absence of UV. However, an incomplete desorption of reaction products may again interfere with the evaluation of this effect.

(c) Regenerated Capacity of Carbon: Regenerated capacity of carbon can be calculated from the free or the adsorbed phenol concentration data. This has been done for experiments 6, 7, and 10 and the results are shown in Tables 7 and 8, respectively In all the experiments, it was noted that unexposed carbon from the feed slurry, when resuspended in a fresh phenol solution adsorbed some more phenol. In calculating the regenerated carbon capacity, this extra pickup was attributed to equilibrium between phenol and carbon at a higher level of concentration and was applied as a correction factor. It has been estimated that the calculated regenerated capacity values in Table 7 are low by 10-20% primarily because the ozone-exposed carbon samples to be suspended in fresh phenol solution contained some moisture and no correction was applied for this factor while preparing suspensions of ozone-exposed carbon samples. By applying a 15% correction to the calculated values in Table 7, the regenerated carbon capacity is seen to be 20-40%. Using the adsorbed phenol concentration data in Table 8, the regenerated capacity is calculated to be in the range of 50-70%. This apparent contradiction between the two sets of values given in Tables 7 and 8 may be explained by that the products of reactions taking place on the carbon surface are not completely desorbed from the surface so that the values calculated in Table 8 are overestimated.

It may also be noted from the data that most of the regeneration seems to occur in the early stages of the reaction. Calculated regenerated capacity estimates at 90 minutes are only marginally higher than those at 20 minutes. Apparently the reaction and the conditions involving oxidation of the adsorbed materials have significantly altered since the beginning.

(d) <u>Phenol Removal Rate</u>: Phenol removal rate is calculated for the O_3/UV, O_3/UV/C, and O_3/C processes from the data in experiment no. 5, 5A, 6 and 7. For 5 and 5A, the rate at various phenol concentrations is calculated graphically while for no. 6 and 7, the calculation is done analytically. For no. 6 and 7, the carbon capacity after regeneration as measured by phenol adsorption after suspension of the exposed carbon in a fresh solution of phenol, is also included. Details of these calculations are given in Table 9.

For all the experiments, the calculated values are summarized in Table 10 and shown in Figure 10. Note that calculations are based on phenol concentration and not on the absolute amount of phenol removed. Also, it is assumed that the feed gas flowrate and the ozone concentrations in the influent and the effluent gas streams are the same in all experiments. Only those points were selected from all the data that satisfied or very nearly satisfied this assumption. Figure 10 clearly shows that under the experimental conditions, the rate of phenol removal is maximum in the O_3/UV/C process, and is high, almost by a factor of 2 compared to the O_3/C and the O_3/UV processes. Due to scatter in the data, the efficiencies of the O_3/C and the O_3/UV processes may be considered essentially the same. For each process, the rate of phenol removal is also seen to depend on the reaction concentration under the experimental conditions selected.

DISCUSSION

Based on the above results, it can be stated that the A/O process removes phenol at a much faster rate than any of the other processes investigated in this study. This effect seems to be most dominant in the initial stages of the process. As the reaction proceeds, the effect appears to slow down as evidenced by values of the calculated regenerated carbon capacity. This slowdown is interpreted as being caused by the intermediate reaction products formed as a result of the phenol-ozone reaction which do not have the same high reactivity, or do not readily desorb off the carbon surface. The explanation is consistent with Gould's[2] studies on oxidation of phenol by ozone in which he found that the COD (chemical oxygen demand) first decreases sharply until all the aromatics are consumed and then the COD reduction rate drops sharply. Obviously such a situation depends primarily on the type of organic contaminant being removed and the adsorbent being used. It may vary from one case to another. For an organic such as phenol, it is clear that additional techniques will have to be developed to improve reactivity of the intermediate products and to help desorb the products of reaction.

From the viewpoint of the A/O process design, the technique based on powdered carbon is considered superior to that based on granular carbon, primarily because the former facilitates intimate contact among all the process elements simultaneously, which is the basis of the process. The experiments with powdered carbon clearly show that both the free and the adsorbed phenol fractions compete fo ozone. In those experiments with granular carbon in which the ozone supply was the limiting factor, availability of ozone to the adsorbe phenol in a measure the same as that in the powdered carbon experimen is very unlikely. Based on the effluent gas analysis in the O_3/UV experiment, all the ozone was consumed by the free phenol in solution. Ozone dissolved in water may have been available to the adsorbed phenol to some extent which can explain the observed 10-20% improved performance of the A/O process over the O_3/UV process. Of a more immediate consequence to this study was the resultant improvement in gas-liquid contact by avoiding bubble coalescence and gas channelling by the use of powdered carbon. Furthermore, the effect of UV on phenol removal although not obvious from the raw data on phenol is clearly seen in Figure 10. Based on the above discussion, it is clear that the contacting scheme for the liquid with the carbon, ozone and UV is the key to the success of the process and that valuable insights would be gained by investigating additional contacting schemes such as those based on spray liquid or a slurry in an O_3/UV environment instead of bubbling gas, and a CSTR (constant stirred-tank reactor) design instead of a column reactor.

Continuing the A/O process design discussion, the study has demonstrated contributions of each of the three components, namely, ozone, UV, and carbon. The importance of UV and carbon is shown by the phenol removal rate data in Figure 10. The role of UV was even more dramatic in the case of DMF removal as shown by data in Table 2. The role of ozone was demonstrated by comparing its performance with oxygen as shown in Figure 3.

The importance of selecting reaction conditions for the A/O process which are compatible with all the three component processes is illustrated by the high pH experiment, no. 8. At a starting pH of 12, the A/O process performance is seen to deteriorate drastically whereas it has been shown in several studies that a high pH is desirable for an ozonation process. Nebel et al[3] have shown that a pH of 11.8 and above is optimum for the ozonolysis of phenol. However, a high pH is not suitable for the adsorption process and consequently the A/O performance suffers.

For phenol removal under the conditions investigated, it is seen that almost 80-90% of the regeneration of the carbon capacity is achieved in the first 20 minutes of the reaction. Allowing the reaction to proceed over a period of 90 minutes yielded the residual 10-20% of the regenerated capacity. This behavior is attributed to important changes in both the reaction and the conditions. The ozone-phenol reaction chemistry is quite complex and has been the subject of a number of studies[2,3,5,6]. Phenol oxidation with ozone has been shown to occur in several steps and result in the formation of several intermediate products of reaction, some of which such as catechol, o-quinone, and oxalic acid have been experimentally verified.

While there is no singular concurrence on the exact mechanism of the total oxidation reaction, it is clear that acidic products are formed before the final oxidation step of carbon dioxide formation. The lowering of pH as a result of ozonation in the A/O and the O_3/UV experiments in this study is consistent with this general description of the mechanism. In the presence of UV while the mechanism of phenol oxidation may change substantially, it is apparent from the pH data that acidic products are still formed. The interaction of ozone and carbon further adds to the complexity of the A/O process. The adsorption properties of a material depend on its surface functionality[4]. By the action of ozone, this functionality may change drastically thereby affecting its adsorption capacity for a given material. Garten and Weiss[7] using an electrochemical reduction procedure altered the surface functionality of carbon from "acid-adsorbing" to "base-adsorbing". The reduction procedure increased the NaOH adsorption capacity by a factor of 2 to 5, while simultaneously reducing the HCl adsorption capacity by a factor of 2 to 7. Ozone which is one of the most powerful oxidants known could also bring about such a fundamental change in the adsorption properties of carbon.

Another type of effect ozone may have on carbon is to completely oxidize it which from a practical standpoint is undesirable because of the carbon lost. No attempt was made in this study to investigate this effect. It is obvious that the adsorption-oxidation process chemistry is extremely complex. For phenol removal, it is evident that the original reactions and the conditions have altered significantly and that regeneration reactions of carbon are retarded after the initial regeneration has been achieved. It is safe to say that the reactions are going to be different for different organics. No attempt was made in this study to investigate the reaction chemistry of the process, yet it is clear that future effort must be directed to this area to fully exploit the potential of the A/O process.

<u>Direction for Proposed Future Work</u>: A number of areas for further work are suggested from the preceding discussion. In the process development area, need for development of additional adsorption-oxidation process schemes which permit intimate contact of the organic material with carbon, ozone, and the UV radiation simultaneously is identified. In order to develop such a scheme successfully, chemistry of various oxidation reactions must be better understood. As described previously, the adsorption-oxidation reaction chemistry is extremely complex. So initially, simple reaction schemes must be devised and tested including identification and oxidation reactions of intermediate products of reaction. As the data base grows,

exceeding complex reactions including the role of UV can be studied. Effects of ozone on the adsorption capacity of carbon and others related to carbon oxidation should be included in the process reaction studies. Possibilities of exploiting change in carbon adsorption characteristics brought about by reaction with ozone should be evaluated in terms of designing new application schemes and for improving process performance.

In the short term, need for extending the data base to a variety of organic chemicals seems to be the most important. Studies on various types of carbon and other adsorbent materials should also be conducted to examine the uniqueness of carbon to the adsorption-oxidation process and to determine if the large surface area of an adsorbent is vital to the A/O effect. Furthermore, it would be useful to conduct regeneration studies similar to the ones conducted in this study on partially saturated carbon. Note that in this study, carbon was completely saturated before regeneration was attempted. Access of ozone to adsorption sites deep inside the pores may be quite limited which can significantly affect the performance efficiency of the process. If, however, adsorption were limited mostly to the surface sites such that carbon is not saturated before it is regenerated which may be the case in several practical applications, the adsorption-oxidation process may have added attractiveness.

CONCLUSIONS AND RECOMMENDATIONS

1. Laboratory schemes were devised to test the A/O process involving the use of powdered carbon, ozone, and UV radiation in a unique combination. Technical feasibility of the process has been demonstrated successfully for the removal of dissolved organics from industrial wastewaters, specifically for phenol.

2. Experimental data have been obtained on phenol removal which shows that the A/O process performs better than any of the other processes investigated. Ozone utilization efficiency for the A/O process is also seen to be higher than that of direct ozonation with or without UV.

3. Phenol adsorbed on carbon can be reacted with ozone in the A/O process leading to regeneration of the adsorbent. However, the regeneration reaction slows down after an initial oxidation phase. A better understanding of the A/O process chemistry is required to fully understand the slowdown in the regeneration reaction and to correct this situation.

4. It is recommended that a number of other organic materials be evaluated using the A/O treatment process to help identify the nature and scope of other problem areas. A heavier emphasis on understanding the reaction chemistry of the A/O process is also recommended.

5. Development of additional A/O process schemes which permit intimate contact of the organic with carbon, ozone, and the UV radiation simultaneously is recommended.

6. Ozone-carbon reaction studies are important for future process development work. There is experimental evidence that upon prolonged contact with ozone containing gases, separation characteristics of powdered carbon change significantly which may be due to particle attrition, surface adsorption of gases, or chemical reactions taking place on the surface.

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FIGURE 1: ADSORPTION-OXIDATION REACTOR

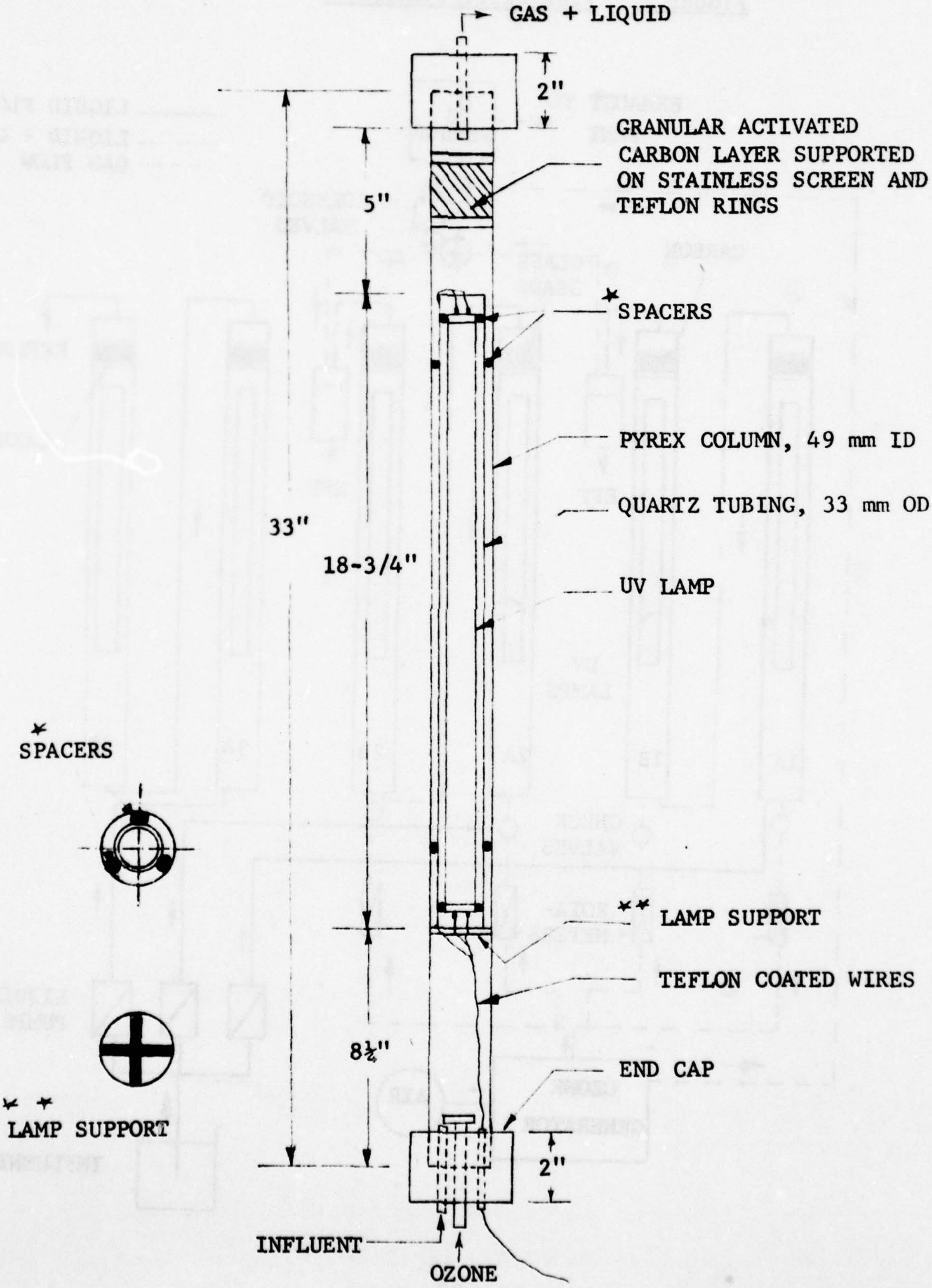


FIGURE 2: TEST SETUP SCHEMATIC

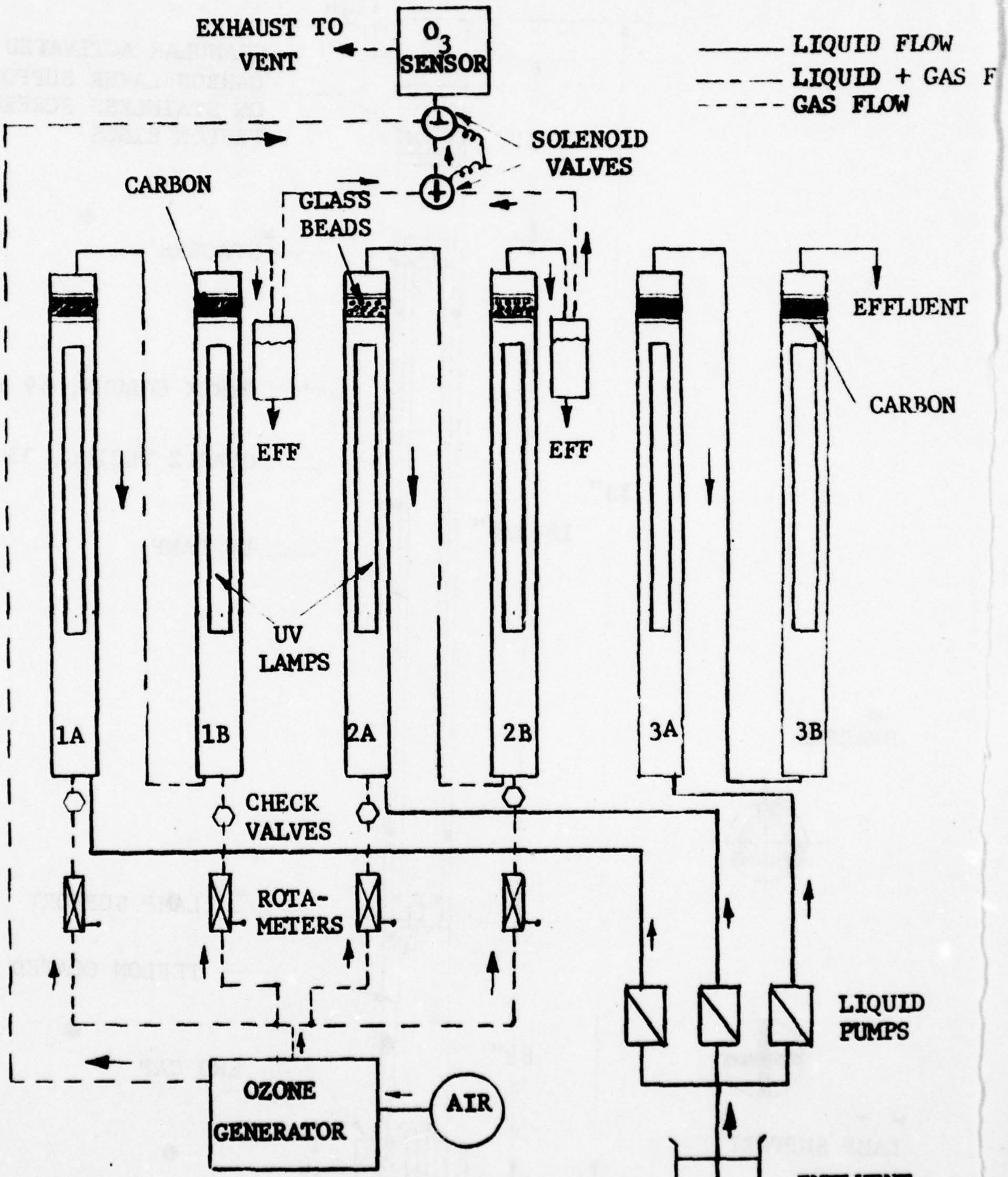


FIGURE 3: O_3 / UV / C VS. O_2 / UV / C FOR PHENOL

INFLUENT: PHENOL = 1108 mg/1 } Actual Waste
DMF = 1942 mg/1

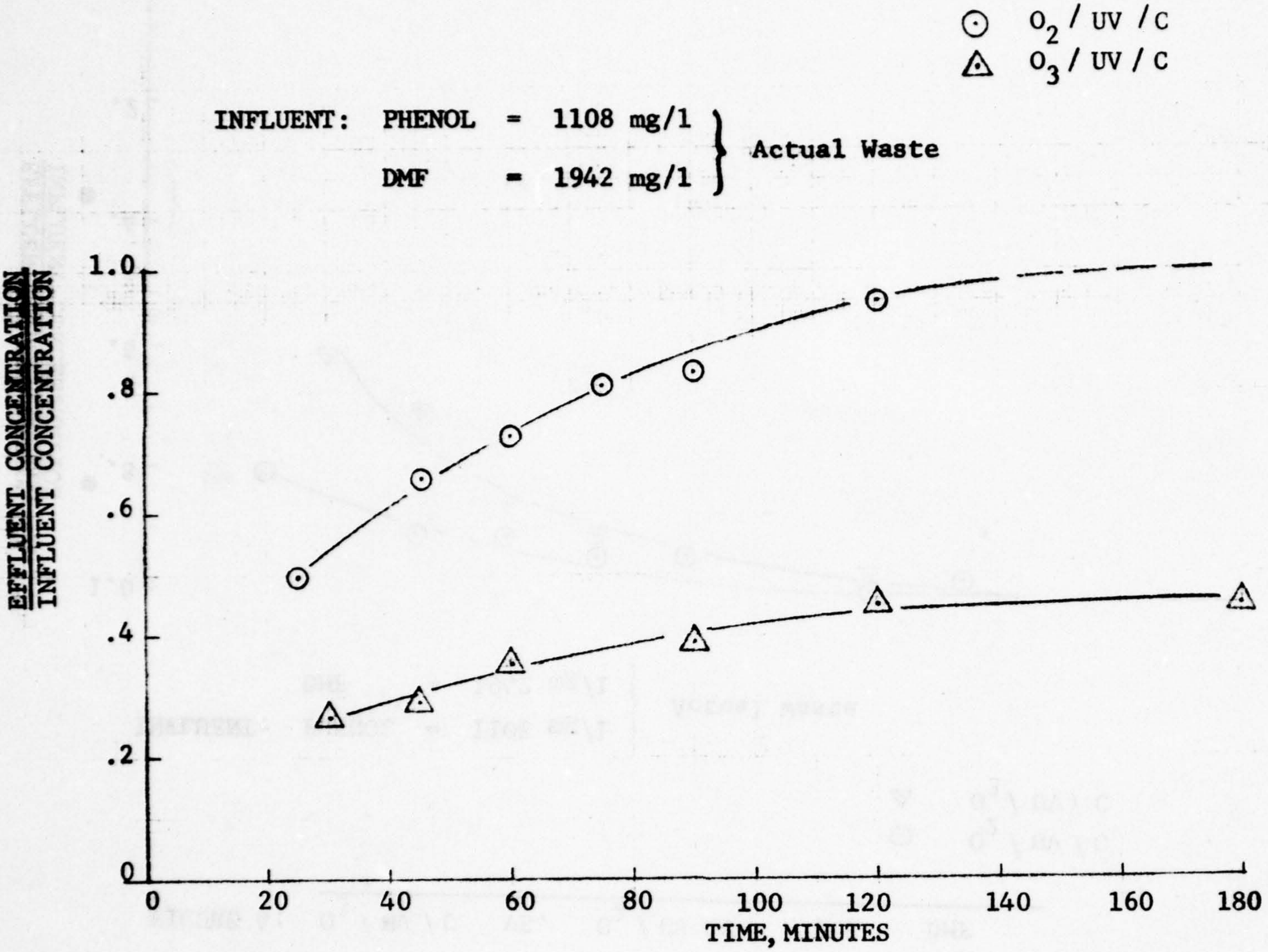
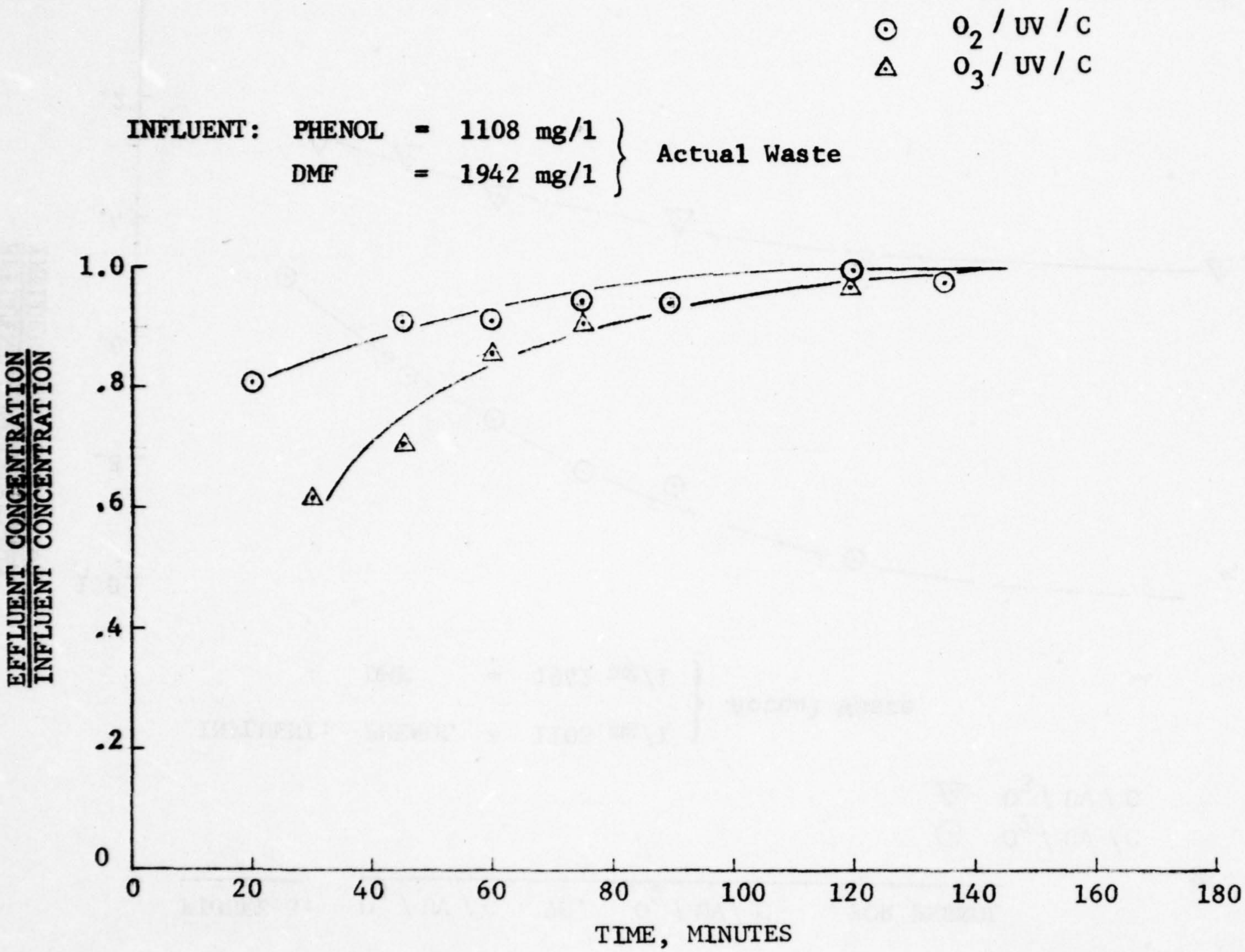


FIGURE 4: O_3 / UV / C VS. O_2 / UV / C FOR DMF



INFLUENT: PHENOL = 1108 mg/1 } Actual Waste
DMF = 1942 mg/1 }

FIGURE 5. REMOVAL OF PHENOL BY VARIOUS PROCESSES

INFLUENT SOLUTION: PHENOL 1050 Mg/L } SYNTHETIC WASTE
DMF 1575 Mg/L

LIQUID FLOWRATE = 25 ML/MIN.
GAS FLOWRATE = 400 ML/MIN
O_3 CONC. = 35 MG/L
AMOUNT OF CARBON = 15 GMS

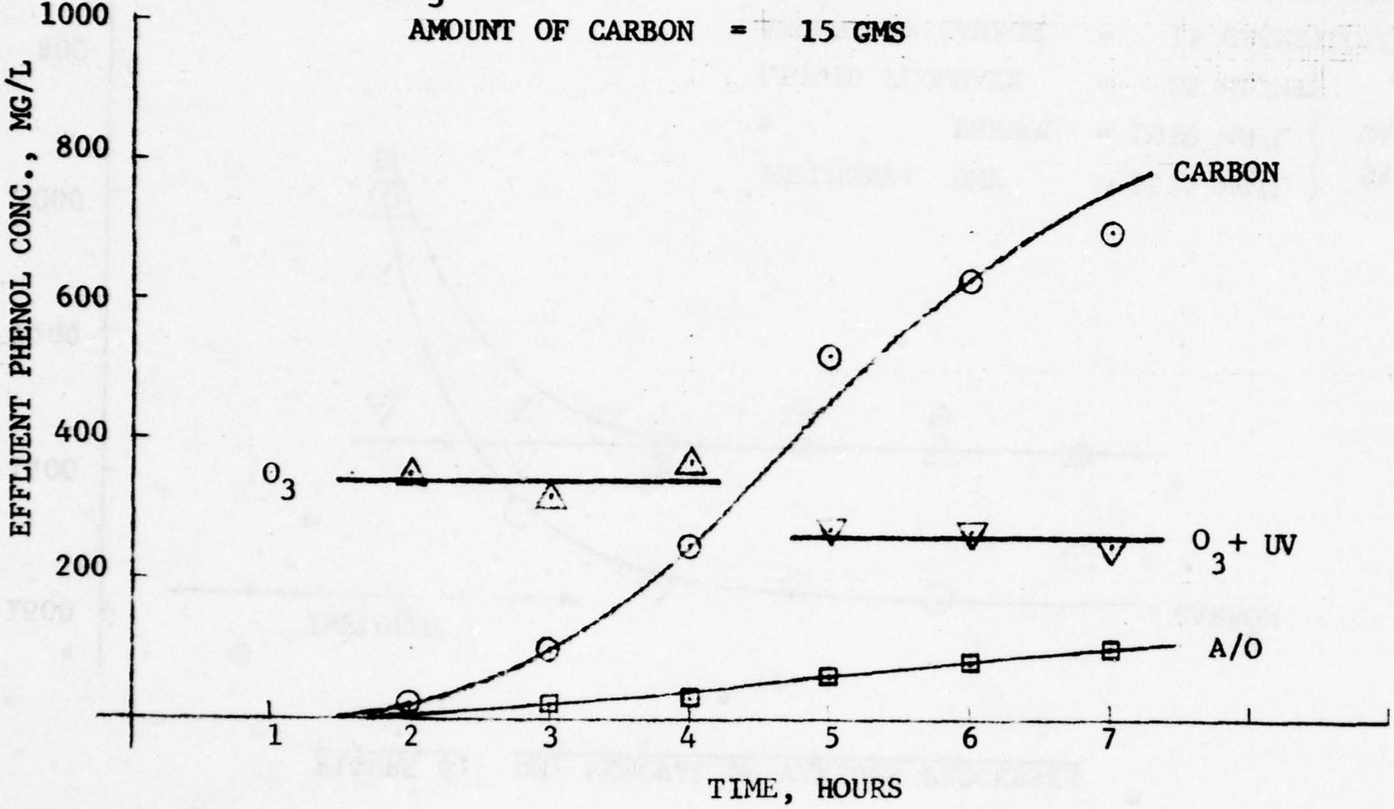


FIGURE 6: DMF REMOVAL BY VARIOUS PROCESSES

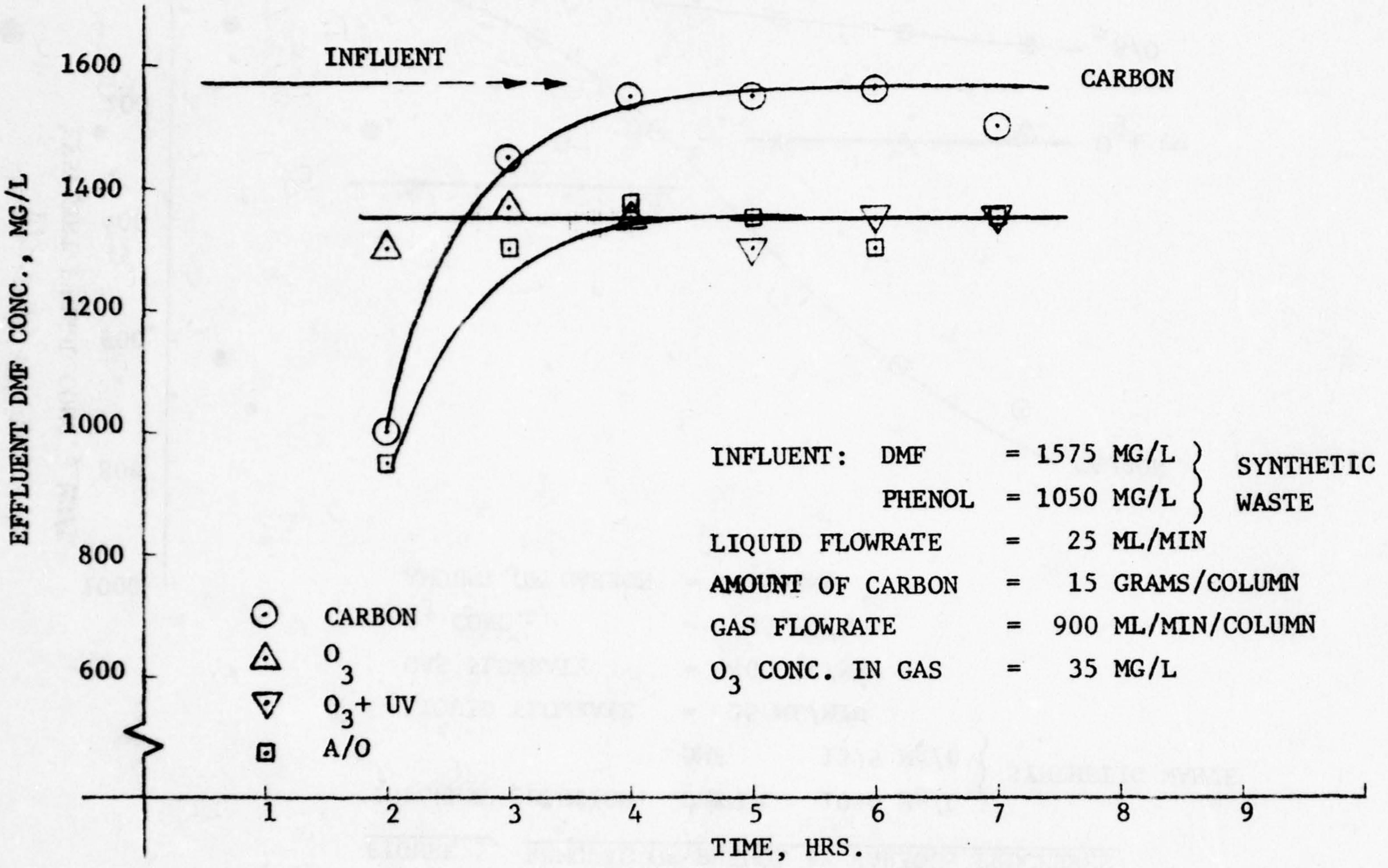


FIGURE 7: A/O EFFECT ON PHENOL BEFORE AND AFTER REGENERATION

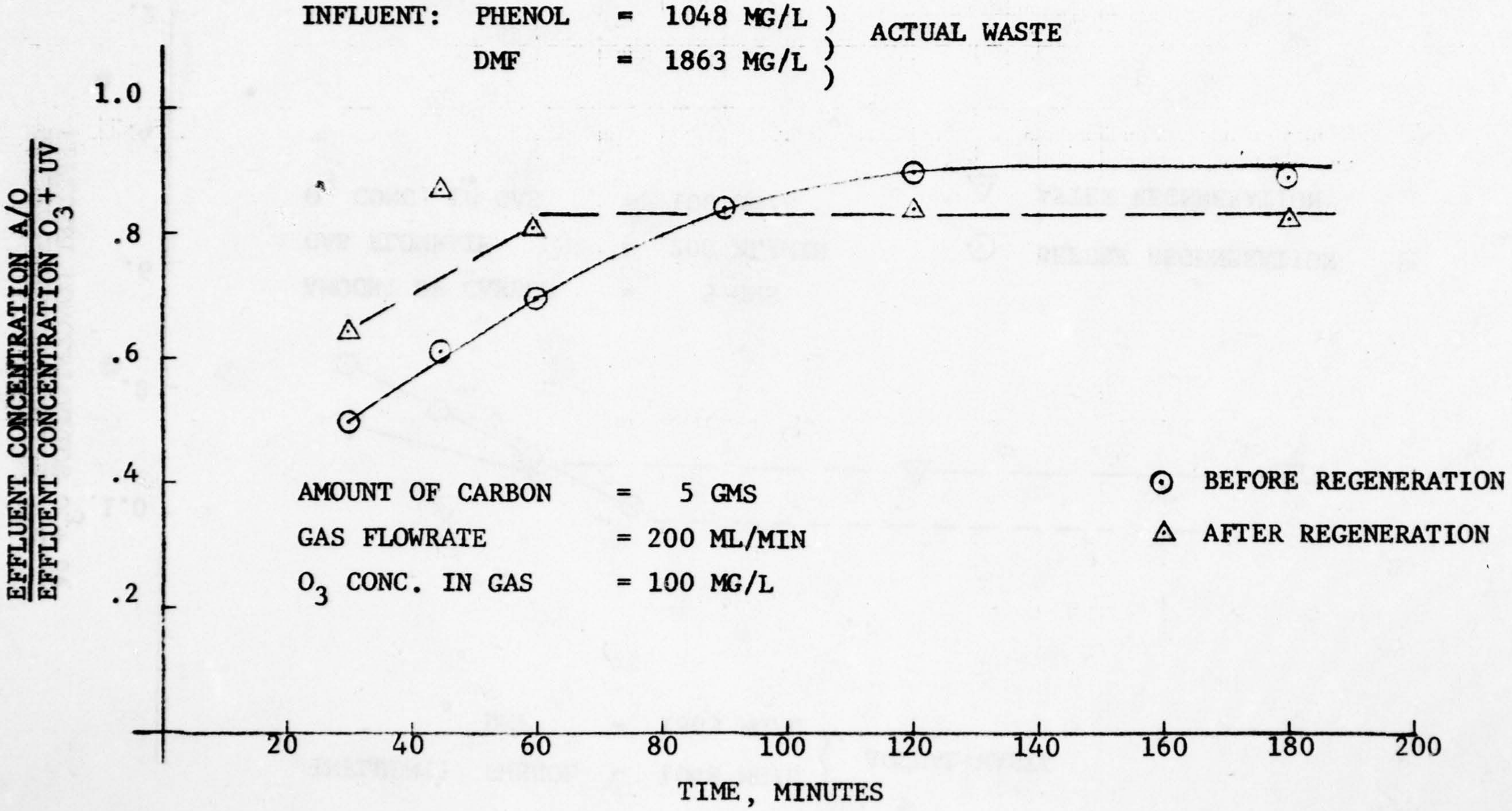


FIGURE 8: A/O EFFECT FOR DMF BEFORE AND AFTER CARBON REGENERATION

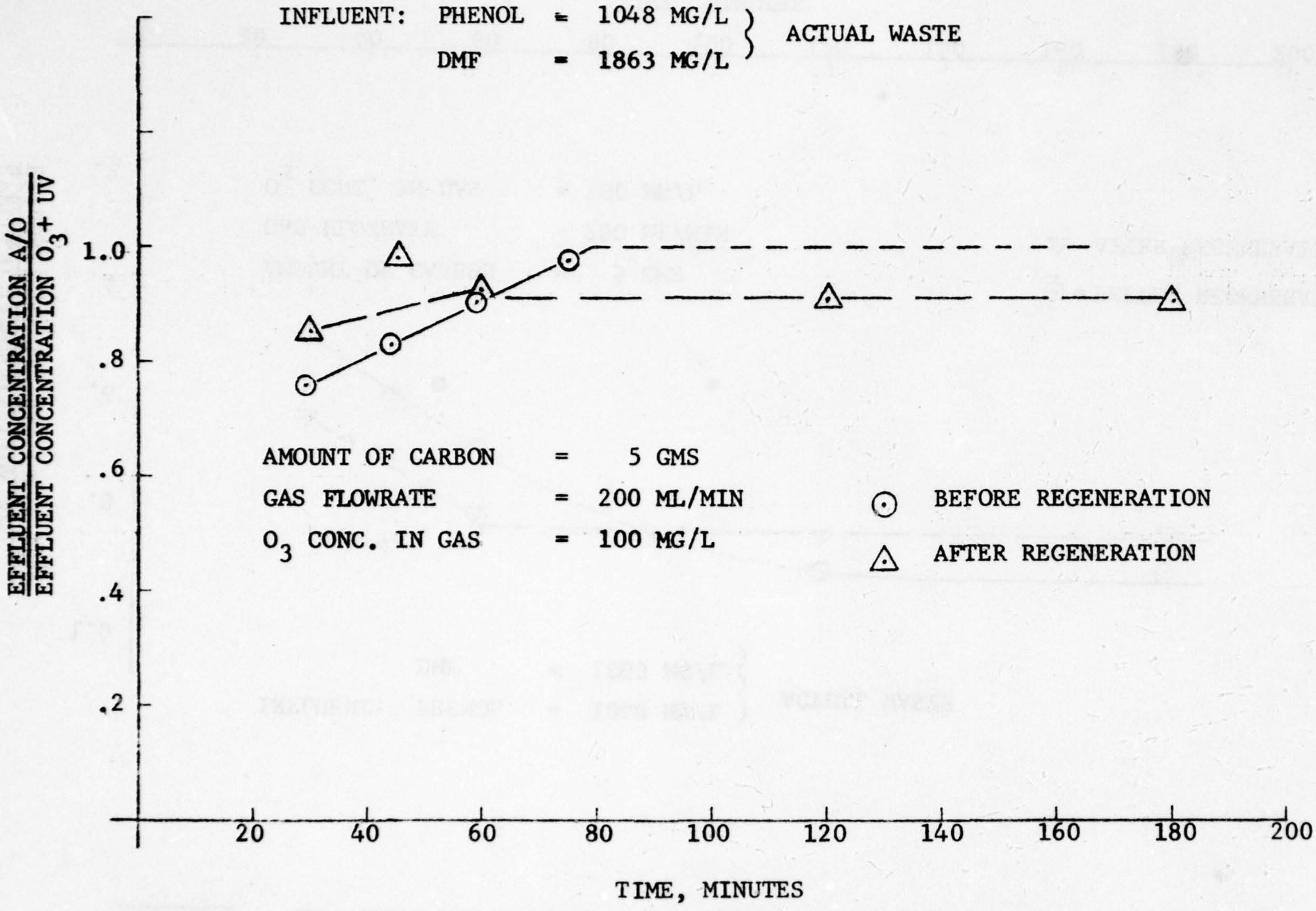


FIGURE 9: EFFLUENT PHENOL AND OZONE MEASUREMENTS (EXPERIMENT 5)

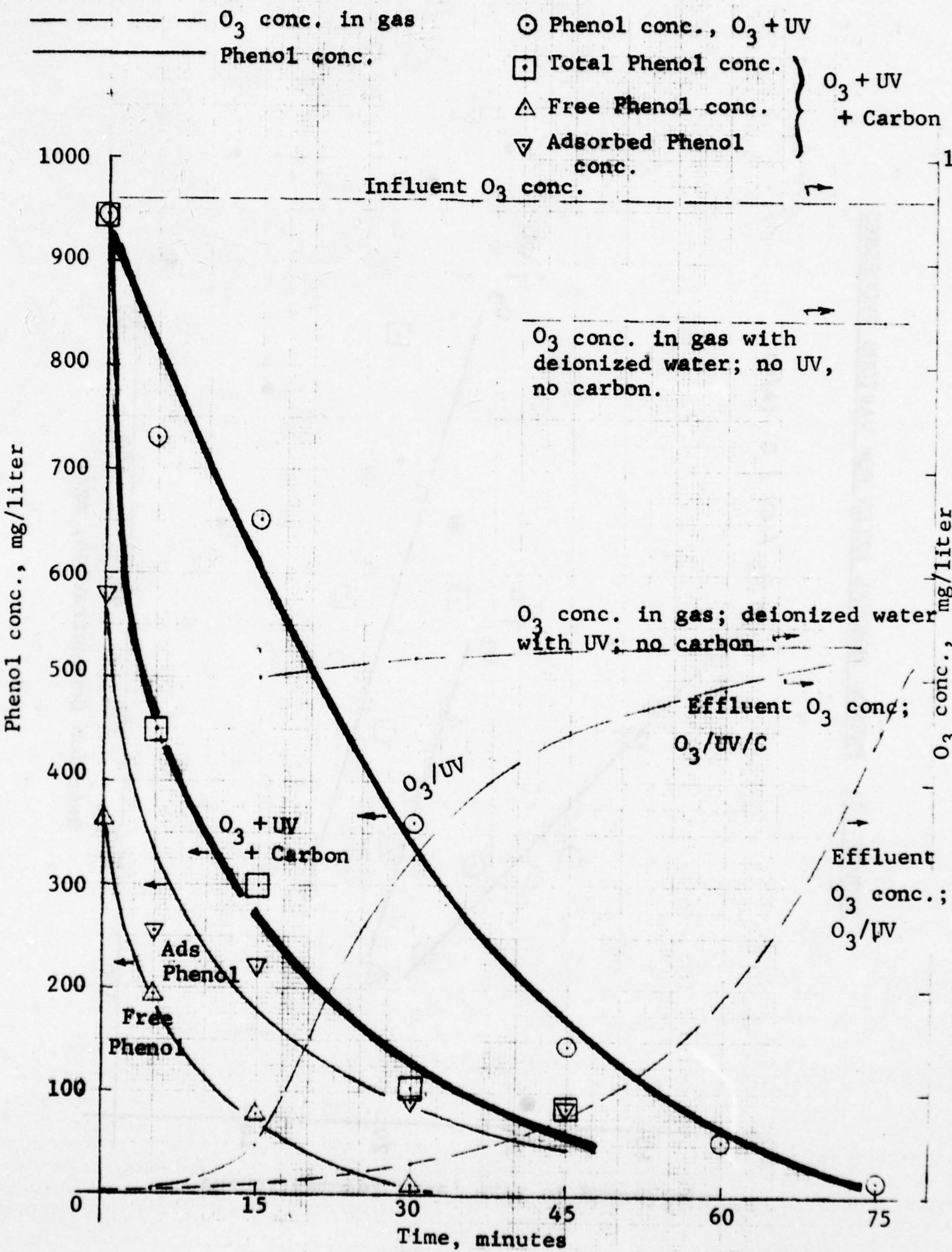


FIGURE 10: PHENOL REMOVAL RATES FOR VARIOUS PROCESSES

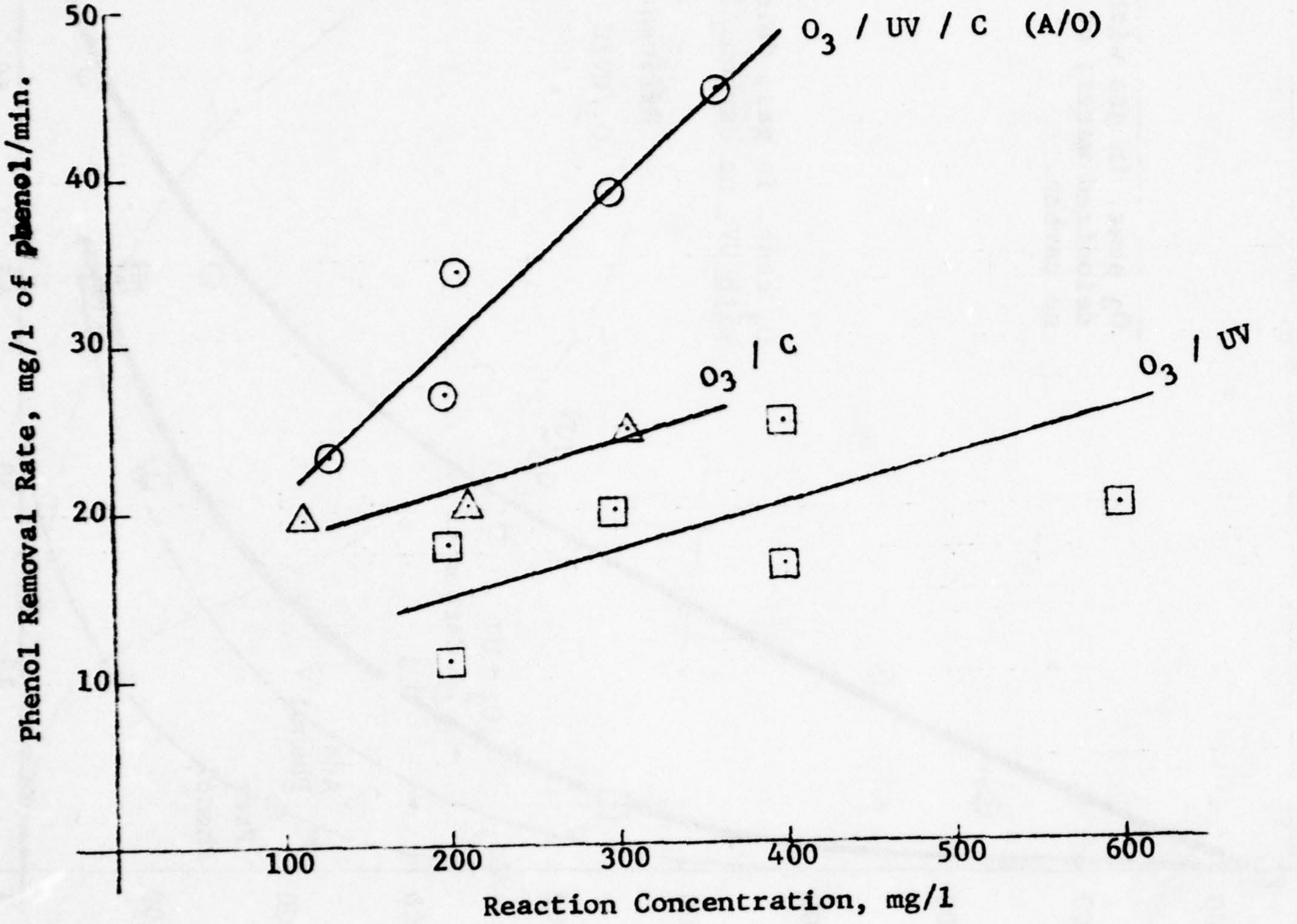


TABLE 1

Experiment No. 1: Removal of Phenol and DMF by Various Processes at High Concentrations

Influent Solution: Phenol = 1050 mg/liter
DMF = 1575 mg/liter
Synthesized Solution

Liquid Flowrate = 25 ml/min
Feed Gas Flowrate = 400 ml/min, each column
Feed Gas Ozone Concentration = 35 mg/liter
Amount of Carbon = 15 gms, each column

	EFFLUENT LIQUID CONCENTRATIONS FOR VARIOUS PROCESSES, mg/l											
	ADSORPTION-OXIDATION				OZONE + UV				ADSORPTION			
Time	IA		IB		IIA		IIB		IIIA		IIIB	
Hrs	Phenol	DMF	Phenol	DMF	Phenol	DMF	Phenol	DMF	Phenol	DMF	Phenol	DMF
2	100	1250	5	950	450	1450	350	1350			20	1000
3	200	1350	20	1300	550	1400	320	1370	650	1600	100	1450
4	200	1270	30	1370	400	1400	370	1350	780	1550	250	1550
					UV Light Turned ON*							
5	500	1500	60	1350	600	1400	270	1300	850	1550	520	1550
6	450	1450	80	1300	600	1450	270	1350	920	1570	630	1570
7	500	1470	100	1350	600	1470	250	1350	950	1600	700	1500

* IIA and IIB only; lights in IA and IB had been turned on since the beginning of the experiment.

TABLE 2

Experiment No. 2: **Removal of Phenol and DMF by Various Processes at Low Concentrations**

Influent Solution:	Phenol	=	87 mg/liter	Synthesized Solution
	DMF	=	143 mg/liter	
	pH	=	6.8	

Liquid Flowrate = 25 cc/min
Gas Flowrate = 400 cc/min, each column
Feed Gas Ozone Concentration = 70 mg/liter
Amount of Carbon = 5 gms, each column

	EFFLUENT LIQUID CONCENTRATIONS FOR VARIOUS PROCESSES, mg/1											
	ADSORPTION-OXIDATION				OZONE + UV				ADSORPTION			
Time	IA		IB		IIA		IIB		IIIA		IIIB	
Hrs	Phenol	DMF	Phenol	DMF	Phenol	DMF	Phenol	DMF	Phenol	DMF	Phenol	DMF
1												
2												
3												
4	0	27	0	-	0	38	0	13				
5	0	34	0	-	0	36	0	15	61	137	43	14
6	0		0	14	0	26	0	11				
7	6	34	0	14	0	31	0	11	62	124	44	13
	UV Lights Turned ON											
8												
9	1	8	1	0	0	6	0	0	79	131	60	13
10												
11	2	3	0	0	0	5	0	0	85	135	68	13

TABLE 3

Experiment No. 3: Ozonation of DMF Solution With and Without UV

Influent DMF Concentration = 780 mg/liter

Feed Gas Ozone Concentration = 56 mg/liter

Liquid Flowrate = 25 ml/min

Feed Gas Flowrate = 400 ml/min, each column

Time	Effluent DMF mg/liter		Effluent Ozone in Gas mg/liter
Hrs	IIA	IIB	IIB
1	--	--	43
2	690	710	43
3	--	--	43
4	720	660	43
		UV Light Turned ON	
5	330	290	2
6	300	190	2
7	--	82	-

TABLE 4

Experiment 4: A/O and O_3/UV Treatment of Pfizer Waste

Influent Solution: Actual Pfizer waste sample diluted by a factor of ~9

Phenol Concentration = 1048 mg/liter
DMF Concentration = 1863 mg/liter

Liquid Flowrate = 50 ml/min
Feed Gas Flowrate = 200 ml/min, each column
Feed Gas Ozone Concentration = 98 mg/liter
Amount of Carbon = 5 gms

Time	EFFLUENT LIQUID CONCENTRATIONS, mg/l							
	ADSORPTION-OXIDATION				O_3 + UV			
	IA		IB		IIA		IIB	
Min	Phenol	DMF	Phenol	DMF	Phenol	DMF	Phenol	DMF
30	268	1156	--	--	549	1519	--	--
45	309	1316	--	--	514	1584	--	--
60	367	1613	266	1528	535	1764	507	1690
75	--	--	--	--	--	--	--	--
90	409	1784	311	1745	490	1747	443	1684
105	--	--	--	--	--	--	--	--
120	472	1813	384	1774	530	1876	460	1767
135	476	1840	--	--	--	--	--	--
180	460	1898	424	1829	521	1950	480	1843
0	Columns drained of liquid and refilled with deionized water; Columns IA and IIA only were used for rest of the experiment.							
30	44	74			21	27		
60	27	23			12	14		
75	24	15						
90	17	8			10	8		
	Ozone gas begun to be introduced along with water.							
120	0	2						
150	0	0			0	0		
0	Columns drained of water and waste solution being introduced.							
30	354	1297			549	1519		
45	446	1566			514	1589		
60	428	1635			535	1764		
75	445	1613						
90								
120	441	1707			530	1876		
180	424	1774			521	1950		
210	448	1702						

TABLE 5

Experiment No. 5: Phenol Removal by A/O and O_3/UV Processes; Liquid Stream Continuously Recirculated

Initial Phenol Concentration	947 mg/liter
Feed Slurry Carbon Concentration for the A/O run	= 3.34 gms/liter
Feed Gas Flowrate	~400 ml/min
Feed Gas Ozone Concentration	~ 96 mg/liter
Liquid Flowrate	= 50 ml/min
UV Lamp	ON

	O_3/UV RUN		A/O RUN		
Time, Min	Effluent Phenol Conc., mg/l	Effluent Ozone Conc., mg/l	Effluent Phenol Conc., (free) mg/l	Phenol Conc. on Carbon mg/gm	Effluent Ozone Conc., mg/l
0	947		363	157	
5	731	0.5	193	69	0.5
15	652	1.0	77	60	4.6
30	361	3.5	12	25	35.5
45	147	8.8	0	23	45.0
60	53	19.4	0	--	49.5
75	17	45.6	0	--	51.2

TABLE 5A

Experiment No. 5A: **Phenol Removal by Ozone/UV; Liquid Stream Continuously Recirculated**

Initial Phenol Concentration	= 432 mg/liter
Feed Gas Flowrate	~ 400 ml/min
Feed Gas Ozone Concentration	= 96 mg/l
Liquid Flowrate	= 50 ml/min
UV Lamp	ON

Time Min.	Effluent Phenol Conc. mg/l	Effluent Ozone Conc. mg/l
0	432	-
5	325	2.4
15	137	1.4
30	6	33.8
45	0	46.6
60	0	48.7

TABLE 6: A/O SEMI-BATCH EXPERIMENTS WITH POWDERED CARBON

Phenol Removal and Carbon Capacity Determination

Experiment No. 6: Nominal Experimental Conditions

Initial Phenol Concentration	=	970 mg/liter
pH of Phenol Solution	=	4.5
Feed Slurry Carbon Concentration	=	3.34 gms/liter
Feed Gas Flowrate	~	430 ml/min
Feed Gas Ozone Concentration	~	95 mg/liter of gas
UV Lamp	=	ON

Reaction Time Min.	Effluent Gas Ozone Concentration mg/l	pH	Free Phenol Concentration mg/l	Adsorbed Phenol Concentration mg/gm of carbon
0		7.3	263	119
	0 at 3 min			
5		4.0	154	94
	0.5 at 8 min			
10		3.2	105	74
	1.0 at 16 min			
20		3.0	28	53
	23 at 30 min			
	35 at 45 min			
	40 at 85 min			
90		2.9	2	13

Exposed carbon samples were filtered and resuspended in original concentration phenol solution for about 2 hours until equilibrium was achieved.

0		6.0	870	145
5		4.4	807	162
10		3.8	739	143
20		3.7	719	154
90		3.6	686	133

After 24 hours of contacting with original concentration phenol solution,

0		6.3	--	133
5		4.6	792	149
10		3.9	733	165
20		3.7	700	171
90		3.5	668	138

TABLE 6 (Continued)

<u>Experiment No. 7</u>: <u>Effect of UV</u>

Initial Phenol Concentration = 1034 mg/liter
Feed Slurry Carbon Concentration = 3.34 gms/liter
Feed Gas Flowrate ~ 430 ml/min
Feed Gas Ozone Concentration ~ 94 mg/liter of gas
UV Lamp OFF

Reaction Time, Min.	Effluent Gas Ozone Concentration mg/l	pH	Free Phenol Concentration mg/l	Adsorbed Phenol Concentration mg/gm of carbon
0		6.7	364	124
5		3.7	250	127
	0.5 at 8 min			
10		3.3	174	110
	0 at 16 min			
20		3.0	55	63
	18 at 30 min			
	32 at 45 min			
	40 at 85 min			
90		3.0	0	9

Exposed carbon samples were filtered from slurries and resuspended in original concentration phenol solution for about 2 hours until equilibrium was achieved.

0		6.7	890	159
5		4.5	881	177
10		4.1	854	188
20		3.8	778	177
90		3.6	745	116

TABLE 6 (Continued)

Experiment No. 8: **Effect of High pH**

Initial Phenol Concentration = 994 mg/liter
Initial pH = 12.0
Feed Slurry Carbon Concentration = 3.34 gms/liter
Feed Gas Flowrate = 4.35 ml/min
Feed Gas Ozone Concentration = 96 mg/liter of gas
UV Lamp = OFF

Reaction Time Min	Effluent Gas Ozone Concentration mg/l	pH	Free Phenol Concentration mg/l	Adsorbed Phenol Concentration mg/gm of carbon
0		12.0	724	22
10		11.7	412	21
	0 at 16 min			
20		10.6	59	24
	25 at 30 min			
	32 at 45 min			
	38 at 85 min			
90		8.2	7	8

Exposed carbon samples were filtered from slurries and resuspended in original concentration phenol solution for about 2 hours.

0		11.9	962	32
5		11.9	990	33
10		12.0	980	26
90		11.9	900	22

TABLE 6 (Continued)

Experiment No. 9: Effect of Carbon Concentration

Initial Phenol Concentration = 1029 mg/liter
Feed Slurry Carbon Concentration = 1.34 gms/liter
Feed Gas Flowrate ~ 220 ml/min
Feed Gas Ozone Concentration ~ 97 mg/liter of gas
UV Lamp ON

Reaction Time, Min	Effluent Gas Ozone Concentration mg/l	pH	Free Phenol Concentration mg/l	Adsorbed Phenol Concentration mg/gm of carbon
0			736	120
10			535	124
	0 at 15 min			
20			421	90
	0 at 26 min			
30			246	53

Samples of carbon from above slurries were filtered and resuspended in phenol solution of original concentration.

0			959	157
10			980	158
20			966	134
30			964	133

TABLE 6 (Continued)

Experiment No. 10: Data on Pfizer Waste Sample

Initial Phenol Concentration	=	1011 mg/liter
pH of the Solution	=	2.4
Feed Slurry Carbon Concentration	=	3.34 gms/liter
Feed Gas Flowrate	=	460 ml/min
Feed Gas Ozone Concentration	=	94 mg/liter of gas
UV Lamp		ON

Reaction Time, Min	Effluent Gas Ozone Concentration mg/1	pH	Free Phenol Concentration mg/1	Adsorbed Phenol Concentration mg/gm of carbon
0		2.5	492	126
	1 at 16 min			
20		2.5	20	24
	2 at 45 min			
	3 at 60 min			
	6 at 85 min			
90		2.5	6	9

Exposed carbon samples from each were filtered and resuspended in original concentration phenolic waste solution for about 2 hours.

Reaction Time, Min	Effluent Gas Ozone Concentration mg/1	pH	Free Phenol Concentration mg/1	Adsorbed Phenol Concentration mg/gm of carbon
0			970	118
20			803	109
90			790	82

TABLE 6 (Continued)

Experiment No. 11: Phenol Removal by O_3/UV

Initial Phenol Concentration = 1061 mg/liter
Feed Gas Flowrate ~ 410 ml/min
Feed Gas Ozone Concentration = 97 mg/liter

Time Min.	Effluent Phenol Concentration mg/liter	Effluent Gas Ozone Conc. mg/l
0	1061	0
5	825	0
15	546	0
30	148	2
45	5	34
60	0	39
90	0	43

TABLE 7

CALCULATION OF REGENERATED CARBON CAPACITY BASED ON FREE PHENOL MEASUREMENTS

Experiment No.	Ozone Exposure Time Min.	Final Free Phenol Conc. mg/l	Phenol Pickup by Carbon ≡ mg/l	Regenerated Capacity of Carbon ≡ mg/l of phenol	% Carbon Capacity Regenerated
6	Initial Phenol Concentration = 970 mg/l				
	Virgin Carbon Capacity for Phenol ≡ 970-263 = 707 mg/l of phenol				
	0	870	100	-	-
	20	719	251	151[a]	21.3%[d]
	90	686	284	184	26.0%
7	Initial Phenol Concentration = 1034 mg/l				
	Virgin Carbon Capacity for Phenol ≡ 1034-364 = 670 mg/l of phenol				
	0	890	144	-	
	20	778	256	112[b]	16.7%[e]
	90	745	289	145	21.6%
10	Initial Phenol Concentration = 1011 mg/l				
	Virgin Carbon Capacity for Phenol ≡ 1011-492 = 519 mg/l				
	0	970	41	-	
	20	803	208	167[c]	32.2%[f]
	90	790	221	180	34.6%

a. 251-100

b. 256-144

c. 208- 41

d. $\frac{151}{707}$

e. $\frac{112}{670}$

f. $\frac{167}{519}$

TABLE 8

CALCULATION OF REGENERATED CARBON CAPACITY BASED ON ADSORBED PHENOL MEASUREMENTS

Experiment No.	Ozone Exposure Time Min.	Adsorbed Phenol Conc. mg Phenol/gm Carbon		Phenol Pickup by Carbon	Percent of Final Capacity Regenerated
		Initial	Final		
6	0	119	145	26	--
	20	53	154	101	51.7[a]
	90	13	133	120	64.8
7	0	124	159	35	-
	20	63	177	114	49.6[b]
	90	9	116	107	45.3
10	0	126	118	0	--
	20	24	109	85	69.6[c]
	90	9	82	73	59.8

a. $\frac{101-26}{145}$

b. $\frac{114-35}{159}$

c. $\frac{85-0}{\left(\frac{126+118}{2}\right)}$

TABLE 9

CALCULATED REACTION CONCENTRATION AND REMOVAL RATE FOR SEMI-BATCH EXPERIMENTS

Experiment No.	Time Min.	Free Phenol Removed mg/1	Adsorbed Phenol Removed* mg/1	Total Phenol Removed mg/1	Phenol Removal Rate mg/1/min	Phenol Reaction Concentration mg/1
6	5	263-154=109	870-807=63	109+63=172	$\frac{172}{5} = 34.4$	$\frac{263+154}{2} = 208.5$
	10	154-105=49	807-739= 68	49+ 68 =117	$\frac{117}{5} = 23.4$	$\frac{154+105}{2} = 129.5$
7	5	364-250=114	890-881=9	114+9=123	$\frac{123}{5} = 24.6$	$\frac{364+250}{2} = 307$
	10	250-174=76	881-854=27	76+27=103	$\frac{103}{5} = 20.6$	$\frac{250+174}{2} = 212$
	20	174-55=119	854-778=76	119+76= 195	$\frac{195}{10} = 19.5$	$\frac{174+55}{2} = 114.5$

* Measured by the amount of phenol adsorbed when exposed carbon is resuspended in a fresh phenol solution.

TABLE 10

CALCULATED PHENOL REMOVAL RATES FOR VARIOUS EXPERIMENTS

No. & Experiment		Phenol Reaction Concentration mg/1	Calculated Phenol Removal Rate mg/1 of Phenol/min
5	O_3/UV/C	363	45
		300	39
		200	27
5	O_3/UV	800	25
		600	20
		400	16.6
		200	11.1
5 A	O_3/UV	400	25
		300	20
		200	18
6	O_3/UV/C	208.5	34.4
		129.5	23.4
7	O_3/C	307	24.6
		212	20.6
		114	19.5