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**STEAM REGENERATION OF ADSORBENTS AND
PHOTOCATALYTIC DESTRUCTION OF
ORGANIC COMPOUNDS
(PREPRINT)**

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Steam Regeneration of Adsorbents, and Photocatalytic Destruction of Organic Compounds

Rominder P.S. Suri, John C. Crittenden, David W. Hand, and Mike Dziobak

ABSTRACT

A treatment strategy is examined where organic compounds in aqueous phase are first removed by fixed-bed adsorption, followed by off-line regeneration of spent adsorbent and clean up of regeneration fluid by photocatalytic oxidation. The regeneration of adsorbents is conducted using saturated steam at 160 °C. This treatment strategy is examined with the following organic compounds: tetrachloroethylene (PCE), carbon tetrachloride (CCl₄), p-dichlorobenzene (p-DCB), o-chlorobiphenyl (o-PCB), and methyl ethyl ketone (MEK). For 6 cycles of adsorption and regeneration with each compound, the adsorption capacity of the adsorbent for PCE, p-DCB, CCl₄, and MEK is completely recovered using the steam regeneration process. In the case of o-PCB, there is about 20% loss in adsorbent capacity after the first cycle, however, the adsorption capacity for cycles 2 through 6 is almost the same. The photocatalytic oxidation process is observed to be effective for the destruction of desorbed organic compounds in the aqueous phase.

Key Words: adsorption, regeneration, steam regeneration, photocatalysis, photooxidation.

INTRODUCTION

The major drawback of currently practiced processes such as activated carbon adsorption or air stripping is that these are nondestructive technologies, as the contaminants are only transferred from one phase to the other. Moreover, the spent carbon may have to be handled as hazardous waste. Another technology which destroys the organics is the heterogeneous photocatalytic oxidation process. This process involves the use of photoactive catalysts illuminated with UV light to generate highly reactive radicals which can mineralize organic compounds to nontoxic forms, such as carbon dioxide and water. However, the major drawbacks of this process are the fouling of the photoactive catalysts, and scavenging of the reactive radicals by inorganic species and natural organic matter present in natural waters.

An alternative treatment strategy which can remove and destroy the organics is the combination of adsorption and photocatalytic oxidation processes. This strategy employs the adsorption process to first remove and concentrate the organic pollutants from water, and then destroy the organics by catalysis. The spent adsorbent column is regenerated off-line using steam. The effluent steam from the regeneration unit carrying the desorbed organics, free from the fouling species present in natural waters, is decontaminated by destroying the organics using the photocatalytic oxidation process.

The potential advantages of employing this treatment strategy are: 1) the spent adsorbents may be efficiently regenerated and reused; 2) the organic contaminants may be mineralized to nontoxic forms; 3) the contaminated water can be treated on-site; 4) sunlight can be used to activate the photocatalysts; and 5) the problem of photocatalyst deactivation by fouling species present in natural waters is eliminated.

The overall objective of this study was to evaluate this process for the removal and destruction of a variety of organic compounds in water. The performance of the adsorbent was examined for multiple cycles of adsorption and regeneration with each organic compound. The adsorbent selected was Ambersorb 563 obtained from Rohm & Haas Co. (Philadelphia, PA). Ambersorb 563 adsorbent has been reported to be resistant to fouling by natural organic matter (Parker and Bortko, 1991; and Hand et al., 1994). Fouling of activated carbon may occur by natural organic matter, and it may be difficult to regenerate using steam. Moreover, certain phenolic compounds have been reported to polymerize in the presence of dissolved oxygen on the surface of activated carbons (Vidic et al., 1993), and it may be difficult to regenerate the carbon. Also, Ambersorb 563 adsorbent has been reported to have catalytic properties at high temperatures for oxidation of organics (Vandersall et al., 1993), which may be beneficial during the steam regeneration process. Five contaminant compounds, tetrachloroethylene (PCE), carbon tetrachloride (CCl_4), p-dichlorobenzene (DCB), o-chlorobiphenyl (o-PCB), and methyl ethyl ketone (MEK) were chosen as they represent different classes of organic compounds - chlorinated aliphatic, aromatic, and polynuclear aliphatic; and oxygenated aliphatic. These compounds have different adsorption affinity with adsorbents, and reactivity with oxidizing radicals during photocatalysis.

PROCESS STRATEGY

The process strategy examined in this study for removal and destruction of organics involves these three steps: adsorption, steam regeneration, and destruction of organics.

Adsorption Process: The organic pollutants were first removed from water using

fixed-bed adsorption. When the adsorbent was saturated with organic compound, it was taken off-line and regenerated using steam.

Steam Regeneration Process: Saturated steam at 160 °C was used to regenerate spent adsorbents. A review of literature shows that regeneration by steam has mainly been applied to adsorbents used for recovery of solvents from gas phase because the compounds in the gas phase generally have low boiling points (Sontheimer et al., 1988). For organics with high boiling points, the steam temperature and pressure must be increased (Sontheimer et al., 1988). In the late 1970s, Rohm & Haas Co. (Philadelphia, PA) developed certain synthetic carbonaceous adsorbents (XE-340, XE-347, and XE-348). Neely and Isacoff (1982) reported that the XE-340 synthetic adsorbent saturated with an aqueous influent chloroform concentration of 1 mg/L could be effectively regenerated using steam at 105 °C for 8 cycles. They also reported that granular activated carbon, which was loaded and regenerated under similar conditions, showed loss in capacity after each regeneration cycle. Recently, steam was used to regenerate Ambersorb 563 adsorbent (an improved version of XE-300 series carbonaceous adsorbents, and which is commercially available) loaded with trichloroethylene from aqueous solution (Parker and Bortko, 1991). The regeneration process was conducted with saturated steam at 150 °C. The adsorbent was loaded with an aqueous influent TCE concentration of 60 mg/L until a breakthrough of about 2 mg/L was observed (about 1400 bed volumes were fed). Their study showed that after three cycles of adsorption and regeneration, there was no significant loss in adsorption capacity. In this study, saturated steam at 160 °C was used to regenerate Ambersorb 563 adsorbent saturated with aqueous phase organics.

Destruction of Organics: The destruction of desorbed organics from the regeneration

process was examined in the aqueous phase using photocatalysis, and also in the steam phase using photocatalysis or thermal catalysis. In the first approach, effluent steam from the regeneration unit was condensed and collected in a teflon bag. The organics in steam condensate were then destroyed using heterogeneous photocatalysis. The heterogeneous photocatalytic process involves the use of an n-type semiconductor as the catalyst to oxidize organic compounds. The primary oxidant responsible for the heterogeneous photocatalytic oxidation of organic compounds is the highly reactive hydroxyl radical (Turchi and Ollis, 1990), although in gas phase the oxidation reaction may also be initiated by chlorine atoms (Nimlos et al., 1993). The mechanism for formation of hydroxyl radical (OH^*) have been discussed in literature (Al-Ekabi and Serpone, 1988; Izumi et al., 1980; Kraeutler and Bard, 1978; Matthews, 1984; Okamoto et al., 1985; Pelizzetti et al., 1990; Serpone et al., 1986; and Turchi and Ollis, 1990). A number of researchers (Suri et al., 1993; Zhang et al., 1994; Al-Ekabi and Serpone, 1988; Barbeni et al., 1985; Herrmann and Pichat, 1980; Hsiao et al., 1983; Ollis et al., 1984; Okamoto et al., 1985; Matthews, 1984, 1986, 1987a,b, and 1988; and Pruden and Ollis, 1983) have reported that a wide variety of aliphatic and aromatic compounds including those with halogen, oxygen, nitrogen or sulfur substitutions, such as polychlorinated biphenyls (PCBs), pesticides, dioxins, alcohols, aldehydes, ketones, carboxylic acids, ethers, amines, thioethers, and mercaptans, can be oxidized using heterogeneous photocatalysis.

For photocatalytic destruction of organic compounds, several researchers have evaluated the option of fixing the catalysts on some support material to avoid the problem of catalyst separation from the aqueous slurry. Matthews (1987a, and 1987b), and Al-Ekabi and Serpone (1988) showed that phenolic compounds could be photocatalytically degraded over titanium oxide

supported on a glass fiber matrix. Zhang (1994) showed that Pt-TiO₂ catalyst supported on silica gel was very effective for destruction of a number of compounds such as benzene, toluene, ethyl benzene, xylenes, trichloroethylene, tetrachloroethylene, p-dichlorobenzene, and o-chlorobiphenyl. In an earlier study (Suri et al., 1993), a number of catalysts were examined for their photoactivity, and 1%Pt-TiO₂ was identified as a very active photocatalyst for destruction of a number of organic compounds. In this study, 1%Pt-TiO₂ catalyst supported on silica gel was used for destruction of organics in aqueous phase.

As a second option, the destruction of the desorbed organics was also examined in the steam phase using photocatalysis. The effluent steam from the regeneration column carrying the desorbed organics was passed through a photocatalyst unit. The photocatalysts evaluated were TiO₂, and Pt-TiO₂ catalysts which were supported on silica gel.

As a third option, a limited study was performed to examine the possibility of oxidizing organics in the steam phase using thermal active catalysts. Vandersall et al. (1993) reported that methylene chloride and some other chlorinated and non-chlorinated compounds could be destroyed in gas phase at 250 °C using Ambersorb 563 adsorbent. They also observed that CoO (or MnO) catalyst fixed on Ambersorb 563 and 572 adsorbents provided significant destruction of toluene, hexane, and butane at 250 °C and 175 °C. Brendley et al. (1993) examined the catalytic degradation of methylene chloride with metal oxide-impregnated Ambersorb 563 adsorbent. Their work suggests that TiO₂ or Pt-TiO₂ as good catalyst choices for catalytic oxidation reactions. They also report that ^{the}presence of hydrogen, either as part of the reactant molecule (as in CH₂Cl₂) or as part of an additive such as water, was important for efficient decomposition of organics to carbon dioxide^s and HX. Excess water in ^{the}reaction stream did not

inhibit the reaction in any way and even promoted the reaction at lower temperature. In this study, a limited effort was directed to examine the feasibility of degrading the organics in the steam phase at 160 °C using some thermally active catalysts. The effluent steam from the regeneration column was directly passed through a thermal catalyst unit. Based on a review of literature (Vandersall et al., 1993; and Brendley et al., 1993), Ambersorb 563, TiO_2 and Pt- TiO_2 impregnated Ambersorb 563, and CoO/SiO_2 catalysts were selected. These catalysts were examined for the degradation of organics in the effluent steam at 160 °C from the regeneration column.

EXPERIMENTAL

MATERIALS:

All the chemicals used were of reagent grade or better. Tetrachloroethylene (PCE), p-dichlorobenzene (DCB), carbon tetrachloride (CCl_4), methyl ethyl ketone (MEK), high purity (99.9+ %) Aldrich TiO_2 , (Lot No. 00108TV), and DavisilTM silica gel (SiO_2) were obtained from Aldrich Chemical Co. (Milwaukee, WI). The o-chlorobiphenyl (o-PCB) was obtained from Pfaltz & Bauer, Inc (Waterbury, CT). Ambersorb-563 adsorbent (20X50 mesh) was obtained from Rohm and Haas Co. (Philadelphia, PA).

Adsorbent Preparation: The commercial grade Ambersorb-563 adsorbent (20X50 mesh; Rohm and Haas Co.) was chosen for this study. The Ambersorb adsorbent was impregnated with 1%Pt- TiO_2 catalyst following the method described elsewhere (Suri, 1994). In short, the impregnation of the adsorbent was conducted in two steps. In the first step, titanium isopropoxide solution (with 20% by volume of 2-propanol) was hydrolyzed on the adsorbent in

a humid environment. The adsorbent was then calcined at 500 °C for 3 hours under an argon atmosphere. With this process, it is expected that the catalyst will be impregnated onto the internal surface of the adsorbent. This may facilitate the regeneration process by reducing the solute diffusion time from the internal to the external surface where the reaction might take place. The impregnation of the catalyst onto the external surface of the adsorbent was performed by immersing the adsorbent in an aqueous slurry of Pt-Aldrich TiO₂ catalyst for 10 minutes. The adsorbent/catalyst was dried at 70 °C for 2 hours, washed with Milli-Q water, and dried at 105 °C for 12 hours. The amount of catalyst loaded onto the adsorbent was determined by ash content analysis, and the total amount was observed to be about 12% by adsorbent weight.

Catalyst Preparation: Platinized TiO₂ was prepared by photo-reducing 1 weight percent of Pt on to the surface of TiO₂ from hexachloroplatanic acid as described by Kraeutler and Bard (1978). The 1%Pt-TiO₂ photocatalyst was fixed on silica gel support (35X60 mesh) following the method outlined by Zhang et al. (1994). The catalyst dosage on the silica gel was about 1% by weight of silica gel. The CoO thermal catalyst supported on silica gel (about 2% by weight of CoO on SiO₂) was prepared by reducing Co(NO₃)₂·6H₂O salt on silica gel following the method outlined by Vandersall et al. (1993).

METHODS:

Analytical Methods: PCE and CCl₄ 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) which was equipped with an electron capture detector. The o-PCB was analyzed by direct aqueous injection using a HP 5890A GC which was equipped with an electron capture detector and a 30 m X 0.32 mm SPB-5 capillary column (Supelco, Inc.,

Houston, TX). The p-DCB was analyzed according to EPA method 601 using a Tekmar (Cincinnati, OH) LSC 2000 purge and trap (P&T) connected to a HP 5880A GC which was equipped with a flame ionization detector. The MEK was analyzed following a modified EPA method 625 using a HP (Palo Alto, CA) 5890 gas chromatograph and 5970 mass spectrometer (GC/MS) system. Chloride ion concentration was measured using Dionex DX500 (Sunnyvale, CA) Ion Chromatograph. Dissolved oxygen (DO) was analyzed using a YSI (Yellow Spring, OH) Model 54 DO meter. Light intensity was measured using EG&G Gamma Scientific (San Diego, CA) Model GS 3100 spectroradiometer equipped with a fiber optic probe. It was calibrated to measure light intensity for wavelengths between 275 to 387.5 nm because this is the range of light which can activate TiO_2 catalysts (Sakata and Kawai, 1983).

Removal of Organics from Water: In this study, small - scale columns (1.5 cm I.D). were used to load the adsorbents with the organic compound of interest. Both ^qimpregnated and virgin (non-impregnated) Ambersorb adsorbents were loaded with the organic compound. The Ambersorb adsorbent was impregnated with 1%Pt- TiO_2 catalyst. Table 1 lists the experimental conditions of the adsorption process.

Table 1 The operation parameters for the adsorption process.

Empty bed contact time:	25 sec
Velocity:	10 m/hour
Adsorbent Mass:	6 gm
Adsorbent Size:	20X50 Mesh (0.048 cm)
Column Diameter:	1.5 cm I.D.
Column Length:	27 cm
Flow Rate:	30 ml/min
Bed Depth:	7 cm
Adsorbent:	Ambersorb 563 - virgin Ambersorb 563 - impregnated with 1%Pt- TiO_2 catalyst; catalyst loading was 12% by adsorbent weight.

The adsorption unit was constructed using glass, teflon, and stainless steel to minimize the loss of organics due to adsorption onto construction materials. A glass column (Ace Glass, Inc.) of 1.5 cm in diameter was used as the adsorption column. A concentrated stock solution of the organic was added using a positive feed displacement pump into a 13 liter mixing tank containing organic free Milli-Q water and then pumped through the test columns. To load the adsorbents in a reasonable amount of time, a high influent concentration of the organic compound was selected. Samples were taken periodically at the influent and the effluent end and analyzed for the organic compound. When the adsorbent was completely saturated with the influent organic compound, the column was taken off-line and regenerated using steam.

Regeneration of Spent Adsorbents: Figure 1 shows the schematic of the steam regeneration unit. The glass columns used for the adsorption process were also employed for regeneration of spent adsorbents using steam. The end caps of these columns were made from a special glass filled teflon material which is resistant to a temperature of about 225 °C and pressure of about 120 psig (ACE Glass Inc., Vineland, NJ). The regeneration unit was pressure tested at about 250 psig prior to conducting the experiments. The stainless steel tubings and the regeneration column were heated with fiber glass heat tape to prevent steam condensation. The temperature of the steam entering and leaving the regeneration column was monitored. The regeneration of the spent adsorbents was conducted using saturated steam at about 160 °C. The run time of the regeneration experiments was about 7 to 10 hours except in the case of MEK where it was about 5 to 7 hours. Table 2 lists the regeneration experimental conditions.

Table 2. The operation parameters for the steam regeneration process

Saturated Steam:	160 °C
Empty Bed Contact Time:	0.9 sec
Space Velocity:	1.1 sec ⁻¹
Steam Condensate Flow Rate:	~ 3 ml/min
Run Time:	~ 7 to 10 hours
Column Diameter:	1.5 cm I.D.

Destruction of Desorbed Organics:

Condensate treatment: In the first approach, the effluent steam from the regeneration unit was condensed and collected in a teflon bag. A known amount of oxygenated deionized Milli-Q water (about 20 liters) was added to the condensate (about 1.5 to 2 liters) to enhance the dissolved oxygen content, and to dissolve any organic phase to the aqueous phase. The solution was then pumped at a flow rate of 5 to 20 ml/minute through the photocatalytic reactor. These reactor units were constructed using plastic tubes (American Energy Technologies, Inc., Green Cove Springs, FL). It has been shown that a 1/8" thick plate of this plastic material has an average sunlight transmittance of 80% in the wavelength range of 300 - 400 nm, and the mechanical and UV transmissive properties of this material are stable under a continuous solar illumination for 5 years. For this study, the artificial light source used was a 1.75 meter long, 88 watts fluorescent tanning lamp (United States Lighting Corp., Fenton, MI; model FS7212/UVB/HO). The light intensity of these lamps was 1.8 mW/cm² (about 50% of the intensity of sunlight at noon on a clear day) in the range of 275 to 387.5 nm and peaked at 310 nm. For all photocatalytic experiments, the reactors were placed at a distance of 1 cm from the lamp. Samples were taken periodically at the influent and effluent ends of the photocatalytic reactor to determine the destruction of organics.

Steam treatment: As ~~an~~^o another option, the effluent steam from the regeneration reactor carrying the desorbed organics was directly passed through a catalytic reactor in an attempt to degrade the organics in the steam phase. The catalysts were packed in glass columns similar to the adsorption/regeneration columns (1.5 cm I.D.) which were rated to withstand temperature and pressure of up^yto 225°C and 120 psig, respectively. For some experiments, oxygen as an electron acceptor was introduced to the steam prior to the catalyst unit. The catalyst unit contained either the thermal catalyst or the photocatalyst. The photocatalyst column was placed between a 450 W and a 1200 W high pressure mercury vapor lamps (ACE Glass Inc., Vineland, NJ). Since the objective of this part of the study was to examine the technical feasibility of the process, very limited attempt^s ~~was~~^{er} made to optimize the photocatalytic reactor. A more appropriate design for practical application may be an annular reactor with the lamp at the center. The effluent steam from the thermal catalyst or photocatalyst unit was condensed, and collected in a clean teflon bag. Periodic samples of the condensate were taken and analyzed for the organic compound and the chloride ion (if applicable). The collected steam condensate was then pumped through an aqueous phase photocatalyst unit (described in the previous section) to destroy any remaining organics present in the solution.

RESULTS AND DISCUSSION

Adsorption / Regeneration Process: The adsorbents were loaded with the organic compound, regenerated using steam, and reloaded under similar conditions. This process was examined with five organic compounds: PCE, p-DCB, CCl₄, o-PCB, and MEK. The adsorbents were impregnated with Pt-TiO₂ catalyst to achieve any catalytic degradation of adsorbed organics

during the regeneration process. Control experiments were conducted with virgin (non-impregnated) adsorbent to ascertain the effect of catalyst impregnation on the regeneration process, and on the adsorbent capacity. The integrated column capacity for the virgin and impregnated adsorbents indicated about 16% loss in adsorbent capacity due to catalyst impregnation with PCE. Similar tests were conducted with other compounds, and a similar loss in capacity was observed, except for o-PCB where the loss was about 30% due to catalyst impregnation.

The effect of catalyst impregnation to degrade the organics during regeneration was ascertained from the chloride ion concentration in the steam condensate. The dissolved oxygen of the Milli-Q water which was used to produce steam was about 3 mg/L, and that of the effluent steam condensate was about 2 mg/L. It was observed that chloride ions produced from the regeneration of impregnated adsorbent were significantly more than those from the regeneration of the virgin adsorbent (the catalytic activity of the virgin adsorbent material has also been reported by Vandersall et al., 1993). However, the maximum destruction achieved with the impregnated adsorbent was only about 5% of the initially adsorbed PCE, and about 7% for CCl₄. No significant destruction was observed for p-DCB and o-PCB. However, there may be a possibility of achieving higher destruction of adsorbed organics on the adsorbent by using more active catalysts, higher contact time, or higher temperature. In this study, the temperature of the regeneration unit was about 160 °C, whereas some researchers observed significant destruction of organics at 250 °C (Vandersall et al., 1993; and Brendley et al., 1993).

The impregnated adsorbent was loaded and regenerated for at least 6 cycles to examine the long term performance of this process. Figures 2 through 6 show the breakthrough profiles

for 6 adsorption cycles with the impregnated adsorbent for PCE, p-DCB, CCl₄, o-PCB, and MEK, respectively. The capacity of the adsorbent can be estimated by integrating the area between the respective influent and effluent profiles. It may be observed from Figures 2 - 6 that for 6 cycles of adsorption, the breakthrough profiles are very similar for PCE, p-DCB, CCl₄, and MEK, respectively. Integrating the area between the influent and effluent profiles revealed that the adsorbent capacity was completely recovered with the steam regeneration process for PCE, p-DCB, CCl₄, and MEK. In the case of o-PCB, there was about 20% loss in adsorbent capacity after the first cycle; however, the adsorption capacity for cycles 2 through 6 were almost the same. Experiments conducted with virgin adsorbent and o-PCB showed similar loss in capacity after the first cycle, as shown in Figure 7.

During regeneration of impregnated adsorbents, some organics may be (1) completely oxidized, or (2) partially oxidized to organics which may be more polar in nature and desorb faster from the adsorbent than the parent compound, thereby enhancing the regeneration process. Experiments conducted with PCE showed that the virgin adsorbent could be successfully regenerated for several cycles, as shown in Figure 8. In the case of p-DCB, CCl₄, and MEK, only one cycle of regeneration was performed with the virgin adsorbent, and it was observed (results not shown here) that the virgin material could also be regenerated successfully. The impregnated adsorbent may provide some oxidation of adsorbed organics, but the virgin adsorbent can be regenerated just as well. In the case of impregnated adsorbent, it may be possible to enhance the regeneration process by achieving higher oxidation of adsorbate on the adsorbent by using more active catalysts, higher contact time, or higher temperature.

Destruction of desorbed organics: The destruction of the desorbed organics was examined in the aqueous phase and in the steam phase. In the first approach, the effluent steam from the regeneration unit was condensed and treated by fixed-bed photocatalysis. A known amount of oxygenated Milli-Q water (about 20 liters) was added to the condensate (about 1.5 to 2 liters) to enhance the dissolved oxygen content, and to dissolve any organic phase to the aqueous phase. This was done to provide sufficient concentration of electron acceptors to match with the theoretical oxygen demand (ThOD) for oxidation of organics. The diluted solution was pumped at a flow rate of 5 to 20 ml/minute through the photocatalytic reactor, and destruction of organics was determined by measuring the concentration of organic compound, total organic carbon (TOC), and chloride ion where applicable. Figure 9 shows the removal of the organics using the photocatalytic reactors. The PCE, o-PCB, and p-DCB compounds in the aqueous phase were completely mineralized, where as only about 53% destruction of CCl_4 was observed. However, a higher destruction of CCl_4 could be achieved using a longer reactor or higher retention time. For MEK, although 97% of the compound was removed, only about 15% removal of TOC was observed thereby suggesting that some by-products were produced that were refractory to oxidation. Similar results for MEK have been reported by Suri et al. (1993) and Zhang (1994).

For practical application of this regeneration process, the condensate may be treated by the following steps: a) separate the organic phase from the steam condensate, and either recycle it or dispose it separately, b) pass the condensate, which has organics in aqueous phase only, through the adsorbent bed to superload the adsorbent before the steam regeneration, c) take the effluent from the superloading step, which will have a lower organic concentration, and

photocatalytically destroy any remaining organics. One aspect of following this strategy is that the concentration of organics in the condensate (prior to photocatalysis) will be lower and the requirement of additional electron acceptor will be reduced.

In this study, the destruction of the desorbed organics was also examined in the steam phase by passing the effluent steam from the regeneration unit directly through a thermal catalytic reactor or a photocatalytic reactor. The objective of this part of the study was only to examine the technical feasibility of destroying the organics in the steam phase at 160 °C, and a very limited study was performed. The chloride ions in the condensate was measured to estimate the degradation of chlorinated organics in the steam phase. The thermal catalysts evaluated were: Ambersorb 563, TiO_2 and Pt- TiO_2 impregnated Ambersorb 563, and CoO supported on silica gel. The photocatalysts evaluated were TiO_2 , and Pt- TiO_2 supported on silica gel. The dissolved oxygen concentration of the Milli-Q water which was used to produce steam was about 3 mg/L. For some experiments, additional oxygen was introduced (at about 30 ml/min under standard conditions) prior to the catalyst column. It was observed that the catalysts tested in this study did not show any significant destruction of organics, although the destruction was slightly higher in the presence of oxygen. The maximum PCE destruction of about 5% was observed using Pt- TiO_2 photocatalyst supported on silica gel and in the presence of additional oxygen. One of the complications of this process is to match the desorbed organic concentration profile in the steam with the required electron acceptor concentration for oxidation. No attempt was made to examine any partial degradation of the organics during the process. It may be possible to achieve higher destruction of organics using more active catalysts, higher contact time, or higher temperature (Vandersall et al., 1993, observed significant destruction of organics

at 250 °C with Ambersorb 563 and metal oxide impregnated Ambersorb 563 catalysts, whereas the temperature used in this study was 160 °C).

CONCLUSIONS

The treatment strategy for removal and destruction of organics in water by adsorption and catalysis was examined with the following five contaminant compounds: tetrachloroethylene (PCE), p-dichlorobenzene (p-DCB), carbon tetrachloride (CCl₄), o-chlorobiphenyl (o-PCB), and methyl ethyl ketone (MEK). The spent adsorbent was regenerated off-line using saturated steam at 160 °C. To examine the feasibility of degrading the adsorbed organics during steam regeneration, the adsorbent was impregnated with Pt-TiO₂ catalyst. Some loss in adsorbent capacity, about 10 to 15%, due to catalyst impregnation was observed for PCE, p-DCB, CCl₄, and MEK, whereas about 30% reduction in capacity was noted in the case of o-PCB.

The impregnated adsorbents were loaded and regenerated for at least 6 cycles to examine the long term performance of this process. It was observed that the adsorption capacity of the adsorbent for PCE, p-DCB, CCl₄, and MEK was almost completely recovered with the steam regeneration process. In the case of o-PCB, there was about 20% loss in adsorbent capacity after the first cycle, however, the adsorption capacity for cycles 2 through 6 were almost the same. Tests conducted with virgin adsorbent for o-PCB showed similar loss in capacity after the first cycle. Just like the results with impregnated adsorbent for PCE, the virgin amborsorb 563 adsorbent was also successfully regenerated for several cycles. In the case of p-DCB, CCl₄, and MEK, only one cycle of regeneration was performed with the virgin adsorbent, and the results showed that the virgin material could be regenerated just as well as the impregnated

adsorbent.

The Ambersorb 563 adsorbent showed some catalytic properties to degrade the adsorbed organics during steam regeneration at 160 °C. Impregnating the adsorbent with Pt-TiO₂ catalyst enhanced the degradation of adsorbed PCE during the steam regeneration process, although the maximum amount of PCE degraded was only about 5% of the initially adsorbed. However, a higher destruction of adsorbed organics may be achieved at a higher temperature, as reported by some researchers, and using more active catalysts and higher contact time.

The desorbed organics in the steam condensate were destroyed by photocatalytic oxidation process. The PCE, o-PCB, and p-DCB compounds in the aqueous phase were completely mineralized, where as only about 53% destruction of CCl₄ was observed. However, a higher destruction of CCl₄ could be achieved using a higher empty bed contact time. For MEK, although 97% of the compound was removed, only about 15% removal of TOC was observed thereby suggesting that some by-products were produced that were refractory to oxidation. The destruction of the desorbed organics was also examined in the steam phase at 160 °C. The thermal catalysts evaluated were: ambersorb 563, and CoO supported on silica gel. The photocatalysts evaluated were TiO₂, and Pt-TiO₂ supported on silica gel. It was observed that the catalysts tested in this study⁹ did not show any significant destruction of organics in the steam phase. Some of the complications of this process are to match the desorbed organic concentration profile in the steam with the required electron acceptor concentration for oxidation, and have appropriate contact time and temperature.

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REFERENCES

- Al-Ekabi, H., and Serpone, N. (1988) "Kinetic Studies in Heterogeneous Photocatalysis. 1. Photocatalytic Degradation of Chlorinated Phenols in Aerated Aqueous solutions over TiO_2 Supported on a Glass Matrix," J. Phys. Chem. 92, 5726 -5731.
- Barbeni, M., Pramauro, E., Pelizzetti, E., Borgarello, E., Gratzel, M., and Serpone, N. (1985) "Photodegradation of 4-Chlorophenol Catalyzed by Titanium Dioxide Particles," J. Chem., 8, 547.

Brendley, W.H., Drago, R.S., Petrosius, S.C., and Grunewald, G.C. (1993) "Deep Oxidation of Chlorinated Hydrocarbons," presented at Symposium on Environmental Catalysis; 205th American Chemical Society National Meeting and Exposition Program, Denver, Colorado.

Hand, D.W., Herlevich, J.A., Perram, D.L., and Crittenden, J. C. (1994) "Evaluation of Synthetic Adsorbents for Trichloroethene Removal," in press, J. AWWA.

Herrmann, J-M., and Pichat, P. (1980) "Heterogeneous Photocatalysis. Oxidation of Halide Ions by Oxygen in Ultraviolet Irradiated Aqueous Suspension of Titanium Dioxide," J. Chem. Soc. Faraday Trans. I, 76, 1138 - 1146.

Hsiao, C., Lee, C., and Ollis D. F. (1983) "Heterogeneous Photocatalysis: Degradation of Dilute Solutions of Dichloromethane, Chloroform, and Carbon Tetrachloride with Illuminated TiO_2 Photocatalyst," J. of Catalysis, 82, 418 - 423.

Izumi, I., Dunn, W., Wilbourn, K., Fan, F., and Bard, A. (1980) "Heterogeneous Photocatalytic Oxidation of Hydrocarbons on Platinized TiO_2 Powders," J. Phys. Chem. 84, 3207 - 3210.

Kraeutler, B., and Bard, A. (1978) "Heterogeneous Photocatalytic Decomposition of Saturated Carboxylic Acids on TiO_2 Powder. Decarboxylative Route to Alkanes," J. Am. Chem. Soc. 100:19, 5985-5992.

Liu, J., Hand, D.W., Crittenden J.C., and Perram, D.L. (1993) "Destruction of Toxic Organics Using Adsorption and Photocatalytic Regeneration with Sunlight or low Intensity Artificial Lights," a report prepared at Michigan Technological University, Houghton, MI, for AWWA Research Foundation, Denver, CO.

Matthews, R. (1984) "Hydroxylation Reactions Induced by Near-Ultraviolet Photolysis of Aqueous Titanium Dioxide Suspensions," J. Chem. Soc. Faraday Trans. 1, 80, 457-471.

Matthews, R. (1986) "Photo-Oxidation of Organic Materials in Aqueous Suspensions of Titanium Dioxide," Water Res. 20, 569.

Matthews, R. (1987a) "Photooxidation of Organic Impurities in Water Using Thin Films of Titanium Dioxide," J. Phys. Chem., 91, 3328-3333.

Matthews, R. (1987b) "Carbon Dioxide Formation from Organic Solutes in Aqueous Suspensions of Ultraviolet Irradiated TiO_2 . Effect of Solute Concentration," Aust. J. Chem. 40, 667.

Matthews, R. (1988) "Kinetics of Photocatalytic Oxidation of Organics Solutes Over Titanium Dioxide," J. of Catalysis, III, 264-272.

Neely, J. W., and Isacoff, E. G. (1982) "Carbonaceous Adsorbents for the Treatment of Ground and Surface Waters," First Edition, Marcel Dekker, Inc., New York, New York.

Nimlos, M. R., Jacoby, W. A., Blake, D. M., Milne, T. A. (1993) "Direct Mass Spectrometric Studies of the Destruction of Hazardous Wastes. 2. Gas-phase Photocatalytic Oxidation of Trichloroethylene over TiO_2 : Products and Mechanisms," *Environ. Sci. & Technol.*, 27, 732-740.

Okamoto, K., Yamamoto, Y., Tanaka, H., Tanaka, M., and Itaya, A. (1985) "Heterogeneous Photocatalytic Decomposition of Phenol over TiO_2 powder," *Chem. Soc. Japan*, 58, 2015- 2022.

Ollis, D. F., Pelizzetti, E., Serpone, E. (1991) "Destruction of Water Contaminants," *Environ. Sci. & Technol.*, 25, 9, 1522-1529.

Ollis, D. F., Hsiao, C., Budiman, L., and Lee, C. L. (1984) "Heterogeneous Photoassisted Catalysis: Conversions of Perchloroethylene, Dichloroethane, Chloroacetic Acids, and Chlorobenzenes," *J. of Catalysis*, 88, 89-96.

Parker G.R., and Bortko, S.M. (1991) "Groundwater Remediation using Ambersorb Adsorbents," Presented at The Florida Environment Chemistry Conference.

Pelizzetti, E., Maurino, V., Minero, C., Carlin, V., Barnauro, E., Zerbini, O., and Tosato, M. L. (1990) "Photocatalytic Degradation of Atrazine and other S-Triazine Herbicides," *Environ. Sci. & Technol.*, 24(100), 1559-1565.

Pruden, L., and Ollis, D. (1983) "Photoassisted Heterogeneous Catalysis: The Degradation of Trichloroethylene in Water," *J. Catal.* 82, 404.

Sakata, T., and Kawai, T. (1984) "Photosynthesis and Photocatalysis with Semiconductor Powders," *Energy Resources through Photochemistry and Catalysis*, edited by M. Gratzel, 331-357.

Serpone, N., Borgarello, E., Harris, R., Cahill, P., Borgarello, M., and Pelizzetti, E. (1986) "Photocatalysis over TiO_2 Supported on a Glass Substrate," *Solar Energy Material*, 14, 121-127.

Sontheimer, J., Crittenden, J.C., and Summers R.S., (1988) "Activated Carbon for Water Treatment," 2nd edition, DVGW-Forschungsstelle.

Spivey, J.J., and Butt., (1987) "Complete Catalytic Oxidation of Volatile Organics," I&EC Research, 26, 2180.

Suri, R. P. S., Liu, J.B., Hand, D.W., Crittenden J.C., Perram, D.L., and Mullins, M.E. (1993) "Heterogeneous Photocatalytic Destruction of Hazardous Organic Contaminants in Water," Water Env. Res., 65, 5, 665-673.

Turchi, C. S., and Ollis, D. F. (1990) "Photocatalytic Degradation of Organic Water Contaminants Mechanisms Involving Hydroxyl Radical Attack," J. of Catalysis, 122, 178-192.

Vandersall, M.T., Maroldo, S.G., Brendley, W.H., Jurczyk, K., and Drago, R.S. (April 1993) "Low Temperature Deep Oxidation of Aliphatic and Aromatic Hydrocarbons," presented at Symposium on Environmental Catalysis; 205th American Chemical Society National Meeting and Exposition Program, Denver, Colorado.

Zhang, Y., Crittenden, J. C., Hand, D. W., and Perram, D. L., (1994) "Fixed-Bed Photocatalysts for Solar Decontamination of Water," Environ. Sci. & Technol., 28, 435-442.

Zhang, Y. (1994) "Detoxification of Water Using Fixed-Bed Photocatalysts," Ph.D. dissertation, Michigan Technological University, Houghton, MI.

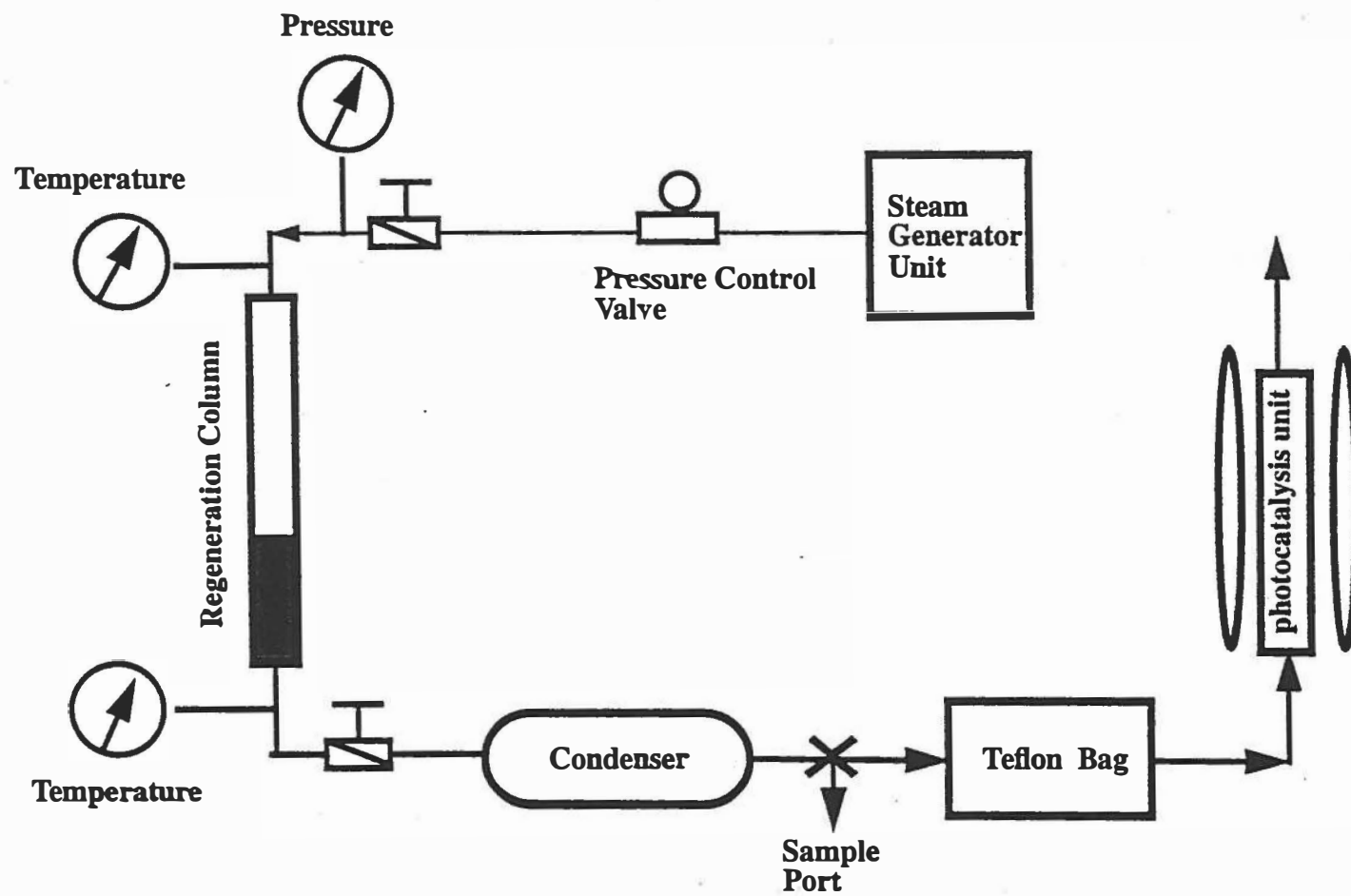


Figure 1. Schematic of the steam regeneration unit.

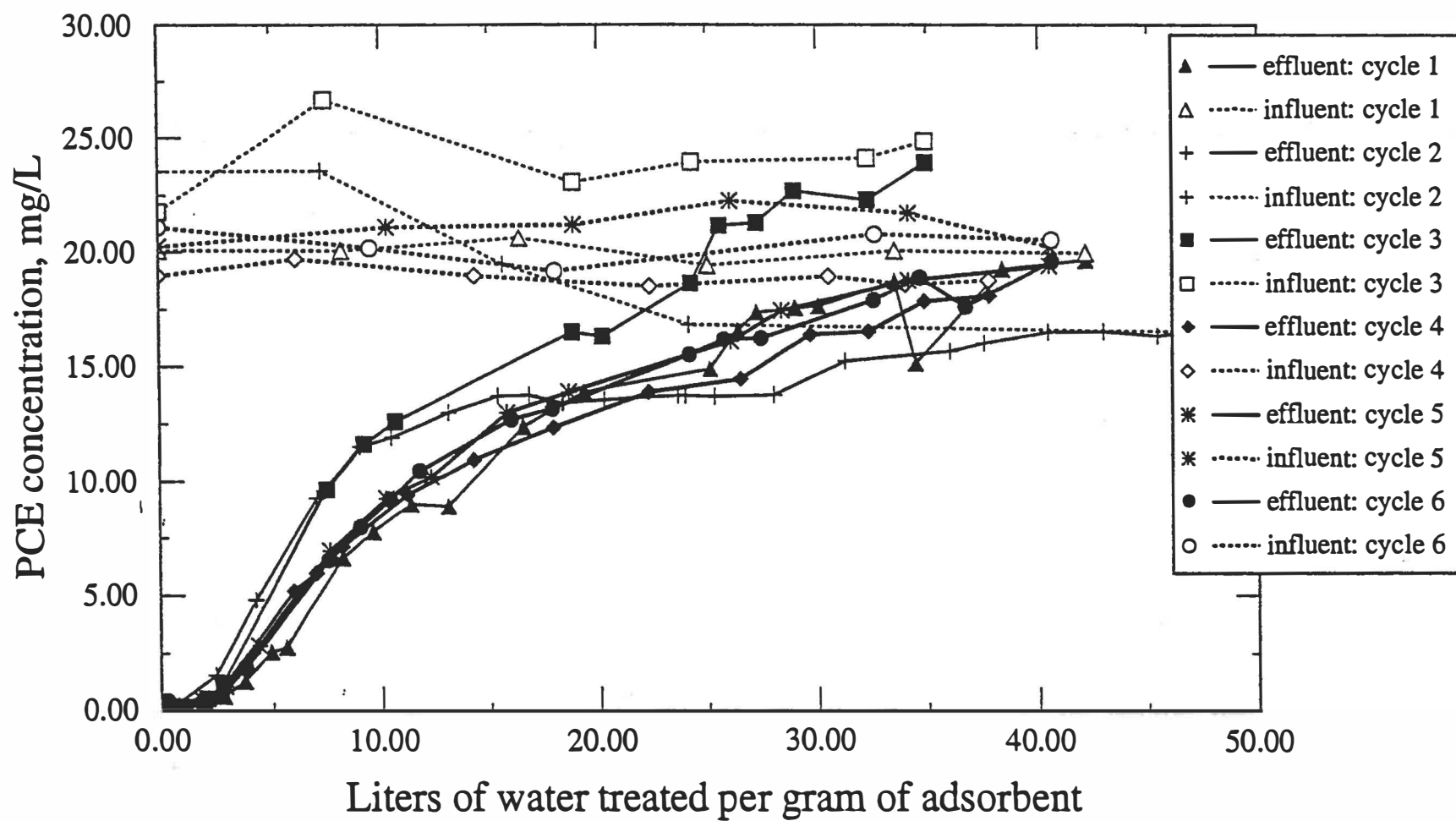


Figure 2. PCE adsorption profiles with impregnated Ambersorb 563 adsorbent; impregnated adsorbent mass: 5.3 gm.

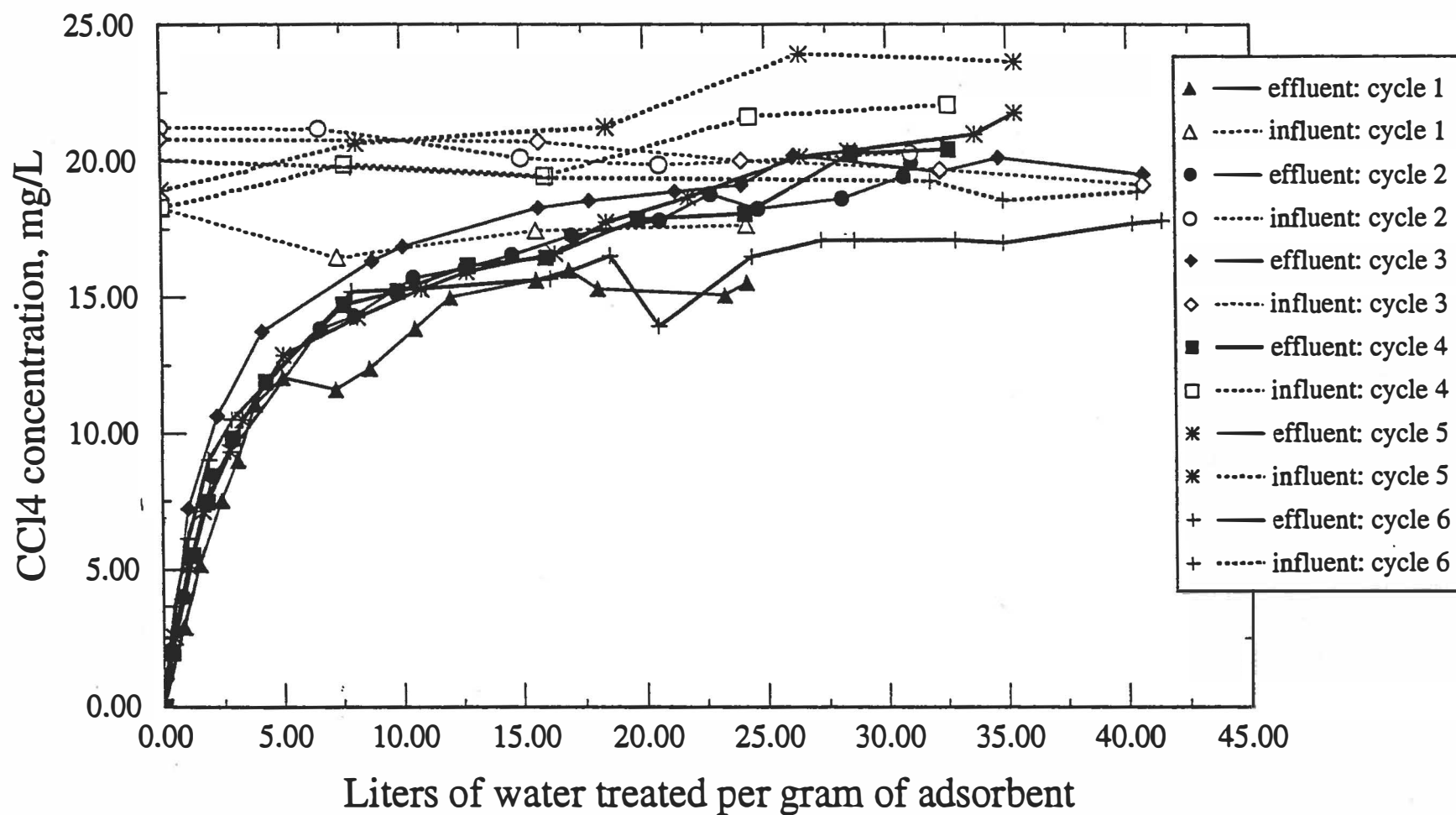


Figure 3. CCl₄ adsorption profiles with impregnated Ambersorb 563 adsorbent; impregnated adsorbent mass: 5.3 gm.

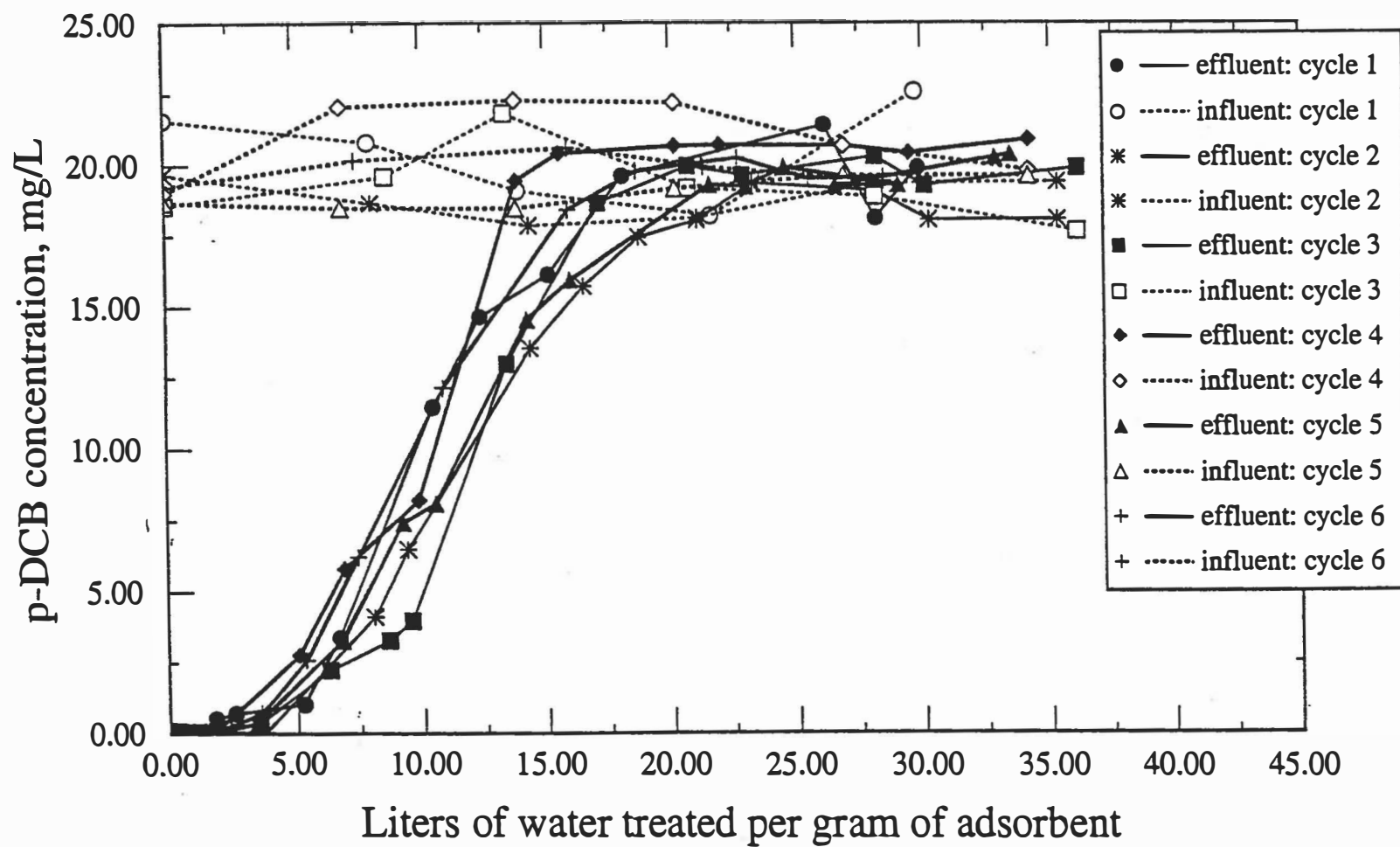


Figure 4. p-DCB adsorption profiles with impregnated Amborsorb 563 adsorbent; impregnated adsorbent mass: 6 gm.

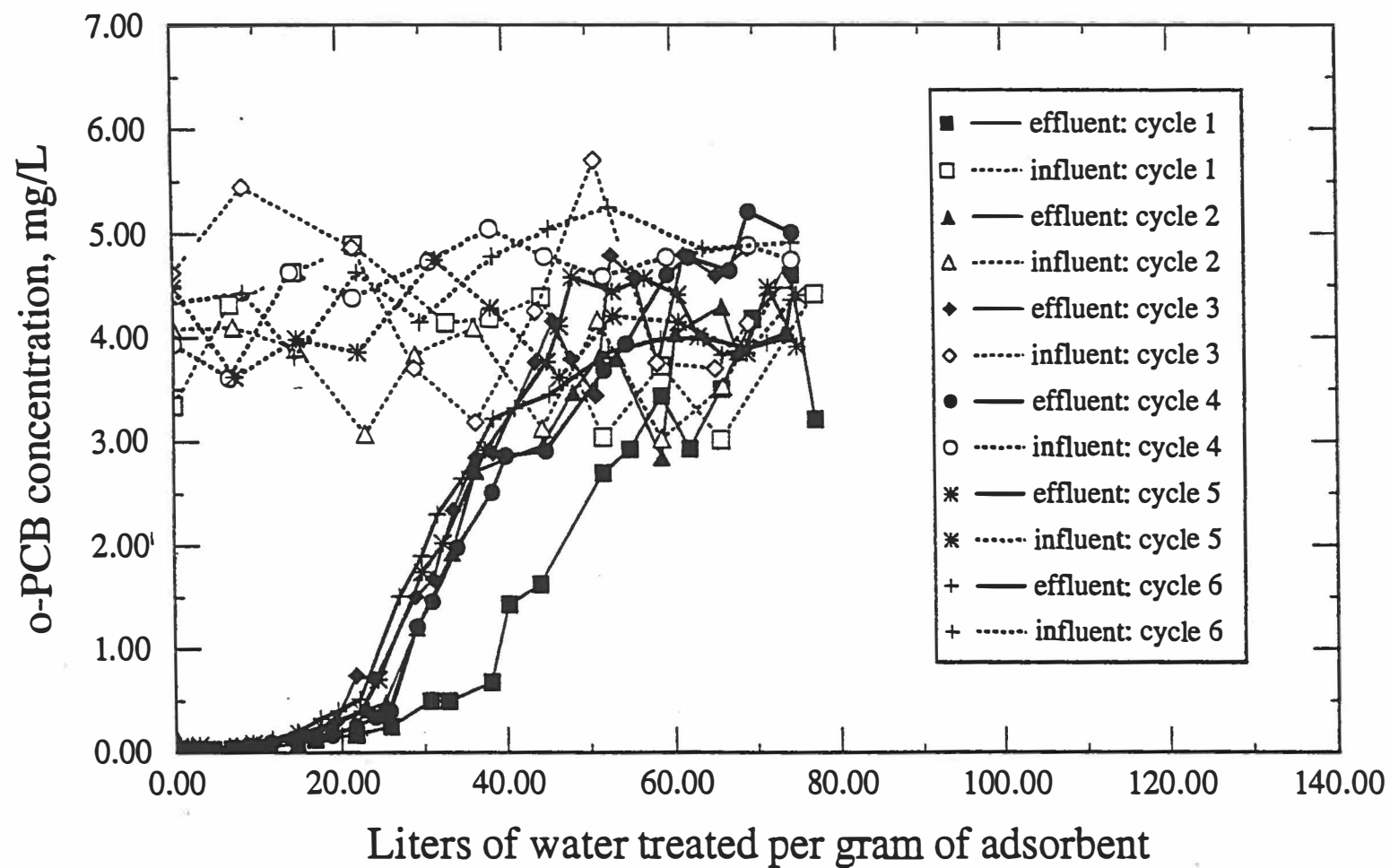


Figure 5. o-PCB adsorption profiles with impregnated Amborsorb 563 adsorbent; impregnated adsorbent mass: 5.3 gm.

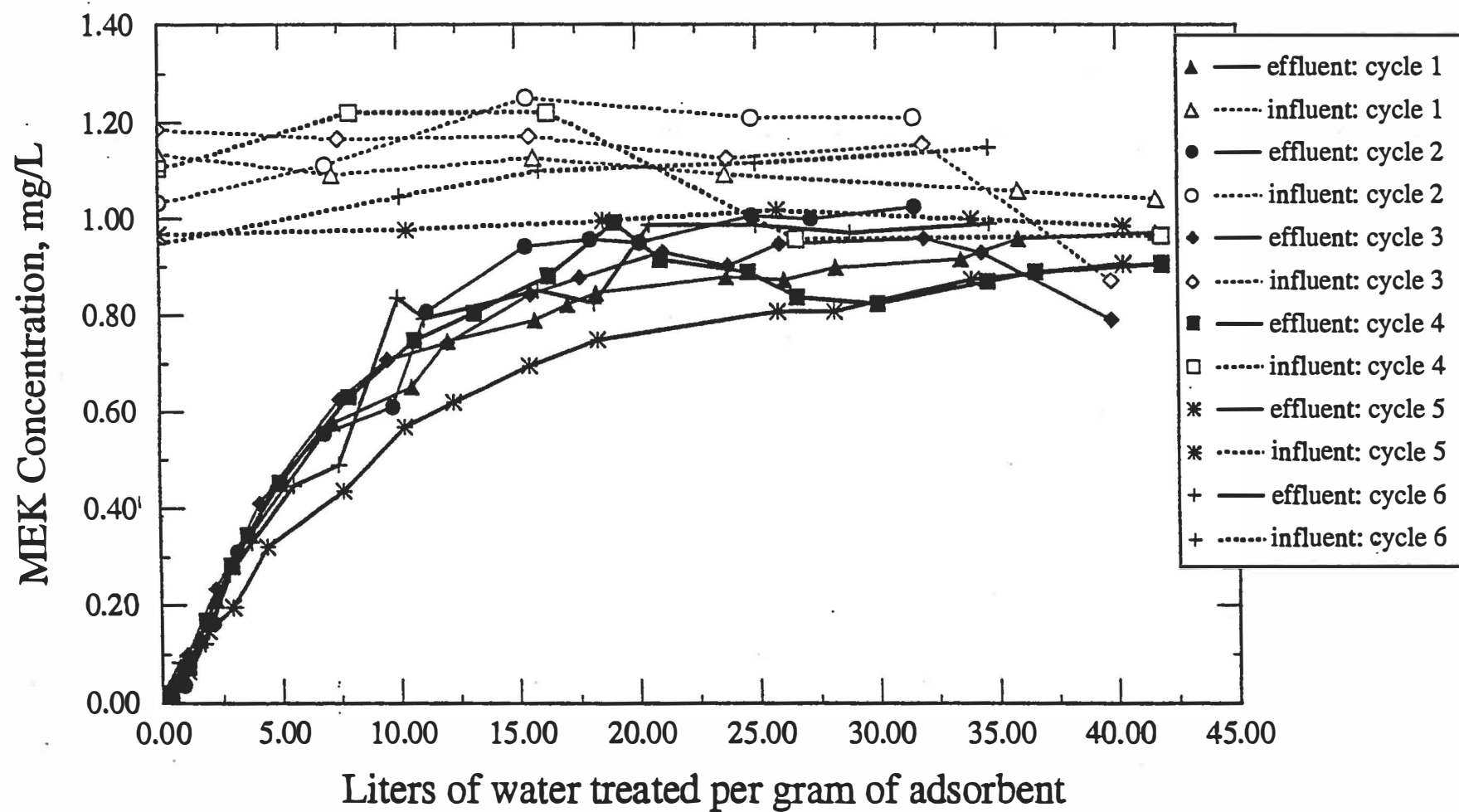


Figure 6. MEK adsorption profiles with impregnated Ambersorb 563 adsorbent; impregnated adsorbent mass: 5.3 gm.

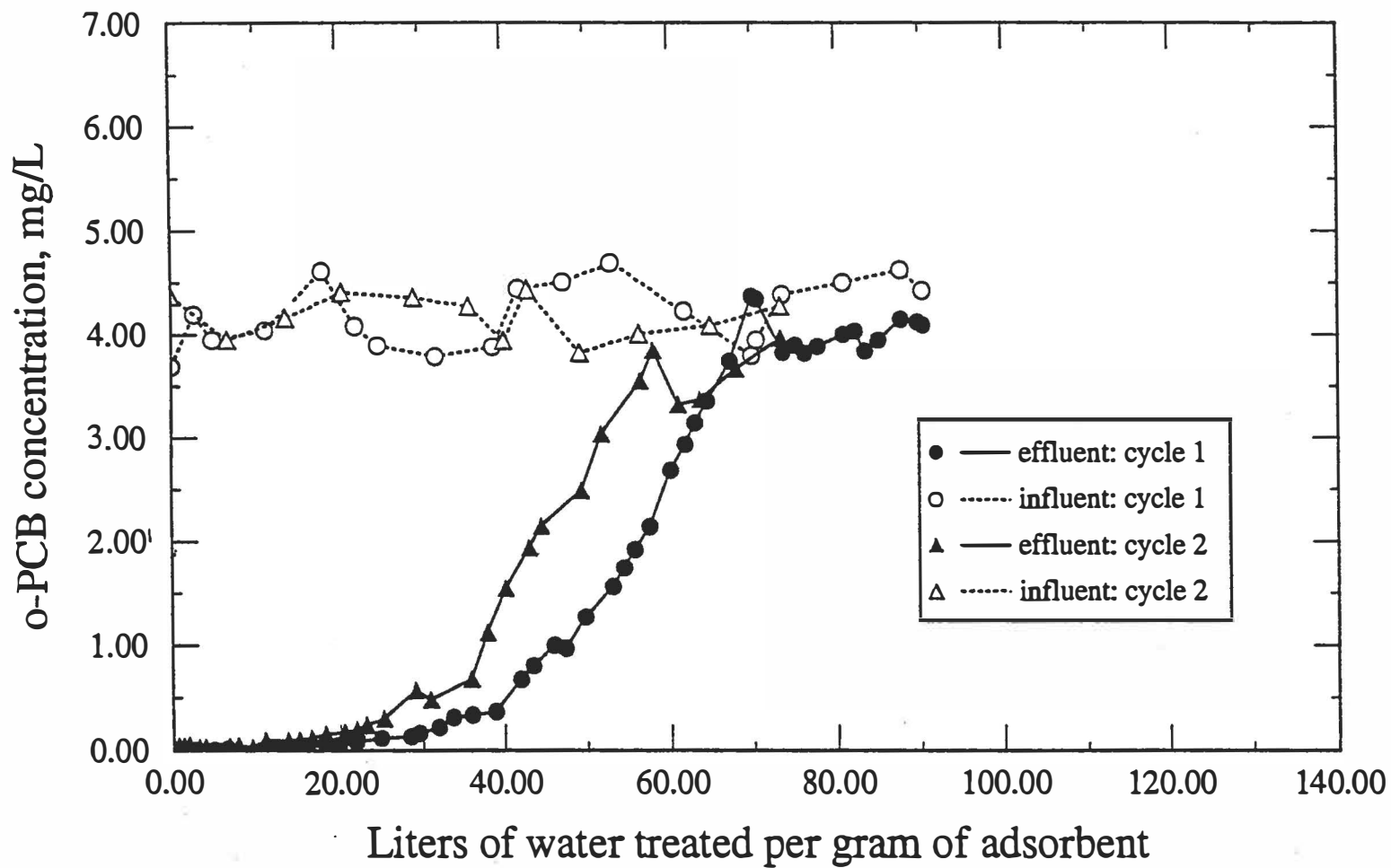


Figure 7. o-PCB adsorption profiles with virgin Ambersorb 563 adsorbent for first two adsorption cycles; virgin adsorbent mass: 6 gm.

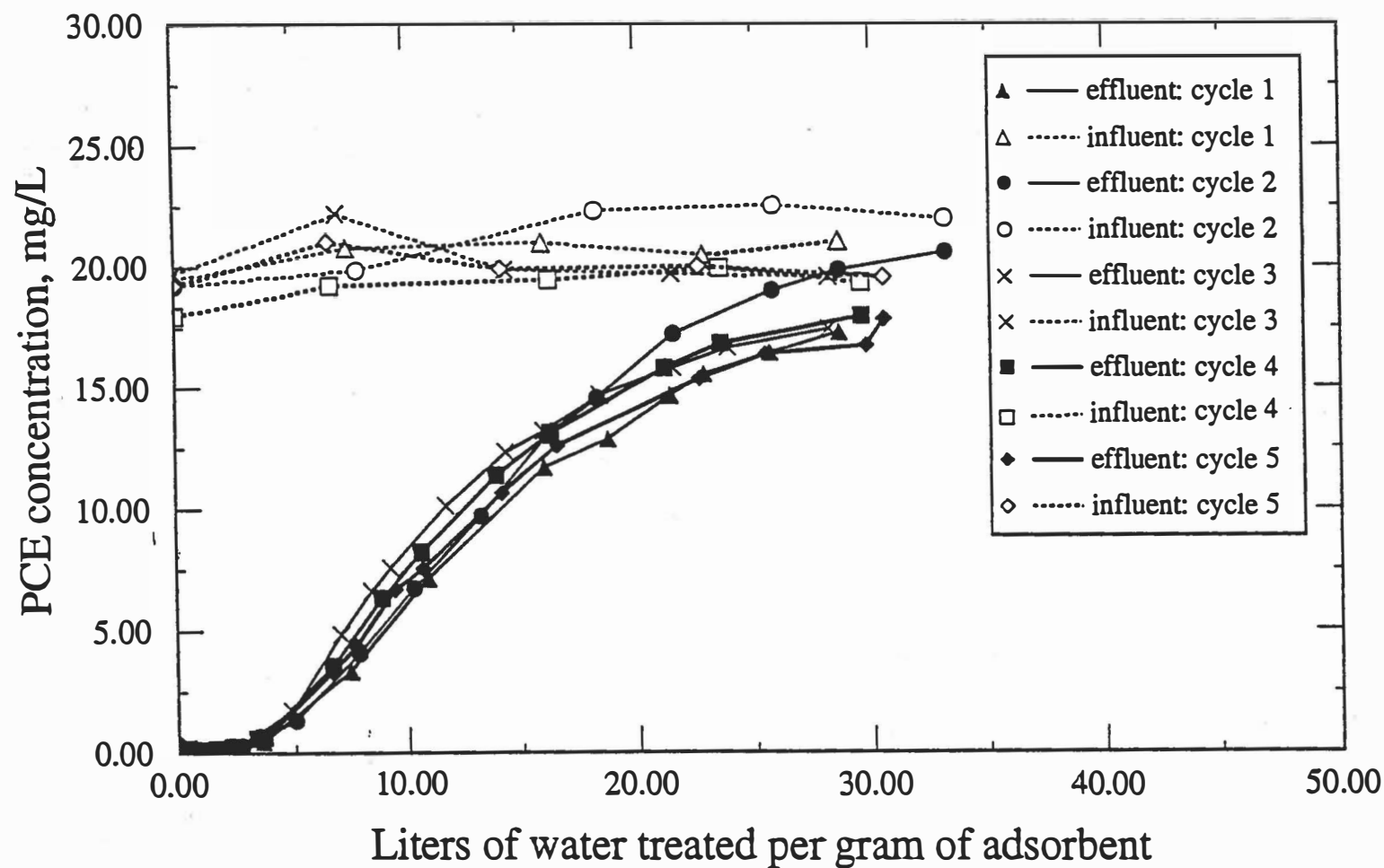


Figure 8. PCE adsorption profiles with virgin Ambersorb 563 adsorbent; virgin adsorbent mass: 6 gm.

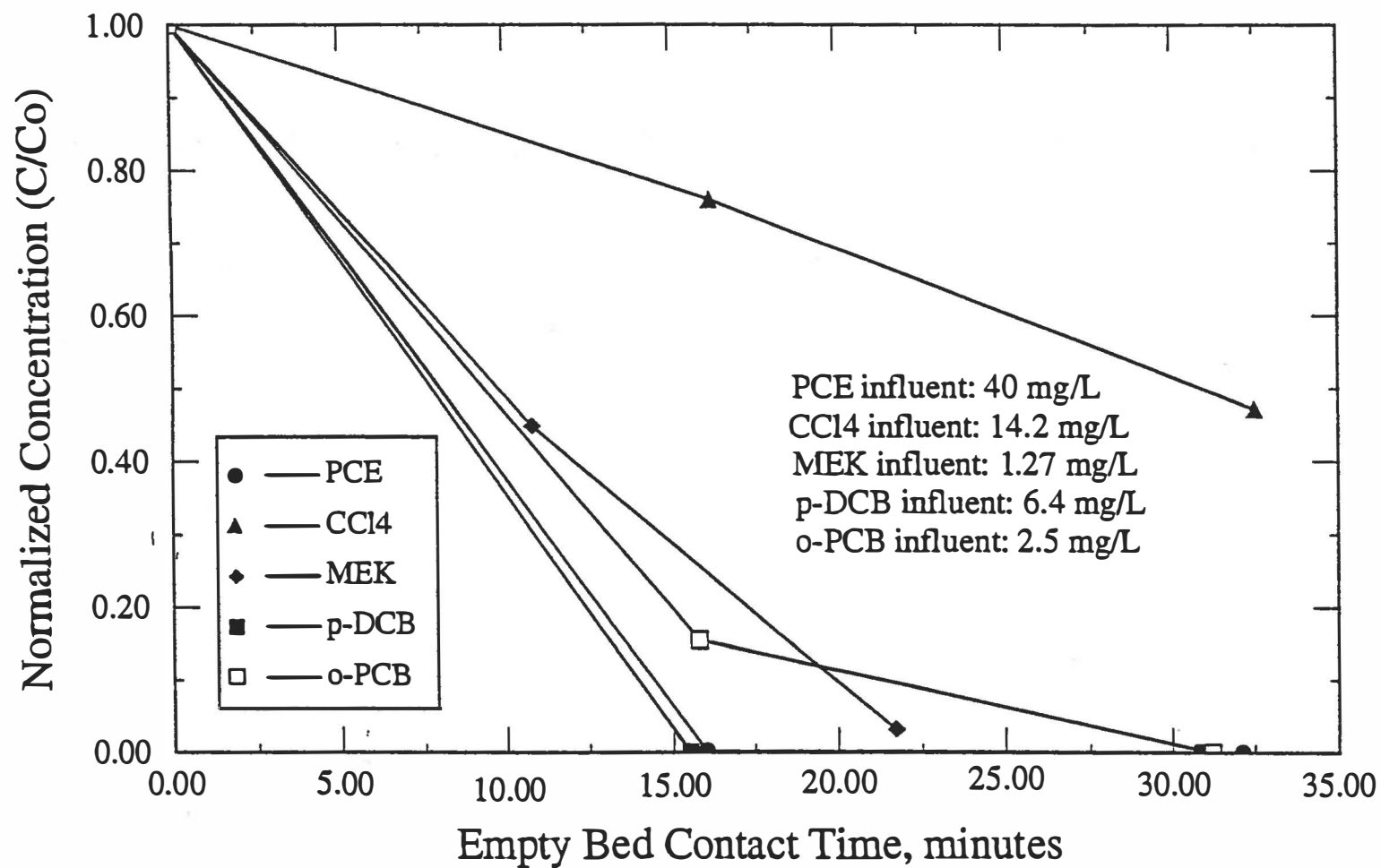


Figure 9. Photocatalytic destruction of organic compounds in water; reactor I.D.: 1.27 cm; used 2 reactors in series of 100 cm each; loading velocity for PCE, CCl_4 , p-DCB, o-PCB = 3.8 m/hours, and for MEK = 5.5 m/hour.

db941209 data

