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Anaerobic Degradation of Tetrachloroethylene Using Different Co-substrates as Electron Donors[1]

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Objective To investigate the biodegradation of tetrachloroethylene (PCE) by acclimated anaerobic sludge using different co-substrates, i.e., glucose, acetate, and lactate as electron donors. **Methods** HP-6890 gas chromatograph (GC) in combination with auto-sampler was used to analyze the concentration of PCE and its intermediates. **Results** PCE could be degraded by reductive dechlorination and the degradation reaction conformed to the first-order kinetic equation. The rate constants are $k_{lactate}>k_{glucose}>k_{acetate}$. The PCE degradation rate was the highest in the presence of lactate as an electron donor. **Conclusion** Lactate is the most suitable electron donor for PCE degradation and the electron donors supplied by co-metabolic substrates are not the limiting factors for PCE degradation.

Key words: Tetrachloroethylene (PCE); Co-metabolic substrate; Biodegradation; Electron donor

INTRODUCTION

With the development in economy, urban industrialization and improvement of the people's living standard, municipal and industrial wastewater is increasingly released into the environment. Chlorinated organic compounds are widely used in electronics, paper making, dry cleaning, and degreasing industries. The chlorinated solvent, tetrachloroethylene (PCE), is one of the most ubiquitous compounds. A nationwide survey revealed that 2.3% of PCE in 590 000 water samples can not meet the drinking water standard in Japan[1]. It has been shown that 61% of PCE is detected from the toxic landfill liquids collected from 1984 to 1991 in USA[2]. Chlorinated aliphatic organic compounds are produced at 2000 million tons each year, and PCE is one of the highest chemicals produced[3]. Due to extensive use, PCE has become one of the most common pollutants in the environment. In general, natural attenuation of PCE is very slow and PCE usually can be metabolized by microorganisms. Recent reports are focused on PCE degradation using glucose, acetate, and lactate as cometabolic substrates[4-6], yet the degradation rate is different between different co-metabolic substrates. Thus, it is difficult to determined which co-metabolic substrate is the most suitable electron donor. Though recent studies indicate that PCE degradation coincides with the first order kinetics, the concretely regression analytical results are not offered.

The objective of this study was to examine the most suitable electron donor and to compare the reaction rate constant for degradation of PCE.

MATERIALS AND METHODS

Synthetic Wastewater

Cultivated sludge was acclimated in an intermittent mode, and then PCE degradation experiment was conducted. Synthetic wastewater was used in this study. Inorganic solution consisted of 0.32 NH_4Cl, 0.063 KH_2PO_4, 0.063 $CaCl_2$, 0.1316 Na_2CO_3, (g/L) and 0.5 mL of the trace element solution was added to each liter of the inorganic solution. Trace element solution comprised 5000 $MgSO_4{\cdot}7H_2O$, 6000 $FeCl_2{\cdot}4H_2O$, 1036.88 $CoCl_2{\cdot}6H_2O$, 100 H_3BO_3, and 640 $ZnSO_4{\cdot}7H_2O$ (g/L). The concentrations of

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lactate sodium, acetate sodium, and glucose as co-metabolic substrates were 0.77 g/L, 6.8 g/L, and 1 g/L, respectively.

Experimental Procedures

Four hundred mL of the acclimated sludge was put into 700 mL reactor sealed with a Teflon-coated silicon cap. The reactor was subsequently filled with dissolved co-metabolic substrates from inorganic solution, trace element solution and PCE stock solution. The total volume of the mixed liquor was 650 mL and the bottle was capped quickly. The schematic diagram of experimental apparatus is shown in Fig. 1.

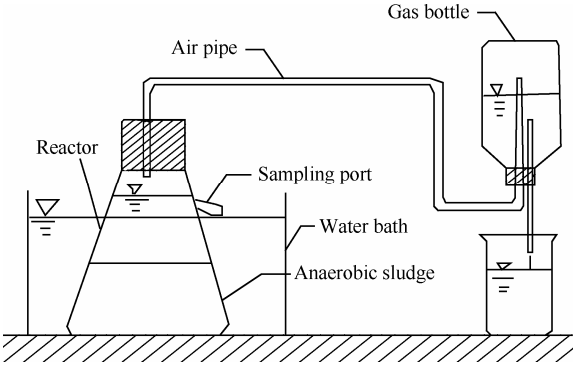

FIG. 1. Schematic diagram of the experimental apparatus.

When the liquor and sludge were well mixed in a steady state for 20 minutes, the content of chlorinated hydrocarbons in the supernatant was measured. PCE and its metabolic intermediates were measured. Then 0.4 mL liquor sample was taken by a glass syringe from sampling port and filled into HP headspace glass with a serum-coated Teflon. The concentration of PCE was determined by the headspace method using gas chromatography.

Analytical Methods

HP-6890 gas chromatograph (GC) with a HP-7694 auto-sampler was used. The concentration of PCE was determined by the headspace method using gas chromatography. The inlet temperature was set at 160℃. The flow rate of chromatographic column was 1.0 mL/min. The initial temperature in GC oven was 70℃, which was maintained for 10 min. The ECD temperature was controlled at 300℃. In headspace, glass temperature was 50℃ and loop temperature 60℃. The equilibrium time was 10 min and injection time 1.00 min. Nitrogen was used as carrier gas at a rate of about 30 mL/min (GB11890-89, 1996). The limit of detection for PCE was 0.05 μg/L.

RESULTS AND DISCUSSION

Degradation of PCE

The microbial degradation of PCE is depicted in Fig. 2. The initial concentration of PCE was 440-480 ug/L. Sodium lactate, glucose, and sodium acetate were used as co-substrates, separately. The removal rate of PCE was relatively high. More than 90% of PCE was removed when lactate or glucose was used as a co-substrate for 3 days, while the removal rate was relatively low when acetate was used as a co-substrate. Only about 77% of PCE was removed on the third day and 85% on the fifth day. The experimental results also revealed that PCE could not be degraded without addition of co-substrates.

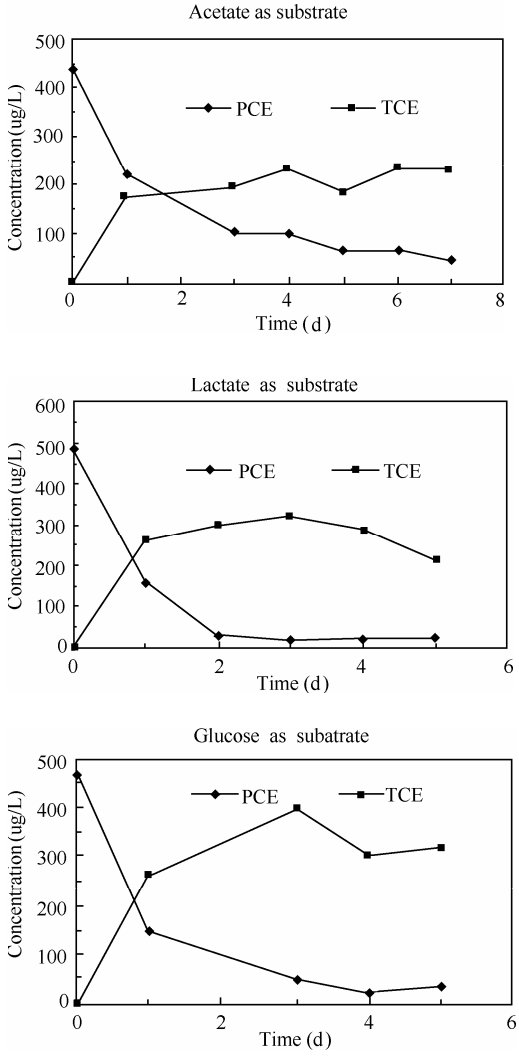

FIG. 2. PCE and its dechlorination products in the experiment.

Trichloroethylene (TCE) was generated during

PCE degradation. From the first two reactions, TCE concentration increased gradually at first and then declined, which probably resulted from TCE reduction. The results indicated that the degradation of PCE was due to reductive dechlorination, being consistent with the previous study[8]. DCEs were not detected in our experiment. According to the previous study, PCE might be transformed into nonchlorinated co-mpounds[9].

Co-metabolic Substrates

In PCE degradation, co-metabolic substrates were the actual electron donors for PCE reductive dechlorination. The changes of co-metabolic substrates in the entire experimental period are presented in Fig. 3.

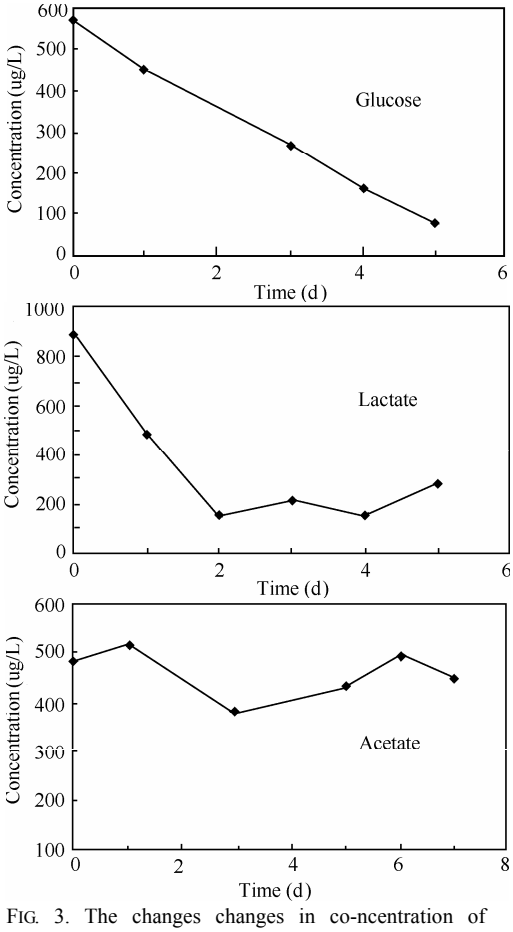

FIG. 3. The changes changes in co-ncentration of co-metabolic substrates.

A significant decrease of glucose and lactate showed that the degradation of PCE occurred simultaneously with the degradation of co-metabolic substrates used as electron donors. While in the case of acetate, the change in acetate was relatively slow. Except for a difference in initial PCE concentrations, the fewer electrons donated might contribute to the lower removal of PCE. According to the half-reaction equations of glucose, acetate, and lactate, Table 1 shows the relationship between consumed co-metabolic substrates and the amount of generated hydrogen and degraded PCE.

Hydrogen generated in the experiment was sufficient to drive the dechlorination of PCE to ethane. The extent and rate of PCE degradation were related to the metabolic capability of microorganisms. The electrons supplied by co-metabolic substrates were sufficient to dechlorinate PCE, indicating that this step was not a limiting factor of PCE degradation. It was possible that decreased microorganism population could dechlorinate PCE in the sludge to limit PCE degradation. But it requires further study.

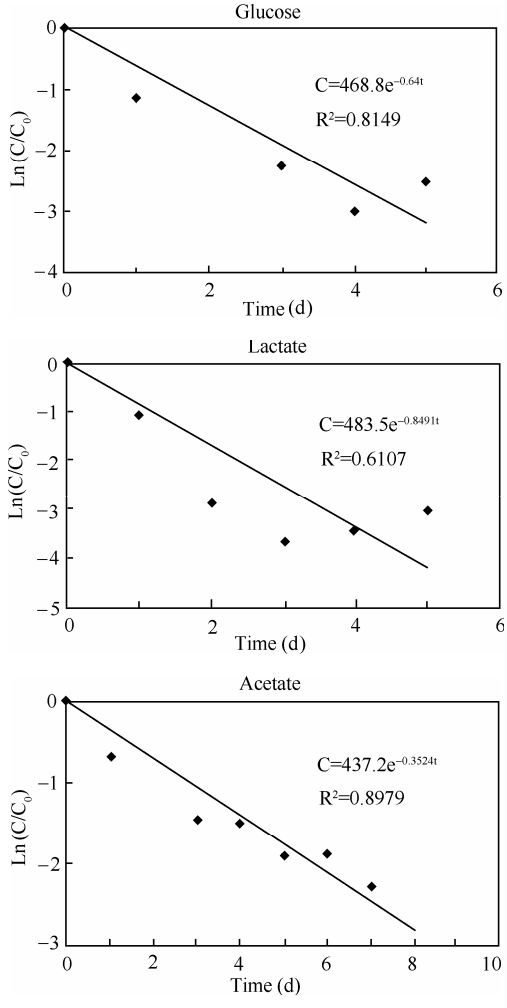

FIG. 4. Regression results Ln (C/C_0)-t.

Kinetics of PCE Degradation

PCE degradation was analysed and the corresponding kinetic equations are shown in Fig. 4 and Table 2.

TABLE 1

Relationship Between Co-substrates, PCE Concentration and Hydrogen

	Co-substrates (mmol/L)		PCE (μmol/L)		Hydrogen Generated	Hydrogen in Theory
	Initial	Consumed	Initial	Consumed	(mmol/L)	(μmol/L)
Glucose	3.18	2.76	2.91	2.67	1.1	10.68
Lactate	7.97	5.5	3.0	2.86	11.0	11.44
Acetate	5.87	0.41	2.72	2.44	1.64	9.76

TABLE 2

Kinetic Parameters of PCE Degradation

Co-substrate	Rate Constant (d^{-1})	Half-life (d)	Degradation Equation	R^2
Glucose	0.64	1.08	$C=468.8e^{-0.64t}$	0.8149
Lactate	0.82	0.82	$C=483.5e^{-0.8491t}$	0.6107
Acetate	0.35	1.97	$C=437.2e^{-0.3524t}$	0.8979

The results showed that the degradation of PCE conformed to the first-order kinetic equation, being consistent with that of Valter Tandol *et al*.[7]. In comparison with these results, we can find that the rate constant is $k_{lactate}>k_{glucose}>k_{acetate}$, indicating that the dechlorination rate of PCE using lactate as an electron donor is 2-fold higher than that using acetate as an electron donor, being consistent with that of Gao *et al*.[4]. However, Ndon *et al.* [6] found that the dechlorination rate of PCE using acetate as an electron donor is higher. The difference may be attributed to the environment of microorganisms, which needs further study. From this study, it seems that lactate is the most suitable co-substrate for degradation of PCE.

CONCLUSIONS

The following conclusions can be drawn based on the results of the experiment.

(1) The removal efficiency of PCE using lactate and glucose as electron donors is higher than that using acetate as an electron donor.

(2) The degradation of lactate and glucose as co-substrates is faster than that of acetate under the sufficient electron donor to dechlorinate PCE.

(3) The degradation rate of PCE using lactate and glucose as electron donors is higher than that using acetate as an electron donor. The rate constant is $k_{lactate}>k_{glucose}>k_{acetate}$, showing that lactate is the suitable electron donor in this study.

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