Modeling of Tetrachloroethylene Degradation by Anaerobic Granular Biological Activated Carbon

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A number of different methods have been used for modeling the adsorption and biotransformation of volatile organic chlorinated compounds such as tetrachloroethylene perchloroethylene (PCE). In this study, PCE was degraded by granular biological activated carbon (GBAC) in an anaerobic Erlenmeyer flask reactor. In order to study GBAC, we performed experiments in which the efficiencies of GBAC, granular activated carbon (GAC) and anaerobic sludge for the removal of PCE were compared. In this paper, we describe how PCE was microbially biotransformed and adsorbed on GBAC. The biotransformational products were trichloroethylene (TCE) and *cis*-1,2-dichloroethylene (*cis*-1,2-DCE), which were adsorbed by GBAC (at solid phase). Thus, the GBAC acted not only as a microbiological carrier, but was also instrumental in adsorbing PCE and the biotransformation products. Since the adsorbed PCE was biotransformed on the GBAC, we concluded that GBAC might be effective in the treatment of PCE in synthetic wastewater. The model confirmed that the GBAC was involved in the degradation of PCE under our conditions. The model confirmed that the GBAC was instrumental in treating PCE.

Key words —— granular biological activated carbon, microbial transformation, tetrachloroethylene, volatile organic chlorinated compound, adsorption, biotransformation

INTRODUCTION

In recent years, the use of biological activated carbon (BAC), activated carbon, and anaerobic sludge for the removal of volatile organic chlorinated compounds from wastewater has been examined. In such studies, BAC has accomplished adsorption and biodegradation under aerobic or anaerobic conditions, and has thus received much attention. Volatile organic chlorinated compounds are a type of contaminant. We consider perchloroethylene (PCE) treatment using granular biological activated carbon (GBAC) under anaerobic conditions to be an essentially microbial process in which PCE is biotransformed into products which are subsequently adsorbed by the GBAC. The transformation process is very complex because GBAC is a composite particle of activated carbon with biotic components. However, the adsorption behavior in anaerobic BAC treatment of PCE remains unclear. Regarding analytic methods for GBAC, we consider it necessary to discuss the adsorption of GAC, the biotransformation of microorganisms, and the adsorption of GBAC.

When contaminants are removed by GBAC, two processes are involved: the first is adsorption due to activated carbon, and the second is biodegradation due to microbial activity, both of which are necessary. First, volatile organic chlorinated compounds such as PCE, TCE, *trans*-1,2-dichloroethylene, 1,1-dichloroethane, vinyl chloride, 1,1,1-trichloroethane and chloroform, which have been adsorbed by GAC,[1,2] are adsorbed by activated carbon. Experimental results also demonstrate that PCE and TCE could be adsorbed by GAC.

During the biotransformation step, some studies have shown that anaerobic biological processes can be used for dechlorination. Biodegradation can transform volatile organic chlorinated compounds to CO_2 and CH_4 under anaerobic conditions.[3] In addition, the anaerobic biotransformation of PCE to TCE, DCE, ethylene and ethane has also been reported.[4–6] Under aerobic or anaerobic conditions, chlorinated hydrocarbons can be fortuitously biotransformed via reductive dechlorination to produce a series of lower chlorinated homologues.

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Highly concentrated synthetic wastewater was treated by a column packed with anaerobic GBAC, and anaerobic biological activity combined with the adsorptive capacity of GAC was studied. It has been reported by Nakhla *et al*. that PCE is adsorbed by GAC and is biodegraded through transformation by anaerobic sludge.[7] A macroscopic partitioning model governed by microbial transformation was developed to elucidate the transport and fate of chlorinated hydrocarbons and microorganisms in porous media.[8] In an earlier paper,[9] we reported the degradation of TCE using a column packed with GBAC under an anaerobic condition.

The current study was conducted to investigate the influences of adsorption and biodegradation on GBAC in a batch system when PCE was degraded by anaerobic GBAC. A modeling study of the PCE concentration adsorbed with biotransformation products on the GBAC was also examined. By studying the desorption behavior of different molecules on the GBAC surface, changes in the concentrations of PCE and biotransformation products can be predicted. Additionally, the PCE would continue to be adsorbed from the synthetic wastewater, resulting in its further decrease. The PCE concentration in the GBAC is lower than that in synthetic wastewater. As the PCE would contribute to its adsorption from synthetic wastewater, resulting in its further decrease, this is instrumental to a PCE decrease. Simultaneous biotransformation products were also adsorbed by GBAC. This adsorption process was not simple because PCE, TCE and *cis*-1,2-DCE were present on the GBAC. The model in which PCE, TCE and *cis*-1,2-DCE change is key to the solid phase (GBAC) under anaerobic condition. The research for the distribution of PCE, TCE and *cis*-1,2-DCE between solution phase (synthetic wastewater) and solid phase (GBAC) revealed that the TCE and *cis*-1,2-DCE were adsorbed when PCE was biotransformed on the GBAC, and thus related PCE of the solid phase with PCE of the solution phase.

MATERIALS AND METHODS

Granular Biological Activated Carbon —— The GBAC used in this experiment was prepared from GAC and the supernatant liquid of anaerobic sludge. Both materials were mixed in an airtight anaerobic container for one day at 22°C.

The anaerobic sludge was obtained from the Kanagawa Prefectural Public Health Laboratories, Japan, and was cultured in the anaerobic state in the laboratory for six months.

The GAC was a carboniferous system Diahope S80 (Mitsubishi Chemical Co., Japan). The pore diameter size distribution was from 10 (Å) to 10^7 (Å) and the specific surface area was 1315 m^2/g (BET): particle size ranged from 1 mm to 2 mm. The GAC was washed with boiling distilled water for 30 min to remove, then dried at 110°C for 24 h and stored in an airtight container at room temperature.[10]

Synthetic Wastewater —— The components of the synthetic wastewater were aqueous PCE solution and nutrient salts. The initial PCE concentration was 152.2 μg/l. The nutrient salts contained 32 mg of potassium dihydrogenphosphate (Kanto Chemical Co., Japan, [G]), 9 mg of urea (Wako Pure Chemical Co., Japan, [G]) and 238 mg of saccharose (Wako Pure Chemical Co., Japan, [G]), solubilized with one litre distilled water, and the pH was 6.2–6.4.

Experiments on the biotransformation by anaerobic sludge, adsorption using GAC and degradation using GBAC were conducted at 22°C, and the samples were filtered through a 0.45 μm membrane filter.

Experiment on Biotransformation by Anaerobic Sludge —— Fifty ml of anaerobic sludge and 100 ml of synthetic wastewater were added to a 200 ml Erlenmeyer flask. In the supernatant liquid of the raw anaerobic sludge, the PCE concentration was 0.038 μg/l, and TCE and *cis*-1,2-DCE were not detectable. Analysis was performed on the supernatant liquid and on hexane extracts of the anaerobic sludge.

Adsorption Experiment Using GAC —— The Erlenmeyer flask was filled with 10 g of GAC and 100 ml of synthetic wastewater. The analytical samples were supernatant liquid and the extractive solvent, hexane, with which GAC received extraction treatment.

Experiment on Degradation Using GBAC —— The Erlenmeyer flask was filled with 10 g of GBAC and 100 ml of synthetic wastewater. The analytical samples were of two types: one was supernatant liquid and the other was an extractive solvent, hexane, with which GBAC received extraction treatment.

Analytical Method —— The PCE, TCE and *cis*-1,2-DCE concentrations were determined using gas chromatography/mass spectroscopy (GC/MS-QP-5000, Shimadzu Co., Japan). GC was performed using a He carrier (130 kPa). Column temperature programming was as follows: 40°C for 2 min; 6°C/min for 10 min to 100°C; 10°C/min for 4 min to

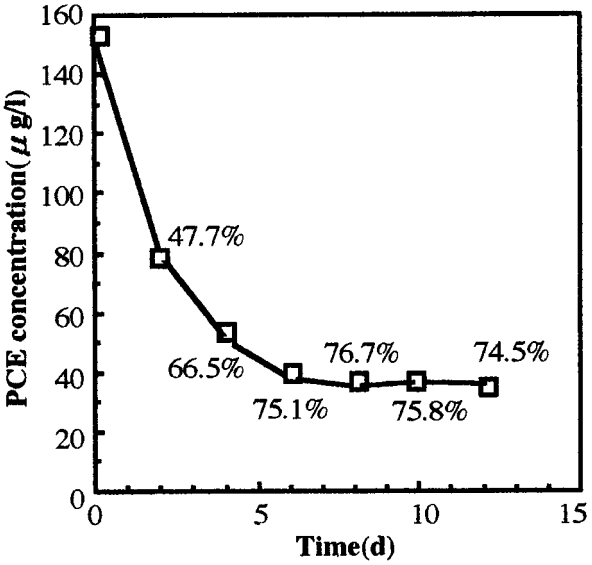

Fig. 1. Course of PCE Adsorption in GAC
Initial concentration is 152.2 μg/l: data % is rate of removal.

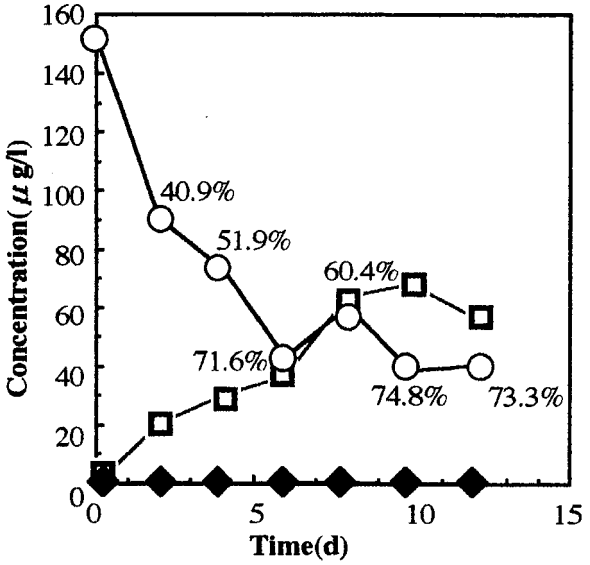

Fig. 2. Course of PCE, TCE and *cis*-1,2-DCE Biotransformation in Anaerobic Sludge
○, PCE; ♦, TCE; □, *cis*-1,2-DCE, Initial PCE concentration is 152.2 μg/l: data % is rate of removal.

140°C; 6°C/min for 7.5 min to 185°C: and finally 15°C/min to the final temperature of 220°C. The calibration software was CLASS-5000 (Shimadzu Co., Japan). Standard stock solution of volatile organic compounds was solution I (Kanto Chemical Co., Japan). Three g of sodium chloride (Kanto Chemical Co., Japan, [G]) before measurement was dissolved into a 10 ml aqueous sample. The analytical method was based on Japanese Industrial Standards (JIS K 0125).

RESULTS AND DISCUSSION

Adsorption of PCE by GAC

As PCE is known to be adsorbed by GAC, which in turn is a component of GBAC, we anticipate a correlation between the adsorption characteristics on these adsorbents. The decrease in PCE concentration in the presence of GAC under anaerobic conditions is shown in Fig. 1. The experiment was conducted for fourteen days. The breakthrough point occurred on the eighth day. The adsorptive rate of derivation was 76.7% at the breakthrough point. In adsorbed synthetic wastewater, only PCE was present (no TCE or *cis*-1,2-DCE). The PCE was decreased solely through adsorption of a single molecule (PCE) from synthetic wastewater by GAC. These results demonstrated that PCE was adsorbed by GAC, and therefore that PCE could be adsorbed by GBAC.

Biotransformation of PCE by Anaerobic Sludge

The biotransformation by microorganisms on GBAC is another way in which PCE is removed by GBAC, because GBAC is a composite particle of activated carbon with biotic components. Therefore, the used GBAC removes PCE in close relationship with biotransformation. The decrease in PCE concentration under anaerobic conditions is shown in Fig. 2. The biotransformation rate of derivation was 60.4% on the eighth day. The maximum biotransformation rate over twelve days was 74.8%, and the minimum was 40.9%. The variability in biotransformation of PCE is related to the microorganism activity in the anaerobic sludge. The biotransformation products of PCE were TCE and *cis*-1,2-DCE, which occurred with an increase in *cis*-1,2-DCE concentration as the PCE concentration degraded. The TCE concentration (average 0.307 μg/l) is lower than the others, because the TCE is inter-medium from PCE to *cis*-1,2-DCE. The results demonstrated that PCE was biotransformed by microorganisms. It is presumed that PCE may be biotransformed in GBAC.

Decrease of PCE by GBAC

The decrease in PCE concentration in an anaerobic Erlenmeyer flask packed with a GBAC is shown in Fig. 3. The removal of PCE by GBAC under anaerobic conditions is shown in Fig. 3. The removal rate of derivation is 85.3% on the eighth day. The maximum removal rate is 91.5% and the minimal is

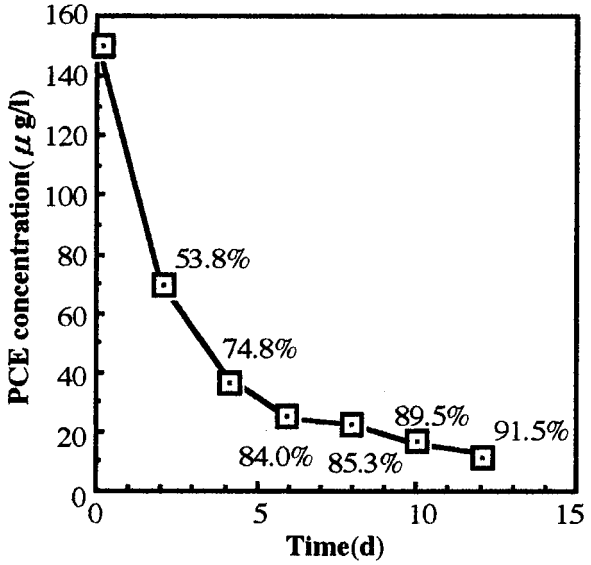

Fig. 3. Course of PCE Decrease in GBAC
Initial concentration is 152.2 μg/l: data % is rate of removal.

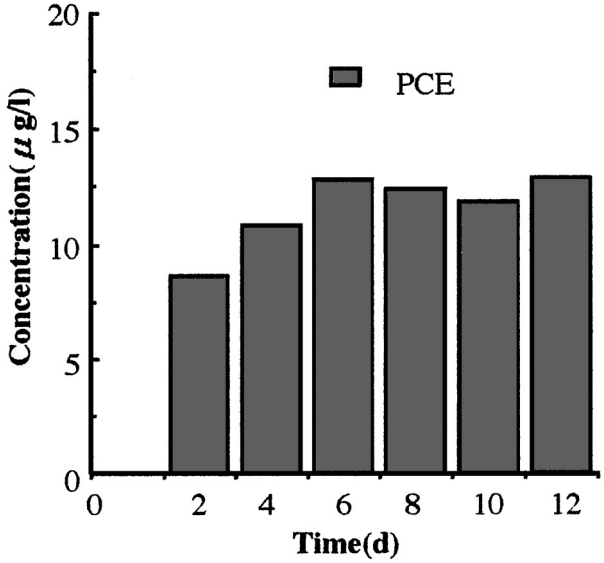

Fig. 4a. Course of PCE on Adsorbed GAC
The sample is extracted by hexane.

53.8% for fourteen days. The observed PCE removal rate was greater in the GBAC than in either the GAC or in the anaerobic sludge. TCE and *cis*-1,2-DCE were not detected in the wastewater. Both, however, may be adsorbed by GBAC.

The PCE decrease caused by GBAC may have been due to both biodegradation and adsorption of PCE. In the samples at that time, PCE was present in synthetic wastewater, but neither TCE nor *cis*-1,2-DCE occurred, because those were adsorbed on the GBAC, though both adsorptions were not the same: one is the single molecular adsorption of PCE from synthetic wastewater (from aqueous phase to solid phase), and the other is the adsorption of TCE and *cis*-1,2-DCE from more molecules on the GBAC (at solid phase), considering that both the adsorption of PCE and the adsorption of biotransformation products (TCE and *cis*-1,2-DCE) were simultaneous. The adsorptive capacity of GBAC is higher than that of GAC because of the presence in GBAC of the biological matrix.[11] Although PCE is adsorbed by GAC, the adsorption decreases with contact time, and an equilibrium state arises. But this saturation only involves PCE, because the adsorptive capacity of GAC does not encompass all. For overall utilization of the adsorptive capacity, PCE concentration was decreased by the GBAC because PCE was biotransformed into TCE and *cis*-1,2-DCE, and the molecular size and molecular weight of these compounds are not the same. The PCE was biotransformed in a range of microbial activity from large to low, or from more chloride to less on GBAC. The low molecule will fit best wherever GBAC is present so that it can extend over using time or adsorptive capacity as usefully as possible. GAC and GBAC were not the same. The GAC adsorbs only PCE in synthetic wastewater. However, the GBAC adsorbs both PCE and biotransformation products (TCE and *cis*-1,2-DCE) in synthetic wastewater. Though Weber *et al*. have conducted a simulation and designed models for adsorption processes, they have not thought of the lump single compound system with more complex systems.[12] In general, the adsorption of complex matters is lower than that of a single matter, and this is attributed to adsorption competition. This is an important point regarding PCE, TCE and *cis*-1,2-DCE, and also regarding GBAC, because the products of biotransformation affect the adsorption of PCE by GBAC.

Distribution of PCE and *cis*-1,2-DCE in the Solid Phase

Hexane extractions were done on GAC, anaerobic sludge and on the GBAC samples discharged from the PCE degradation experiment. This experiment was performed to confirm that the PCE was biotransformed into *cis*-1,2-DCE, which remained adsorbed on the GBAC.

The experimental results are shown in Fig. 4a, Fig. 4b and Fig. 4c. Figure 4a shows that only PCE was present in the case of GAC. This means that PCE was adsorbed by GAC, and the adsorbed PCE was not biotransformed to TCE or *cis*-1,2-DCE, because there was no anaerobic sludge on the GAC.

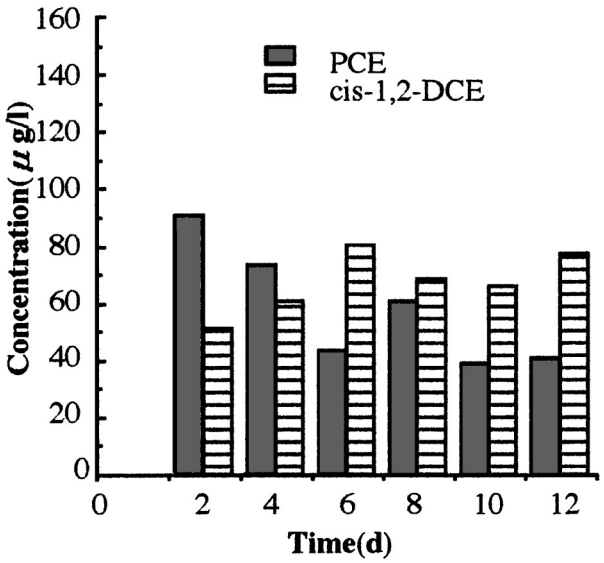

Fig. 4b. Course of PCE and *cis*-1,2-DCE on Biotransformed Anaerobic Sludge
The sample is extracted by hexane.

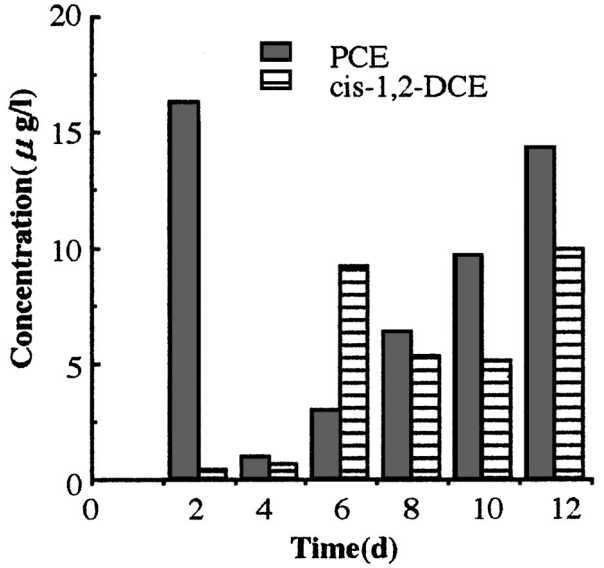

Fig. 4c. Course of PCE and *cis*-1,2-DCE on Decreased GBAC
The sample is extracted by hexane.

Figure 4b shows that PCE and *cis*-1,2-DCE were present in the case of anaerobic sludge. Figure 4c shows that PCE and *cis*-1,2-DCE were also present in the case of GBAC. The average concentration of PCE in the case of GBAC was higher than *cis*-1,2-DCE, because the PCE contained both the remaining part for nonbiotransformation and the re-adsorption part from synthetic wastewater. The result demonstrated that PCE could be biotransformed and adsorbed on the GBAC.

In Fig. 4b and Fig. 4c, TCE was not detected. It may be that the TCE concentration on the anaerobic sludge or the GBAC was too low to be detected.

The data in Fig. 4a, Fig. 4b and Fig. 4c are qualitative. The PCE and *cis*-1,2-DCE were not quantitative because hexane cannot extract PCE, TCE and *cis*-1,2-DCE completely from the solid phase.[13] However, it is feasible to use the method to predict changes in PCE and *cis*-1,2-DCE in the solid phase.

Model

The experimental results demonstrated that PCE could be degraded by GBAC. Anaerobic bio-sorption is mainly a physico-chemical process.[14] The quantity of PCE adsorbed or biotransformed on the GBAC were unknown until this current work. In this paper, a mathematical model is developed to investigate the interaction between the adsorption and biodegradation of PCE on GBAC.

A comprehensive equation has been developed to determine the PCE quantity adsorbed (or remaining) and the quantity biotransformed, based on the total quantity, which is the remaining PCE total quantity (R_n) and the biotransformed PCE total quantity (B_n). The equation is derived using the summation formula as follows:

$$S = a_1(1 - q^n) / 1 - q \quad (0 < q < 1),$$

Where S is the sum, a_1 is the first term of the geometric progression, and q is the common ratio of the geometric progression. On the GBAC, R_n and B_n are described by the following equation (1) and (2).

$$\begin{aligned} U_1 &= (C_1 - C_1k) + [(C_1 - C_1k) - (C_1 - C_1k)k] \ ..... \\ &= C_1(1-k) + C_1(1-k)^2 + ... + C_1(1-k)^n \\ &= C_1(1-k)\,[1-(1-k)^n] / k \end{aligned}$$

The others are described as follows:

$$U_2 = C_2\,(1-k)\,[1-(1-k)^n] / k$$

$$U_n = C_n\,(1-k)\,[1-(1-k)^n] / k$$

Where U_1 is total quantity of C_1 remaining, U_2 is total quantity of C_2 remaining, and U_n is total quantity of C_n remaining.

$$R_n = U_1 + U_2 + ... + U_n$$

$$R_n = (C_1 + C_2 + ...+ C_n)\,(1-k)\,[1-(1-k)^n] / k \quad (1)$$

$$\begin{aligned} P_1 &= C_1k + (C_1 - C_1k)k \\ &\quad + [(C_1 - C_1k) - (C_1 - C_1k)\,k]\,k \ ..... \\ &= C_1k + C_1(1-k)k + C_1(1-k)^2k .....+ C_1(1-k)^nk \\ &= C_1[1-(1-k)^n] \end{aligned}$$

The others were described as follows:

$$P_2 = C_2\,[1-(1-k)^n]$$

$$P_n = C_n\,[1-(1-k)^n]$$

Where P_1 is the total quantity of C_1 biotransformed, P_2 is total quantity of C_2 biotransformed, and P_n is total quantity of C_n biotransformed.

$$B_n = P_1 + P_2 + ... + P_n$$

$$B_n = (C_1 + C_2 + ...+ C_n)\,[1-(1-k)^n] \quad (2)$$

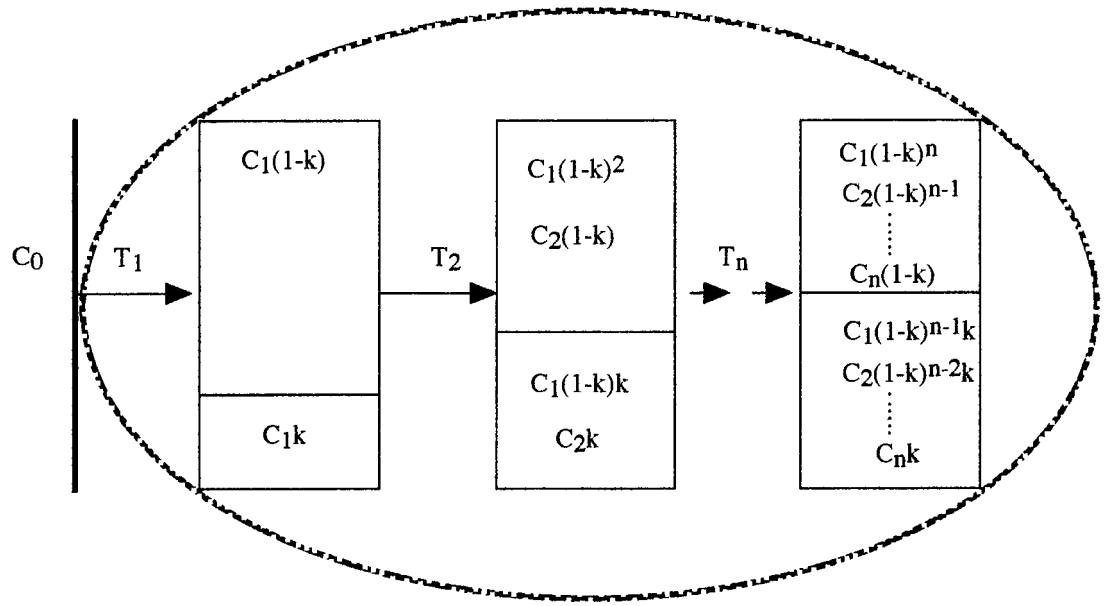

Fig. 5. Model of Adsorption and Biotransformation of PCE on the GBAC
C_0: PCE quantity in synthetic wastewater
T_n : Time
k : Biotransformation PCE coefficient on GBAC
C_1: At T_1, adsorption PCE quantity by GBAC from synthetic wastewater
C_1k: At T_1, biotransforming PCE quantity on GBAC
$C_1(1-k)$: At T_1, PCE remaining quantity of C_1 on GBAC
C_2: At T_2, adsorption PCE quantity by GBAC from synthetic wastewater
C_2k: At T_2, biotransforming PCE quantity on GBAC
$C_2(1-k)$: At T_2, PCE remaining quantity of C_2 on GBAC
C_n: At T_n, adsorption PCE quantity by GBAC from synthetic wastewater
C_nk: At T_n, biotransforming PCE quantity on GBAC
C_n(1-k) : At T_n, PCE remaining quantity of C_n on GBAC

The decrease in total PCE quantity (S_n) is described by the following equation (3):

$$S_n = R_n + B_n$$
$$S_n = (C_1 + C_2 + \ldots\ldots + C_n)\,[1 - (1-k)^n] / k \quad (3)$$

equation (1) / equation (3) is $R_n = (1-k)S_n$ (4)

equation (2) / equation (3) is $B_n = k\,S_n$ (5)

Where, C_1, C_2, C_n and k of equations (1)–(5) are defined in Fig. 5, and k ($0 < k < 1$) was the assumed condition in which the biotransformation PCE coefficient was a constant (or a mean-value). From equation (4) and equation (5), then,

$k = 0.5 \rightarrow B_n = R_n$,
$k > 0.5 \rightarrow B_n > R_n$, $k < 0.5 \rightarrow B_n < R_n$

For simplicity, R_n is related to B_n by the following equation (6):

equation (4) / equation (5) is $R_n = (1/k - 1)B_n$ (6)

In addition, the removal ratio of PCE (X%) is described by the following equation (7):

$$(X\%) = C_0 - C_r \;/\; C_0$$
$$= S_n / C_0 \quad (7)$$

From equation (4) and equation (5) into equation (7), where C_0 is PCE initial quantity, and C_r is remaining PCE quantity in synthetic wastewater, X% is related to R_n, B_n and k by the following equation (8):

$$(X\%) = R_n / (1-k)\,C_0 = B_n / k\,C_0 \quad (8)$$

B_n can be obtained from the experiment of Kimura *et al.* ($B_n = Q_1 - Q_2$), where Q_1 is the equilibrium adsorption quantity, Q_2 is the adsorptional quantity after bio-regeneration. X% can also be obtained from the experiment. Therefore, R_n and k can be determined.[15] The model above indicates that biodegradation plays a prominent role in GBAC.

We have made several attempts to understand the underlying processes, and reproducible results have been nearly obtained in some cases when microorganisms were tightly attached to activated carbon.

However, it is difficult to delineate different model variants because of microorganism exfoliation.

We are currently reexamining mechanisms of microorganism exfoliation in an attempt to incorporate these aspects into our model.

The main conclusions of this study can be summarized as follows:

1. PCE degradation using GBAC was more efficient

than with GAC or extended treatment with anaerobic sludge.

2. The adsorption by GBAC was lower than that by GAC in the earlier stage: with GBAC, adsorption is competetive because the PCE was biotransformed to *cis*-1,2-DCE, *etc*. This means that the adsorption type changed from single molecule adsorption to multi molecule adsorption.

3. A mathematical model demonstrated that when $k > 0.5$, the amount of PCE on the GBAC is low, and therefore, the amount of PCE adsorbed from synthetic wastewater is enhanced. Conversely, when $k < 0.5$, the quantity of PCE is higher on the GBAC, and therefore the amount of PCE adsorbed from synthetic wastewater is reduced.

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