Reductive dechlorination versus adsorption of tetrachloroethylene in fluidized-bed reactors

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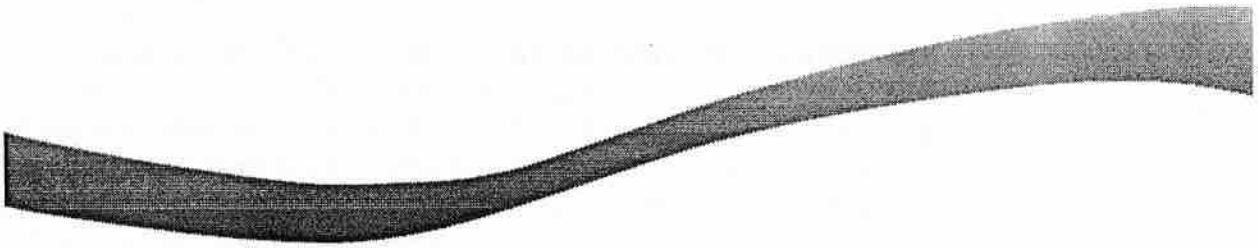

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REDUCTIVE DECHLORINATION VERSUS ADSORPTION OF TETRACHLOROETHYLENE IN FLUIDIZED BED REACTORS

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ABSTRACT: In this study, the PCE treatment efficiency of two anaerobic fluidized bed reactors (AFBRs) were investigated and compared under different hydraulic loads. Granular activated carbon (GAC) and Biolite™ were used as a support media in the first and second reactor, respectively. The results showed that the GAC AFBR achieved close to 100% PCE removal under all the loading conditions studied. Both adsorption and dechlorination accounted for this total PCE removal. With the exception of one hydraulic loading, adsorption was the main PCE removal mechanism for the duration of this investigation for the GAC reactor. The maximum PCE removal efficiency achieved by the Biolite™ AFBR was approximately 70%. Dechlorination was the only removal mechanism for this reactor. The highest specific chloride ion production rate for both reactors was achieved under the lowest loading condition and methanol activity.

INTRODUCTION

Tetrachloroethylene (also known as perchloroethylene, PCE) is one of the volatile organic compounds which is most frequently detected in groundwaters used as drinking water sources. In addition to being used as dry cleaning-solvent and as a degreaser, PCE also serves as a starting material for other man-made chemicals such as fluorocarbons. Agencies worldwide have classified PCE as being possibly carcinogenic.

It has been demonstrated that PCE can be reductively dehalogenated under methanogenic conditions (De Bruin *et al.*, 1992). In this process, PCE, the electron acceptor, is sequentially reduced to TCE, DCE isomers (*cis*-1,2-DCE, *trans*-1,2-DCE, or 1,1-DCE), VC, ethylene and ethane. An electron donor such as methanol, acetate, or hydrogen must be available to provide reducing equivalents for reductive dechlorination and for cell growth.

The anaerobic fluidized bed reactor (AFBR) has been shown to rapidly and efficiently degrade PCE (Carter and Jewell, 1993). Many parameters such as the hydraulic retention time (HRT), the organic load and the supporting media used for cell immobilization influence the PCE treatment efficiency and still need to be investigated in order to optimize treatment efficiency. These variables form the basis for this research.

The objective of this study is to investigate the ability of an anaerobic fluidized bed reactor to dechlorinate PCE using two different supporting media; granular activated carbon (GAC) and Biolite™ (particles of expanded clay). The

performance of each reactor was assessed by evaluating overall PCE removal. For the GAC anaerobic fluidized bed reactor, the role played by adsorption in the total PCE removal was also examined. The details of this research are provided in Marcoux (1997).

MATERIALS AND METHODS

Parallel experiments were performed using two separate AFBRs, reactor 1 (R1) and reactor 2 (R2), operating simultaneously at 35°C. The AFBRs were glass columns with cone-shaped inlets and with working volumes of 15.8 L. A recycling line ensured the fluidization of the bioparticles. Granular activated carbon (GAC) (Sigma, St-Louis, MO) and Biolite™ (Degrémont, France) were used in R1 and R2, respectively. The specific gravity of GAC and Biolite™ equalled 1.64 g/g and 2.10 g/g, respectively. For the GAC AFBR and Biolite™ AFBR, the upflow velocities equalled 4.02 m/hr and 7.95 m/hr, respectively. These upflow velocities resulted in an initial static bed expansion of 30% and were kept constant throughout the entire experiment. A nutrient solution and PCE-methanol solution were fed to each reactor.

Anaerobic sludge used for inoculating the reactors was obtained from a food industry (Champlain Industries, Cornwall, Ontario). Methanol served as the electron donor and as the carbon source for the microorganisms. The methanol:PCE mass concentration ratio was kept constant at 10:1 for the entire experiment. The influent PCE and methanol concentrations were equal to 10 mg/L and 100 mg/L, respectively.

PCE, TCE, DCEs and VC in the effluent were analyzed using the GC headspace method. In the off gas, concentrations of PCE and its metabolites were determined using a gas chromatograph and FID. The inorganic chloride concentration in the effluent was measured using the Hach Mercuric Thiocyanite Method and a Hach DR/3000 spectrophotometer set at 455 nm. The methanol concentration in the reactors and during the activity test was determined using a gas chromatograph and FID.

This study was divided in four phases. The only variable parameter was the HRT. It varied from 24 hrs (phase 1), to 48 hrs (phase 2), to 12 hrs (phase 3), and to 18 hrs (phase 4). The duration of each phase was determined by the time taken by each reactor to reach steady-state in terms of inorganic chloride and aqueous PCE concentration. The entire experiment lasted 130 days.

RESULTS

During PCE addition, the methanol activity for both reactors was highest at a HRT of 0.75 day and lowest at a HRT of 2 days. The methanol activity was lower at a HRT of 0.5 day than at a HRT of 0.75 day for both reactors.

Figure 1 shows the variation of the percentage of total PCE removed with respect to the hydraulic retention time of each phase. The removal of PCE and its metabolites by escaping into the gas phase represented less than 1% for both reactors during all HRTs except for the Biolite™ AFBR (R2) at a 0.5 day HRT where it approximately equalled 2% of the total PCE removal. TCE was the only

metabolite present in measurable quantities in the reactors' effluent with a maximum value of 0.99 mg/d in the Biolite™ reactor. For the GAC AFBR (R1), the total PCE percentage removal was greater than 99.3% for each HRT. For the Biolite™ AFBR, the total PCE percentage removal reached a maximum value of 69.5 ± 13.1% at a HRT of 2 days.

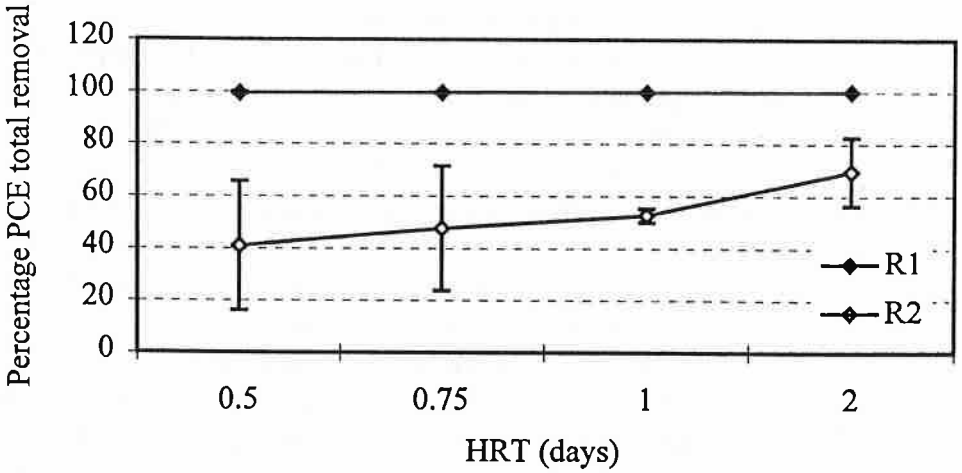
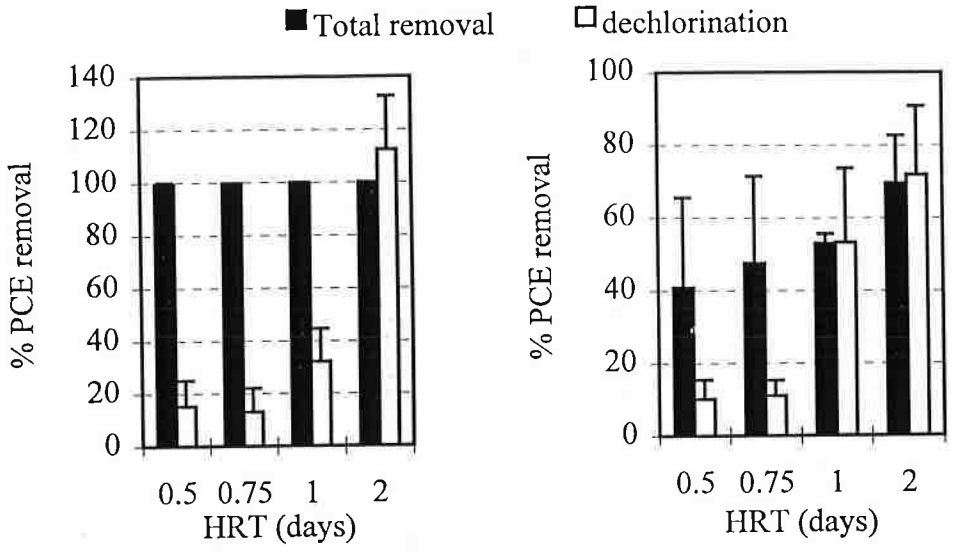


FIGURE 1. Percentage of total PCE removal versus HRT.

The maximum specific chloride ion production for GAC AFBR (R1) occurred at a 2 day HRT (phase 2). The minimum specific chloride ion production occurred at a HRT of 0.75 days (phase 4). These values, in PCE equivalents, equalled 9.82 ± 1.56 and 5.58 ± 0.89 mg PCE/g prot/d. For the Biolite™ AFBR (R2), the specific chloride ion production decreased constantly from phase 1 to phase 4 (from 7.46 ± 1.76 to 4.21± 1.63 mg PCE/g prot/d).

Figures 2(a) and 2(b) show the percentage of total PCE removal and the percentage of PCE removed by dechlorination. For the GAC AFBR, the percentage of PCE being adsorbed to the GAC was always higher than the percentage of PCE being dechlorinated (totally or partially) with the exception of the 2 day HRT where the dechlorination of PCE was higher than the total PCE removed. For the Biolite™ AFBR, the percentage of PCE removal due to dechlorination almost equalled the percentage of PCE total removal at HRTs of 1 and 2 days.



(a) (b)

FIGURE 2. Percentage of PCE total removal and of PCE dechlorination for (a) GAC AFBR (R1) and (b) Biolite™ AFBR (R2).

DISCUSSION

PCE Removal. The GAC AFBR experienced more than 99.5 % PCE removal for the entire experiment. It is obvious that adsorption of PCE onto GAC particles played a major role in the removal efficiency of the system because of the imbalance between the chloride ion production and the total PCE removed (Figure 2(a)). The presence of PCE metabolites in the gas and liquid phase as well as chloride ions confirmed PCE biodegradation.

Chloride Ion Production. The specific chloride production rate was better at high HRTs where the methanol activity was lower than at low HRTs where the methanol activity was higher. From these results, it appears as if a low methanol activity favored the dechlorination of PCE. Two hypotheses may explain why low methanol activity might favor dechlorination. First, a low methanol activity might favor the acetogenic metabolism of methanol and increase the H_2 available for the dechlorinators. Second, the slow release of H_2 during low methanogenic activity might favor the dechlorination over the hydrogenotrophilic methanogens, as dechlorinators could use H_2 at lower concentration than the hydrogenotrophilic methanogens (Fennell *et al.*, 1997).

From the formulated observations, it is suggested that the methanol load to be provided for optimal PCE removal should result in a low methanol activity, but an activity that is high enough to provide sufficient H_2 for dechlorination.

Role of Adsorption and Dechlorination. As seen in Figure 2(a), at a 1 day HRT, most of the PCE was adsorbed on the GAC particles and the remainder was biodegraded. In this case, the rate of PCE adsorption was greater than the rate of

PCE biodegradation. This low rate of dechlorination might be explained by the high methanol activity of the reactor. This methanol activity value was also higher for the GAC AFBR than for the Biolite™ AFBR while the specific chloride production was lower for the GAC AFBR than for the Biolite™ AFBR.

At a HRT of 2 days, when the methanol activity was at its lowest, the specific chloride production in the GAC AFBR tends to be higher than its maximum possible chloride ion production. This is explained by a PCE biodegradation rate higher than a PCE adsorption rate. The higher dechlorination rate (which shifted the equilibrium) caused a desorption of the PCE that had been adsorbed in the previous phase so as to maintain a PCE equilibrium between the solid and liquid phase. As seen from Figure 2(b), for the GAC AFBR, the removal of PCE by dechlorination at a HRT of 1 and 2 days is equal to the total PCE removed. These results demonstrate that the PCE removal mechanism was through biodegradation. When the Biolite™ AFBR was operated at a HRT of 0.5 and 0.75 days, approximately 30% and 35%, respectively, of the PCE was removed by adsorption. One potential explanation would be that PCE adsorbed on the recently replaced inflow part of PCE inflow Viton tubes. This adsorption did not affect the results of the first two phases since the interior tubing wall had probably reached saturation. The higher standard deviations of the total PCE removal show that at low HRTs, where the average PCE percentage removal is lower, the system performance fluctuated.

For the Biolite™ AFBR, the chloride ion production at HRTs of 1 and 2 days can be considered as the total PCE removal since both values are equal. At HRTs of 0.5 and 0.75 days, if the total PCE removal was represented by the chloride ion production, it would be equal to approximately 10% of the influent PCE concentration (Figure 2(b)).

Applications of GAC versus Biolite™ in an AFBR. The specific chloride ion production was more or less the same for both reactors. Therefore, one can conclude that in terms of chloride ion production, both systems resulted in a very similar performance. Since the Biolite™ AFBR never achieved 100% PCE removal, it had reached its maximum dechlorination capacity under the highest specific chloride production measured. This corresponds to a value of 6.40 ± 1.51 mg Cl^-/g prot/d. However, since the GAC AFBR achieved a maximum chloride ion production of 8.46 ± 1.34 mg Cl^-/g prot/d which equalled to a PCE removal greater than 100%, it is possible that the system had not reached its optimum PCE removal capacity.

CONCLUSIONS

The following conclusions can be drawn from these experiments:

(1) The GAC reactor achieved a higher PCE percentage removal than the Biolite™ reactor. PCE metabolites were measured in very low concentrations in the effluent and in the gas phase of both reactors.

(2) The specific chloride production was similar for the GAC and Biolite™ AFBRs under the same loading conditions for both reactors. Both reactors achieved the highest percentage of PCE removal by dechlorination under the lowest methanol activity.
(3) For the GAC AFBR, with the exception of the 2 day HRT, adsorption was the main PCE removal mechanism.

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