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**REGENERATION OF SPENT ADSORBENTS
USING ADVANCED OXIDATION
(PREPRINT)**

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ABSTRACT

The removal of organic contaminants from water by adsorption processes results in spent adsorbents; and, in this research, the use of advanced oxidation processes for regeneration of adsorbents and destruction of adsorbed contaminants is investigated.

These two advanced oxidation processes are examined: (1) hydrogen peroxide /ozone and (2) UV light/hydrogen peroxide. The impacts of size and type of adsorbent, adsorbate, and temperature on the destruction efficiency of adsorbed contaminants, the rate, and the required quantity of oxidants are investigated.

This study demonstrates that the regeneration of adsorbents by advanced oxidation is not practical. The regeneration rate was found to be much faster for smaller particle size adsorbents and weakly adsorbed compounds; and, in some cases, nearly 100% of the virgin capacity was recovered after regeneration. However, in all cases, the regeneration process consumes more oxidants than would be required by simply using a conventional advanced oxidation process for destroying organic contaminants. The high consumption of oxidants may be due to the slow rate of organic desorption and redox reactions with the adsorbent surface. Accordingly, regeneration processes using advanced oxidation is not practical unless an adsorbent is developed that exhibits fast desorption kinetics, and the surface does not react with the oxidants.

KEY WORDS: Regeneration, Adsorption, Advanced Oxidation,
Hydrogen Peroxide, Ozone, UV light.

INTRODUCTION

New regulations for air, water, and solid residuals have stimulated engineers to search for water treatment technologies that either destroy or immobilize toxic organics. Considerable research is being directed at effective and economical treatment strategies to meet the new standards. Some of the current methods for the removal of organic contaminants from water include: granular activated carbon (GAC)/synthetic resins, air stripping, and advanced oxidation processes (AOPs). The major drawback of GAC/resin adsorption or air stripping process is that these are nondestructive technologies, as the contaminants are only transferred from one phase to another. Moreover, the spent carbon/resin may have to be handled as hazardous waste, and the air stripping tower off-gas may require further treatment before its release in the near future, according to the stringent VOC emission regulations under the 1990 Clean Air Act Amendments (e.g. air toxic VOCs are subject to the lesser quantity emission rate).

Alternative technologies that destroy the organics are the advanced oxidation processes (AOPs). AOPs involve the generation of highly reactive species such as the hydroxyl radical, which can mineralize the organic compounds to non-toxic forms such as carbon dioxide, mineral acids, and water. AOPs have been used to mineralize a wide-spectrum of organic compounds (Aieta et al. 1988; Bellamy et al. 1991; Glaze et al. 1988; Hager et al. 1988; Paillard et al. 1988; Sundstrum et al. 1989; Symons et al. 1989). The main disadvantages of AOPs are that some compounds require large detention times, some by-products appear in the product water for recalcitrant organic compounds, and the free radicals may be scavenged by bicarbonate and carbonate ions in the wastewater.

A water treatment strategy that has received considerable attention is the removal of organic contaminants by adsorption followed by regeneration of the spent adsorbents. Several researchers (Johnson et al. 1964; Rodman and Shunney 1971; Martin and Ng 1984; Ashcroft et al. 1992) have investigated the chemical regeneration of adsorbents, a cheaper alternative to traditional means of steam regeneration or reactivation. The ineffectiveness of chemical regeneration and the potential for using AOPs for regeneration has initiated this research on the use of the phase-transfer advanced oxidation process. The phase-transfer oxidation process consists of two consecutive operational steps: fixed-bed adsorption followed by regeneration of the adsorbent using advanced oxidation. Advantages of the phase transfer oxidation process are: (1) on-site regeneration of spent adsorbents and destruction of the adsorbed organics (this may minimize the adsorbent inventory and completely eliminate unloading, transporting, and repacking the adsorbent); (2) no additional treatment of the regeneration solution is required since the adsorbates may be destroyed or mineralized into non-toxic forms such as CO₂, mineral acids, and H₂O; (3) a broad spectrum of organic chemicals can be effectively destroyed; (4) longer reaction times for complete destruction can be used; and, (5) the contaminants are concentrated prior to destruction avoiding the impact of free radical scavengers, such as carbonate and bicarbonate ions.

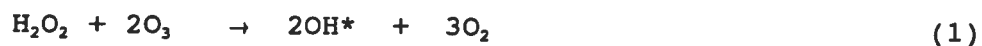
The main objective of this study was to compare these AOP strategies for the regeneration of adsorbents: (1) ozone/hydrogen peroxide; and (2) hydrogen peroxide/UV light. Limited studies were aimed at the impacts of the size and type of adsorbent, temperature, adsorbate on the destruction efficiency of adsorbed organics, the regeneration rate, and the required oxidants.

MECHANISMS IN THE DESTRUCTION OF ORGANIC CONTAMINANTS BY HOMOGENEOUS ADVANCED OXIDATION PROCESSES

Advanced oxidation processes involve the generation of the hydroxyl radical which is a very reactive intermediate and has a higher oxidation potential (2.8 eV) than either ozone (2.07 eV) or hydrogen peroxide (1.77 eV). Hydroxyl radical, is one of the strongest oxidizing species, attacks organic molecules by abstracting a hydrogen atom or by adding to the double bonds. Farhataziz and Ross (1977) have shown that the reactions of hydroxyl radicals with organic compounds follows a second-order rate expression with constants on the order of 10^9 - 10^{10} $M^{-1}sec^{-1}$, which is on the same order as acid-base reactions (Stumm and Morgan, 1981). In a recent study prepared for the EPA by Haag (1990), the oxidation pathway for a wide variety of organic contaminants were classified. The majority of the organic contaminants were destroyed by hydroxyl radical oxidation at a much higher rate. For instance, the hydroxyl radical rate constant for TCE ($4.2 * 10^9 M^{-1} s^{-1}$) was found to be much greater than the ozonation rate constant ($15 M^{-1} s^{-1}$).

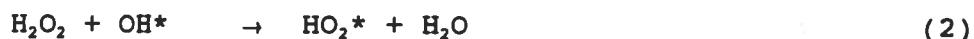
Regeneration Using Ozone/Hydrogen Peroxide

Organic compounds may be destroyed by a hydroxyl radical (OH*), which is formed according to:



The regeneration process that uses H_2O_2/O_3 depends upon two design parameters, the molar ratio of H_2O_2/O_3 , and the quantity of the oxidants to be used. The stoichiometry of equation (1) suggests the production of OH* will be achieved using a ratio of 2 moles O_3 to 1 mole H_2O_2 . The work of Glaze et al. (1988) and Bellamy et al. (1991) confirms this molar ratio for the most efficient use of the oxidants in the production of

hydroxyl radicals. A potential problem using H₂O₂ and O₃ is controlling the H₂O₂ concentration because hydroxyl radicals can be scavenged in the presence of excess hydrogen peroxide and produce the perhydroxyl radical (HO₂*), which is a much weaker oxidant than hydroxyl radical:



Our regeneration experiments were designed to maintain a 2:1 ratio of O₃:H₂O₂ and other ratios were not investigated.

Another consideration in the oxidation of the adsorbed compounds is the quantity of oxidants required in the regeneration experiment. In this study, TCE (Cl₂C=CHCl) was used and according to the stoichiometry of equations (1) and (3), six moles of O₃ and three moles of H₂O₂ are needed for the destruction of one mole of TCE.



The stoichiometric quantity of oxidants needed in this study were compared to previous studies that treated the water directly using conventional AOPs because the use of the adsorption step can not be justified if the quantity of oxidants is much greater than conventional AOPs. Both Bellamy *et al.* (1991) and Glaze *et al.* (1988) demonstrated that TCE could be destroyed using three to six times the theoretical stoichiometric requirement. Consequently, in most cases, three to six times the stoichiometric requirement of oxidants were used to regenerate the adsorbents.

Regeneration Using Hydrogen Peroxide/UV Light

Hydroxyl radicals are produced from H₂O₂ and UV light when photons of sufficient energy are absorbed:

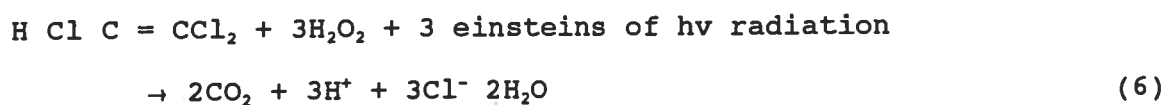
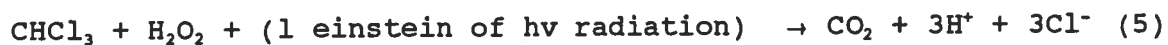


The dissociation energy of the O-O bond in the H₂O₂ molecule is 48.5 kcal mole⁻¹, and UV-radiation with wavelengths of 200-280 nm leads to usable

radical yields (Overath, 1979).

Research has shown that the major process variables influencing reaction rates are the oxidant dosage and intensity of UV radiation. In one study, Sundstrum (1989) found the H₂O₂/UV light process to be effective for the destruction of a number of aromatic compounds using up to 10 times the stoichiometric requirement of oxidants. However, many by-products due to partial oxidation were detected. Light transmission is also an important technical and economical issue in AOPs involving H₂O₂/UV light. The light transmission can be much greater in regeneration solutions than in wastestreams because it can be controlled. Accordingly, the use of UV/H₂O₂ to regenerate adsorbents may be more effective than using UV/H₂O₂ to treat the wastewater because of the higher light transmission in the former than in the latter.

In this study, H₂O₂ and UV light were used to regenerate adsorbents that were loaded with TCE and chloroform. The following reaction establishes the stoichiometric requirement of H₂O₂ and light for the destruction of chloroform and TCE.



The quantity of H₂O₂ and light consumed in the regeneration experiments were compared to the stoichiometric requirements to determine its efficiency.

EXPERIMENTAL MATERIALS AND METHODS

Adsorber Design and Set-up

In most cases, the adsorbent was loaded with the compound of

interest using rapid small scale column tests (RSSCTs). RSSCTs use smaller adsorbent particle sizes, smaller column lengths and diameters, and much less water than a pilot scale system. RSSCTs were used because they can be performed in much less time than pilot scale units, and this will allow a faster evaluation of the effectiveness of regeneration. The design of the RSSCTs are described by Crittenden et al. (1986, 1987, and 1991). In this study, it was assumed that the intraparticle diffusivity did not change with particle size. RSSCTs were set up in a temperature-controlled room that was maintained at 12 to 14°C. The unit was constructed using glass, teflon, and stainless steel to minimize the loss of the organic due to adsorption on the RSSCT components. A glass column (Ace Glass, Inc., Vineland, NJ) of 1.1 cm in diameter was used for the RSSCT column. The adsorbents chosen for this study were Filtrasorb-400 (F-400) Carbon (Calgon Carbon Corp., Pittsburgh, PA) and two synthetic carbonaceous adsorbents, Ambersorb-572F and Ambersorb-563 resins (Rohm and Haas Co., Philadelphia, PA).

Regeneration Reactors

After adsorption, the adsorbents were transferred from RSSCT columns into regeneration units. The design and operation of the regeneration units for each advanced oxidation process are described below.

Regeneration With H₂O₂/O₃ Process

The regeneration reactor for the H₂O₂/O₃ process is shown in Figure 1. Ozone, hydrogen peroxide, and the adsorbent to be regenerated were mixed in a reactor, that was approximately 800 ml in volume (7-cm diameter, 20-cm long). Hydrogen peroxide was added at a continuous flow rate from a stock solution of known concentration. The pH of this solution was about 7. The ozone was produced from a Model V10-0 Ozonator, manu-factured by the Ozone Research & Equipment Corporation (Phoenix,

Arizona). The ozone was introduced at the bottom of the reactor and bubbled through a porous diffuser. A constant stream of ozone gas was diverted from the influent ozone line for measurement. Samples were taken from the reactor effluent sample port at regular intervals (6 hours) and analyzed for TCE and H_2O_2 concentration. The cumulative chloride production was determined from periodic measurements on the reservoir.

Regeneration With H_2O_2 /UV Light at Room Temperature

Figure 2 illustrates the schematic of the reactor used for the H_2O_2 /UV light regeneration conducted at room temperature (25°C). The adsorbent was regenerated in a batch mode using a continuously stirred, two-liter glass beaker that contained the suspended adsorbent particles, H_2O_2 solution, and the UV-light source. A 450- Watt, Hanovia, high-pressure, mercury-vapor lamp (ACE Glass Co., Vineland, NJ) was used as a UV light source. The incident UV-light intensity for this reactor was measured to be about 625 μ Einstein/L-min using the potassium ferrioxalate actinometry method (Hatchard and Parker, 1956). Based on the radiation surface area, the light intensity was calculated to be 2.62 μ Einsteins/cm²-min. Samples were periodically taken from the reactor and analyzed for chloroform, hydrogen peroxide, UV absorbance at 254 nm (using a 1-cm cell), and chloride ion. The adsorbent was regenerated until no chloroform was detected in the regeneration solution, and no increase in the mass of chloride was found.

Regeneration With H_2O_2 /UV Light at High Temperature

The schematic of the regeneration unit used for the high temperature H_2O_2 /UV light experiment is shown in Figure 3. The destructive oxidation of the organics was conducted in the reactor, which contained an original solution volume of 1.6 liters and has a detention time of 45 minutes

based on the recycled flow rate through the column. The light source was a 450-Watt, Hanovia, high-pressure, mercury-vapor lamp (ACE Glass Co., Vineland, NJ) placed in a quartz cooling vessel. The intensity of the light received by the solution in the reactor vessel was 256 μ Einsteins/(L-min). Following the regeneration reactor, the solution was passed through a heat-exchanger which raised the temperature to 90° C. The hot solution was passed through the adsorbent bed and entered the reactor. During regeneration, a stock solution of H₂O₂ was continuously fed into the reactor using a chemical-feed pump. Samples were periodically taken from the regeneration reactor, and the adsorbent column effluent and analyzed for TCE, hydrogen peroxide, and chloride ion concentrations. The aqueous concentration of TCE in the reactor was low enough to assume negligible loss due to volatilization. The adsorbent was regenerated until the TCE leaving the adsorbent was negligible (compared to its initial loading) and the mass of chloride did not increase in the regeneration solution.

Analytical Techniques

Gas phase ozone was determined by the iodometric method, Method 422 in Standard Methods, 16th edition (1985). The iodometric method is accurate to concentrations as low as 0.06 mg/L. The amount of ozone transferred in the experiment was determined from the difference in the inlet and exit-gas phase concentrations.

The determination of the aqueous-phase ozone concentration was measured by the indigo method (Bader and Hoigne, 1982).

Aqueous phase hydrogen peroxide, at concentrations greater than 1.2 mg/L were analyzed by titrating with KMnO₄, which provides a faint pink color at the end point. The amount of hydrogen peroxide that reacted in the experiment was determined from the difference in the inlet and outlet

hydrogen peroxide concentrations.

The organic chemicals were analyzed by direct aqueous injection (Supelco GC Bulletin 816A, Supelco, Inc., Houston, TX) using a Hewlett-Packard (HP; Palo Alto, CA) 5880A gas chromatograph (GC) that was equipped with an electron capture detector.

The chloride ion concentration was analyzed by a Dionex Model 12 ion chromatograph with 4G-1 guard column and AS-3 analytical column (Dionex, Sunnyvale, CA).

The pH was measured by using an Orion (Cambridge, MA) pH meter Model No. 501. For some regeneration experiments, light intensity was measured using an EG&G Gamma Scientific (San Diego, CA) Model GS 3100 spectroradiometer equipped with a fiber optic probe.

EXPERIMENTAL APPROACH AND THE QUANTIFICATION OF REGENERATION EFFECTIVENESS

The regeneration of adsorbents may be influenced by many parameters including (a) the adsorbent type and size; (b) adsorbate; (c) the type of advanced oxidation process; (d) the quantity and rate of oxidant addition; (e) temperature; and, (f) the reactor design. In this study these operational parameters were examined: (a) temperatures of 25°C and 90°C were used; (b) activated carbon and synthetic resins were employed as adsorbents; and (c) ozone/hydrogen peroxide, and hydrogen peroxide/UV light were used to regenerate the adsorbent.

Ozone/Hydrogen Peroxide Regeneration of the Adsorbents

For a given reactor, the efficiency of the O_3/H_2O_2 process for the destruction of organics is affected by two important parameters, the

ratio of O₃ to H₂O₂, and the quantity of oxidants added to the regeneration system. An oxidant feed ratio of 2:1 was maintained for O₃:H₂O₂. The other important consideration in our experiments was the quantity and rate that the oxidants were added. The effectiveness of using O₃/H₂O₂ for regeneration, as it related to the oxidant dosage, and the type of adsorbent was also examined. The following experiments were conducted: (1) Regeneration of F-400 (60x80 mesh) carbon saturated at a TCE influent concentration of 1000 µg/L using four times the stoichiometric requirement of oxidants; (2) Regeneration of Ambersorb-563 resin (20x50 mesh) saturated at a TCE influent concentration of 2.5 mg/L using three times the stoichiometric requirement of oxidants; and, (3) Regeneration of Ambersorb-563 resin (20x50 mesh) saturated at a TCE influent concentration of 2.5 mg/L using six times the stoichiometric requirement of oxidants.

Prior to each regeneration experiment, the adsorbent was saturated with TCE, and the mass of TCE adsorbed was determined. From the stoichiometry of Equations 1 and 3, the total mass of O₃ and H₂O₂ required to oxidize the TCE were then calculated. The oxidant mass feed rates were then based on a regeneration time equal to the time of adsorption.

The effectiveness of the O₃/H₂O₂ regeneration process was evaluated in terms of destruction efficiency.

$$\% \text{ Destruction efficiency} = \frac{\text{Mass of chloride measured from experiment}}{\text{Mass of chloride calculated from stoichiometry}} \times 100 \quad (7)$$

To calculate the stoichiometric mass of chloride, it was assumed that the adsorbed TCE was totally mineralized.

Hydrogen Peroxide/UV Light Regeneration of the Adsorbents

For a given reactor and light source, the efficiency of the H₂O₂/UV light process for the destruction of organics is affected by the rate of hydrogen peroxide addition, light intensity, and the pH. The use of H₂O₂ and UV radiation at neutral pH is more effective than at high pH. At high pH, H₂O₂ decomposes to form the perhydroxyl ion. The perhydroxyl ion can react with a hydroxyl radical to form the perhydroxyl radical, which is a much weaker oxidant than OH*. More-over, the perhydroxyl ion absorbs more UV light than H₂O₂ (Schumb et al. 1955) and can prevent the formation of hydroxyl radicals. In this study, the effectiveness of the H₂O₂/UV light regeneration process was evaluated for different adsorbents, adsorbates, temperatures, and pH values. The experiments were conducted at a pH of 7 and 11. The following experiments were conducted: (1) Regeneration of Ambersorb-572F resin saturated at a chloroform influent concentration of 139 µg/L using H₂O₂/UV light at room temperature and pH values of 7 and 11; and, (2) Regeneration of Ambersorb-563 resin saturated at a TCE influent concentration of 1000 µg/L using H₂O₂/UV light at high temperature.

The effectiveness of the H₂O₂/UV light process was evaluated in terms of destructive efficiency (Equation 6), capacity recovery, quantum efficiency, and H₂O₂ consumption, which are defined as follows:

$$\% \text{ Capacity Recovery} = \frac{\text{capacity after regeneration}}{\text{capacity before regeneration}} \times 100 \quad (8)$$

$$\text{Quantum Efficiency} = \frac{\text{moles of organic compound completely destroyed}}{\text{moles of photons received by the regeneration solution}} \quad (9)$$

$$\text{H}_2\text{O}_2 \text{ Consumption} = \frac{\text{moles of H}_2\text{O}_2 \text{ spent}}{\text{moles of H}_2\text{O}_2 \text{ required by stoichiometry}} \times 100 \quad (10)$$

To calculate the quantum efficiency, the moles of the organic compound completely destroyed were determined from the measured concentrations of chloride ions, which were produced from the mineralization. To calculate adsorbent capacity recovery, the adsorbents were saturated with the organic compound of interest in RSSCT columns after they were regenerated. The adsorption capacities were determined from the integrated area between influent and effluent concentration profiles.

RESULTS AND DISCUSSION

Regeneration of F-400 Carbon Using H₂O₂/O₃

In this experiment, F-400 carbon (Calgon, PA) granular activated carbon was used as the adsorbent. Three grams of the (60x80 mesh size) carbon was saturated at a TCE influent concentration of approximately 1000 µg/L in a RSSCT column. The RSSCT column had an EBCT of 11.6 seconds, operating temperature of 20°C, and a loading rate of 20.77 m/hr. This RSSCT would simulate a large-scale adsorber (using the adsorbent with an original size of 12x40 mesh) with an EBCT of 4.5 minute and a loading rate of 4.29 m/hr. After being saturated with TCE, the spent adsorbent was carefully transferred into the regeneration reactor shown in Figure 1, and the desired quantity of oxidants were fed for six days, which was the same time period as the adsorption step.

From the effluent concentration history profile, it was determined that 217.5 mg of TCE was adsorbed on the carbon. For this experiment, 0.67 of the stoichiometric requirement of oxidants (SRO), hydrogen

peroxide and ozone, were fed per day. The pH of the regeneration solution was about 7. The experimental conditions and results are given in Table 1. Complete mineralization of the TCE would have produced 176.0 mg of chloride. As shown in Figure 4, the cumulative chloride produced in the regeneration experiment corresponds to 48% destruction efficiency. The absence of TCE in the reactor solution suggests the regeneration may not be limited by the reaction kinetics but rather the slow rate of organic desorption. It is suspected that the adsorbent was not completely regenerated in the experimental time frame. The adsorbent, however, was not re-loaded to identify the fraction of capacity that was recovered by regeneration.

Regeneration of Ambersorb-563 Resin Using H_2O_2/O_3

Two experiments were conducted with Ambersorb-563 (20x50). The adsorbent was saturated in a pilot column with an average influent concentration of 2.5 mg/L of TCE (Hand et al. 1992). The regeneration experiments used approximately 10 grams of the adsorbent (about 5% of the pilot column's total mass), and the adsorbent was regenerated for 5-6 days. This regeneration time was much shorter than the total operation time for the pilot column which was 112 days.

From the effluent concentration history profile, it was determined that 2160 mg of TCE were adsorbed onto the 10 grams of adsorbent. In this study, the effect of oxidant dosage (H_2O_2 and O_3) on the destruction efficiency was investigated. The experimental conditions and results for the two experiments are given in Table 2.

In the first regeneration experiment, referred as REGENA, a feed rate of 0.5 the stoichiometric requirement of oxidants (SRO) were fed per day. In the second regeneration experiment, referred as REGENB, 0.86 of the SRO/day was added. The complete mineralization of the TCE would have

produced 1749 mg of chloride. As shown in Figure 5, the feed rate of oxidants had no effect on the rate of destruction of the adsorbed TCE, and the destruction efficiency for each experiment was only 10%. The gas chromatograph results did not reveal the formation of by-products, and indicated TCE destruction can be measured from chloride data alone. The experimental results, particularly the chloride production, demonstrate the rate of regeneration appears to be limited not by destruction kinetics but by the slow rate of organic desorption out of the adsorbent and into the bulk aqueous phase.

In comparing the O_3/H_2O_2 regeneration data for TCE on F-400 (60x80) carbon and Ambersorb-563 (20x50) resin, it is evident that the regeneration rate is much faster for the former than the latter. Two reasons may contribute to the slow regeneration rate of Ambersorb-563 resin. The Ambersorb-563 had a larger particle size and has a smaller surface diffusivity than F-400 carbon. It has been shown (Thacker *et al.* 1983) that the overall rate of desorption decreases with increasing particle size and decreasing surface diffusivity.

Regeneration of Ambersorb-572F Resin Using H_2O_2 /UV Light at Room Temperature

Notthakun (1991) investigated the phase-transfer process using H_2O_2 at a wide range of concentrations (100 μ M-10M) and pH values (7-11). These experiments revealed the regeneration to be most effective for dilute H_2O_2 concentrations (100-3000 μ M) and neutral pH. Three grams of the (60x80 mesh) Ambersorb-572F resin (Rohm & Haas) were saturated at a chloroform influent concentration of 139 μ g/L in a RSSCT column. The RSSCT column had an EBCT of 12.1 seconds, an operating temperature of 20°C, and a loading rate of 18.75 m/hr. This RSSCT would simulate a large-scale adsorber (using the adsorbent with an original size of 20x50

mesh) with an EBCT of 1.1 minute and a loading rate of 8.28 m/hr. From the effluent concentration history profile, 33.3 mg of chloroform were adsorbed onto the 3 grams of resin. After exhaustion, the adsorbent was carefully transferred into the regeneration reactor shown in Figure 2. The reactor contained an initial H_2O_2 concentration of $100\mu M$, and a H_2O_2 solution was continuously fed into the reactor at 161.8 the stoichiometric requirement of oxidants (SRO)/day (A $0.1M H_2O_2$ solution with a flow rate of 0.30 ml/min). The pH of this solution was about 7. The adsorbent was regenerated until no chloroform was detected in the regeneration solution (after 250 hours) and the destruction efficiency (based on chloride ion production) did not increase.

Figure 6 shows the chloride produced during the regeneration period was 96% of the expected chloride predicted from stoichiometry (assuming the chloroform is completely mineralized). The regeneration time was slightly longer than the adsorption time, which reveals that the destruction oxidation is likely to occur in the bulk solution rather than on the surface or inside the pores of the adsorbent particle. The effectiveness for the regeneration is summarized in Table 3.

The influent and effluent concentration data obtained from the RSSCTs for the virgin and regenerated adsorbents is plotted against liters of water treated and shown in Figure 7. The effectiveness for the regeneration is summarized in Table 4.

Although the capacity recovered was found to be lower than 100%, some of the original adsorbent was lost during adsorbent transfer. The ultimate adsorption capacity per mass of adsorbent was found to be about the same, i.e. 11,100 and 10,801 $\mu g/g$, for the virgin and regenerated resin, respectively. Although the adsorbent was regenerated, the process is infeasible because too much oxidant, H_2O_2 , is required.

Regeneration of Ambersorb-563 Resin Using High Temperature/ H_2O_2 /UV Light

For this experiment, two grams of the (60x80 mesh) Ambersorb- 563 resin (Rohm & Haas) were saturated at a TCE influent concentration of 1000 $\mu\text{g/L}$ in a RSSCT column. The RSSCT column had an EBCT of 6.5 seconds, an operating temperature of 20°C, and a loading rate of 24.8 m/hr. This RSSCT would simulate a large-scale adsorber (using the adsorbent with an original size of 20x50 mesh) with an EBCT of 0.56 minutes and a loading rate of 10.95 m/hr. From the effluent concentration history profile 311 mg of TCE were adsorbed onto the 2 grams of resin. After about 230 hours of loading, exhaustion was observed and the adsorbent column was put in line with the high temperature (90° C) regeneration set-up shown in Figure 3. Hydrogen peroxide was continuously fed into the reactor at 22 times the stoichiometric requirement of oxidants (SRO)/day (A 0.22 M solution with a flow rate of 0.37 ml/min). The adsorbent was regenerated until the TCE leaving the column was negligible (compared to its initial loading), and the destruction efficiency (based on chloride ion production) did not increase.

Regeneration was carried out for 94 hours, at which time the TCE leaving the adsorbent column was less than 30 $\mu\text{g/L}$. Figure 8 shows the chloride production observed during the regeneration period, as compared to the total mass of chloride predicted from stoichiometry (assuming the adsorbed TCE is completely mineralized). The experiment revealed a very fast rate of TCE destruction efficiency during the first 24 hours (about 30%); however, further regeneration time revealed a considerable decrease in the destruction rate (only 35% after 94 hours). The effectiveness for the regeneration is summarized in Table 5.

The influent and effluent concentration data obtained from the

RSSCT's for the virgin and regenerated adsorbents are plotted against liters of water treated per gram of resin and is shown in Figure 9. The operational parameters for the RSSCTs are given in Table 6.

The capacity recovery was only about 30%. The capacity loss could be attributed to: (1) residual TCE, or by-products, remaining on the adsorbent surface; and (2) the increase of surface oxides on the adsorbent caused by oxi-dative reactions between the adsorbent and oxidants in the regeneration solution. The surface oxygen groups on adsorbents have been shown to decrease the adsorption capacity for many compounds (Couglin, 1970).

Results indicate that the application of a higher temperature may increase the initial rate of desorption. However, the higher temperature fails to completely desorb the organic contaminants, and the regeneration process may still be limited by desorption kinetics. The high consumption of hydrogen peroxide makes this process infeasible. It appears that H_2O_2 was consumed not only for the organic destruction but also for the decomposition into H_2O and O_2 through many intermediate reactions including reactions with the adsorbent surface.

CONCLUSIONS

These two advanced oxidation processes were investigated for the destructive regeneration of exhausted adsorbents: (1) ozone/hydrogen peroxide; and, (2) hydrogen peroxide/UV light.

The adsorbents were not effectively regenerated by using the O_3/H_2O_2 process. For example, F-400 carbon saturated with TCE (1000 $\mu\text{g/L}$) could not be completely regenerated using O_3/H_2O_2 for a regeneration time equal to the adsorption time. The regeneration rate and efficiency of F-400

carbon (60x80) was much higher than that of Ambersorb-563 resin (20x50). This may be attributed to the smaller size and faster desorption kinetics for F-400 carbon. No increase in the destruction rate was observed with an increase in oxidant dosage, (O_3 and H_2O_2). Furthermore, the quantity of oxidants required in the regeneration process appears to be much more than simply using homogeneous advanced oxidation for organic destruction.

Two regeneration experiments were investigated using H_2O_2 /UV light. The impact of adsorbent, adsorbate, and temperature on the regeneration efficiency was also examined. The complete regeneration of Ambersorb-572F saturated with chloroform using H_2O_2 /UV light at room temperature was observed with a regeneration time slightly longer than the adsorption time. However, too much H_2O_2 is needed to be considered a viable option. The regeneration of Ambersorb-563 saturated with TCE using H_2O_2 /UV light at high temperature ($90^\circ C$) was not effective. When comparing the two regeneration experiments for chloroform and TCE on Ambersorb-572F resin and Ambersorb-563 resin respectively, it can be seen that the regeneration rate is much faster for the chloroform than the TCE. One reason may be that TCE is more strongly adsorbed and desorbs more slowly than chloroform. The batch reaction desorption model (BRDM) developed by Notthakun (1991) was used to confirm that desorption rates for chloroform are much faster than that for TCE.

This study demonstrates that regeneration of carbonaceous resin and carbon adsorbents by advanced oxidation is not practical. The regeneration process consumes a substantial amount of oxidants, more than would be required by simply using conventional treatment methods, such as homogeneous advanced oxidation, for destroying organic contaminants. Consequently, the adsorption step may not be justified. For the destructive regeneration process to occur the organic contaminants must

desorb from the adsorbent and into the bulk solution to be oxidized. The slow rate of desorption and the redox reactions with the adsorbent surface result in a high consumption of oxidants. Therefore, this process is not feasible unless an adsorbent is developed that exhibits fast desorption kinetics and the adsorbent surface does not react with the oxidants.

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Table 1

Experimental conditions and results for the regeneration of F400 carbon (60x80 mesh) loaded with TCE using H₂O₂/O₃

Adsorption Time (hours)	149
Mass of TCE adsorbed	72.5 mg TCE/g-carbon
Mass of adsorbent used	3 grams
Regeneration Time (hours)	127
Feed rate: In terms of Stoichiometric Requirement of Oxidants (SRO)	0.67 SRO / day
Ozone mass feed rate	0.213 mg O ₃ /min
Ozone concentration	2.13 mg O ₃ /L-air
Hydrogen Peroxide concentration	15 mg H ₂ O ₂ /L-water
Destruction Efficiency (%)	48

Table 2

Comparative investigation on the effect of changing oxidant dosage on the regeneration of Ambersorb (20x50 mesh) saturated with TCE using H₂O₂/O₃

Adsorption Time for Pilot Column (days)	112	
Mass of TCE adsorbed	216 mg/g-resin	
Mass of adsorbent used	10 grams	
Experiment name	REGENA	REGENB
Regeneration Time (hours)	140	167
Feed rate in terms of Stoichiometric Requirement of Oxidants (SRO)	0.5 SRO/day	0.86 SRO/day
Ozone mass feed rate	1.7 mg O ₃ /min	2.81 mg O ₃ /min
Ozone concentration	1.1 mg O ₃ /L of air	1.56 mg O ₃ /L of air
Hydrogen peroxide mass feed rate	0.6 mg H ₂ O ₂ /min	1.0 mg H ₂ O ₂ /min
Hydrogen peroxide concentration	100 mg H ₂ O ₂ /L water	99.7 mg H ₂ O ₂ /L water
Destruction Efficiency (%)	10.5	8.6

Table 3

Experimental conditions and results for the regeneration of Ambersorb-572F (60x80 mesh) resin saturated with chloroform using H₂O₂/UV light at room temperature

Adsorption time (hours)	236
Mass of chloroform adsorbed	11.1 mg chloroform/g-resin
Mass of adsorbent used	3 grams
Regeneration time (hours)	264
Feed rate: In terms of Stoichiometric Requirement of Oxidants (SRO)	161.8 SRO / day
H ₂ O ₂ feeding rate	1800 μ moles/hr
H ₂ O ₂ concentration	0.1 M
Quantum Yield	1.35×10^{-5}
Destruction Efficiency (%)	96
No. of stoichiometric requirements fed of H ₂ O ₂	1780
Capacity Recovery (%)	92

Table 4

Operational Parameters for the RSSCTs using Ambersorb-572F (60x80 mesh) resin

	Virgin adsorbent	Regenerated adsorbent
Adsorbent mass	3 grams	2.85 grams
Bulk density	0.5 g/ml	0.5 g/ml
Column diameter	1.1 cm	1.1 cm
Average Flow Rate	29.7 ml/min	30.8 ml/min
EBCT, small scale	12.1 seconds	11.1 seconds
Superficial Velocity, ss	18.75 m/hr	19.45 m/hr
EBCT, large scale	1.1 minutes	0.95 minutes
Superficial Velocity, ls	8.28 m/hr	8.59 m/hr
Average Influent Concentration	139.4 μ g/L	140.2 μ g/L
Temperature	14 $^{\circ}$ C	14 $^{\circ}$ C

Table 5

Experimental conditions and results for the regeneration of Ambersorb-563 (60x80 mesh) resin loaded with TCE using H₂O₂/UV light at high temperature

Adsorption time (hours)	230
Mass of TCE adsorbed	155.5 mg TCE/g-resin
Mass of adsorbent used	2 grams
Regeneration time (hours)	95
Feed rate: In terms of Stoichiometric Requirement of Oxidants (SRO)	22.0 SRO / day
H ₂ O ₂ feeding rate	4835 μmoles/hr
H ₂ O ₂ concentration	0.22 M
Quantum Yield	9.75 X 10 ⁻⁶
Destruction Efficiency (%)	35
H ₂ O ₂ Consumption	107
Capacity Recovery (%)	30

Table 6

Operational Parameters for the RSSCTs using Ambersorb-563 (60x80 mesh) resin

	Virgin adsorbent	Regenerated adsorbent
Adsorbent mass	2 grams	2 grams
Bulk density	0.468 g/ml	0.468 g/ml
Column diameter	1.1 cm	1.1 cm
Average Flow Rate	39.3 ml/min	40.2 ml/min
EBCT, small scale	6.52 seconds	6.38 seconds
Superficial Velocity, ss	24.8 m/hr	25.4 m/hr
EBCT, large scale	0.56 minutes	0.55 minutes
Superficial Velocity, ls	10.95 m/hr	11.21 m/hr
Average Influent Concentration	1032 μg/L	850 μg/L
Temperature	20 °C	20 °C

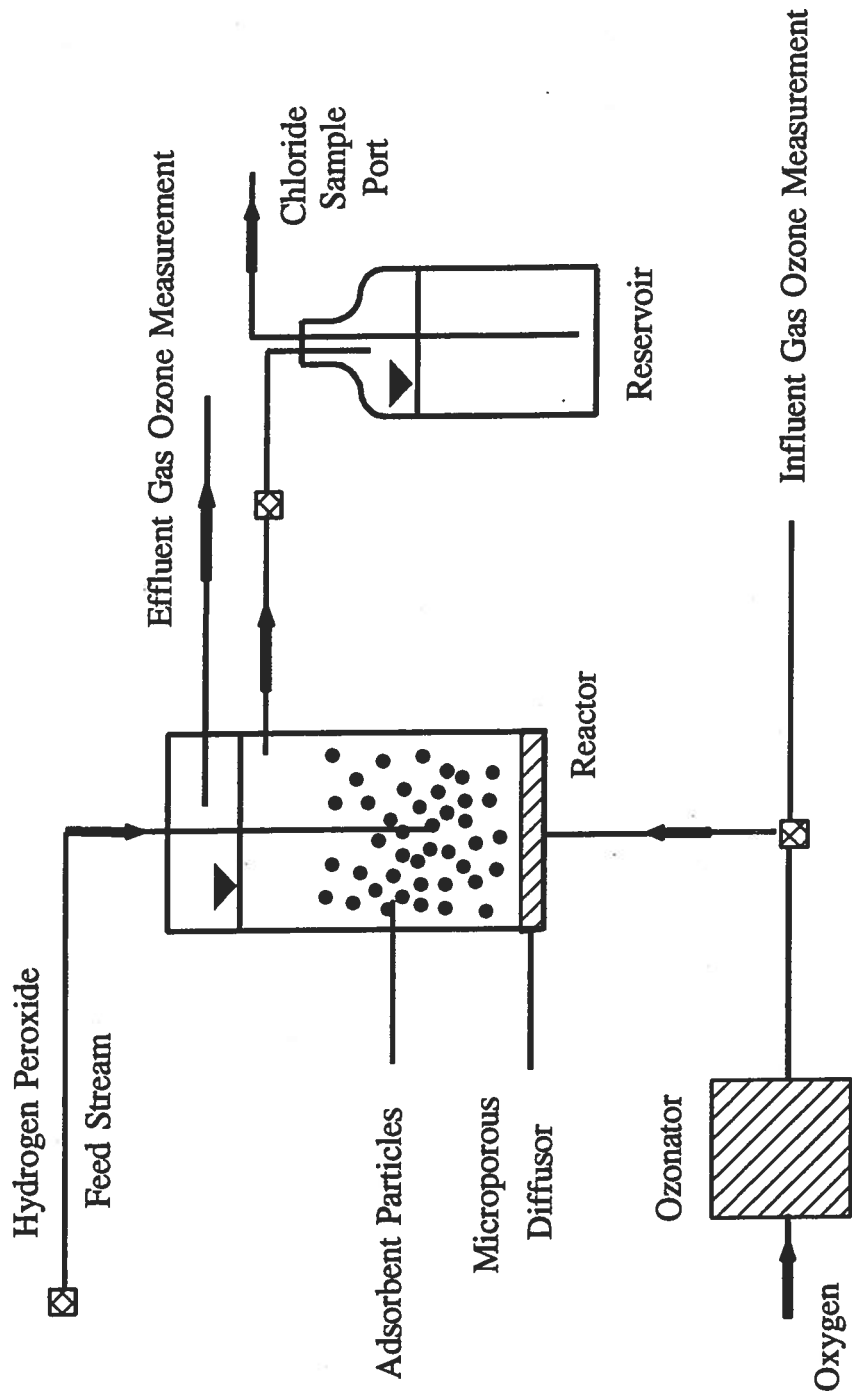


Figure 1. Schematic of the Regeneration Unit used for the Ozone/Hydrogen Peroxide process.

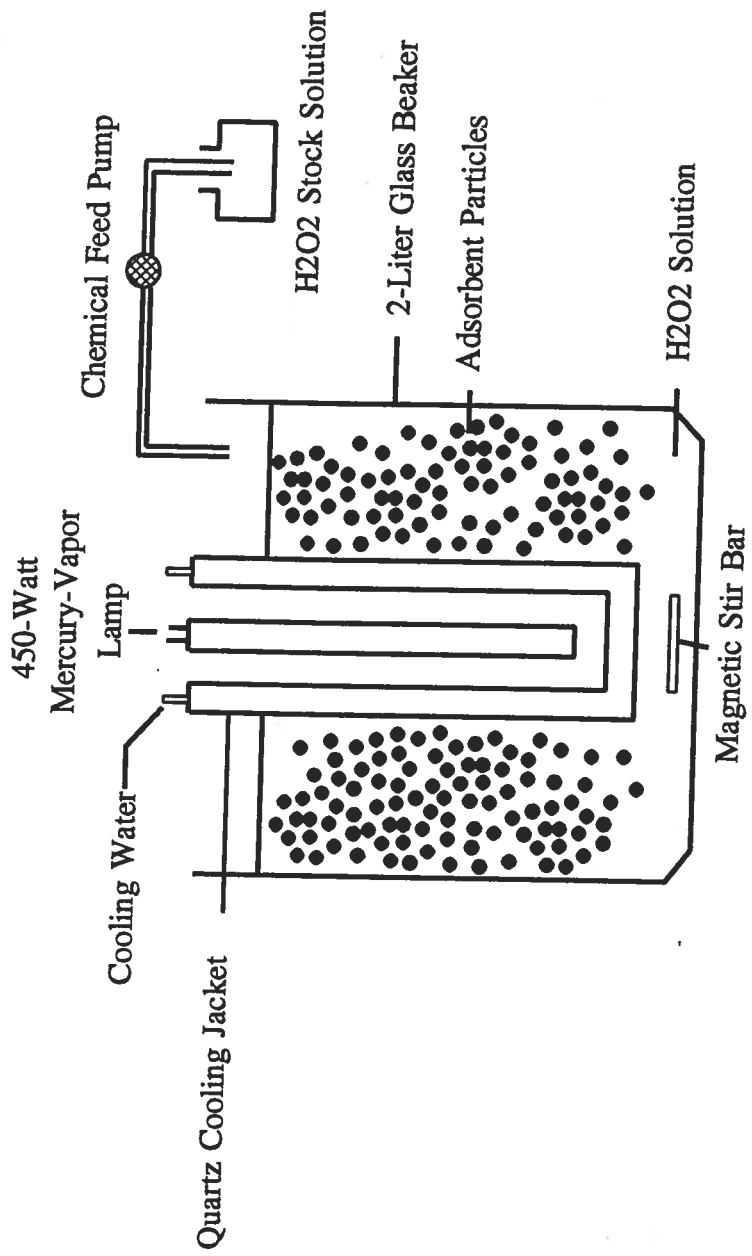


Figure 2. Schematic of the Regeneration Unit used for the Hydrogen Peroxide/UV light experiment conducted at room temperature (Notthakun, 1991).

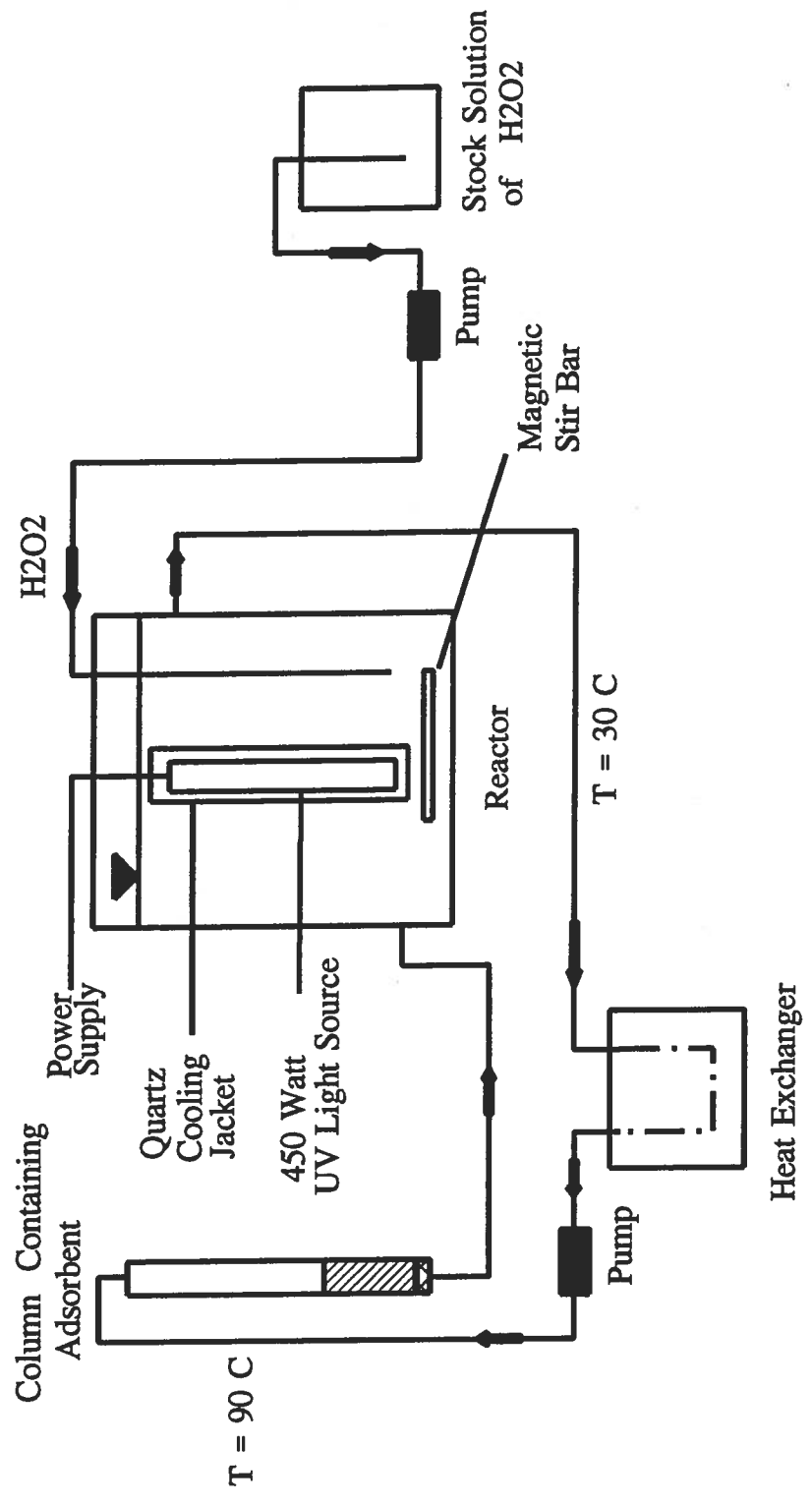


Figure 3. Schematic of the Regeneration Unit used in the high temperature H₂O₂/UV light experiment.

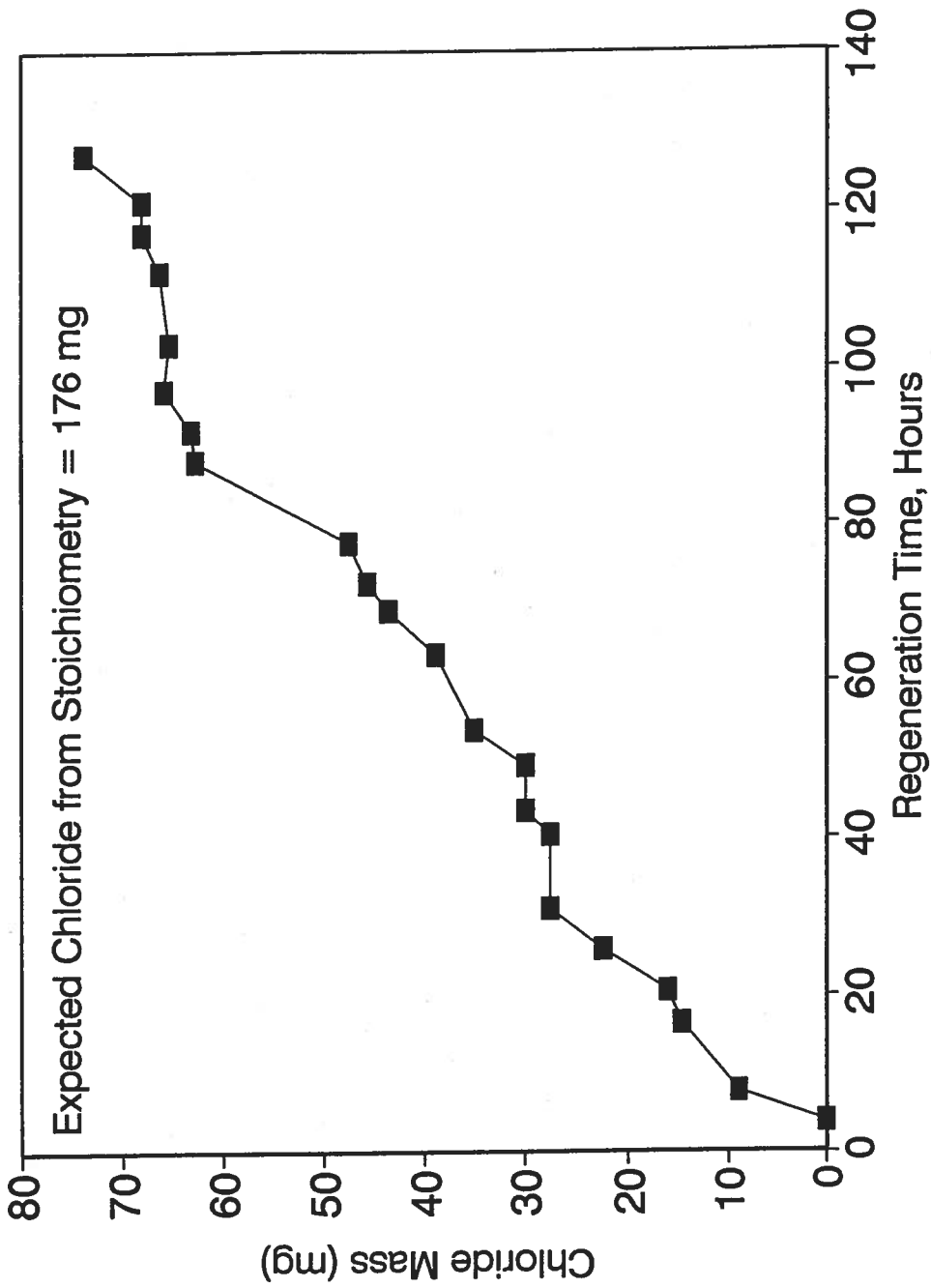


Figure 4. Mass of chloride produced during the regeneration of F-400 Carbon using H₂O₂ and O₃. (The adsorbent was regenerated using a feed rate of 0.67 Stoichiometric Requirement of Oxidants (SRO) / day).

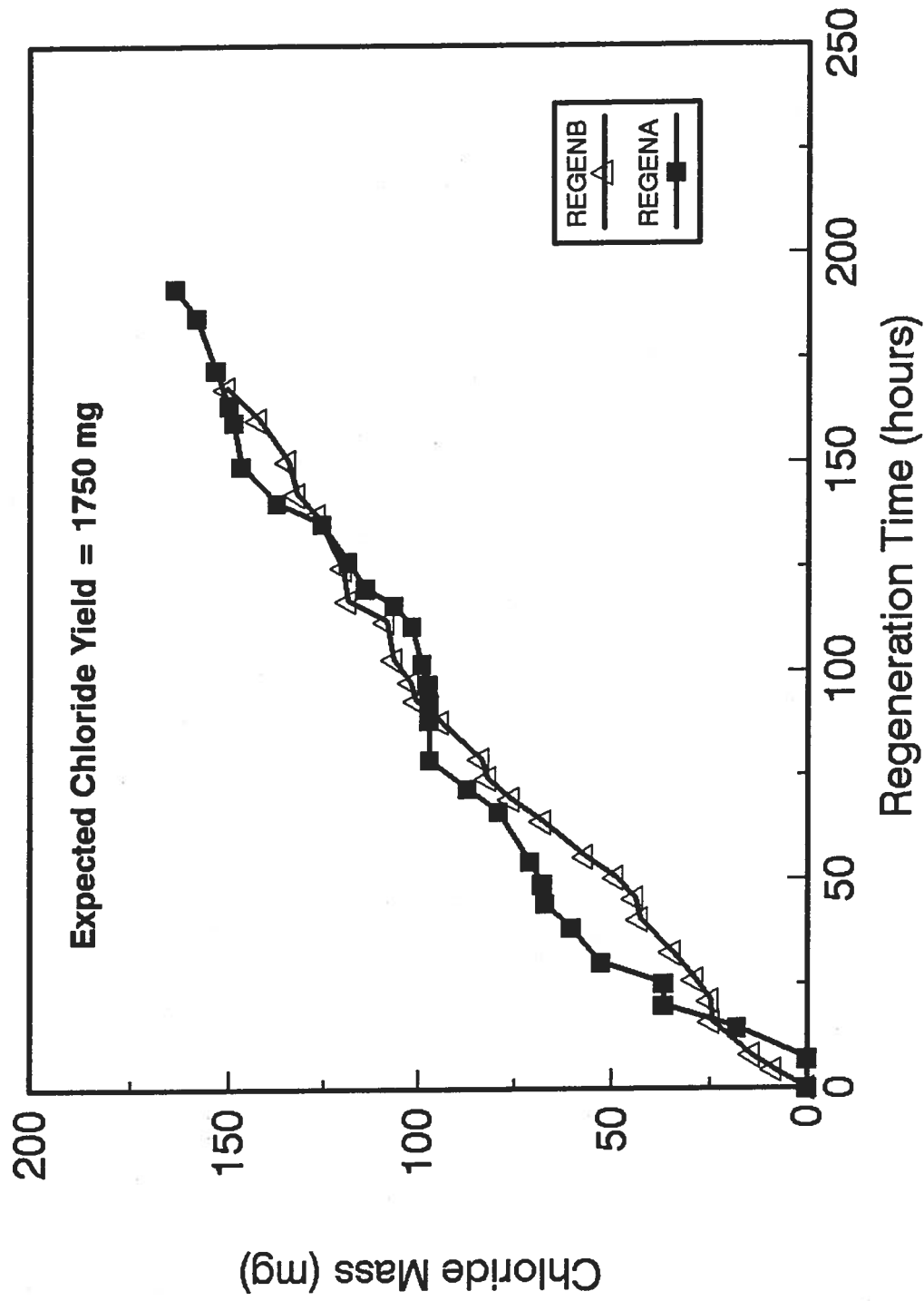


Figure 5. Mass of Chloride Produced: Comparative Investigation on the effect of changing oxidant (H₂O₂ and O₃) dosage on the destruction efficiency. REGENA used a feed rate of 0.5 the Stoichiometric Requirement of Oxidants (SRO) / day. REGENB used a feed rate of 0.86 the SRO / day.

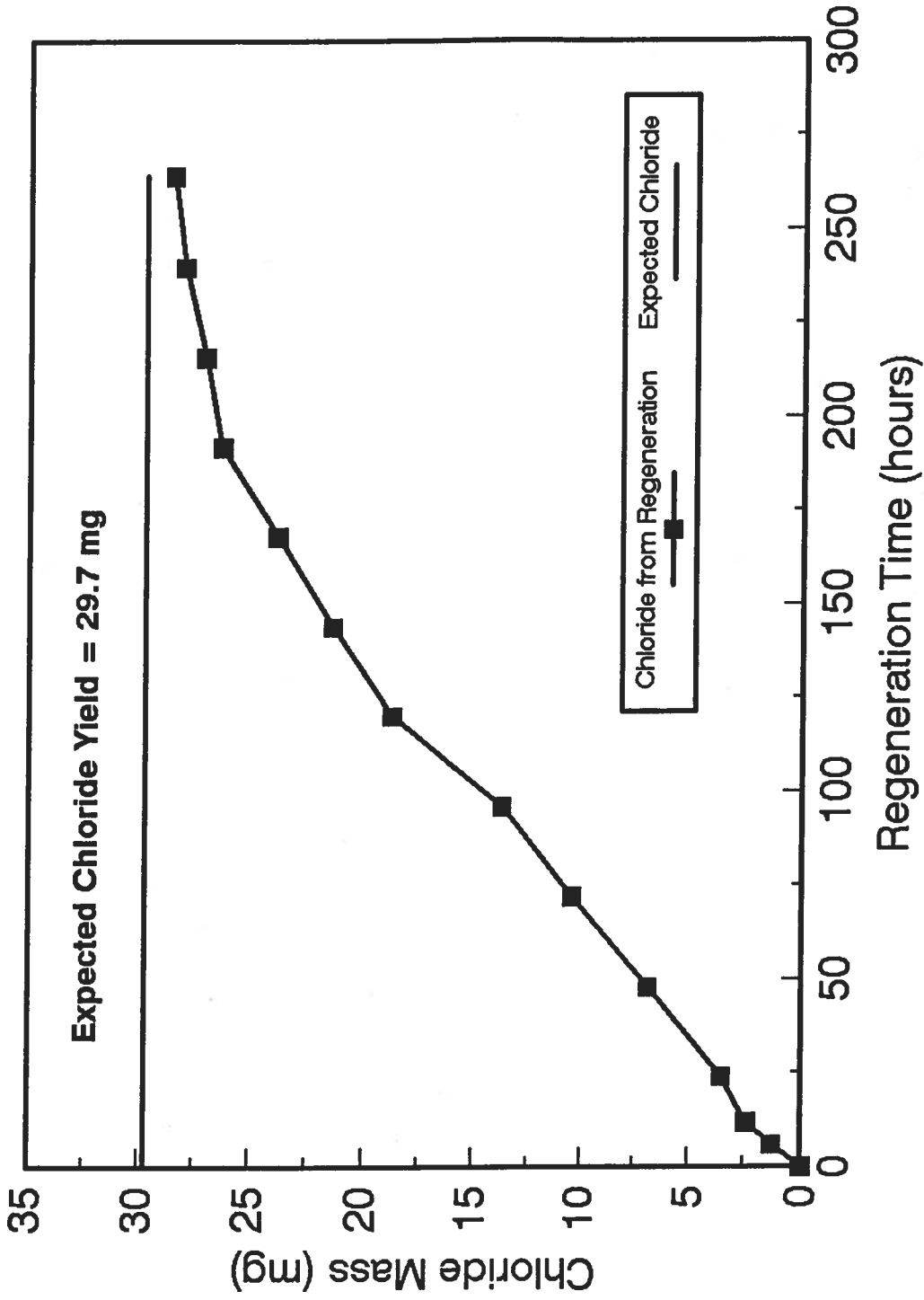


Figure 6. Mass of Chloride produced during the regeneration of Ambersorb-572F resin. The adsorbent was regenerated using H₂O₂/UV light at room temperature using a feed rate of 161.8 the SRO/day (Notthakun, 1991).

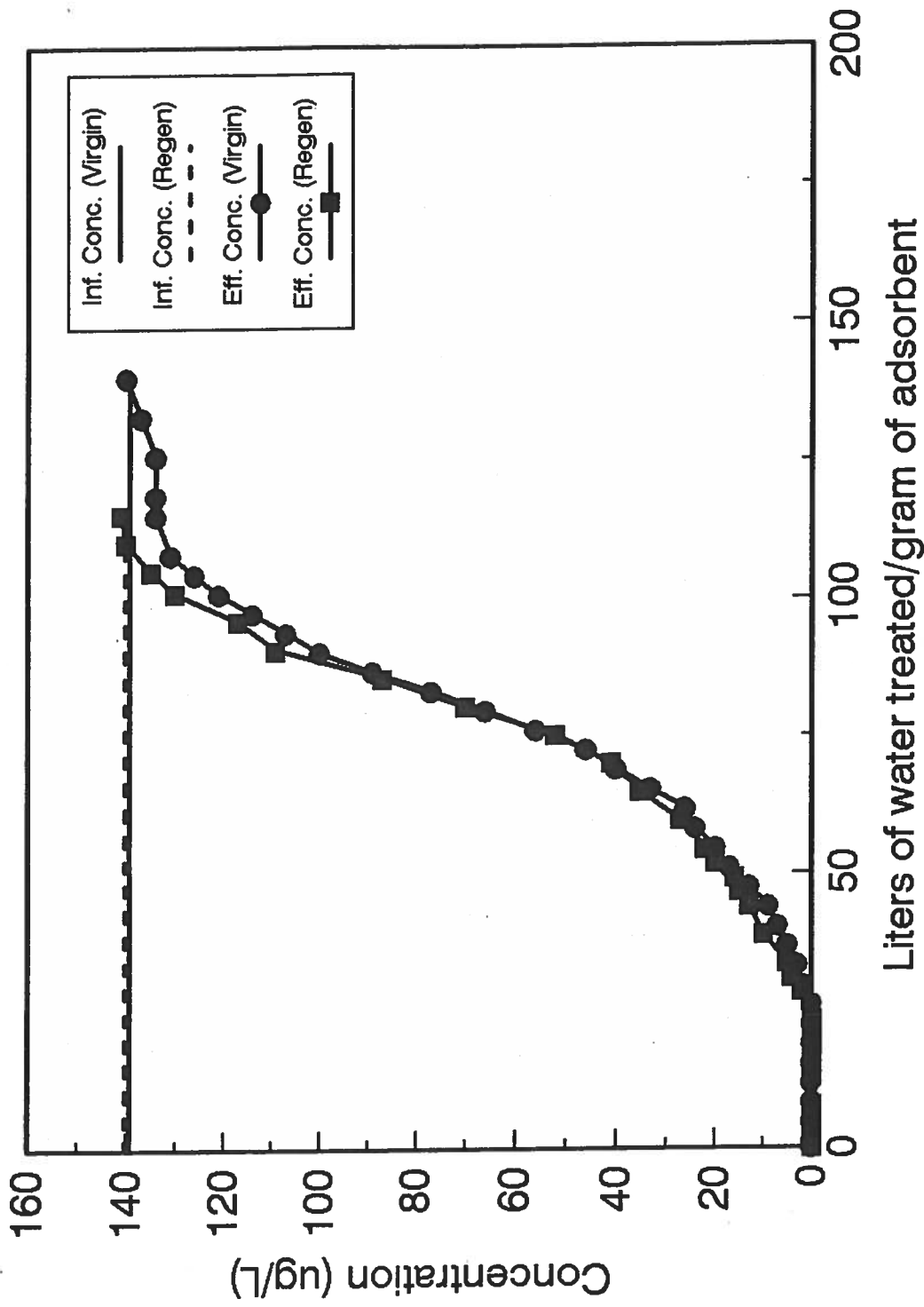


Figure 7. Comparison of breakthrough profiles of virgin and regenerated Ambersorb-572F. (The operational parameters for the RSSCTs are given in Table 4). The adsorbent was regenerated using a feed rate of 161.8 the SRO/day (Notthakun, 1991).

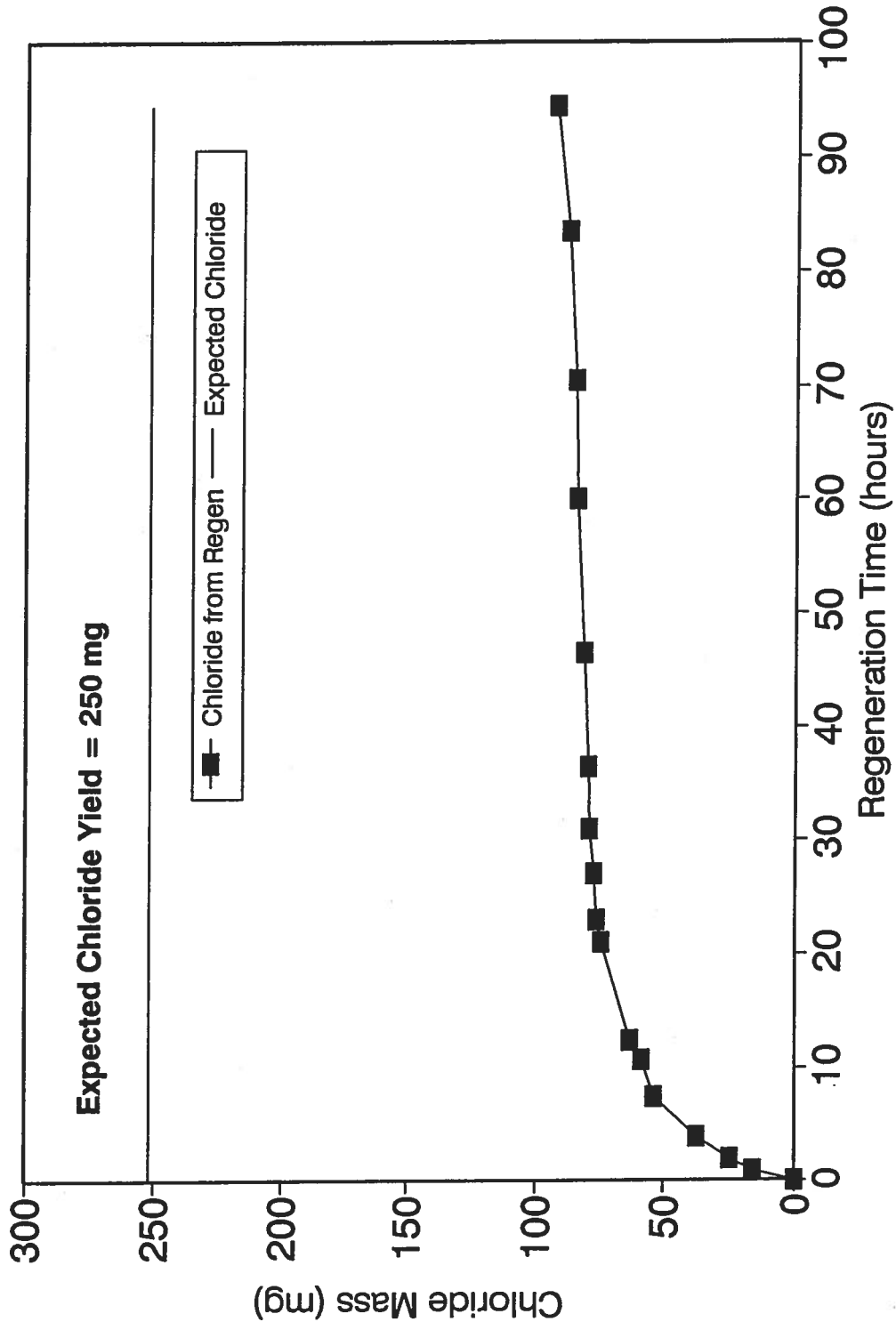


Figure 8. Mass of Chloride produced during the regeneration of Ambersorb-563 resin (The adsorbent was regenerated using high temperature / H2O2 / UV light using a feed rate of 22.0 the SRO / day).

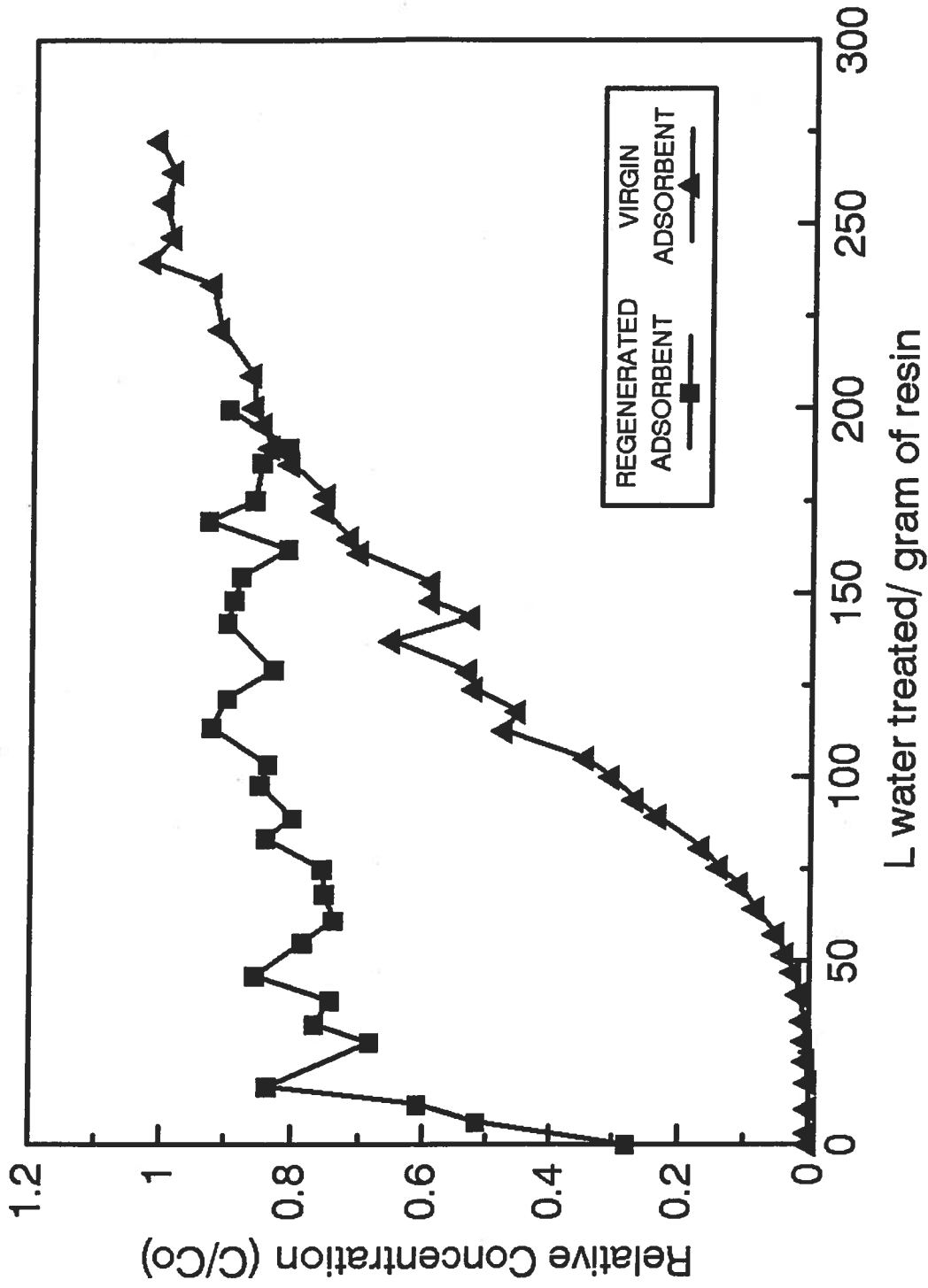


Figure 9. Comparison of breakthrough profiles of virgin and regenerated Amborsorb-563 resin. (The operational parameters for the RSSCTs are given in Table 6). The adsorbent was regenerated using a feed rate of 22.0 the SRO / day.