



Short communication

Electrochemical detection of perchloroethylene using differential pulse voltammetry

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ABSTRACT

We demonstrate the application of differential pulse voltammetry (DPV) for the electrochemical detection of perchloroethylene (PCE) on an unmodified glassy carbon electrode surface. Detection sensitivity was substantially improved using DPV, in which dechlorination was denoted by a cathodic peak observed at approximately -0.6 V (vs Ag/AgCl). Peak current intensity was found to correlate linearly with concentration over a tested range of 0 to 10 μ M. The utility of this technique was subsequently evaluated for PCE-spiked environmental samples containing either *Methylobacterium adhaesivum* (1×10^6 cells/mL) or creek water (10% v/v). In all environmental samples, a linear dynamic range was also observed from approximately 0 to 10 μ M. The limit of detection was determined to be 0.3 μ M in blank buffer, 0.4 μ M in bacteria-containing samples and 1.2 μ M in creek water samples.

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1. Introduction

Chlorinated aliphatic hydrocarbons are one of the most prevalent recalcitrant pollutants especially in areas surrounding industrial facilities and hazardous waste sites [1,2]. Perchloroethylene (PCE) is a highly chlorinated hydrocarbon that is chemically stable, undergoes slow decomposition and accumulates persistently within ground water due to low aqueous-phase solubility [3,4]. PCE has been linked to toxicity of the liver and kidneys, increased risk of developing neurodegenerative diseases and is potentially carcinogenic [5]. In anaerobic conditions, PCE can undergo reductive dechlorination resulting in the production of several more toxic degradation products: trichloroethylene (TCE), dichloroethylene (DCE) and vinyl chloride (VC) [6]. Complete dechlorination is regarded as a viable strategy for remediation but is limited by the tendency of PCE to remain separated from the aqueous-phase [7]. Consequently, there remains interest in the development of novel methods for improved detection and remediation of PCE contaminated sites [8].

While the legal limit of PCE in drinking water established by the Environmental Protection Agency is 30 nM, substantially higher concentrations have been observed for well-water (>139 μ M) and ground water (>6 μ M) [9]. Currently, the most sensitive method for detecting chlorinated hydrocarbon-based pollutants employs gas-chromatography (GC) coupled with mass spectrometry (MS) [10,11]. The primary advantages of GC-MS include low nanomolar detection limits for PCE in water,

improved resolution of target analytes from a matrix and rapid screening of a wide range of contaminants via m/z library matching [9]. However, GC-MS is unsuitable for analysis in non-centralized areas due to high-cost, requirement for specialized personnel and inability to perform rapid on-site measurements. Moreover, due to the low concentrations of chlorinated hydrocarbons at contaminated sites, samples are often first isolated and pre-concentrated prior to chromatographic separation, which is both time consuming and tedious [12]. In this regard, electrochemical detection platforms pose a number of advantages due to their high sensitivity and portability [13,14]. Carbon-based electrodes in particular offer a number of advantages as they are low-cost, readily modified and chemically inert. Carbon, silver and gold are developed into inexpensive inks and pastes to be implemented in screen-printed electrodes, ideal for applications in non-centralized areas [14].

Bacteria-modified electrode surfaces have previously been employed for effective detection of TCE, in which the ionic side products formed from bacteria-mediated degradation are correlated to initial TCE concentrations using impedance spectroscopy and potentiometry [8,15,16]. Alternatively, metalloporphyrin-modified graphite foil electrodes have also shown great utility in the detection of a wide range of chlorinated hydrocarbons. Notably, cobalt-porphyrin complexes are capable of catalyzing organohalide reduction at less negative potentials compared to reductive processes [17]. However, both methods require surface modifications that are time consuming to prepare. Saez and co-workers [18] have recently demonstrated that surface modifications were not necessary for direct detection of PCE on an unmodified glassy carbon rotating disk electrode using linear sweep voltammetry (LSV). In this study, we present an improved method for employing highly sensitive differential pulse voltammetry (DPV) on an unmodified glassy carbon electrode surface in environmental samples.

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2. Experimental

2.1. Chemicals and reagents

Analytical grade perchloroethylene (PCE), potassium ferrocyanide ($K_4Fe(CN)_6$), potassium ferricyanide ($K_3Fe(CN)_6$) and sodium sulfate were purchased from Sigma–Aldrich (Oakville, ON) and used without any further purification. Unless otherwise described, solutions were prepared using 18.2 M Ω water obtained from a Cascada LS water purification system (Pall Co., NY). A stock solution of 500 μ M PCE was prepared in 50 mM sodium sulfate, pH 7.4, and diluted to the appropriate concentration prior to electrochemical measurement. Environmental samples were also collected from a local creek (suspended sediment level 1140 mg/L), diluted in Na_2SO_4 (50 mM), then spiked with desired concentrations of PCE. The concentration of *Methylobacterium adhaesivum* was estimated by measuring optical density at 600 nm (OD_{600}).

2.2. Instrumentation

Voltammetric studies were conducted using a μ Autolab-III potentiostat system (Metrohm, Switzerland). The general purpose electrochemistry software (GPES) was used to operate potentiostat and analyze voltammogram data using a Pt counter electrode, Ag/AgCl (3 M KCl) reference electrode and glassy carbon working electrode (GCE, geometric working area: 7.07 mm², CH Instruments, TX). Electrochemical detection of PCE was performed using DPV conducted at room temperature (25 ± 1 °C) using a sodium sulfate supporting electrolyte (50 mM, pH 7.4). Electrodes were immersed in the electrolyte solution followed by 5 min degassing period using high-purity oxygen-free nitrogen. A stock solution of PCE was diluted into the electrolyte to the desired concentration followed by DPV analysis between -1 V and 0 V under the following conditions: step potential, 5 mV; amplitude, 25 mV. Between measurements the surface of the GCE was cleaned by polishing in an aqueous slurry of alumina (0.05 μ m and 0.03 μ m). Electrodes were rinsed and sonicated in a 50:50 mixture of ethanol–water for 10 min. Raw voltammograms were treated using Savitzky–Golay smoothing and baseline-correction with a moving average peak width of 0.004 V. All measurements were performed for $n \geq 3$ and peak current values obtained from PCE reduction were measured by subtracting sample signal from the one obtained from the blank electrolyte.

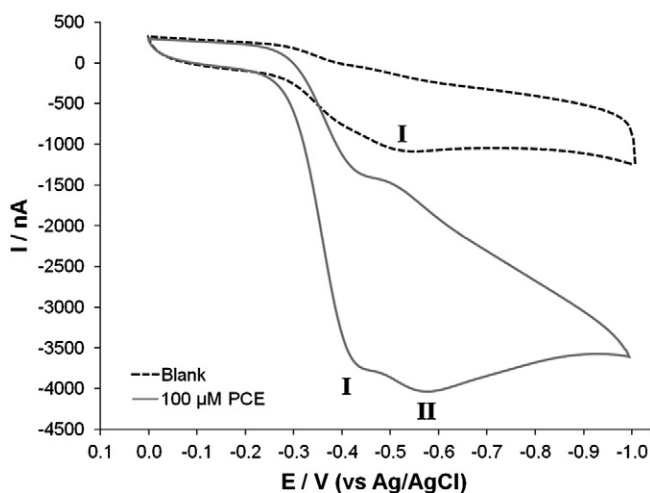


Fig. 1. Cyclic voltammogram of PCE measured for a 100 μ M PCE sample (—) and blank solution (---) containing only the supporting electrolyte (50 mM Na_2SO_4 , pH 7.4). Potential was applied between 0.0 V and -1.0 V on a GCE at a scan rate of 50 mVs^{-1} .

3. Results and discussion

Initial characterization of the electroactive properties of perchloroethylene (PCE) was performed by cyclic voltammetry (CV) on a glassy carbon electrode (GCE). Fig. 1 compares the voltammetric profiles obtained for a 100 μ M sample PCE relative to a blank solution containing only the supporting electrolyte (50 mM Na_2SO_4 , pH 7.4) measured at a scan rate of 50 mVs^{-1} . No oxidation peaks were observed over an applied potential range of 0 V to -1 V (vs Ag/AgCl) as the potential was ramped in the anodic direction. Conversely, ramping the electrode potential from -1 V to 0 V in the cathodic direction resulted in the formation of two distinct reduction peaks detected at approximately -0.4 V (I) and -0.6 V (II). Peak I, was attributed to oxygen since the current intensity could be decreased by increasing N_2 degassing periods. Peak II was also found to vary in intensity between electrolyte, creek-water samples and bacteria-spiked samples. Peak II was related to the reductive dechlorination of PCE, which has been previously reported to occur at high negative potentials [18] and was not significantly affected by the presence of oxygen.

Although CV indicated that PCE exhibited a strong voltammetric signal at -0.6 V, the overlapping peak potential from oxygen renders detection and quantification difficult. Thus, in order to further improve

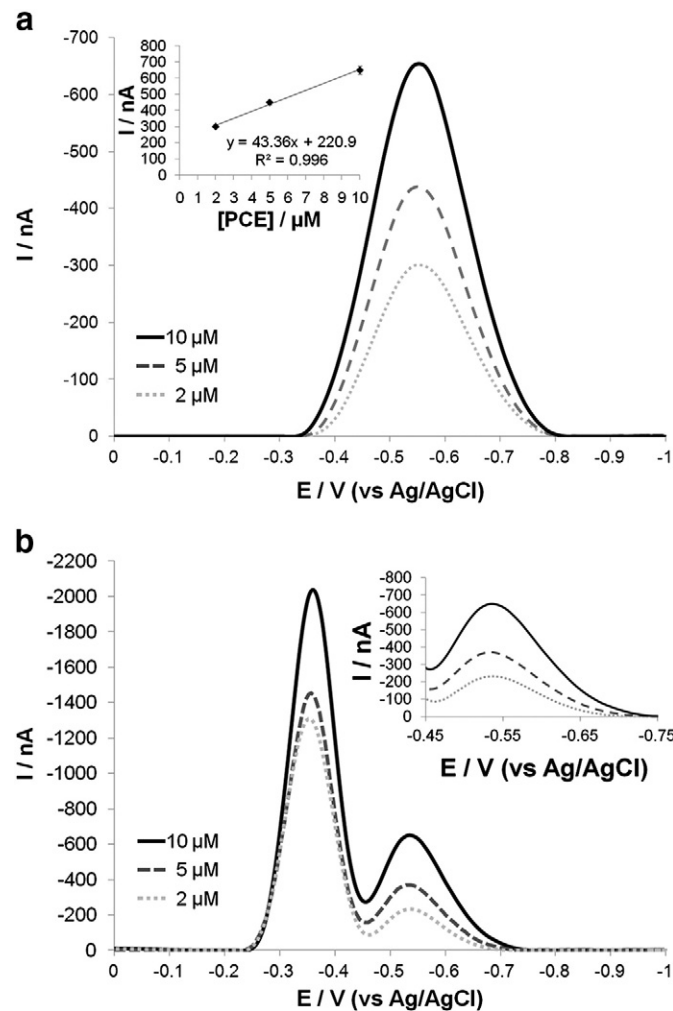


Fig. 2. Differential pulse voltammograms of various PCE concentrations (2, 5 and 10 μ M) on GCE in: (a) 50 mM Na_2SO_4 with 30 min N_2 degassing measured under N_2 blanket and (b) 50 mM Na_2SO_4 spiked with *Methylobacterium adhaesivum* (1×10^6 cells/mL) with 5 min N_2 degassing. DPV parameters were set to: step potential, 5 mV; amplitude, 25 mV and 20 ms pulse width. Measurements were repeated for $n \geq 3$. Raw voltammograms were treated using Savitzky–Golay smoothing and baseline-correction with a moving average peak width of 0.004 V.

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