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Feasibility study for reductive destruction of carbon tetrachloride using bare and polymer coated nickel electrodes

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Abstract

This research investigated the feasibility of an electrochemical reductive dechlorination method for removing carbon tetrachloride (CT) from contaminated waters. Reaction rates and Faradaic current efficiencies were measured for CT dechlorination in small flow-through reactors utilizing bare and silicone polymer coated nickel cathodes. CT dechlorination resulted in near stoichiometric production of methane. Rates of CT reduction were found to follow a first-order kinetic model for all CT concentrations investigated. CT disappearance was limited by its reaction rate, and the performance of the reactor could be approximated with an ideal plug-flow reactor model. Destruction half-life values for CT with the bare nickel electrode ranged from 3.5 to 5.8 min for electrode potentials ranging from −652 to −852 mV with respect to the standard hydrogen electrode (SHE). The apparent electron transfer coefficient for CT reduction was only 0.06. The low transfer coefficient can be attributed to oxides coating the electrode surface that contributed to mass transfer resistance for CT reduction. Faradaic current efficiencies for CT reduction were found to decline with decreasing electrode potential. This can be attributed to an electron transfer coefficient for water reduction of 0.33 that was significantly greater than that for CT reduction. Faradaic current efficiencies could be increased by 100–360% by coating the electrode with a silicone polymer. In addition to decreasing the rate of water reduction by acting as hydrophobic mass transfer barrier, the polymer coating resulted in small increases in CT reaction rates. The energy cost per volume of water treated was strongly dependent on the electrode potential, but only weakly dependent on the influent CT concentration over the range of practical interest. The energy costs for reductive dechlorination appear to be lower than the carbon costs for adsorptive treatment of CT. This indicates that low current efficiencies at low CT concentrations are not a significant obstacle for developing a practical treatment process. The main impediment to electrochemical treatment for removing CT from water is the slow reaction rate that requires large reactors for obtaining sufficient hydraulic detention time to meet effluent water standards.

1. Introduction

In recent years there has been considerable interest in developing destructive treatment methods for removing chlorinated organic compounds from contaminated waters. The presently used treatment methods of air-stripping and adsorption on activated carbon merely transfer the chlorocarbons from water to another medium, which then requires treatment or disposal. Disposal often involves internment in hazardous waste landfills or incineration. Landfill disposal is becoming increasingly expensive due to the liability involved with the long-term storage of hazardous materials. Incineration of chlorocarbons is difficult due to their low flammability, and their production of highly corrosive hydrochloric acid upon combustion. Additionally, expensive precautions must be taken to avoid incomplete combustion that often produces highly toxic products, such as dioxins, furans, and phosgene [1].

Reductive destruction of chlorinated solvents in water has been a very active research area since Gillham and O'Hannesin [2] showed that metallic iron filings could be utilized in passive groundwater remediation schemes [2–6]. In this process, the zerovalent iron serves as an electron donor to reductively dechlorinate the halocarbons to their nonchlorinated analogs and chloride ions. Due to the slow reaction kinetics, dechlorination using corroding iron requires contaminant-iron contact times ranging from hours to days [7–9], and is therefore only suited for in situ groundwater treatment.

In addition to treatment methods utilizing zerovalent iron, several investigators have focused on reductive dechlorination methods that can be employed in above ground canister treatment systems [10–14]. Many of these methods use palladium or platinum as a reduction catalyst and hydrogen as the electron donor. Other investigators have attempted electrochemical reduction of chlorinated compounds using palladium supported on carbon and graphite cathodes [12, 13, 15, 16]. Although rapid dechlorination rates have been achieved using noble metals, the effectiveness of the catalyst is short-lived due to fouling by dissolved carbon dioxide and reduced sulfur compounds [17, 18], and to loss of catalyst from the electrode surface [15, 16].

To avoid problems with catalysts, several investigators have used porous iron and copper cathodes for reductive dechlorination of carbon tetrachloride (CT) [19, 20]. These systems are capable of steady long-term performance without fouling [19]. However, reduction of CT by copper and iron cathodes often produces significant amounts of chloroform [21]. Chloroform production from CT reduction is undesirable because chloroform dechlorination rates are up to an order of magnitude slower than those for CT [4, 5, 19]. A recent study in our laboratory has found that CT reduction at nickel surfaces results in near stoichiometric production of methane as the first detectable product [22]. The absence of significant chloroform production makes nickel cathodes attractive for developing a practical treatment scheme for CT reductive dechlorination.

A practical dechlorination scheme must possess fast reaction rates, high Faradaic current efficiencies, and not be susceptible to catalyst fouling. A major impediment to achieving these objectives is the polar surface of metal electrodes that results in low halocarbon concentrations adsorbed on the electrode surface. This makes it difficult to achieve both high reaction rates and high current efficiencies. The goal of this research was to obtain kinetic and current efficiency data for CT reduction in a flow-through reactor using a porous nickel cathode. The effectiveness of a hydrophobic polymer coating on the electrode surface for increasing reaction rates and Faradaic current efficiencies was also investigated. The lab reactor data was then used in a technical and economic feasibility analysis to assess the potential for development of a practical treatment process.

2. Materials and methods

All experiments were performed using the flow-through reactor shown in Figure 1. The working electrode consisted of a porous nickel cylinder that was 2 cm in diameter and 6.1 cm in length. The porous nickel cylinder was produced by lightly sintering 800 μm diameter nickel spheres (Aesar, Ward Hill, MA) at 550 °C under an argon atmosphere. The electrode had a surface area of 18 m^2 and 6.5 ml of internal pore volume. The anode consisted of carbon cloth (Electrosynthesis Co., Lancaster, NY), that was wrapped around the cathode. The anode and cathode were separated by an ESC-7000 cation exchange membrane (Electrosynthesis Co., Lancaster, NY). The electrode assembly was contained within a 2.5 cm outer diameter (o.d) glass tube fitted with stainless steel pipe fittings at each end. In this configuration, the water passed only through the cathode compartment of the reactor. The working electrode potentials were controlled by a potentiostat and an Ag/AgCl reference electrode. All potentials are reported with respect to the standard hydrogen electrode (SHE).

Experiments were also conducted with a silicone polymer coated nickel electrode. Silicone adhesive (Dow Corning®) was dissolved in toluene to produce a 12.8% (w/w) polymer solution. The electrode was coated with the polymer by immersion into the silicone solution for 10 min. The polymer coated electrode was then allowed to dry at room temperature under a nitrogen atmosphere for 6 days. The amount of silicone on the electrode was gravimetrically determined to be 0.66 g. Based on a polymer density of 0.97 g ml^{-1} and the 18 m^2 of nickel surface area, the average silicone thickness on the electrode surface was 380 Å.

All experiments were conducted using a 10 mM $CaSO_4$ background electrolyte solution that was purged with nitrogen gas prior to entering the reactor. Prior to performing the experiments investigating CT dechlori-

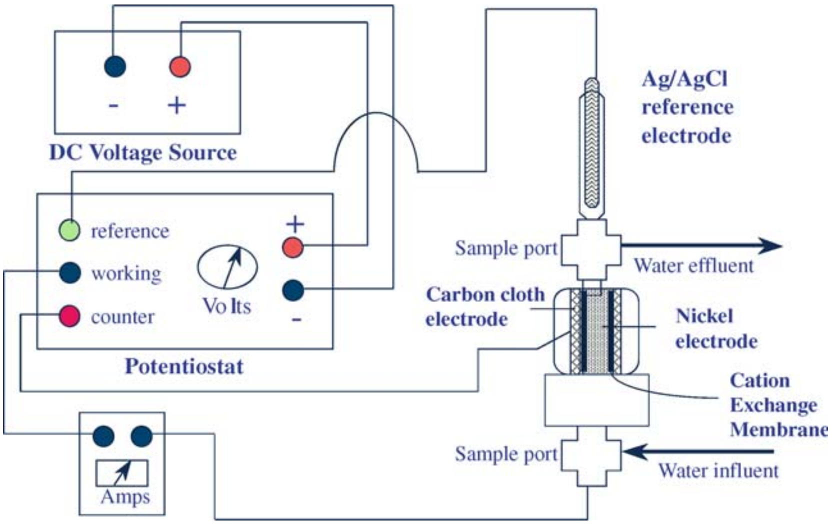

Fig. 1. Schematic diagram of the flow-through reactor and experimental setup.

nation, the electrode was equilibrated with the feed solution at a potential of −752 mV for 7 days. The flow-through reactor was operated at flow rates ranging from 1.66 to 6.14 ml min^{-1} at potentials ranging from −652 to −852 mV. For each set of operating conditions, the reactor was operated for at least 2 days before sampling in order to achieve steady state performance. CT concentrations in the feed stream were controlled using a water–gas contactor consisting of 1 m of 0.25 cm o.d., silicone rubber tubing contained inside a 1 l sealed glass vessel. The water–gas contactor was purged with nitrogen gas containing CT at different concentrations. Influent and effluent CT concentrations were determined by analysis of five replicate samples prepared by injection of 100 μl aqueous samples into 1 g of pentane. Chlorocarbon analyses were performed with a Hewlett-Packard 5890 series II gas chromatograph equipped with an electron capture detector and autosampler. Methane analyses were performed using a Hewlett-Packard 5790 gas chromatograph equipped with a flame ionization detector.

3. Results and Discussion

3.1. *Experimental Results*

Methane was the predominant reaction product of CT dechlorination. Only trace levels of chloroform and methylene chloride were observed. The sum of all chlorinated daughter products accounted for less than 5% of the CT disappearance. These products indicate that eight equivalents of electrons were required for each mole of CT destroyed.

Both mass transfer and reaction rate limitations may affect the degree of reactant conversion in flow-through reactors. The effect of flow rate on CT dechlorination rates can be used to assess the importance of boundary layer mass transfer limitations in the flow-through reactor. Previous research has found that over the concentration range used in this study, CT reaction rates at nickel electrodes are first-order in CT concentration [22]. Therefore, the destruction half-life can be used as a measure of the reaction rate [23]. Half-life values for CT disappearance at three electrode potentials are shown in Figure 2 as a function of the flow rate. At each potential, the half-life values for flow rates between 3 and 6.14 ml min^{-1} were statistically identical at the 95% confidence level. However, the half-life values were greater for a flow rate of 1.66 ml min^{-1}. The mass transfer correlation of Wilson and Geankoplis [24] for a packed bed of spherical particles can be used to estimate the hydrodynamic boundary layer mass transfer coefficient for the reactor. At a flow rate of 1.66 ml min^{-1}, the fluid velocity of 0.5 cm min^{-1} yields a mass transfer coefficient of 1.24×10^{-3} cm s^{-1}. This value is 4 orders of magnitude greater than the reaction rate constant of 8.55×10^{-8} cm s^{-1} at this flow rate, indicating that boundary layer mass transfer limitations had no impact on the observed reaction rates. The slower reaction rates observed at a flow rate of 1.66 ml min^{-1} can be attributed to blocking of the electrode surface by hydrogen bubbles produced from water reduction. Increasing the flow rate to 3.0 ml min^{-1} resulted in mechanical scouring of the hydrogen bubbles from the electrode, which then resulted in increased reaction rates.

Conformance of the CT reaction rate to a first-order kinetic model was confirmed by measuring the CT half-life as a function of the influent concentration at a flow rate of 3.0 ml min^{-1}. As shown in Figure 3 for an electrode potential of −652 mV, the CT half-life values were independent of the influent concentration. This confirms that the reaction rates were well-described by the first-order kinetic model given by:

$$\frac{\mathrm{dC}}{\mathrm{dt}} = -kC \tag{1}$$

where C is the CT concentration, k the first order rate constant and t is the time. The dependence of the rate constant on the electrode potential (E) can be used to determine the electron transfer coefficient ($\vec{\alpha}$) for CT reduction in the flow-through reactor. The relationship between the potential, rate constant, and electron transfer coefficient is given by [25]:

$$k = k_\mathrm{o} \exp\left[\frac{-\vec{\alpha}F(E - E_0)}{RT}\right] \tag{2}$$

where k_o is the rate constant at an arbitrary reference potential (E_o), F the Faraday constant, R the gas constant and T is the temperature. The half-life data in Figure 2 for flow rates greater than 3 ml min^{-1} yield an apparent $\vec{\alpha}$ value of 0.06. This value is considerably smaller than the value of ~0.5 determined using quantum chemistry techniques [26], and is also smaller than the value of 0.23 that was recently measured using a nickel rotating disk electrode (RDE) [22]. The electron transfer coefficient for water reduction measured in the flow-through reactor of 0.33 was close to that measured

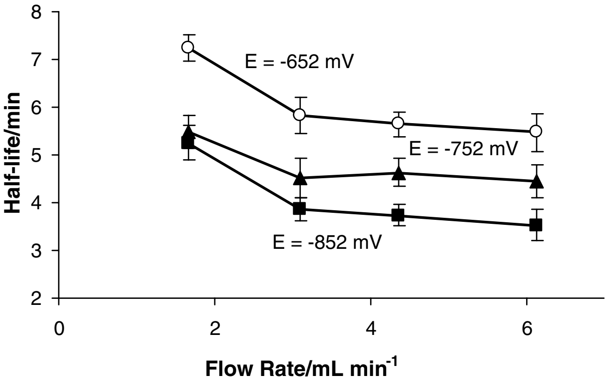

Fig. 2. Reaction half-life for CT reduction to methane as a function of the flow rate for three electrode potentials. Error bars represent upper and lower 95% confidence intervals.

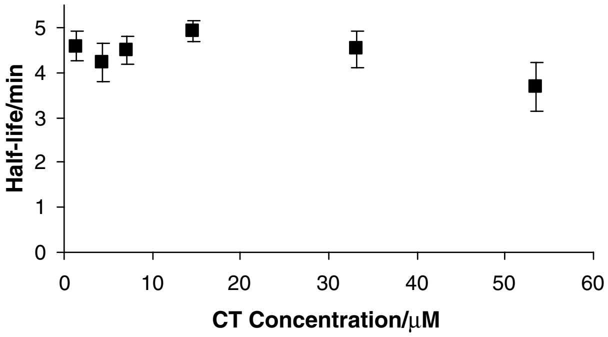

Fig. 3. Reaction half-life for CT reduction to methane as a function of the CT concentration for a flow-rate of 3.09 ml/min^{-1}.

using a nickel RDE [22]. This suggests that CT reduction in the flow-through reactor was affected by mass transfer limitations arising from CT diffusion through oxides coating the nickel surface.

Visible black oxides were observed to form on the electrode during the first several days elapsed. Concomitant with the oxide formation was an order of magnitude drop in the current for water reduction at a fixed potential. Although there was considerable oxide formation during the first several days of operation, after the initial equilibration period there was no measurable change in the reactor performance over a 9-month period of continuous operation. Temporarily polarizing the electrode to lower potentials had no effect on reduction of the oxides as evidenced by the steady state currents for hydrogen evolution. This is consistent with past observations of the recalcitrance of β-Ni(OH)$_2$ towards cathodic reduction [27].

The Faradaic current efficiency, defined as the fraction of the cell current going towards CT reduction, is one of the main factors affecting the economic feasibility of reductive dechlorination as a treatment technique. Figure 4 shows the current efficiencies for CT reduction as a function of the CT concentration for three different electrode potentials. In addition to lower current efficiencies with decreasing CT concentrations, the current efficiencies also decreased with decreasing electrode potential. This can be attributed to a smaller $\vec{\alpha}$ value for CT reduction as compared to that for water. Experiments in the blank electrolyte measured an $\vec{\alpha}$ value of 0.33 for water reduction. Therefore, as the potential was lowered, water reduction increased at a faster rate than CT reduction.

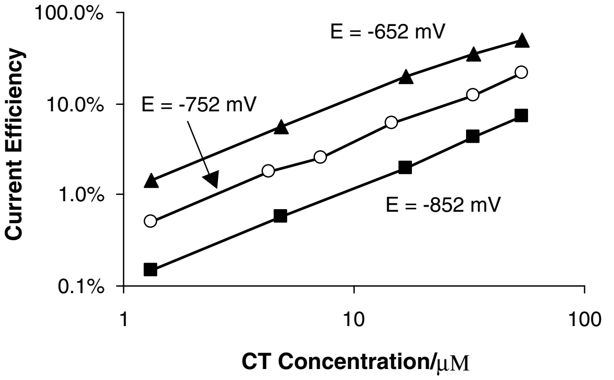

Fig. 4. Faradaic current efficiencies for CT reduction to methane as a function of electrode potential and CT concentration.

Competition between water and CT reduction is greatly affected by the relative concentrations of each species on the electrode surface. The hydrophilic oxide coated nickel surface resulted in low concentrations of CT adsorbed to reactive sites. A previous investigation found that adsorbed CT covered less than 1% of the surface of a nickel electrode under open circuit conditions at an aqueous concentration of 2000 μM [22]. This indicates that there is room for substantial improvement in current efficiency if CT adsorption can be increased and water adsorption decreased.

The effect of a silicone polymer coating the electrode was investigated in blank and CT containing solutions. Figure 5(a) compares currents for water reduction as a function of potential for uncoated and silicone coated nickel electrodes. At all three potentials, lower rates of water reduction were observed on the silicone coated electrode. This can be attributed to the silicone polymer acting as a mass transfer impedance for water reduction. The small effect of the polymer at −652 mV can be attributed to mass transfer rates that were only slightly below the reaction rate on the uncoated electrode. The large effect of the polymer at −852 mV can be attributed to reaction rates on the uncoated electrode that were much faster than the rate that water was able to diffuse through the polymer coating.

In addition to decreasing the rate of water reduction, the silicone polymer resulted in a slight increase in CT reaction rates at potentials of −752 and −852 mV, as shown in Figure 5(b). This indicates that despite introducing mass transfer limitations, the silicone polymer was able to increase CT concentrations at the electrode surface. First-order reaction kinetics were also observed with the polymer coated electrode. The measured half-lives were independent of the influent concentration and the flow rate. Although the increases in CT reaction rates were small, the combined polymer effect on water and CT reduction yielded 100–360% increases in current efficiency, as shown in Figure 5(c). The effects of the polymer coating were long-lasting, with negligible change in performance over a 6 month period of continuous operation.

3.2. *Feasibility Assessment*

Because mass transfer and dispersion effects were found to have a negligible impact on CT reaction rates, the reactor can be approximated as an ideal plug-flow reactor for modeling purposes [23]. For a plug-flow reactor, the influent (C_{in}) and effluent (C_{out}) CT concentrations are related by:

$$C_{\text{out}} = C_{\text{in}} \exp[-k\theta] \tag{3}$$

where θ is the hydraulic detention time. Rate constants determined from the data in Figure 2 can be used to

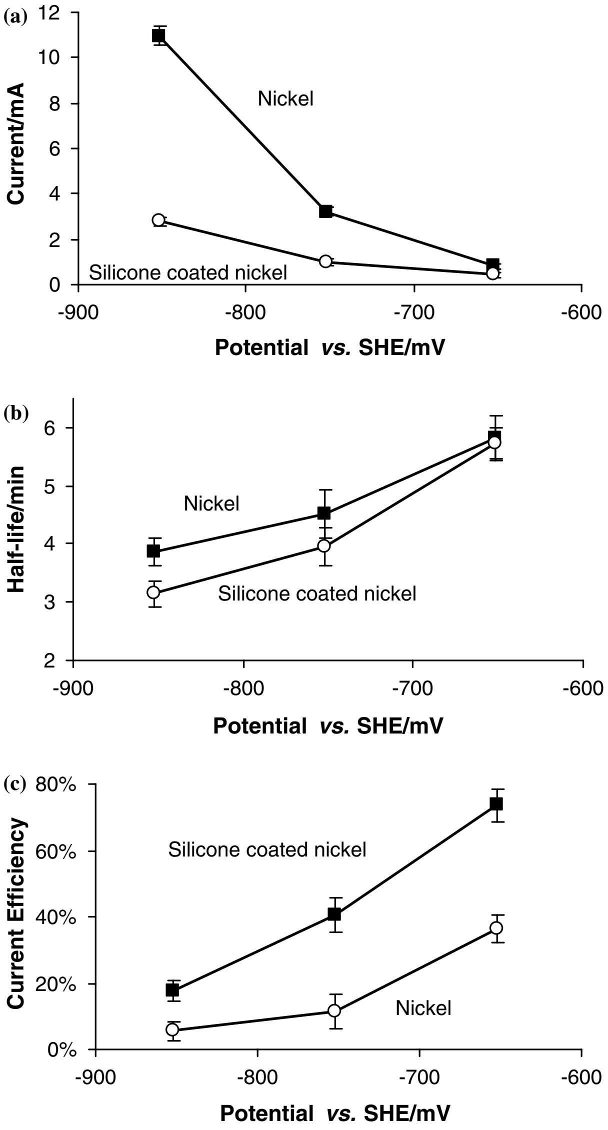

Fig. 5. Performance comparison for bare and silicone coated nickel electrodes as a function of potential: (a) Currents for hydrogen evolution, (b) CT reaction half-lives, and (c) CT current efficiencies.

determine the relationship between the influent and effluent concentrations and the hydraulic detention time. Figure 6 shows effluent CT concentrations as a function of the detention time for an influent concentration of 5000 μg l^{-1}. For the uncoated electrode, hydraulic detention times ranging from 39 to 58 min are required to reach the drinking water maximum contaminant level (MCL) of 5 μg l^{-1} [28]; while for the polymer coated electrode, a θ value as short as 32 min can be used. These times are considerably longer than typical hydraulic detention times on the order of 10 min that are normally used in activated carbon treatment systems [29]. Thus, the reactor volume required for electrochemical treatment of water saturated with CT will likely be too large to make electrochemical treatment a favorable alternative to adsorption systems. However, for lower influent concentrations, the process may be technically feasible, with detention times ranging from 11 to 20 min per order of magnitude decrease in CT concentration.

The energy requirements to remove CT to the drinking water MCL are shown in Figure 7 as a function of the influent concentration. The reaction stoichiometry requiring 8 moles of electrons per mole of CT, and the current efficiency as a function of the CT concentration and electrode potential, were used to determine the energy requirement to reach an effluent concentration of 5 μg l^{-1}. The parameter most affecting the energy requirement is not the influent concentration, but rather the electrode potential. Although operation at lower potentials decreases the required hydraulic detention time, decreasing the potential rapidly increases the energy requirement due to the decreasing current efficiency with decreasing potential.

For power at a cost of \$0.10 kW^{-1}h^{-1}, the energy costs for electrochemical treatment are less than the carbon costs for adsorptive treatment. For example, for an influent CT concentration of 100 μg l^{-1}, the carbon cost for adsorptive treatment is approximately \$0.25 m^{-3} of treated water [30]. For all potentials tested, this carbon cost is higher than the energy cost for electrochemical treatment. For an influent concentration

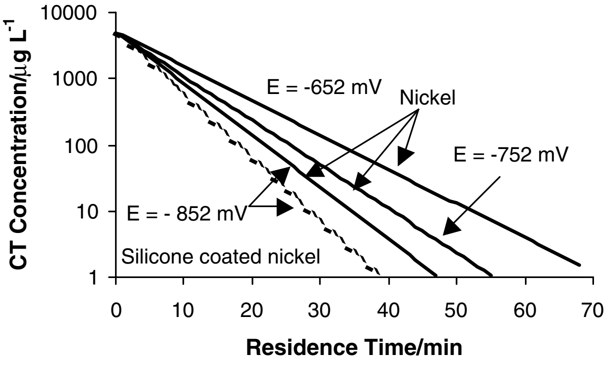

Fig. 6. CT concentrations as a function of the hydraulic detention time calculated using the ideal plug-flow reactor model and CT rate constants determined from the data in Figure 5.

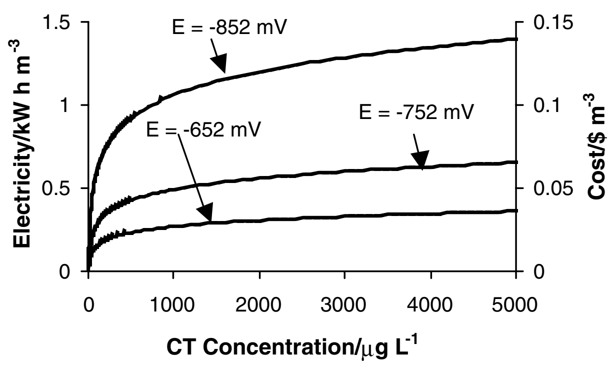

Fig. 7. Energy requirements and costs per m^3 of water treated (based on \$0.10 kW^{-1}h^{-1}) as a function of the influent CT concentration and electrode potential.

equal to 5000 $\mu g\ l^{-1}$, the carbon cost of \$13 m^{-3} is significantly greater than the energy cost for electrochemical treatment [30]. The reasonable energy costs for electrochemical treatment indicate that low current efficiencies at low CT concentrations are not a major obstacle for developing a practical treatment process. This suggests that slow reaction rates may be the most significant impediment to developing electrochemical methods for removing chlorinated solvents from contaminated water. Of course, issues associated with scale-up to a practical reactor size, and corrosive waters leading to the release of toxic nickel ions, must also be considered.

Acknowledgements

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