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ABSTRACT

Carbon aerogel electrodes have been used to remove NH_4ClO_4 and heavy metals from aqueous waste streams. Photochemical oxidation with H_2O_2 has been used to destroy organic contamination and is proposed as a means of avoiding the fouling of carbon aerogel electrodes.

I. INTRODUCTION

Hot water is used to dissolve ammonium perchlorate (NH_4ClO_4) in solid rocket propellants during decommissioning. The solubility of this salt in water is approximately 424.5 g/liter. This process requires that dissolved NH_4ClO_4 be separated from the process water so that the water can be discharged or recycled. Electrochemical cells with carbon aerogel electrodes have been used to remove a variety of contaminants, including NH_4ClO_4, from aqueous waste streams. The solution to be separated was passed through a stack of carbon aerogel electrodes, each having a very high specific surface area (400 to 1100 m^2/g) and very low electrical resistivity ($\leq$ 40 mΩ-cm). After polarization, non-reducible and non-oxidizable ions were removed from the electrolyte by the imposed electric field and held in electric double layers formed at the surfaces of electrodes. As desired, the effluent from the stack was purified water. This process was also used to remove heavy metal and colloidal impurities by a combination of double-layer charging, electrodeposition and electrophoresis. During treatability tests with contaminated ground water at Lawrence Livermore National Laboratory (LLNL), it was demonstrated that hexavalent chromium ($Cr_2O_7^{-2}$) contamination could be lowered from 35 to 2 ppb, well below the acceptable level of 11 ppb. Copper, zinc, nickel, cadmium, chromium, lead and uranium were removed from sea water and 0.1 M KNO_3. This electrolytic separation process has several potential advantages over other more conventional technologies. Since regeneration is accomplished by electrical discharge or reverse polarization, no secondary waste is generated. This is in sharp contrast to ion exchange, which requires concentrated solutions of salt, acid, or base for regeneration of the resin. Furthermore, this approach is much more energy efficient than evaporation. Finally, it offers operational advantages over reverse osmosis (RO) since high-pressure pumps and membranes are not necessarily required. When streams contain organics, steps have to be taken to prevent fouling of the electrodes. Complete photochemical oxidation can be used to convert organics into carbon dioxide, while partial photochemical oxidation can be used to produce acetate, formate, carbonate, chloride, fluoride, and sulfate ions which can be electrostatically removed with the carbon aerogel electrodes. This approach has been applied to aqueous streams that contain a fluoroalkyl surfactant, an organic used as a foaming agent by the United States Air Force (Table 1).

II. CELL WITH CARBON AEROGEL ELECTRODES

Double-sided electrodes were made by gluing two sheets of carbon aerogel composite (CAC), a novel material developed by LLNL, to both sides of a titanium plate that served as both a current collector and a structural support. Thin sheets of CAC were synthesized by infiltrating a 70% w/v resorcinol-formaldehyde (RF) solution into a porous carbon paper. After infiltration, the RF/carbon paper was cured between glass plates in a closed vessel which prevented evaporation. The cured paper was then exchanged into acetone, which was subsequently evaporated at room temperature. Finally, the

RF/carbon paper was pyrolyzed at 1050°C in a nitrogen atmosphere. This fabrication process resulted in monolithic, open-cell structures composed of chains of interconnected carbon particles with characteristic diameters of 10 nm. This unique material has a high specific surface area (400-1100 m^2/g), an optimal pore size (~50 nm), and an exceptionally low electrical resistivity (40 mΩ-cm). In fact, the resistivity is so low that it may be possible to eventually eliminate the titanium plates. Each sheet of CAC was 6.86 cm x 6.86 cm x 0.0125 cm, had a total active surface of approximately 2.8×10^6 cm^2, and had a through (front-to-back) resistance of about 10 μΩ. A thin film of conductive, graphite-filled epoxy was used to glue the sheets of CAC to the titanium plates. After gluing, the epoxy was cured for 24 hours at 85°C. A pattern of holes was located around the perimeter of each titanium plate and accommodated 12 threaded rods that held the stack together. Even electrodes served as cathodes while odd electrodes served as anodes. The electrodes and headers were aligned by the threaded rods. A separation of about 0.12 to 0.16 cm was maintained between electrodes by rubber compression seals (gaskets) and cylindrical Delrin (acetyl resin) spacers concentric with the threaded rods. Note that the height of each spacer, measured from shoulder to end, was 0.127 cm (0.050 inches). A rectangular orifice in each titanium plate admitted flow into the downstream electrode gap. This orifice was located inside the pattern of holes, as well as inside the rubber compression seal, and was aligned with one edge of each CAC sheet. Since the orifices alternated from one side of the stack to the other, the flow path through the stack was serpentine. Note that the orifice was divided by a center tab. Four assembled stacks included 192 double-sided electrodes (384 sheets of CAC; 192 individual electrochemical cells) and had a total active cathodic (or anodic) surface area of approximately 1.1×10^9 cm^2. Flow through the stack was generated by a programmable, magnetically-coupled, gear pump with a 304 stainless steel head. The maximum flow rate that could be achieved with this pump was 3.5 liter/min. Due to the unrestricted path, the differential pressure across a single stack of 48 double-sided electrodes was only 5 psi at a flow rate of 1.7 liter/min. As expected, the differential pressure across four stacks in series (192 double-sided electrodes) was slightly greater, 14 psi at a flow rate of 1.5 liter/min. All lines were made of Teflon and had a nominal diameter of 1/4 inch. The cells were polarized by a programmable power supply that had a voltage range of 0 to 12 V or a current range of 0 to 60 A. Sensors were placed on the inlet and outlet lines of the stack. Electrical conductivity, pH, individual ion concentrations, and temperature were continuously monitored. A computerized data acquisition system logged important operating parameters such as voltage, current, conductivity, pH, and temperature. Data acquisition system was based on an Intel 486DX-33 microprocessor, a National Instruments 8-channel A/D converter, and LabTech Notebook data acquisition software for Microsoft Windows.

III. AMMONIUM PERCHLORATE SEPARATION

The process to remove NH_4ClO_4 from water is known as carbon aerogel capacitive deionization (CDI).[1-5] Earlier versions of the process used activated carbon electrodes.[6-12] Upon application of a voltage between adjacent CAC electrodes, cations and anions were drawn towards the cathodes and anodes, respectively. These ions were held in the electric double layers formed at the extensive surface of the CAC electrodes until the voltage was reduced. Tests demonstrated that CDI with CAC electrodes could effectively remove NH_4ClO_4 from water. As shown in figure 1, deionization was accomplished during charging, while regeneration was accomplished during discharge. The concentration and conductivity of the NH_4ClO_4 solution was cycled up and down numerous times by charging and discharging the stack. The ability of the CAC electrodes to remove ions from water, i.e., the electrosorption capacity, had a strong dependence on cell voltage. The best results were achieved at 1.2 V, with relatively poor performance below 0.4 V. At 1.2 V and 100 ppm NH_4ClO_4, the anion capacity was determined to be approximately 2.5×10^{-5} equivalents per gram of CAC. No severe irreversible degradation in performance was observed after cycling the stacks several months. During experiments without recycle, a characteristic breakthrough time was observed for each of several salts tested, which is indicative of ionic selectivity. Deionization of more concentrated solutions will require more CAC electrodes.

IV. REMOVAL OF HEAVY METALS

A single electrochemical cell with only two CAC electrodes, one cathode and one anode, was used to remove various heavy metals from a fixed 500 ml volume of sea water. The starting concentration of each contaminant, which included Cr, Mn, Co, Ni, Pb, and U, was 100 ppb. The flow rate was 50 ml/min and the cell voltage was 1.2 V. Results for Co, Pb, and U are shown in figure 2. More electrodes would have resulted in faster, more complete separation.

V. DESTRUCTION OF ORGANICS

A photochemical (UV-H_2O_2) reactor was built around a 25 cm long, 450 W, medium-pressure mercury lamp (Canrad-Hanovia). The total volume of the system was approximately 2 liters. A peristaltic pump was used to add the 30% hydrogen peroxide (H_2O_2) solution to the reactor and a magnetic stir bar was used for agitation. All solutions were prepared with deionized water. After turning on the lamp, the H_2O_2 feed pump was started. Within a few minutes, the solution was heated to 40°C and maintained at that temperature by auxiliary cooling. Samples for chemical analysis were collected through a plastic valve. Since the volume of each sample removed from the reactor was equivalent to the amount of 30% H_2O_2 solution added, the liquid inventory was kept constant. Analysis of total organic carbon (TOC) in solutions was done by using a standard peroxydisulfate-based TOC analyzer. The destruction of FC-203 CE surfactant by photochemical oxidation in a relatively large volume of H_2O is shown in figures 3 through 6. The liquid inventory in the reactor, the amount of surfactant solution added, the feed rate of 30% H_2O_2 solution (oxidant), and the lamp power were respectively: (fig. 3) 1.6 liters, 5 ml, 0.23 ml/min and 450 W; (fig. 4) 1.5 liters, 15 ml, 0.23 ml/min and 450 W; (fig. 5) 1.5 liters, 15 ml, 1 ml/min and 450 W; and (fig. 6) 1.5 liters, 15 ml, 3 ml/min and 200 W. By comparing the data shown in figures 4 and 5, it is evident that the half life of the surfactant in the reactor was reduced from 3.5 to 2.0 hrs by increasing the flow rate of hydrogen peroxide solution from 0.23 to 1 ml/min. Apparently, the reaction was H_2O_2 limited. Furthermore, by comparing the data shown in figures 4 and 6, it appears that about the same rates of destruction were achieved with (a) 450 W of lamp power and an oxidant feed rate of 0.23 ml and (b) 200 W of lamp power and an increased oxidant feed rate of 3 ml/min. Thus, an optimum combination of lamp power and oxidant must exist. Most important, it was concluded that essentially complete photochemical destruction of the foaming agent was accomplished. Residual ions such as fluoride could be removed by carbon aerogel CDI or electrolysis. Photochemical destruction requires no such additions and promises to be an excellent pretreatment for carbon aerogel CDI. Note that other low-temperature, low-pressure aqueous phase processes require the addition of troublesome inorganic reagents.[13-18]

VI. SUMMARY

In summary, it has been shown that CDI with CAC electrodes is capable of effectively removing NH_4ClO_4 from water. Therefore, this process could be used to separate such contamination from aqueous streams leaving facilities where propellants are decommissioned. It has also been shown that electrolysis with CAC electrodes is capable of effectively removing trace heavy metals from contaminated sea water and ground water. The process may have site remediation applications. Finally, it has been shown that the UV-H_2O_2 process is capable of destroying low concentrations (≤ 3 wt. %) of foaming agents in water. Carbon aerogel CDI and electrolysis could be used to remove residual organic and inorganic ions downstream of such photochemical processes. The exceptionally low electrical resistivity of the CAC, due to its unique nanostructure, should make it possible to eliminate metal substrates in more advanced cell designs.

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Table 1. AFFF Surfactant Composition

No.	Component	Percent	Function
1	2-(2-butoxyethoxy)-ethanol	30	foam stabilizer
2	methyl-1H-benzotriazole	< 0.1	corrosion inhibitor
3	anionic and non-ionic detergents	< 6.0	surfactant
4	Anionic and amphoteric fluoroalkyl surfactants	< 5.0	surfactant
5	water	60	solvent

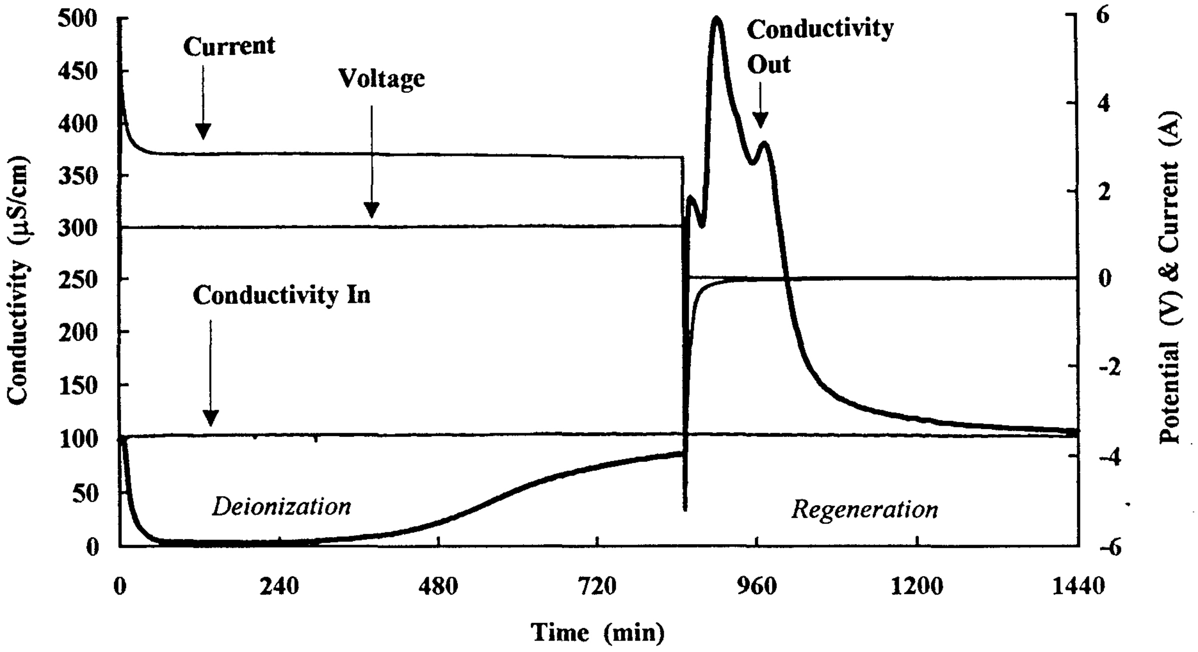

Fig. 1. The treatment of 100 ppm NH_4ClO_4 solution by carbon aerogel capacitive deionization.

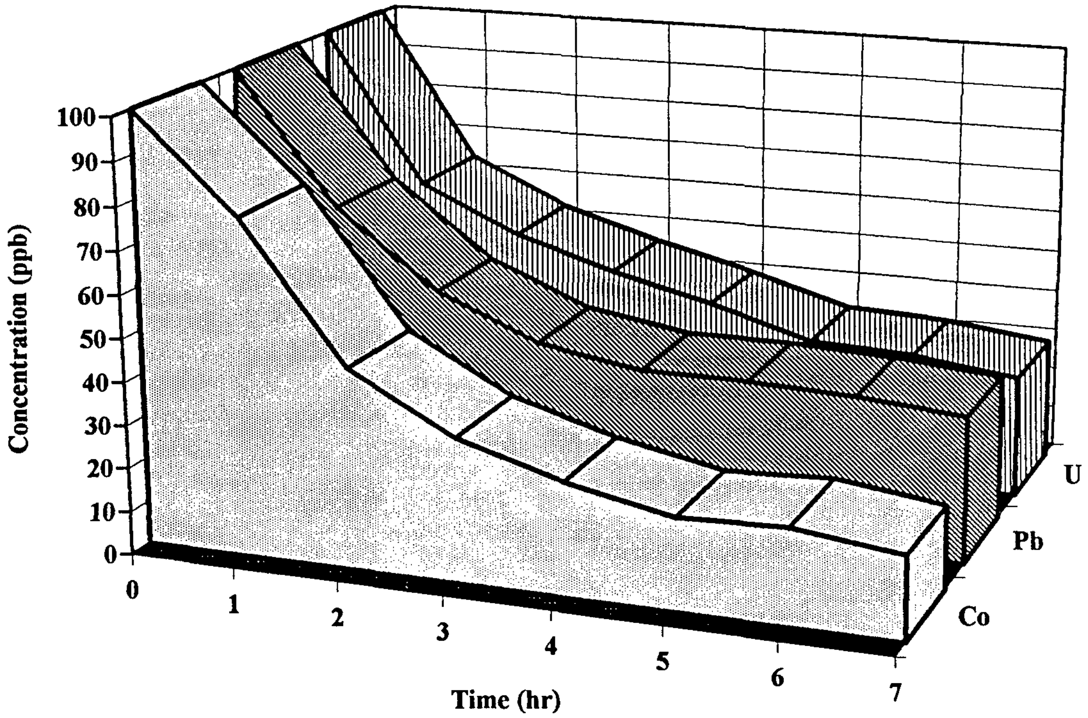

Fig. 2. Removal of heavy metals from sea water with carbon aerogel electrodes.

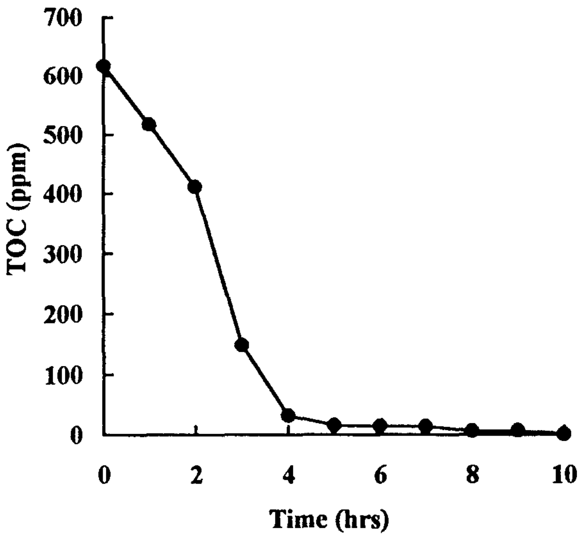

Fig. 3. The photochemical destruction of 5 ml of FC-203 CE in 1.6 liters of water. The feed rate of 30% H_2O_2 solution was 0.23 ml/min and the lamp power was 450 W.

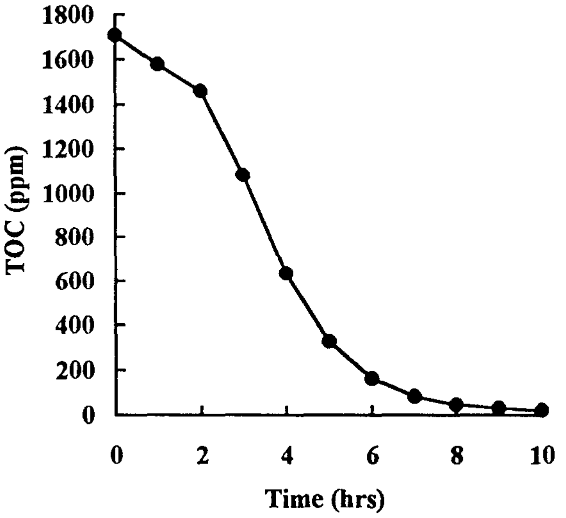

Fig. 4. The photochemical destruction of 15 ml of FC-203 CE in 1.5 liters of water. The feed rate of 30% H_2O_2 solution was 0.23 ml/min and the lamp power was 450 W.

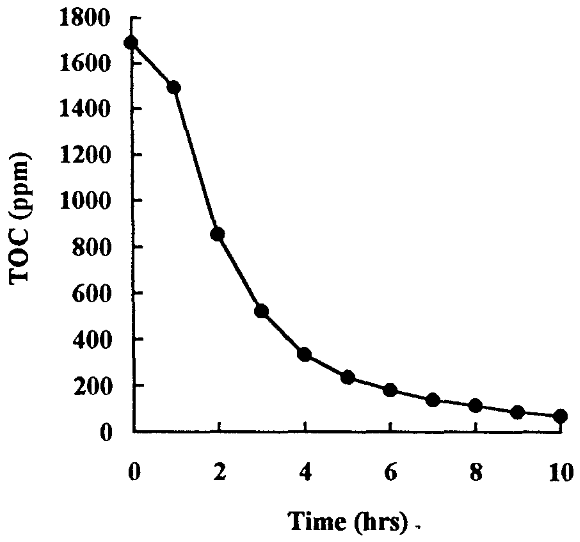

Fig. 5. The photochemical destruction of 15 ml of FC-203 CE in 1.5 liters of water. The feed rate of 30% H_2O_2 solution was 1 ml/min and the lamp power was 450 W.

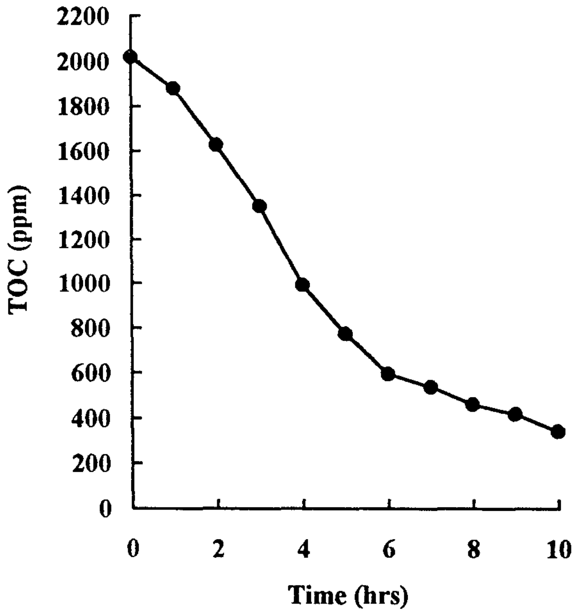

Fig. 6. The photochemical destruction of 15 ml of FC-203 CE in 1.5 liters of water. The feed rate of 30% H_2O_2 solution was 3 ml/min and the lamp power was 200 W.