Effect of current density on electrolytic transformation of benzene for groundwater remediation☆

Hussam Sarahney, Akram N. Alshawabkeh *

Department of Civil and Environmental Engineering, Northeastern University, 400 Snell Engineering Center, 360 Huntington Avenue, Boston, MA 02115, USA

Available online 14 January 2007

Abstract

Electrolytic transformation of benzene in water is evaluated as a potential mechanism that can be implemented for in situ remediation of benzene in groundwater. Electrolytic transformation experiments were conducted using inert electrodes that are separated by a membrane. Electrolytes that consist of sodium chloride or sodium nitrate solutions with 40 mg/L benzene concentration were used. Electric currents of 1, 5 and 10 mA (1.8, 9.0 and 18.1 mA/L, respectively) were applied and the transformation of benzene was monitored and compared with a control. The results show that electrolytic transformation of benzene occurred under different rates that depend upon the type of electrolyte and the current density. Transformation results in formation of chlorinated benzene when sodium chloride is the electrolyte. However, processing for long enough time (up to 300 h) resulted in transformation of the chlorinated benzene byproducts. Benzene transformation occurred when the electrolyte was sodium nitrate but the rate was slower than the case with sodium chloride. The results did no show formation of byproducts in this case. The transformation rate was dependent on the current density. The results with sodium chloride showed that the rate increases with increasing the current density, but there is an optimum value, beyond which increasing the current density will not increase the transformation rate.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Electrochemical; Redox; Benzene; Reactive barriers

1. Background

Benzene, also known as benzol is a colorless liquid with a sweet odor that is found in the environment mainly as a result of human activities. Benzene is a very stable (non-reactive) organic compound. Because of its wide use, benzene ranks among the top 20 chemicals produced in the United States. Industrial processes are the main sources of benzene in the environment. Industrial discharge, disposal of products containing benzene, and gasoline leaks from underground storage tanks can release benzene into water and soil. Groundwater contamination by benzene is very common in industrialized countries specially United States, Western Europe and countries that produced oils in economical levels. Petroleum contamination is a result of surface leakage, leakage from tank storage and landfill leachate.

Methods used for benzene treatment in soil and groundwater include biological degradation (aerobic or anaerobic), chemical oxidation, adsorption, and soil washing with surfactants. Rooney-Varga et al. [1] investigated the composition of microbial community during benzene oxidation by in situ Fe (III)-reducing conditions in a petroleum-contaminated aquifer. Weiner and Lovely [2] showed that [14C] benzene was converted to $^{14}CH_4$ and $^{14}CO_2$ by methanogenesis without an apparent lag. Phenol, acetate, and propionate were intermediates in benzene mineralization. Lo et al. [3] showed that tricaprylmethyl-ammonium (TCMA)–bentonite complexes could be used as an adsorbent to enhance the purification of aromatic hydrocarbon-contaminated water or act as a liner material for removing non-polar contaminants. While benzene, and other contaminants, can be transformed by biological and chemical methods, there are always challenges. For example, biological methods tend to require a relatively long time (on the order of weeks) for degradation, and chemical methods require injection of significant volumes of additives, such as hydrogen peroxide or chlorine gas.

Electrolytic methods can be used for transformation of organic contaminants, such as benzene. Electrolytic methods are based on passing a direct current (dc) across electrodes in

an aqueous medium. If the electrolytes are separated to prevent mixing but allow charge flow, then two main pH and redox conditions may develop: at the anolyte (anode solution), protons and oxygen are produced (oxidizing, acidic conditions develop); at the cathode, hydroxyl anions and hydrogen gas are produced (reducing, alkaline conditions develop). Other electrolysis products may result depending on the availability of ions and their electrochemical redox potentials. Although some secondary reactions might be favored at the cathode because of their lower electrochemical potential, the water reduction half-reaction is dominant. Within the first few days of processing, electrolysis reactions drop the pH at the anode to below 2 and increase it at the cathode to above 10 [4]. The presence of chloride ions may result in the formation of chlorine gas instead of oxygen gas at the anode.

The process can be used for in situ transformation of contaminants in groundwater. Electrochemical redox barriers (ERBs) are permeable electrodes that can inserted in aquifers to intercept and treat contaminated flowing groundwater. The concept is introduced in recent studies [5,6]. Oxidizing or reducing conditions can be developed at the electrodes, depending on the transformation kinetics of the target contaminants. Once the contaminated water flows through the electrochemical redox barriers, transformation will occur. The ERB's can be used for transformation of petroleum products, such as benzene. Several studies have indicated that electrolytic transformation of benzene and other organics is feasible.

Ito et al. [7] evaluated electrochemical effects on benzene using an aqueous sulfuric acid containing 10 ml of benzene per 100 ml solution as an anolyte and an aqueous 0.1 M acetate solutions with some acetonitrile and 10 ml of benzene as a catholyte. Benzene was oxidized to hydroquinone at the cathode compartment indirectly, while at the anode, benzene was oxidized to benzoquionone. To generate the indirect oxidation conditions at the cathode, oxygen was bubbled through the catholyte during electrolysis producing OH$^\bullet$ radicals that are required for the oxidation of benzene. Zaveri and Flora [8] demonstrated the performance of laboratory-scale two compartment septic tanks in response to electrolytic aeration of the septic tank compartment to stimulate biodegradation. In a study of electrochemically enhanced oxidation of naphthalene, Franz et al. [9] evaluated the characteristics of oxygen generation, and side reactions of an electrolytic cell assembly that could be used to remediate sites with contaminants that are amenable to aerobic biodegradation. The distance between the electrodes was 1.4 cm, which does not allow separation of electrolysis products at the cathode and anode. Removal of 98% of naphthalene was reported when chlorine concentration in the electrolyte was 35 mg/L at pH 4. The removal efficiency was orders of magnitude higher than that at neutral pH. Goel et al. [10] investigated naphthalene removal by electrochemical aeration and evaluated the role of anodic oxidation of chloride, formation of HOCL and cathodic reduction of oxygen, producing hydrogen peroxide for direct oxidation of naphthalene. Alshawabkeh and Sarahney [5] evaluated the effect of current density on electrolytic transformation of naphthalene. The results showed that transformation rates were dependent on the current density. Most of naphthalene

transformation occurred in the first four hours under rates of 2.24 and 1.11 mg/L h under 18.2 and 9.0 mA/L, respectively. Naphthalene transformation was attributed to electrochemically enhanced oxidation at the anolyte by chlorine gas produced by electrolysis.

Direct electrochemical oxidation at the anode may result in breakdown of some organic contaminants, depending upon the electrode type and the electrochemical redox potential of the target. Arapoglou et al. [11] used a Ti/Pt anode and a stainless steel cathode to electrochemically detoxify methyl-parathion (MeP) pesticide in 2 h. The transformation of MeP was more effective when the pH of the brine solution was acidic. Torres et al. [12] demonstrated electrochemical oxidation of industrial wastewaters containing 5-amino-6-methyl-2-benzimidazolone (AMBI), on Pt anodes in 45 min. Pulgarin et al. [13] showed that electrooxidation of 1,4-benzoquinone in water solution depends on the typo of electrode. Primary oxidation (i.e., the breakdown of the benzene ring), was attained at the IrO$_2$ anode, resulting in an accumulation of carboxylic acids formation as final non-toxic products. Using the SnO$_2$ anode, carboxylic acid was formed as an intermediate product by oxidation to form CO$_2$ as the final product.

Based on these studies, a technology for electrochemically enhanced transformation of contaminants, such as benzene, can be developed for in situ or ex situ treatment of contaminated groundwater. However, it is necessary to evaluate electrochemically enhanced transformation of contaminated water prior to engineer in situ electrochemical remediation technologies. This study focus on batch reactors to demonstrate electrochemically enhanced transformation of benzene. The specific objective of this study is to evaluate benzene transformation at the anode using different electrolytes and under different electric current densities.

2. Materials and methods

The electrochemical transformation experiments were conducted using glass reactors. Glass was used as the reactor material to minimize cell wall adsorption. Each reactor consists of two 550 ml, bottle shaped compartments that are connected together by a glass tube at the bottom (Fig. 1). A proton-permeable membrane (Nafion$^®$[1]-112) was used as a cell junction that physically separates the electrolytes in the two compartments. Nafion$^®$ membranes perform as a separator and solid electrolytes that selectively transport cations across the electrochemical cell junction. They are chemically resistant and durable. Each compartment has one port that is used for both fitting the electrodes into the solution and sampling. The electrodes, made of a titanium core with mixed metal oxide coating (MMO) and having a mesh structure, are 10.2 cm × 1.3 cm × 0.12 cm (4 in. × 0.5 in. × 1/16 in.). A lab bench dc power supply (HPE3612A) is used to deliver direct electric current.
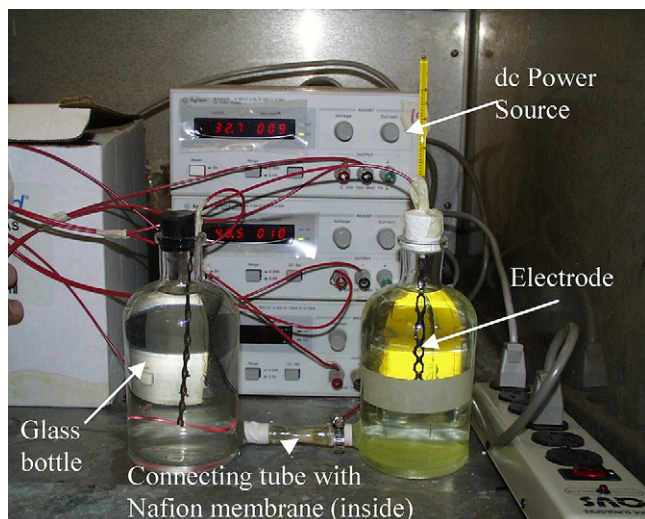
Fig. 1. Experimental setup.

The study evaluated the effects of three current densities: 1.8, 9.0 and 18.2 mA/L (1, 5 and 10 mA, respectively) on 40 mg/L initial benzene concentration. The current densities are presented per volume of electrolyte to indicate the amount of electric charge applied per specific volume of electrolyte, which is useful for evaluating the electrochemical changes in the electrolyte. This is different than the electrokinetic or electrophoresis applications in which the current densities are measured per cross sectional area, an important parameter for species transport rates. After 9 days of processing, the electrode polarity was reversed for 3 days to assess the role of electrochemically enhanced reduction following the electrochemically enhanced oxidation. Another cell was used as a control (no electric current applied) to account for physical losses through volatilization, the losses through adsorption onto the electric cell glass walls and the losses into the Teflon coated port cover.

Fifty millilitres of NaCl (0.2 M) was used to increase the conductivity of the electrolyte. To assess the effects of chloride, tests were also conducted using similar concentrations of sodium nitrate solution as an electrolyte. All electrochemical redox cells, including the control, were conducted inside dark boxes to prevent any potential photo-oxidation. Replicate experiments were also conducted to assess the effect of the anolyte (as a medium) on the benzene degradation. A current density of 18.9 mA/L was applied for 3 days on a 0.018 M NaCl solution in deionized water without injecting benzene. The anolyte was transferred to 100 ml serum bottles and benzene was injected into the solution to form 45 mg/L concentration.

Measurement of pH was conducted using ThermoOrion combination electrode with a VWR Scientific Model 200 Meter. The pH electrode was standardized using commercial buffer of pH 7 and appropriate buffer of either pH 4 or pH 10. Redox potential (Eh) of the electrolytes was determined using a Cole–Parmer combination Ag/Ag/Cl reference electrode with a platinum (Pt) band and an Accumet Basic meter. The electrode was standardized by YSI Zobell ORP calibration solution. Millivolt readings were converted to Eh, using the electrode readings plus the standard potential of reference electrode at a

given temperature. Conductivity measurements were conducted using a Cole–Parmer conductivity cell, model 19550-60, and a Cole–Parmer conductivity meter, model 30. Chemical injection and liquid sampling were conducted using Hamilton series 1700 Gastight Syringes equipped with Teflon fluorocarbon Resin Luer Look (TLL).

Benzene was purchased from ACROS ORGANICS (NJ, USA), with 99% or greater purity. Ultra pure deionized water was used to prepare the stock solution for the reactors with 18 MΩ cm. Benzene was analyzed by SRI 8610 C gas chromatograph (GC) equipped photo ionization detector (PID) with a Purge and Trap terminal (SRI P&T 10 A/S) and a DF 3 capillary column, 15 m × 0.53 mm, Restek Corp. Helium was used as a carrier gas, and it was purified by pretreatment through a Lab Clear disposable gas filter that is installed between the gas cylinder and the GC.

3. Results and discussion

Fig. 2 shows the changes in benzene concentration, dichlorobenzene products and total byproducts after applying a current density of 1.8 mA/L. The figure summarizes the average values achieved in two tests for each case as tests were conducted in duplicates. The results show transformation of 56% of benzene in the first 48 h and more than 96% after 216 h under 1.8 mA/L. Monitoring the byproduct of transformation show formation of 1,2-dichlorobenzene, up to 8 mg/L, at a constant rate in the first 150 h. Beyond that, dichlorobenzene concentration decreased to less than 3 mg/L. Other products, including 1,4-dichlorobenzene, did not show significant buildup during treatment.

A similar behavior is noted under 9.0 mA/L, but at a much faster rate. Fig. 3 shows that more than 87% of benzene was transformed in the first 50 h of treatment. While the current density is five times the previous experiment (1.8 mA/L), the transformation percentage increased from 56% to 87%. In other
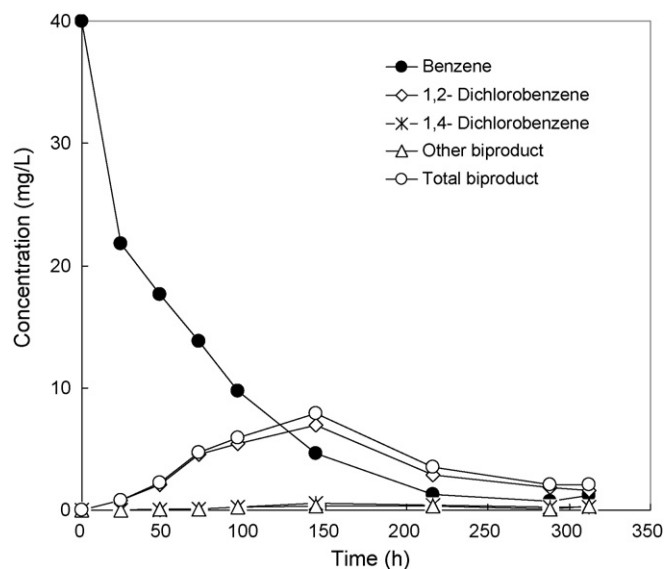

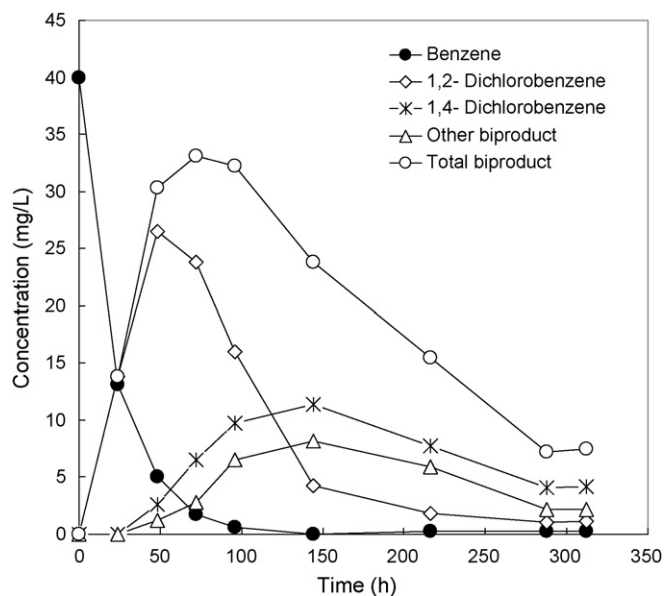Fig. 2. Benzene breakdown under 1 mA (1.8 mA/L).

Fig. 3. Benzene breakdown under 5 mA (9 mA/L).

words, increasing the current density did not cause a linear increase in transformation percentage. Formation and buildup of 1,2 dichlorobenzene is also observed with significant buildup to more than 30 mg/L in the first 50 h. The build up was followed by a steep drop in the concentration of 1,2 dichlorobenzene to less than 5 mg/L after 150 h. The buildup and transformation of 1,4 dichlorobenzene was not as dramatic. Its concentration increased to above 10 mg/L after 150 h and then decreased to below 5 mg/L after 300 h. The results show that while benzene concentration almost disappeared after 100 h, the total concentration of the byproduct was around 7 mg/L after 300 h. Fig. 4 shows the concentration profile for benzene and byproducts under 18.1 mA/L. The behavior is similar under 9 and 18.1 mA/L. Fig. 4 shows that more than 300 h were required for
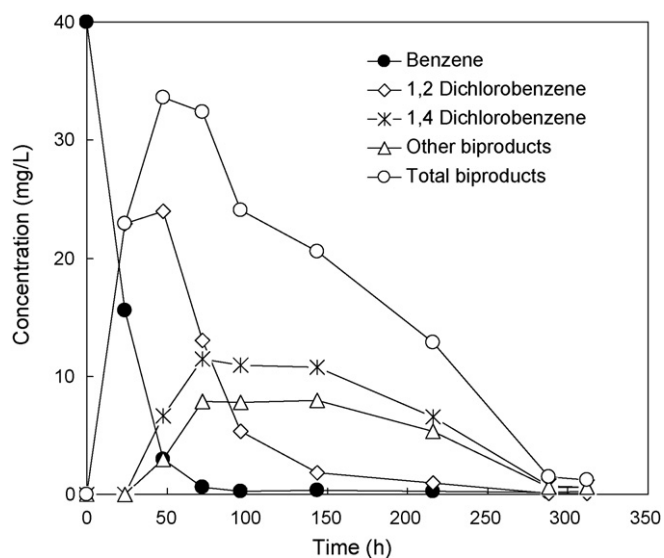

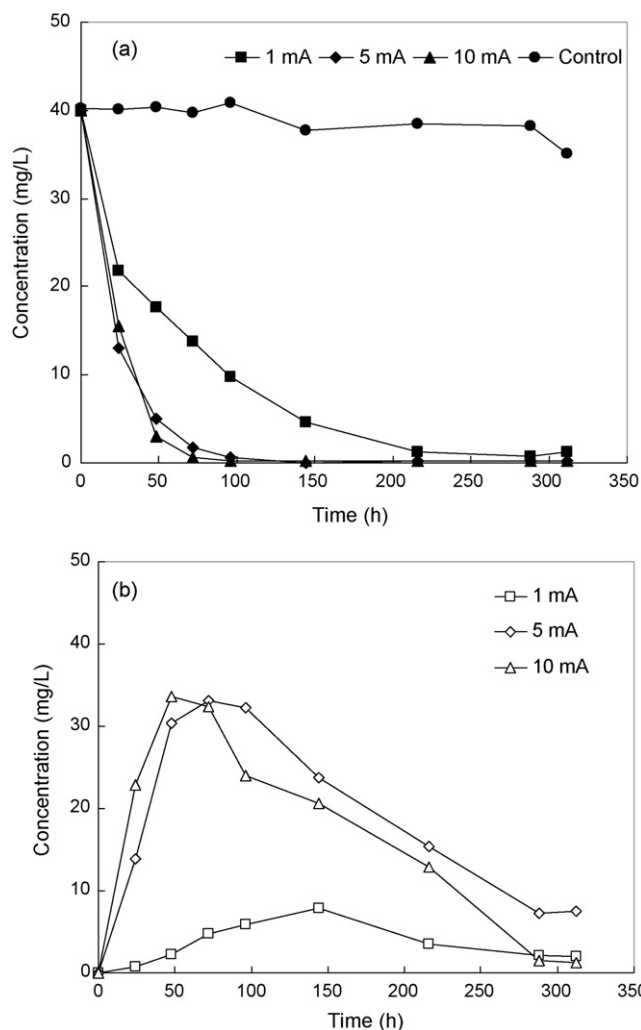Fig. 4. Benzene breakdown under 10 mA (18.1 mA/L) current.

Fig. 5. Comparison of (a) benzene breakdown rates and (b) byproducts under different currents.

decay of the byproducts, even though benzene was transformed in less than 100 h.

A comparison of the results under 1.8, 9.0 and 18.1 mA/L is presented in Fig. 5a. The effect of current density is clear on the rate of transformation. Increasing the current density from 1.8 to 9.0 mA/L improved the rate of transformation. However, increasing the current density beyond 9 mA/L (to 18.1 mA/L) did not cause any significant increase in transformation rate. Therefore, there is an optimum for the effect of increasing the current density.

Fig. 6 shows transformation rates in time under different current densities. Under 1.8 mA/L, the transformation started at a high rate (0.77 mg/L h) in the first 24 h and then was steady at 0.14–0.2 mg/L over the next 200 h. For the higher current densities, the rate started significantly high within the first 24 h and then decreased to less than 0.05 mg/L after 96 h. The results show the differences between high and low currents.

More than 300 h are required for transformation of the byproducts under the three current densities (Fig. 5b). The high currents caused faster transformation of benzene and significant buildup of the byproducts, while the lower current
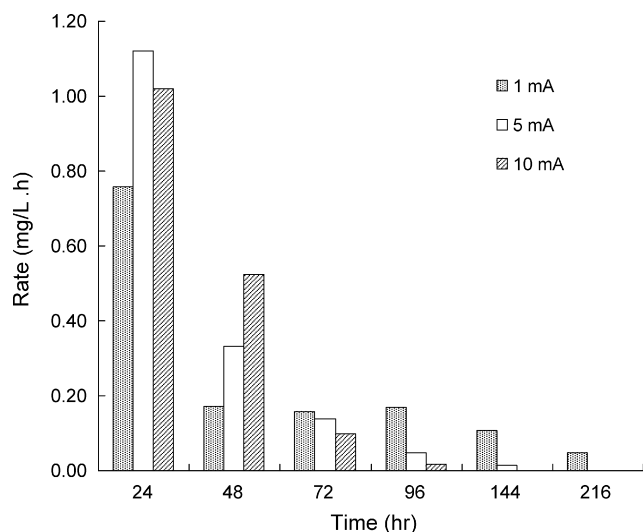
Fig. 6. Benzene transformation rates in mg/L h under 1, 5 and 10 mA currents (1.8, 9 and 18.1 mA/L), respectively.

produced slower transformation rate and less buildup of the byproducts. This effect indicates that benzene transformation rate should not be the primary factor for selecting the current density. The byproduct buildup and transformation should also be considered. Rate of formation of byproducts, which are mainly chlorinated benzene such as 1,4-dichlorobenzene and 1,2-dichlorobenzene, is dependent on current density. In case of 1.8 mA/L, the maximum concentration of dichlorobenzene was 7.8 mg/L after 144 h. After that, the total byproducts went through the transformation and their concentrations reached 2 mg/L after 300 h. The increase in chlorine production under 9.0 and 18.1 mA/L led to buildup of high concentrations of 33.1 and 33.6 mg/L total byproducts after 72 and 48 h, respectively. The byproducts are also toxic and their buildup is not practical or acceptable. Complete transformation is important. This leads to the point that lower current densities on the order of 1–2 mA/L should be more efficient and cost effective than higher current densities (on the order of 9.0–20 mA/L), even though higher currents cause faster transformation rate of benzene.

The results are summarized in detail in Table 1. The table also shows the changes of benzene concentrations in the control

reactor. During the period of 312 h the change in concentration in the control setup was from 40.2 to 35 mg/L, which represent 12.6% loss. The control shows that the losses are reasonable and that the effect of volatilization and/or adsorption was limited. The reactors are made of glass and were completely sealed to minimize the effect of potential losses.

To assess the role of the electrolytes on the transformation, experiments were conducted using sodium nitrate solution instead of sodium chloride. The experiments also assess the impacts of chlorine gas formation at the anode. The standard reduction potential for oxidizing water to oxygen gas and hydrogen ions is very close (1.33 V) to the standard reduction potential for the formation of chlorine gas from chloride ions (1.36 V), as given by

$$O_2(g) + 4\,H^+(aq) + 4\,e^- \leftarrow 2\,H_2O(l) \quad E^0 = -1.23\,V$$

$$Cl_2(g) + 2\,e^- \leftarrow 2\,Cl^- \quad E^0 = -1.36\,V$$
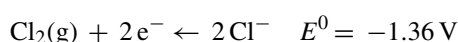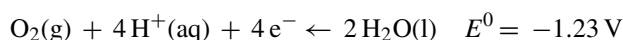
The effect of secondary reaction, such as the oxidation of sodium nitrate, in the anode reactor may be minimized. It is known that nitrate can be reduced to nitrate, nitrous oxide, nitrogen, ammonia and ammonium. It is possible to oxidize the ammonium, ammonia, nitrogen and nitrite to nitrate but it is difficult to oxidize the nitrate which considered as a terminal nitrogen oxidation process.

Fig. 7 shows the transformation of benzene under 18.1 mA/L using sodium chloride and sodium nitrate as electrolytes. Degradation of benzene occurred from 41 mg/L to almost 1 mg/L within 120 h, which indicates that the rate of transformation is slower than using sodium chloride solution. However, the transformation is significant. Note that the change in the control concentration was from 41 to 37 mg/L. Furthermore, the transformation in the absence of chloride ions is important since chlorinated benzene products will not be anticipated in this case. In fact, analysis of the byproducts of transformation showed that using of sodium nitrate as an electrolyte in the reactor resulted in benzene transformation without any significant buildup of byproducts. This indicates that the transformation at the anode is possible without the formation of the chlorine gas (which usually serves as oxidant).

Table 1
Average benzene concentrations, piece transformation rates and percent under electrochemical redox

| Time (h)	Current = 10 mA, current density = 18.1 mA/L			Current = 5 mA, current density = 9.0 mA/L			Current = 1 mA, current density = 1.8 mA/L			Control 0 mA
	Concentration (mg/L)	Transformation		Concentration (mg/L)	Transformation		Concentration (mg/L)	Transformation		Concentration (mg/L)
		Rate mg/L h	%		Rate mg/L h	%		Rate mg/L h	%	
0	40.2	0	0	40.2	0	0	40.2	0	0	40.2
24.00	15.56	1.03	61.10	13.08	1.12	67.31	21.78	0.77	45.82	40.07
48.00	3.01	0.52	92.48	5.07	0.33	87.32	17.64	0.17	56.12	40.41
72.00	0.64	0.10	98.40	1.78	0.14	95.55	13.82	0.16	65.62	39.78
96.00	0.25	0.02	99.39	0.64	0.05	98.40	9.77	0.17	75.70	40.85
144.00	0.31	0.00	99.23	0.01	0.01	99.97	4.67	0.21	88.38	37.75
216.00	0.24	0.00	99.41	0.30	0.00	99.26	1.31	0.14	96.74	38.46
288.00	0.19	0.00	99.53	0.25	0.00	99.38	0.71	0.03	98.23	38.2
312.00	0.25	0.00	99.38	0.28	0.00	99.29	1.19	-0.02	97.04	35.11
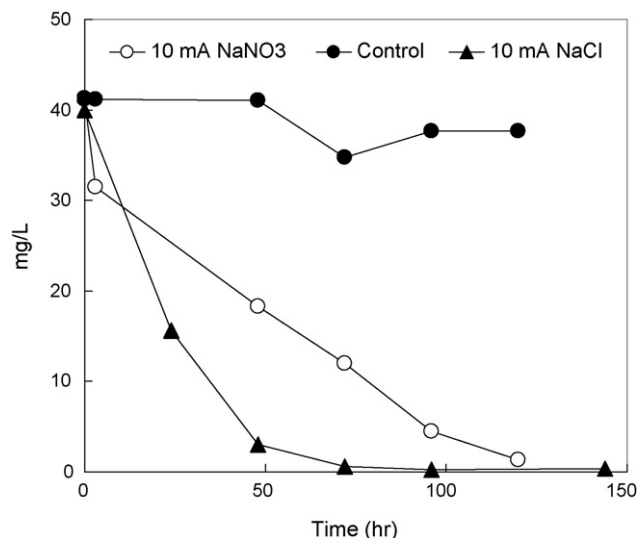
Fig. 7. Benzene breakdown in NaCl and NaNO₃ electrolytes under 10 mA (18.1 mA/L).

Changes in pH and redox potential were consistent with previous studies (see for example [5]). Since non-reactive electrodes were used, the anode pH dropped to around 2 and the redox potential increased to more the 1000 mV. The most significant changes were under 18.1 mA/L, where the potential reached around 1300 mV.

4. Conclusions

The study findings are summarized below:

- Electrolytic transformation of benzene in a sodium chloride electrolyte occurred forming byproducts that include dichlorobenzene. Continuous treatment under electric currents resulted in transformation of the chlorinated benzene byproducts.
- Benzene electrolytic transformation is dependent on the current density. Increasing the current density results in a faster transformation until an optimum is reached beyond which there is no increase in the transformation rate. However, the higher current densities (9.0–18.1 mA/L) result in buildup of higher concentration of chlorinated benzene byproducts when compared to lower current densities (1.8 mA/L). The transformation of the byproducts occurs at a slower rate, such that the time required for complete transformation of benzene and its byproducts is independent of the current density. In this study, about 2 weeks were required for the transformation of benzene and the byproducts.
- When sodium nitrate was used as the electrolyte, transformation of benzene also occurred, but under a slower rate than that of the sodium chloride electrolyte. However, the advantage is the byproducts were not detected in this case.

Acknowledgement

References

[1] J.N. Rooney-Varga, R.T. Anderson, J.L. Fraga, D. Ringelberg, D.R. Lovley, Microbial communities associated with anaerobic benzene degradation in a petroleum-contaminated aquifer, Appl. Environ. Microbiol. 65 (7) (1999) 3056–3065.

[2] J.M. Weiner, D.R. Lovley, Rapid benzene degradation in methanogenic sediments from a petroleum-contaminated aquifer, Appl. Environ. Microbiol. 64 (1998) 1937–1939.

[3] I.M. Lo, L. Cheng-Hao, H.M. Liljestrand, Tricaprylmethyl-ammonium bentonite complexes as adsorbents for benzene, toluene, ethylbenzene and xylene, Water Sci. Technol. 34 (7–8) (1996) 319–325.

[4] Y.B. Acar, A.N. Alshawabkeh, Principles of electrokinetic remediation, Environ. Sci. Technol. 27 (13) (1993) 2638–2647.

[5] A.N. Alshawabkeh, H. Sarahney, Effect of current density on enhanced transformation of naphthalene, Environ. Sci. Technol. (39) (2005) 5837–5843.

[6] D.M. Gilbert, T.C. Sale, Sequential electrolytic oxidation and reduction of aqueous phase energetic compounds, Environ. Sci. Technol. 39 (23) (2005) 9270–9277.

[7] S. Ito, R. Katayama, A. Kuni, A novel paired electrosynthesis of *p*-benzoquinone and hydroquinone from benzene, Tetrahedron Lett. 30 (2) (1989) 205–206.

[8] R.M. Zaveri, J.R.V. Flora, Laboratory septic tank performance response to electrolytic stimulation, Water Res. 36 (2002) 4513–4524.

[9] A.J. Franz, J.W. Rucker, J.R.V. Flora, Electrolytic oxygen generation for subsurface delivery: effects of precipitation at the cathode and an assessment of side reactions, Water Res. 36 (2002) 2243–2254.

[10] R.K. Goel, J. Flora, J. Ferry, Mechanisms for naphthalene removal during electrolytic aeration, Water Res. 37 (4) (2003) 891–901.

[11] D. Arapoglou, A. Vlyssides, C. Israilides, A. Zorpas, P. Karlis, Detoxification of methyl-parathion pesticide in aqueous solutions by electrochemical oxidation, J. Hazard. Mater. 98 (1–3) (2003) 191–199.

[12] R.A. Torres, V. Sarria, W. Torres, P. Peringer, C. Pulgarin, Electrochemical treatment of industrial wastewater containing 5-amino-6-methyl-2-benzimidazolone: toward an electrochemical–biological coupling, Water Res. 37 (13) (2003) 3118–3124.

[13] C. Pulgarin, N. Adler, P. Péringer, C. Comninellis, Electrochemical detoxification of a 1,4-benzoquinone solution in wastewater treatment, Water Res. 28 (4) (2003) 887–893.