Journal of Applied Electrochemistry (2005) 35:897–902
DOI 10.1007/s10800-005-4722-9

# Evaluation of electrolysis for oxidative deodorization of hog manure

DORIN BEJAN, FARIDA SAGITOVA and NIGEL J. BUNCE*
*Department of Chemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada*
*(*author for correspondence, tel.: +1-519-824-4120, ext. 53962; fax: +1-519-766-1499;*
*e-mail: bunce@chembio.uoguelph.ca)*

Received 10 January 2005; accepted in revised form 17 March 2005

*Key words:* boron-doped diamond anode, electrolysis, liquid hog manure, titanium–tin dioxide anode

## Abstract

Electrolysis was investigated as a method for the amelioration of odor from the supernatant phase of centrifuged liquid hog manure. Methods examined included the use of dual anodes to provide both oxidizing intermediates from water electrolysis and a sacrificial input of iron into solution to remove organic constituents of hog manure by coagulation. The most promising approaches used a "dimensionally stable anode" composed of tin dioxide coated on a base of titanium, and the newly developed material boron-doped diamond, which has an exceptional stability to both oxidizing and reducing electrolytic conditions. These anodes promote the formation of hydroxyl radicals which initiate oxidation of organic constituents of the manure.

## List of Abbreviations

| | |
|---|---|
| BOD | biological oxygen demand |
| COD | chemical oxygen demand |
| TC | total carbon |
| TOC | total organic carbon |
| IC | total inorganic carbon |
| TN | total nitrogen |
| DSA | dimensionally stable anode |
| BDD | boron-doped diamond electrode |
| DC | direct current |
| HPLC | high-performance liquid chromatography |

## 1. Introduction

Offensive odors from intensive hog operations cause increasingly adverse public attention, especially during land disposal of liquid hog manure. Odor components are formed when anaerobic bacteria reduce organo-nitrogen and -sulfur compounds in the anoxic environments of the porcine gut and liquid manure tank. Purging the liquid manure tank with air fails to maintain oxygenated conditions because of the high bacterial load and oxygen demand. In this research we investigated at a laboratory scale the possibility of "neutralizing" the odor of liquid hog manure by electrochemical oxidation.

Electrochemical remediation methods have been used as "niche technologies" when biological treatments are unsatisfactory, e.g., with contaminants that are recalcitrant towards biological remediation or toxic to the microflora of bioreactors. Electrolysis offers prospective advantages of relatively simple equipment, oxidative or reductive chemistry, and operation at ambient temperature and pressure [1]. By comparison with chemicals, electricity is cheap: at a cell potential of 2 V and with electricity costing 8 ¢ per kWh, $1.00 purchases >200 mol of electrons. Challenges include parasitic processes such as water electrolysis that lower current efficiency, formation of insulating deposits on the electrode surface, and the need for inexpensive electrode materials.

Electrolysis has been suggested, *inter alia*, for the oxidation of wastes such as municipal landfill leachates [2], tannery waste water [3], pesticide wastes [4], wastewater containing phenolics [5] and, germane to the present research, animal wastes. Gibson et al. [6] electrolyzed the supernatant from anaerobic sewage digesters, using $PbO_2$/graphite or $PbO_2$/Ti anodes and a cylindrical cathode made of copper, stainless steel, or iron. $PbO_2$ anodes promote the production of hydroxyl radicals by water electrolysis [7]; $PbO_2$ was investigated in our laboratory with the model odor compound 3-methylindole [8]. Gibson et al. [6] claimed that even a "relatively slight" electrolytic treatment completely suppressed putrescent odor and "significantly" lowered both BOD and COD, but provided no information about current efficiency, which is key to determining the economic feasibility of electrochemical technologies.

Gibson et al. [6] also achieved disinfection of sewage using an electrochemical hypochlorinator (producing hypochlorite from added brine). Hypochlorination, using the $Cl^-$ present in sewage, was suggested by Preis and Cole [9] (who used carbon anodes and various metal cathodes), and by Morichon and Serpaud [10], to bleach colors, remove odors, and oxidize suspended organic material. However, hypochlorination inevitably affords chlorinated organic byproducts, some of which may be recalcitrant to further treatment.

Tennakoon et al. [11] achieved "electrochemical incineration" (i.e., electrochemical oxidation to $CO_2$ and water [12, 13]), of a synthetic human waste, using Ebonex particles coated with $Sb_2O_3$-doped $SnO_2$ in a packed bed reactor. The current efficiency was limited by accumulation of gas bubbles between the particles.

Gustafson [14] employed electrolytic oxidation to lower the concentration of urea in manure slurry. The concept was that removal of urea, which inhibits algal growth, would stimulate photosynthetic activity to produce oxygen. Hydrogen sulfide off-gas from a treatment lagoon was reduced to barely perceptible levels within hours of starting electrolysis, but since the algae required 5–10 days to become established, it is unclear whether electrolysis promoted removal of urea or direct degradation of odor compounds.

Although several authors have reported odor inhibition by electrolysis of manure at copper anodes [15–17], these methods all appear to rely on the toxicity of dissolved $Cu^{2+}$ towards the odor-causing bacteria. Contamination by $Cu^{2+}$ mitigates against land-disposal of liquid hog manure thus treated.

Other proposed sacrificial anodes comprise metals whose hydroxides can coagulate manure solids to lower the TOC. As early as 1919, Creighton and Franklin [18] compared lime, electrolysis at iron electrodes, and lime + electrolysis for sewage treatment. Lime alone gave a very disagreeable odor, presumably through conversion of amines to non-ionic, volatile forms at high pH. Electrolysis alone gave high levels of free $H_2S$, probably by cathodic reduction of sulfur-containing precursors. Electrolytic-lime treatment ameliorated odor and lowered the bacterial count >90%. This chemistry involves sacrificial dissolution of the iron anode, followed by air oxidation of $Fe^{2+}$ to $Fe^{3+}$; precipitation of a material with composition in the range FeOOH to $Fe(OH)_3$ [19, 20] allows co-precipitation of bacteria, as in drinking water treatment.

Brainard [21] precipitated metal sulfides from sewage using sacrificial anodes (preferably cast iron; also Mn, Co, Ni, or Zn) in combination with a less electropositive cathode (*e.g.*, stainless steel, Ni-Resist, or Inconel). Stoichiometric removal of sulfide requires sufficient dissolution of the anode to titrate away sulfur, making the process both costly and likely to introduce toxic metal ions into the treated waste. Marconato et al. [22] proposed a related electrolytic approach, using cast iron or aluminum sacrificial anodes, to remove sulfides from fowl slaughterhouse waste and lower COD by coagulating small particles with the M(III) hydroxide. Iron was more effective because of the high water solubility of aluminum sulfide. Dutil et al. [23] added metal particles, (*e.g.*, steel, Al, Fe, or Mg) which dissolved during electrolysis of liquid manure at inert electrodes, achieving both coagulation due to hydroxide formation and removal of phosphate by precipitation of insoluble phosphates.

Moniwa et al. [24] remediated wastewater using the electro-Fenton reaction. Oxygen supplied to the cathode generated hydrogen peroxide, which reacted with $Fe^{2+}$ dissolved from a sacrificial anode to form reactive hydroxyl radicals ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$).

Previous work in our laboratory involved electrolysis of the model odor compound 3-methylindole. In exploratory studies at a Pt anode, polymeric deposits on the electrode inhibited electrochemical oxidation [25], whereas at $PbO_2$, 3-methylindole was oxidized with high current efficiency [8]. The difference in behavior is explained by the oxidation chemistry at these two anodes [12]. At Pt, the substrate is directly oxidized at the electrode surface, whereas at $PbO_2$, oxidation occurs by the action of hydroxyl radicals formed by partial oxidation of water.

In the present work, we studied the oxidation of the aqueous fraction of liquid hog manure at various anodes. The objectives were to find anodes suitable for oxidative odor remediation and to correlate loss of odor with reduction in the TOC of the solution.

## 2. Materials and methods

### 2.1. *Materials*

Liquid hog manure was collected from the Arkell Research Station of the University of Guelph, and stored in the dark at 5 °C for no longer than 2 weeks. Centrifugation (480× *g* per centrifuge bottle) at 10,000 rpm for 15 min, yielded ~100 g of black semi-solid, 5 g of suspended matter, and ~375 ml of yellow-greenish liquid, which was used as the liquid fraction of hog manure. $Na_2SO_4$ (used as an additional supporting electrolyte in some experiments) and $FeSO_4$ (Fisher Scientific, Toronto ON) and $Fe_2(SO_4)_3$ and $H_2O_2$ (Aldrich, Mississauga, ON) were used as received.

Mild and stainless steel electrodes were fabricated from scrap material by the Machine Shop, College of Physical and Engineering Science, University of Guelph. Graphite electrodes were purchased from Aldrich. Boron doped diamond electrodes (BDD) were supplied by Swiss Center for Electronics and Microtechnology, Inc., Neuchâtel. Dimensionally stable anodes (DSAs) of $Ti/IrO_2$ and $Ti/SnO_2$ were supplied by ELTECH Systems Corporation, Painesville, OH.

### 2.2. *Apparatus*

Electrolyses were performed in both flow and batch cells. The batch cell was an undivided open-top glass electrochemical reactor that could accommodate variable volumes of solution and both one anode–one cathode and two anodes–one cathode systems. The electrodes had dimensions 5.5 × 4.0 cm; they were mounted vertically and connected by bronze bars (mild steel electrodes and DSAs) or directly (graphite electrodes) to the power supply connectors. The solution was mixed with a mechanical stirrer. Foaming, due both to anodic evolution of $O_2$ and the natural surfactants present in manure, was removed manually at intervals. At higher currents it was necessary to cool the electrochemical cell because of joule heating.

The flow cell was a Plexiglas undivided electrochemical reactor, of volume 7.8 ml, built in our laboratory and operated at 1 ml $min^{-1}$ flow rate, using a Masterflex C/L peristaltic pump, either in single pass mode, or in recirculation mode with the effluent directed into a reservoir. In recirculation mode, the number of equivalent passes was given by "Flow rate (ml $min^{-1}$) × Electrolysis time (min)/Liquid volume (ml)". The liquid volume was normally 40 ml. The electrodes (5 × 1.5 cm) were mounted vertically and employed pieces of Pt wire (Aldrich) and stainless steel wire as electrode feeders. The cathode was stainless steel. The potential difference between the electrodes was 5–12 V depending on the current. Foaming was more pronounced with the Ti/$SnO_2$ and Ti/$IrO_2$ anodes, perhaps because their grid shape caused more turbulence in the reactor than the smooth-surfaced BDD.

The DC power supplies were a Model 363 potentiostat/galvanostat supplied by EG&G, a DC power supply built by the Chemistry Department Electronic Shop (10 V-1.5 A), and a Golden Source DC power supply (30 V-20 A). All electrolyses were conducted galvanostatically (constant current) with the electrical circuit also including an ammeter and voltmeter.

### 2.3. *Analysis*

Before electrolysis, the liquid hog manure had a repulsive and nauseating odor. We defined smell as follows: A = hog manure smell (offensive nauseating odor); B = disagreeable barn-like smell; C = mild barn-like smell (but non-offensive); D = almost no smell (faint organic solvent-like odor). After electrolysis the solutions to be analyzed for Total Carbon (TC), Inorganic Carbon (IC) and Total Nitrogen (TN) were refrigerated prior to analysis with a Shimadzu TOC analyser, model TOC-VCSH). Total Organic Carbon (TOC) was calculated as the difference between TC and IC.

## 3. Results and discussion

### 3.1. *Preliminary experiments*

The individual odor compounds in hog manure were present at concentrations too low to monitor by conventional instrumental methods such as gas and liquid chromatography, and, as other researchers have reported [26], we had to use our subjective sense of smell to judge the success of different treatments. Although unidentified chromatographic peaks could be detected by reverse-phase HPLC, none of their intensities correlated with either the rate of disappearance of known odor components such as 3-methylindole (spiked into the solution [27]) or with the changing smell of the electrolyzed solutions.

Preliminary experiments without electrolysis were conducted using either iron salts as coagulants, or 30% aqueous $H_2O_2$ as an oxidant, or combining both in conventional Fenton chemistry [28], in which $Fe^{2+}$ catalyzes the decomposition of $H_2O_2$, producing hydroxyl radicals (*cf.* [24]). Only the latter treatment, using $>10\%$ v/v of 30% $H_2O_2$ and incubation times $>3$ h removed the odor completely.

To simplify the experimental design of our electrolyses, manure samples were centrifuged before use to minimize electrode fouling by their solids. Because liquid hog manure already contains sufficient inorganic salts to carry the current, it was unnecessary to add $Na_2SO_4$ as supporting electrolyte.

Little success was achieved using iron-based anodes, including mild steel, stainless steel, or pure iron, using either batch cells or plug-flow cells. Only with the addition of hydrogen peroxide was the odor of hog manure dissipated, and then only at high currents (2–4 A) (*cf.* [29]). We also studied two independently powered anodes, for example, a graphite anode operated at 4–5 A, and an iron-based sacrificial anode operated at 1–1.5 A. The concept was that the graphite anode would principally function to provide oxidation products from water (e.g., hydroxyl radicals and $H_2O_2$), while $Fe^{2+}$ from the steel anode would convert any $H_2O_2$ into hydroxyl radicals. However, complete odor amelioration was only achieved when $H_2O_2$ was added as an auxiliary oxidant.

Attention was therefore turned to "dimensionally stable anodes" (DSAs), and to boron-doped diamond (BDD). DSAs are composed of a $\mu$m deposit of conductive metal oxide on a base of metallic titanium. We used Ti/$IrO_2$ and Ti/$SnO_2$, which are members of different mechanistic families [30]. BDD is made by high temperature chemical vapor deposition to give an electrically conducting film having remarkable stability towards both oxidation and reduction. Ti/$SnO_2$ and BDD were much superior to Ti/$IrO_2$, using the subjective parameter of odor reduction and the objective metric of TOC reduction (Table 1). Under anodic polarization, Ti/$IrO_2$ yields a surface layer of a higher oxide, possibly $IrO_3$, which is the actual oxidant for the substrate, whereas BDD and Ti/$SnO_2$ act as sources of hydroxyl radicals, from partial oxidation of water [5, 31–34]. Oxidation of substrate (RH) is initiated by OH, allowing efficient radical chain autooxidation by the molecular oxygen that is also present in the solution from electrolysis of water.

*Table 1.* Electrolysis of liquid hog manure in a batch cell with DSA anode

| Entry number | Anode | Volume of solution (ml) | Current (A) | Supporting electrolyte | Time | Odor |
|---|---|---|---|---|---|---|
| 1 | Ti/IrO$_2$ | 40 | 0.2 | – | 2.5 h | A |
| 2 | Ti/IrO$_2$ | 40 | 0.5 | – | 5 h | B |
| 3 | Ti/IrO$_2$ | 80 | 0.2 | – | 5 h | A |
| 4 | Ti/IrO$_2$ | 100 | 0.2 | – | 5 days | A |
| 5 | Ti/IrO$_2$ | 200 | 5 | – | 45 min | B |
| 6 | Ti/SnO$_2$ | 40 | 0.5 | – | 3 h | C |
| 7 | Ti/SnO$_2$ | 40 | 0.5 | – | 4 h | C |
| 8 | Ti/SnO$_2$ | 200 | 1.0 | – | 3 h | A |
| 9 | Ti/SnO$_2$ | 200 | 4.5 | 0.2 M Na$_2$SO$_4$ | 1 h | C |
| 10 | Ti/SnO$_2$ | 200 | 4.5 | 0.2 M Na$_2$SO$_4$ | 2 h | C |
| 11 | Ti/SnO$_2$ | 200 | 4.5 | 0.2 M Na$_2$SO$_4$ | 3 h | C |

$$H_2O \rightarrow H^+ + OH + e^-$$

$$OH + RH \rightarrow H_2O + R$$

$$R + O_2 \rightarrow R{-}O{-}O \rightarrow \text{further oxidation}$$

In no case were significant changes in pH, from the initial values near pH 8, observed upon electrolysis.

### 3.2. *Odor reduction correlated with TOC*

In recirculation mode, odor intensity and TOC fell progressively with the increased current and/or increased electrolysis time at Ti/SnO$_2$ and BDD, along with a lightening of the color of the solution: see Table 2 and Figure 1 (panel a for BDD and panel b for SnO$_2$/Ti). Samples of solution were briefly removed from the reservoir after each equivalent pass (40 min) and analyzed for smell, which underwent well-defined changes upon electrolysis. The nauseating smell of liquid hog manure (A) was replaced by a non-offensive odor that we describe as “barn-like” (B). Upon prolonged electrolysis this odor diminished progressively (C) and was replaced, in the case of BDD by a faint “solvent-like” smell (D), which we attribute to Kolbe decarboxylation of aliphatic carboxylic acids to hydrocarbons: *e.g.*, butyric acid affords hexane as the volatile product. Carboxylic acids are formed as intermediates in the mineralization of complex organic molecules to CO$_2$ + H$_2$O.

$$2CH_3CH_2CH_2CO_2^- \rightarrow CH_3CH_2CH_2CH_3CH_2CH_3 + 2CO_2 + 2e^-$$

At both Ti/SnO$_2$ and BDD, the TOC declined steadily with total charge passed. Odor removal was

*Table 2.* Comparison of electrolyses of liquid hog manure with BDD and Ti/SnO$_2$ anodes in the plug-flow reactor

| BDD | | | | Ti/SnO$_2$ | | | |
|---|---|---|---|---|---|---|---|
| Current (mA) | Odor | Pass number | Final color | Current (mA) | Odor | Pass number | Final color |
| 100 | C | 3 | Transparent green | 100 | B | 3 | Opaque green |
| 200 | C | 2 | Transparent yellow | 200 | C | 2 | Transparent green |
| 400 | D | 1 | Transparent light yellow | 400 | C | 1 | Transparent yellow |

B – barn-like smell; C – slight barn-like smell; D – solvent-like smell or almost no smell.

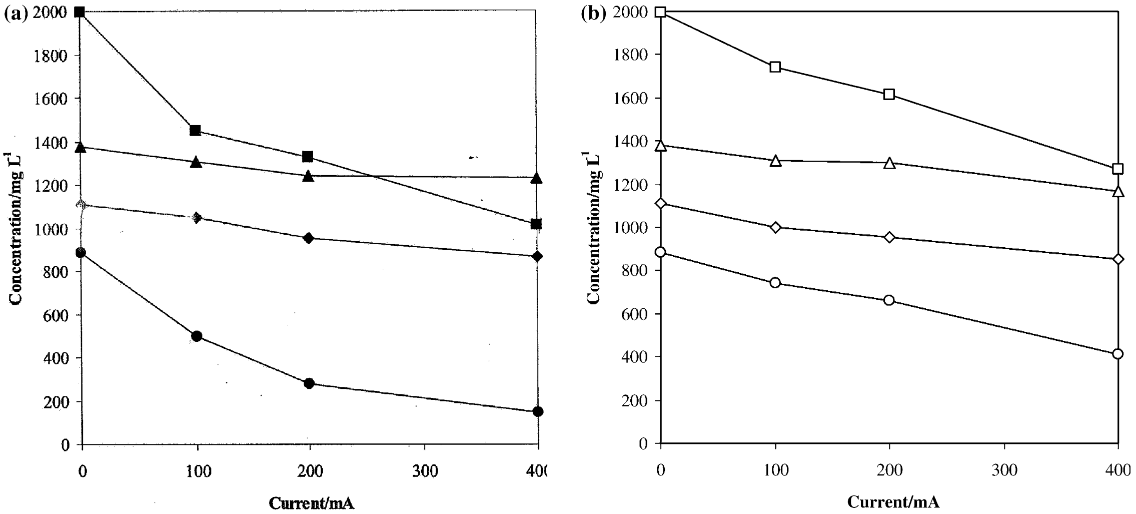

*Fig. 1.* panel a: Electrolysis of hog manure liquid at BDD anode in the plug flow reactor in recirculation mode (four equivalent passes). Variation of total carbon (square), inorganic carbon (diamond), total organic carbon (circle) and total nitrogen (triangle) with current. panel b: Electrolysis of hog manure liquid at the Ti/SnO$_2$ anode in the plug flow reactor in recirculation mode (four equivalent passes). Variation of total carbon (square), inorganic carbon (diamond), total organic carbon (circle) and total nitrogen (triangle) with current.

faster than loss of TOC, parallel to the results of Gibson et al. [6]. Almost complete loss of TOC was achieved at BDD at an applied current of 400 mA in four passes through the reactor. Although the applied currents were equal at both electrodes, the current densities were higher at $Ti/SnO_2$, which was supplied in the form of a grid, whereas BDD was supplied as a solid sheet.

Besides the loss of TOC, Figure 1 shows a progressive decline in inorganic carbon (IC) but no loss of total nitrogen (TN). Lowered IC is attributed to stripping $CO_2$ out of solution by the $O_2$ formed by electrolysis of water. TN remained constant because nitrogenous compounds are oxidized to $NO_3^-$ rather than to volatile nitrogen oxides.

Figure 2 (panels a and b for BDD and panel c for $Ti/IrO_2$ anodes) presents the progress of electrolysis when the plug-flow reactor was operated in simulated cascade mode. At BDD there was progressive loss of both IC/TOC and smell, but at $Ti/IrO_2$ (panel c) there was little amelioration of odor, even after several passes through the reactor. TOC declined very little, and IC dropped slightly, due to stripping $CO_2$ by the $O_2$ evolved at the anode.

Although current efficiencies are difficult to evaluate, we suggest that mineralization involves a four-electron change per carbon atom, assuming that the organic material in hog manure can be approximately represented as carbohydrate $(CH_2O)_n$.

$$CH_2O + H_2O \rightarrow CO_2 + 4H^+ + 4e^-$$

The TOC data from Figure 2a suggest overall current efficiencies for mineralization at BDD of $\sim 10^{-4}$. The values increase with current because the potential difference across the cell increases with current (Ohm's Law). Our miniaturized plug-flow reactor used planar electrodes, which did not promote optimum charge transport, and at higher currents was limited by the difficulty of dissipating heat.

Upon starting this work, we expected that electrolysis would not achieve long-term odor amelioration, because the electrolyzed solution would still retain BOD and hence revert to an anaerobic state over time. In practice, solutions electrolyzed to the near-odorless state could be stored for several weeks without developing any off odor. This is probably the result of killing bacteria upon electrolysis due to electroporation [35], but we have not yet quantified this. An ideal practical technology would allow successful treatment of liquid hog manure in a single pass through the electrochemical reactor, followed by land application. The goal is not complete TOC removal, merely sufficient "sweetening" that the treated material can be applied to land, while minimizing energy costs. Retention of TN in the solution shows that its fertilizer nitrogen value is preserved, as also are potassium and phosphorus.

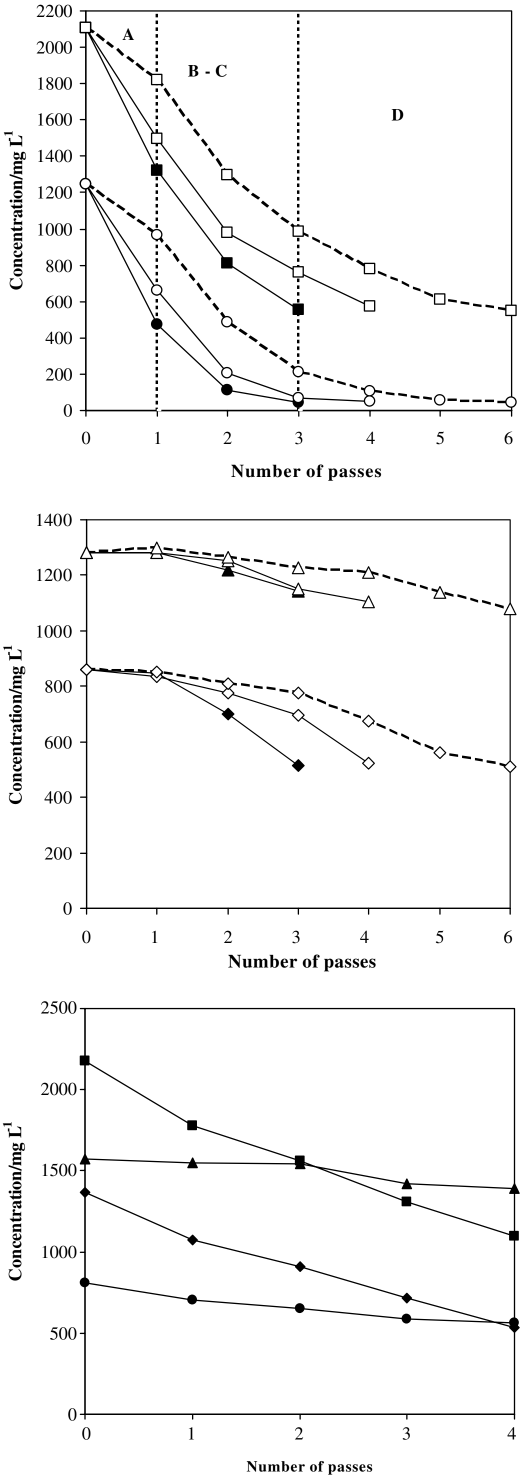

*Fig. 2.* panel a: Variation of total carbon (square) and total organic carbon (circle) at the BDD anode, as a function of the current in a simulated cascade of plug flow reactors. 400 mA – interrupted line, empty symbol; 600 mA – plain line, empty symbols; 800 mA – plain line, full symbols. Symbols for smell: A – offensive; B – barn-like; C – slight barn-like; D – solvent-like, or almost no smell. panel b: Variation of inorganic carbon (diamond) and total nitrogen (triangle) at the BDD anode function of the current in a simulated cascade of plug flow reactors. 400 mA – interrupted line, empty symbol; 600 mA – plain line, empty symbols; 800 mA – plain line, full symbols. panel c: Variation of total carbon (square), inorganic carbon (diamond), total organic carbon (circle) and total nitrogen (triangle) at the $Ti/IrO_2$ anode in a simulated cascade of plug flow reactors at 400 mA (a similar result was obtained at 200 mA).

## 4. Conclusion

We have demonstrated proof of concept that electrolytic oxidation can ameliorate the odor of the liquid fraction of hog manure. Salts naturally present in the excreta make electrolysis a "green" technology in the sense of not requiring extra chemicals as a supporting electrolyte. Loss of offensive odor correlated with TOC reduction, although no specific chemical marker was found to correlate with the change in odor. We are presently developing a pilot plant with the specific objectives of remediating liquid hog manure in one pass with acceptable current efficiency.

Successful approaches to electrolytic odor amelioration will involve indirect-acting anodes at which reactive intermediates such as hydroxyl radicals are produced. Although the $PbO_2$ electrodes (actually $Pb/PbO_2$) used in our preliminary studies [8] also function by promoting the formation of hydroxyl radicals, $Ti/SnO_2$ and BDD are regarded as more friendly environmentally, as there is no chance of contaminating the effluent with the toxic metal lead.

Not mentioned so far is the fouling that we observed over time at the cathode (mild steel and stainless steel were used most often), and which was only partly soluble in organic solvents. The ideal electrode material would be stable to both anodic and cathodic polarization, so that the cell polarity could be periodically reversed in order to oxidize the developing deposit. $Ti/SnO_2$ is not suitable for this application, because $SnO_2$ is unstable towards reduction. Although BDD is stable to both anodic and cathodic polarization, it is too expensive and insufficiently rugged at the present time to be considered for long-term practical use. Further work will be directed towards finding electrode materials free of these limitations.

### Acknowledgements

We thank Ontario Pork and the Ontario Ministry of Agriculture and Food for financial support.

### References

1. K. Rajeshwar and J.G. Ibanez, *Environmental Electrochemistry* (Academic Press, San Diego, CA, 1997) Chapter 2.
2. R. Cossu, A.M. Polcaro, M.C. Lavafnola, M. Mascia, S. Palmas and F. Renold, *Environ. Sci. Technol.* **32** (1998) 3570.
3. M. Paniza and G. Cerisola, *Environ. Sci. Technol.* **38** (2004) 5470.
4. M. Zhou, Q. Dai, L. Lei, C. Ma and D. Wang, *Environ. Sci. Technol.* **39** (2005) 363.
5. A.M. Polcaro, A. Vacca, S. Palmas and M. Mascia, *J. Appl. Electrochem.* **33** (2003) 885.
6. F.D. Gibson, R.C. Rhees, J.I. Gibson and B.B. Halker, US Patent 3 764 500 (1973).
7. U. Schumann and P. Grundler, *Water Res.* **32** (1998) 2835.
8. P.G. Keech and N.J. Bunce, *J. Appl. Electrochem.* **33** (2003) 79.
9. W.R. Preis and W. Cole, Jr., US Patent 3 766 033 (1973).
10. R. Morichon and B. Serpaud, *Techniques, Sciences, Methodes: Genie Urbain– Genie Rural* **1** (1989) 37–44, through Chem. Abstr., 111, 83329.
11. C.L.K. Tennakoon, R.C. Bhardwaj and J. O'M. Bockris, *J. Appl. Electrochem.* **26** (1996) 18.
12. G. Foti, D. Gandine, C. Comninellis, A. Perret and W. Haenni, *Electrochem. Solid-state Lett.* **2** (1999) 228.
13. C.A. Martinez-Hiutle, M.A. Quiroz, C. Comninellis, S. Ferro and A. De Battisti, *Electrochim. Acta* **50** (2004) 949.
14. G.M. Gustafson, US Patent 6 146 507 (2000).
15. W. Muller, US Patent 4 654 071 (1987).
16. G. Ranalli, R. Chiumenti, L. Donantoni and C. Sorlini, *J. Environ. Sci. Health* **A31** (1996) 1705.
17. E. Zanardini, A. Valle, C. Gigliotti, G. Papagno, G. Ranalli and C. Sorlini, *J. Environ. Sci. Health* **A37** (2002) 1463.
18. H.J.M. Creighton and B. Franklin, J. *Franklin Institute*, **1919**, 157.
19. M.L. Pierce and C.B. Moore, *Water Res.* **16** (1982) 1247.
20. K.P. Raven, A. Jain and R.H. Loeppert, *Environ. Sci. Technol.* **32** (1998) 344.
21. E.C. Brainard, US Patent, 5 935 412 (1999).
22. J.C. Marconato, E.D. Bidoia and R.C. Rocha-Filho, *Bull. Electrochem.* **14** (1998) 228.
23. C. Dutil, G. Gagne, R. Chabot and Y. Comeau, US Patent 2 166 819 (2002).
24. S. Moniwa, T. Menju and S. Kazuo, Japanese Patent, 126 861, 2003, through *Chem. Abstr.*, 138, 343040.
25. P.G. Keech, M.M.G. Chartrand and N.J. Bunce, *J. Electroanal. Chem.* **534** (2002) 75.
26. K.V. Lo, A. Chen and P.H. Liao, *J. Environ. Sci. Health* **A29** (1994) 83.
27. P.G. Keech, Electrochemical oxidation of simple indoles. MSc Thesis, University of Guelph, 2001.
28. M.L. Kremer, *J. Phys. Chem.* **107** (2003) 1734.
29. M. Arienzo, J. Chiarenzelli and R. Scrudato, *J. Hazard. Mater.* **B87** (2001) 187.
30. C. Comninellis and C. Pulgarin, *J. Appl. Electrochem.* **23** (1993) 108.
31. S. Stucki, R. Kotz, B. Carcer and W. Suter, *J. Appl. Electrochem.* **21** (1991) 99.
32. B. Marselli, J. Garcia-Gomez, P.-A. Michaud, M.A. Rodrigo and C. Comninellis, *J. Electrochem. Soc.* **150** (2003) D79.
33. M. Panizza and G. Cerisola, *Electrochim. Acta* **49** (2004) 3221.
34. P. Cañizares, J. Garcia-Gomez, C. Saez and M.A. Rodrigo, *J. Appl. Electrochem.* **34** (2004) 87.
35. J.C. Weaver and Y.A. Chizmadzhev, *Bioelectrochem. Bioenerg.* **41** (1996) 135.