Electrochemical Technologies for Water Treatment, Management, and Efficiency

by Gerardine G. Botte

Fresh water is one of the world’s scarcest resources. Only 2.5% of the earth’s water is fresh water, of which 70% is frozen in icecaps. Most of the remaining fresh water is too deep underground to access; leaving only 1% of the earth’s fresh water available for human consumption. This scarcity makes water management a vital aspect of human subsistence as well as a multibillion dollar market. Each year around US$150 billion is spent worldwide on wastewater treatment. Water treatment, management, and recycling are also of critical importance for industrial processes, power generation, the chemical industry, and the pharmaceutical industry. Efficient management of the industrial water cycle can influence production performance, operating costs and the environment.

Water management and efficiency were identified as critical sustainability goals for the Chemical and Allied industry in a recent roadmap, “Electrochemical Pathway for Sustainable Manufacturing” (EPSuM), which was funded by The National Institute of Standards and Technology (NIST) through the Advanced Manufacturing Technology Consortia (AMTech) Program. Partners in the EPSuM program Phase I included the Center for Electrochemical Engineering Research at Ohio University (CEER), the National Science Foundation Industry University Cooperative Research: Center for Electrochemical Processes and Technology (CEProTECH), PolymerOhio Inc., The Electrochemical Society, and multiple companies. Rising concerns associated with water scarcity are becoming more of a significant issue across a greater number of regions, and especially in areas susceptible to drought and water shortages. Diminishing water supply is particularly disruptive to industries that are reliant on high quality process water for use in manufacturing.

A wide variety of products (over 100,000) are manufactured in the chemical and pharmaceutical manufacturing industries. As a consequence, waste streams generated in these industries can be heavily laden with contaminants, toxins, nutrients, and organic content, presenting unique challenges in terms of treatment especially as regulations become more stringent. Chemical industry waste streams can be highly complex, unique, and can exhibit a considerable amount of variation in terms of volume, quality, and composition. On the other hand, industrial-manufacturing processes in the pharmaceutical industry produce wastewater that is generally characterized as high strength organic effluent—waste streams that can be challenging to manage with conventional wastewater treatment. The main constituents in pharmaceutical waste streams that regulators are generally concerned with include oil and grease, pH, suspended solids, biological oxygen demand/chemical oxygen demand levels, and mineral content.

Electrochemical technologies can be implemented efficiently in different processes to address water treatment issues. As a result, it is timely to revisit different electrochemical technologies that are used for water treatment and to introduce examples of new economically efficient solutions to challenges related to industrial water treatment in hydraulic fracking and nitrogen removal.

Electrochemical Technologies for Water Treatment

Classical electrochemical technologies that have been used for water treatment include: metal recovery and removal, electrowinning, electrocoagulation, electroflotation, and electrooxidation.

Metal Recovery and Removal

Metals such as Ni, Co, Cr, Ag, Au, Fe, Cu, Zn, and V are widely used as base catalysts for multiple applications, including: oil refining, batteries, chemical processes, air emissions control, etc. In addition, in the electronics industry, these metals represent a significant waste from circuit boards. The production of such wastes (spent catalysts, batteries, and circuit boards) is a major environmental concern due to their toxicity potential for emissions to the environment in the transportation, post-processing, and disposal stages. Other industries leading to metal waste production include surface treatment and hydrometallurgy. Electrolysis has been widely used to extract metals (Cu, Zn, Ni, Au, etc.) from various solutions and, therefore, to remove metals from water and to recycle these metals. The electrolytic recovery of metals involves two steps: collection of heavy metals and stripping of the collected metals. The electrochemical mechanism for metal recovery is based on the cathodic deposition of the metal:

\[ M^{n+} + ne^- \rightarrow M \]  

Metals are removed from the water in the cathodic compartment of the electrochemical cell, while water is oxidized at the anode of the electrochemical cell. The development of the electrochemical process is highly affected by the current efficiency (CE) as well as the space-time yield (STY) of the reactor—defined as the mass of product produced by the reactor volume per unit time. Areas of improvement for the process include minimization of the cell voltage and improvement of the CE. The high overpotential of the water oxidation reaction causes a high cell voltage, which also reduces the efficiency of the metal recovery process and affects the purity and the quality of the material recovered. This also limits the removal of metals from water when the concentration of ions is low (ppm level).

Different types of electrochemical reactors have been implemented for metal recovery, including plate and frame cells, tank cells, rotating cells, fluidized beds, and packed beds. Because of the high oxidation potential in the electrochemical reactor caused by water oxidation, anode materials for metal recovery are typically made of steel or dimensionally stable anodes (DSA).

To address challenges related to selectivity, low concentration of ions, current efficiency, and energy consumption, new technologies are being developed based on the concept of selective or inorganic compound with a lower oxidation potential than water is oxidized at the anode of the electrochemical cell, while metals are removed by cathodic deposition. The selective organic/inorganic compound must be inexpensive when compared to the metals that will be (continued on next page)
removed and/or recovered from water. Figure 1b shows a comparison of the SRE process implementing ammonia as the selective reductant with the traditional metal removal process (water oxidation at the anode) for the recovery of Ni. The anode and cathode of the cell were separated using a Nafion cation exchange membrane; similarly to the application in the chlor-alkali process. The cell voltage for the SRE process to recover nickel decreased from 2.35 V to 0.54 V, which represents 77% lower energy consumption when compared to the traditional metals removal process.

**Electrocoagulation**

Electrocoagulation (EC) has been used for the treatment of wastewater for the removal of suspended solids, the removal or destruction of microorganisms, algae, iron, silicates, and humus. EC applications include the treatment of wastewater from textile, petroleum and oils shale wastewater, municipal sewage, oily wastewater, etc. EC involves the generation of coagulants in situ by electrically dissolving either Al or Fe ions from Al or Fe electrodes, respectively. The generation of metal ions takes place at Al and Fe anodes in either alkaline or acidic media, according to:

\[ \text{Al} \rightarrow \text{Al}^{3+} + 3e^- \quad E^0 = -1.66 \text{ V vs. SHE} \]  
(2)

\[ \text{Al}^{3+} + 4\text{OH}^- \rightarrow [\text{Al(OH)}_4]^- \quad \text{in alkaline pH} \]  
(3)

\[ \text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{H}^+ \quad \text{in acidic pH} \]  
(4)

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad E^0 = -0.44 \text{ vs. SHE} \]  
(5)

\[ \text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 \quad \text{in alkaline pH} \]  
(6)

\[ 4\text{Fe}^{2+} + \text{O}_2 + 10\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3 + 8\text{H}^+ \quad \text{in acidic pH} \]  
(7)

Hydrogen gas is released from the cathode. The hydrogen generated can also be used to flocculate particles out of the water (see Electrocoagulation). The oxidation reactions (2) and (5) compete with the oxygen evolution reaction:

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \]  
(8)

Al\(^{3+}\) and Fe\(^{2+}\) ions are very efficient coagulants for particulates flocculating. These ions are thoroughly dispersed throughout the fluid to facilitate the elimination of suspended solids and colloids by gathering these together to form floc. Sedimentation, flotation and/or filtration systems are then used to separate the floc. Mechanisms for the coagulation-flocculation and sedimentation have been described in the literature. Factors that affect the EC process include current density, electrode type (typical electrodes include Fe and Al for the anode and stainless steel for the cathode), electrolyte concentration (typically NaCl is used as electrolyte, about 20% Cl\(^-\) concentration is recommended to ensure normal operation), pH (affects solubility of species), temperature (higher current efficiencies have been reported when increasing temperature), and power supply (polarization switching has been implemented to minimize passivation of the electrodes).

Different designs of electrochemical reactors have been used for EC. The orientation of the electrode plates for the cell can be horizontal or vertical. The electrodes are typically connected in bipolar mode.

**Electroflotation**

Electroflotation (EF) has been used for different applications in wastewater treatment including mineral recovery, separation of oil and low-density suspended solids, spent cooling lubricant, wastewater from coke production, food processing wastewater, etc. In the EF process tiny bubbles of hydrogen and oxygen are generated from water electrolysis; the bubbles lead to the flotation of pollutants to the surface of the water. Typical EF systems consist of two electrodes, a power supply, and a sludge-handling unit. Electrodes are typically placed at the bottom of the cell and they can be placed vertically or horizontally. A simple blower system eliminates any pollutants to the surface of the water. Typical EF systems are then used to separate the floc. Mechanisms for gathering these together to form floc.

1. The electrode grids can be arranged to provide good coverage of the whole surface area of the flotation tank, enhancing mixing of the wastewater and the gas bubbles;
2. Gas production and residence time can be checked quickly and are easily controlled with a power source. Typical cell voltages are in the range of 5-20 V;
3. Gas generation is a function of the current and the salinity of the process; therefore, it is easy to control by monitoring pH and applied power;
4. It can be implemented in cases where air could be difficult to dissolve in a particular effluent.

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**Fig. 1.** Selective reductant electrowinning process for the removal/recovery of metals. (a) Schematic representation of the SRE process. (b) Electrochemical cell voltage of the SRE process using ammonia as the reductant chemical for the recovery of nickel from water. The cell voltage for the SRE process to recover nickel decreased from 2.35 V to 0.54 V, which represents 77% lower energy consumption when compared to the traditional metals removal process.
The performance of an EF system is reflected by the pollutant removal efficiency and the power and/or chemical consumption. The removal efficiency is affected by the size of the bubbles. The power consumption is affected by: the design of the reactor, the type of electrodes, concentration of the electrolyte, temperature, pH, and arrangement of the electrodes. The electrode system is the most important part of the EF unit. Typically, electrodes that are not dissolved are recommended for the EF unit. TiO$_2$-RuO$_2$ DSA electrodes have been used but do not have high durability/lifetime for oxygen evolution. Most recently, IrO$_x$-based DSA electrodes have been successfully implemented.\textsuperscript{10}

**Electrochemical Oxidation**

Electrochemical oxidation (EO) has been used for the removal of organic compounds from wastewater produced in/by distilleries, agrochemical industries, pulp and paper mills, textile industries, oilfields, hospitals, pharmaceutical industries, micro-pollutants (e.g., pesticides), etc.\textsuperscript{13} Numerous studies at the pilot scale have demonstrated the removal of organics by EO including phenolic compounds,\textsuperscript{34-38} chlorinated organics,\textsuperscript{39} disinfection byproducts,\textsuperscript{40,41} pharmaceuticals,\textsuperscript{42-45} and various industrial streams.\textsuperscript{46-55} Several critical reviews on this topic are available in the literature.\textsuperscript{10,33,56,57}

EO of pollutants can be performed by indirect electrochemical oxidation (IEO) and direct electrochemical oxidation (DEO). Figure 2 presents the differences between the two approaches.

**Indirect Electrochemical Oxidation** In the IEO process, strong oxidants are produced. The oxidants lead to the oxidation of the pollutant at the bulk of the solution. Typically, the oxidation of the pollutant with the oxidant is fast, however, the process is limited by the generation of the oxidant and its mass transport to the bulk of the solution. This technique can effectively oxidize many inorganic and organic pollutants. The most common processes are the electro-Fenton process (for organics) and the electrochlorination process (for organics and inorganics), which rely on hydrogen peroxide and chlorine as the oxidants, respectively.

In the electro-Fenton process hydrogen peroxide is produced at the cathode of the cell. Hydrogen peroxide is one of the most powerful oxidants known, and through catalysis, H$_2$O$_2$ can be converted into hydroxyl radicals (•OH) with reactivity second only to fluorine. In such a system, the cathodic reaction is:

$$\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$$ \hspace{1cm} (9)

The efficiency of the electro-Fenton system depends mostly on the efficiency of the cathode, typical cathodes include\textsuperscript{38} porous carbon with polytetrafluoroethylene (PTFE), carbon felt, graphite, carbon sponge, and activated carbon fibers, among others.

Iron (Fe$^{2+}$) salts can be added into the wastewater or generated in situ from an iron anode to initiate the electro-Fenton reaction, in which iron is a mediator:

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^{-} + \text{OH}^+$$ \hspace{1cm} (10)

At the anode of the electrochemical cell, the oxidation of water takes place as shown in Eq. 8. The anode needs to withstand the overpotential of water oxidation. Different forms of Pt are the most stable material.\textsuperscript{16} However, because of the economic impact other materials have been implemented such as boron-doped diamond (BDD), titanium coated with IrO$_2$/RuO$_2$, RuO$_2$/Ti mesh, and iron. Different type of reactor configurations and electrode materials have been evaluated for the electro-Fenton process, a summary of the different specifications can be found in the literature.\textsuperscript{18}

Despite the advantages that the electro-Fenton process enables in terms of removing organic pollutants, its application has been hindered due to the energy consumption and cost. On the other hand, electrochlorination has been widely implemented for the removal of inorganic and organic pollutants because it obviates the need for storing chlorine gas on-site. Hypochlorite, an oxidant-disinfectant, is frequently used in water treatment. From a safety and procurement point of view, electrochlorination provides a way to generate hypochlorite in situ, this abolishes the constraints created by the need to store chlorine or to transport and store dilute hypochlorite solutions. Electrochlorination was primarily developed to protect cooling circuits found on offshore platforms, electricity generating stations and factories supplied with seawater, against the proliferation of algae and mollusks, but this process has also been implemented in swimming pools.\textsuperscript{11} The main electrochemical reactions involved in the process are the oxidation of Cl$^-$ and the reduction of water at the anode and cathode of the cell, respectively:

$$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$$ \hspace{1cm} (11)

$$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$$ \hspace{1cm} (12)

Chlorine will react with hydroxyl ions to form hypochlorite ions, which forms hypochlorous acid in equilibrium with water:

$$\text{Cl}_2 + 2\text{OH}^- \rightarrow \text{ClO}^- + \text{Cl}^- + \text{H}_2\text{O}$$ \hspace{1cm} (13)

$$\text{ClO}^- + \text{H}_2\text{O} \rightleftharpoons \text{HClO} + \text{OH}^-$$ \hspace{1cm} (14)

This process requires chlorine concentrations larger than 3 g/l.\textsuperscript{10} Industrial units consume approximately 4 kWh per kilogram of chlorine equivalent produced.\textsuperscript{11}

As an example, ammonia can be removed from wastewater by breakpoint chlorination.\textsuperscript{35} Ammonium ions react with hypochlorous acid to produce chloramines. Further addition of chlorine to the breakpoint converts the chloramines to nitrogen gas as shown below:

$$\text{NH}_4^+ + \text{HOCI} \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O} + \text{H}^+$$ \hspace{1cm} (15)

$$\text{NH}_2\text{Cl} + \text{HOCI} \rightarrow \text{NHCl}_2 + \text{H}_2\text{O}$$ \hspace{1cm} (16)

$$\text{NHCl}_2 + \text{HOCI} \rightarrow \text{NCl}_3 + \text{H}_2\text{O}$$ \hspace{1cm} (17)

$$2\text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{NH}_3$$ \hspace{1cm} (18)

$$2\text{NH}_2\text{Cl} + \text{HOCI} \rightarrow \text{N}_2 + 3\text{HCl} + \text{H}_2\text{O}$$ \hspace{1cm} (19)

In a study performed by the U.S. Environmental Protection Agency (EPA) based on the operation of a wastewater treatment plant (in the Blue Plains locale of Washington, D.C.) implementing the breakpoint

(continued on next page)

![Direct electro-oxidation](image)

![Indirect electro-oxidation](image)

**Fig. 2.** Approaches for the electrochemical oxidation of organic pollutants. Direct electrooxidation takes place at the anode electrodes where pollutants are directly oxidized. In the indirect electrooxidation, strong oxidants—such as chlorine and hydrogen peroxide—that lead to the oxidation of the pollutant at the bulk of the solution are produced. Mediators include metal ions.
chlorination process for the removal of ammonia, 10 parts by weight of Cl₂ are required to remove 1 part by weight of NH₃-N (this type of unit form uses the molecular weight of only the nitrogen atoms). If the chlorine was provided via electrolysis (4 kWh per kg of Cl₂), the energy consumption for the process will be 40 kWh per kg of NH₃-N. However, one of the concerns on the de-coupled implementation of breakpoint with chlorine electrolysis is the excess of HCl produced in the wastewater treatment plant, which represents a high consumption of NaOH and/or lime to regulate pH. Because excess of chlorine is required, wastewater treatment plants (WWTPs) will also require a downstream de-chlorination process.

One alternate approach evaluated at several water treatment facilities including Blue Plains⁶⁶ and South Tahoe⁶¹ is the combination of an ion exchange column with electrochlorination, provided via chlorine electrolysis cells. A schematic of the process is presented in Fig. 3. Zeolites that are selective for ammonia relative to calcium, magnesium, and sodium were evaluated, for example clinoptilolite, a natural zeolite that occurs in several extensive deposits in the western United States.⁶⁰ During the operation cycle (Fig. 3a) wastewater with ammonia flows through the ion exchange bed until the column reaches the breakpoint. After about 150-200 bed volumes of normal-strength municipal waste have passed through the bed, the capacity of the clinoptilolite was to the point that ammonia begins to leak through the bed. At this point, the clinoptilolite must be regenerated so that its capacity to remove ammonia is restored.

The key to the applicability of this process is the method of handling the spent regenerant, see Fig. 3b. The zeolite is regenerated by passing concentrated salt solutions through the exchange bed when the ammonia concentration reaches the breakpoint. Following regeneration, the ammonia-laden spent-regenerant volume is about 2.5 to 5 percent of the throughput treated before regeneration, therefore, the concentration of ammonia in the regenerant is higher than in the inlet wastewater; for example 500 mg/L for a 5% of the throughput treated assuming an inlet concentration of 25 mg/L. The spent regenerant is then treated by indirect electrooxidation (via electrochlorination) providing a fresh regenerant ready to be reused in the process. Because of the IEO process, see Eq. 11-19, the only byproducts of the process are nitrogen and hydrogen gas. However, it was reported that the electrical energy consumption during the IEO is high, 50 kWh per kg of NH₃-N removed.⁵⁹

![Image](https://example.com/image.png)

**Fig. 3.** Selective ion exchange process combined with electrochlorination. The process is effective in removing ammonia from water but the energy consumption is high 50 kWh/kg of NH₃-N.

The selective ion exchange process combined with the IEO was found to have multiple advantages for the removal of ammonia⁶⁹ such as high efficiency, insensitivity to temperature fluctuations, removal of ammonia with minimal addition of dissolved solids, and the ability to eliminate any discharges of nitrogen to the atmosphere other than nitrogen gas. However, the process has relatively high costs due to the high energy consumption. Improvements in the system would require more efficient processes for electrolysis, for example, the use of direct electrolysis of ammonia (ammonia electrolisis⁶³-⁷³), instead of indirect electrolysis. The ammonia electrolisis process is described in the Example Applications section below.

**Direct Electrochemical-Oxidation** Electrooxidation of organic pollutants occurs directly on oxide anodes (MOₓ⁺₁) in which water (in alkaline or acidic media) is also partially oxidized (Eq. 20) to generate physically adsorbed active oxygen (adsorbed hydroxyl radicals, ·OH). Furthermore, the adsorbed hydroxyl radicals may interact with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hydroxyl radical to the lattice of the oxide anode, forming a higher oxide, MOₓ⁺₂ (chemisorbed active oxygen, see Eq. 21).⁷⁴ The physically adsorbed active oxygen causes the complete combustion/oxidation of the organic compounds (R) (see Eq. 22), and the chemisorbed active oxygen participates in the formation of selective oxidation products (see Eq. 23):⁷⁴

\[
MO_x + H_2O \rightarrow MO_x(OH) + H^+ + e^- \quad (20)
\]

\[
MO_x(OH) \rightarrow MO_x + H^+ + e^- \quad (21)
\]

\[
R + MO_x(OH) \rightarrow CO_2 + zH^+ + ze + MO_x \quad (22)
\]

\[
R + MO_x \rightarrow RO + MO_x \quad (23)
\]

In general, ·OH radicals are more effective for organic pollutants oxidation than the O in the MOₓ⁺₁. Selection of the anode material is critical for the process. Specifically, electrode materials must have a high overpotential for oxygen evolution to increase the current efficiency of the process towards the removal of the organic pollutants. Exemplary anode materials include BDD film on titanium substrate,⁷³ Ti/PbO₂⁶ granular graphite,⁷⁷ and PbO₂.⁷⁸ Different designs of electrochemical reactors have been implemented. The simplest electrooxidation reactor design is the bipolar cell. Besides planar electrodes, cylindrical electrodes and packed bed electrodes have also been used.⁶⁰

**Example Applications: Hydraulic Fracking and Nitrogen Removal**

As described in the previous section, electrochemical technologies offer great opportunities for water treatment, management, and efficiency. This section highlights applications on electrochemical technologies within the context of hydraulic fracturing process water and the removal of ammonia from municipal water treatment plants and fertilizer run-off.⁷⁹

**Advanced Water Treatment for Hydraulic Fracking Water**

In the last decade, the use of hydraulic fracturing or fracking process to extract natural gas from shale formations has skyrocketed. Hydraulic fracturing (HF) consists of injecting water, containing sand and chemicals, into wells under extremely high pressure to fracture or crack open pores in the shale formation to release the oil and gas. The hydraulic fracturing process injects large quantity of water (~100 million gallons) per well. Ground water and surface water resources are withdrawn to account for the large volume of water needed for the hydraulic fracturing process, which directly influences the availability...
of ground and surface water for other consumption. The flow-back water and produced water obtained during the hydraulic fracking process contains organic chemicals, dissolved metal ions, dissolved solids, and chemical additives. If the flow-back and produced waters are not sufficiently treated and discharged to bodies of water, the contamination of ground and surface water will be significant. Therefore, water management and wastewater treatment presents a major techno-economic challenge to hydraulic fracking technology.

Challenges when treating HF produced water include variability of the produced water, access of the water treatment technology to the well, and cost. Table I shows an example of the variability range of certain contaminants in HF produced water. The concentration of the contaminants varies as the produced water ages.

A cooperation between the Center for Electrochemical Engineering Research (CEER) at Ohio University and De Nora Tech was established via CEProTECH (industry/university cooperative consortium) to evaluate and demonstrate the performance of a pilot scale skid mobile system that incorporated electrochemical oxidation (mechanical treatment) and UV-ozone to treat HF produced water with a capacity of 400 gpm. Figure 4 presents a picture of the skid system that was installed at CEER and evaluated with HF water that was provided by De Nora Tech. The system was designed with two tanks to allow for full evaluation of the water quality through different passes from the units in the skid. The electrochemical reactor consisted of three bipolar electrodes with DSA anodes. The electrochemical cell was designed and built by De Nora Tech to perform both direct and indirect electrochemical oxidation (mediated with chlorine). The water quality was characterized before and after treatment including: TDS, TOC, COD, TKN, chloride, BTEX, barium strontium, boron, pH, arsenic, cadmium, iron, manganese, mercury, silica, and sulfates.

The skid system was tested through multiple passes: 1, 5, 10, and 20. Successful treatment of the produced HF water was demonstrated at the different passes. Over 80% removal of BTEX was achieved demonstrating complete abatement of volatile organic compounds. The concentration of iron was reduced by 83.3%, manganese concentration was lowered by 87.5%, and concentration of nitrogen-containing compounds expressed in terms of total Kjeldhal nitrogen (TKN) was reduced by 95%. The concentrations of BTEX, nitrogen-containing compounds (TKN), and manganese in the treated water were compliant with the National Primary Drinking Water Regulations after 20 passes through the skid. Current estimated cost for treating the produced water varies and it could be up to $8.50 per barrel based on the technology, location (on-site or off-site), and end use. The ability to remove key constituents (BTEX, manganese, nitrogen-containing compounds, iron) from produced water to meet water regulations using the current configuration of the skid is a strong indicator for efficient treatment of the technology. The economic target of the project is to bring the cost for treating the produced water between $2 and $4 per barrel.

Advanced Water Treatment for Nitrogen Removal

Ammonia emissions into air (ambient ammonia) and water represent an environmental challenge. Ambient NH₃ contributes to inorganic PM₂.₅ (particulate matter with an aerodynamic diameter of less than 2.5 μm) directly and plays an important role in secondary organic aerosol formation by interacting with gaseous phase organic acids and forming condensable salts. Various industries are considered ammonia emitters, including fertilizer manufacturing, livestock management, coke manufacture, fossil fuel combustion, and refrigeration methods. Fossil fuel combustion is included in

![Image](https://example.com/image.png)

**Figure 4.** Pilot system for the treatment of hydraulic fracking produced water. The hydrodynamic cavitation unit is at the forefront, the UV-ozone generator is mounted on the wall, and there are two storage containers for testing of the hydraulic fracking produced water.

Table I. Example of hydraulic fracking water characteristics and comparison with water standards.

| Parameter                  | Produced water range (5 days post fracture) | Produced water range (14 days post fracture) | Water standard | Standard Source          |
|----------------------------|---------------------------------------------|-----------------------------------------------|----------------|--------------------------|
| Total Dissolved Solids (TDS), mg/L | 38,500-238,000                             | 30,010-261,000                                | 500            | U.S. EPA Secondary Standard |
| Total Organic Carbon (TOC), mg/L          | 3.7-388                                    | 3.7-388                                       | 2-20           | Typical values in surface waters |
| Chemical Oxygen Demand (COD), mg/L         | 195-17,700                                 | 228-21,900                                    | 10             | WHO* standard for drinking water |
| Total Kjeldahl Nitrogen (TKN), mg/L as N  | 38-204                                     | 5.6-261                                       | 2-6            | Widely recognized as an acceptable range of total nitrogen |
| Chloride, mg/L                           | 26,400-148,000                             | 1,670-181,000                                 | 250            | WHO                      |
| BTEX (benzene, toluene, ethylbenzene, xylene), µg/L | Non-detect                                | 1-350                                         | Benzene: 5 Toluene: 1,000 Ethylbenzene: 700 Xylene: 10,000 | U.S. EPA National Primary Drinking Water Standards |
| Barium, mg/L                             | 21.4-13,900                                | 43.9-13,600                                   | 2              | U.S. EPA National Primary Drinking Water Standards |
| Strontium, mg/L                         | 345-4,830                                  | 163-3,580                                     | 8              | U.S. EPA National Primary Drinking Water Standards |
| Boron, mg/L                              | 25-30                                      | 100-150                                       | 24             | WHO                      |

*WHO: World Health Organization

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the list of ammonia emitters because of their NOx emission control methods. The exhaust gas from fossil fuel processing plants has nitrogen oxides. Therefore, this gas must be treated with urea or ammonia via selective catalytic reduction to convert the NOx into nitrogen gas before discharge to the atmosphere. However, a portion of the ammonia may exit along with the exhaust gas, which is known as ammonia slip.83 Similarly, even though not considered an industry, combustion gases from diesel vehicles also contribute to ammonia emissions. Other sources of ambient ammonia are caused by the volatilization of ammonia from inappropriate control in water (e.g., livestock, fertilizer run-off). Meng, et al., presented a recent inventory of ambient ammonia for 2011.82 The authors reported that 8.77 Tg of ammonia were emitted from combustion and industrial sources, and this amount accounts for one-eighth of the overall ambient ammonia emissions in 2011.82 According to this, the overall NH3 ambient emissions in 2011 correspond to 70.16 Tg. When comparing to the total amount of ammonia produced worldwide in 2010, 159 million tons,44 the total ambient ammonia emissions in 2011 represent 48.5% of the global ammonia production in 2010. Ammonia emissions in water are associated with environmental problems such as algae bloom.79

Methods for the removal of ammonia include biological and physicochemical methods. Biological methods are not the most appropriate for industrial wastewater treatment. Currently, wastewater treatment solutions for ammonia (biological and chemical treatments) consume a significant amount of energy (4.5 to 50 kWh per kg of ammonia removed); have high operational costs ($4 per lb of ammonia removed); require significant capital investment ($658,000 per MGD for retrofit and $9,000,000 per MGD for grassroots plants/new constructions); are not easily adaptable to tighter emissions regulations; take a long time to start up (i.e., for the micro-organisms to stabilize in the biological reactors); and are large in size.85 For example, the combination of ion exchange with indirect electrooxidation requires at least 50 kWh per kg of NH3-N removed.

An alternative for efficient ammonia water treatment is the ammonia electrolysis technology, illustrated in Fig. 5. This technology has been under development at CEER for the treatment of wastewater.63-69 In this process, the direct oxidation of ammonia takes place at the anode of the electrochemical reactor in alkaline media producing nitrogen gas (Eq. 24), while hydrogen is produced at the cathode of the cell (Eq. 25):

$$2NH_3 + 6OH^- \rightarrow N_2 + 6H_2O + 6e^- \quad E^\circ = -0.77 \text{ V vs. SHE} \quad (24)$$
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad E^\circ = -0.829 \text{ V vs. SHE} \quad (25)$$

The overall cell reaction is:

$$2NH_3 \rightarrow N_2 + 3H_2 \quad E^\circ = 0.059 \text{ V} \quad (26)$$

Because the cell voltage for the oxidation of ammonia is lower than for water electrolysis, ammonia can be removed from the water. Based on the thermodynamic cell voltage, 0.33 kWh per kg of NH3-N removed are needed for water treatment, which is much lower energy.
consumption than for electrochlorination. This value does not include the energy that can be recovered in the process via the combustion or conversion of hydrogen to heat and/or heat and power.

A partnership between CEER and the City of Athens (Ohio) Wastewater Treatment Plant\textsuperscript{48} was established to evaluate and demonstrate the performance of a pilot scale ammonia electrolysis system—Ammonia GreenBox. The ammonia electrolysis cell was combined with zeolite ion exchange columns as shown in Fig. 3. The main difference is that ammonia electrolysis cells were used instead of chlorination electrolysis cells. The system had a capacity to manage 760 gallons of wastewater per day. The Ammonia GreenBox consisted of 5 electrolysis cells with electrode size of 300 cm\textsuperscript{2} and a power consumption of up to 20 W. The components of the system were installed in a mobile trailer and connected to the water treatment plant as an electrical appliance (with minimum plumbing and direct connection to power). Figure 6 presents the different components of the system and the progress during its construction. The whole system was built and assembled in two months (June – July 2015), which is relatively a short time when compared to major construction of systems for WWTPs. For example, the Athens WWTP went through significant renovations and the whole process from design to installation took 2.5 years. The unit was plugged in at the entrance of the influent after primary filtration.

The water treatment system was tested and evaluated for four months. Successful removal of ammonia was demonstrated. Figure 7 presents examples of the evaluation. The concentration of ammonia at the inlet of the treatment system varied from 20 to 85 ppm. As shown in Fig. 7a, the concentration at the exit of the column or exit from the water treatment unit was mostly zero. The saturation point for the column was set to a concentration >1 ppm of ammonia. The system was designed to achieve column saturation in 12 hours as shown in Fig. 7a. After saturation, the column was recovered and a spent regenerant was produced with a concentration of ammonia of ~1,200 ppm. The spent regenerant was sent to the ammonia electrolysis stack for the removal of ammonia and the recovery of the regenerant, as shown in Fig. 7b. The system operated with recirculation. An average ammonia removal rate per cell of 10.5 mg/min was achieved. The average energy consumption was ~6 kWh per kg of NH\textsubscript{3}-N without recovery of energy from the hydrogen produced. This energy consumption is 88% lower than electrochlorination. The ability to remove the ammonia to levels (less than 1 ppm) much lower than current regulations (~10 ppm) is a strong indicator for the efficient treatment of the technology. The pilot system demonstrated an energy efficient technology for ammonia removal. Optimizing the flow through the electrolyzer as well as implementing some minor changes on the electrodes could further reduce the energy consumption for ammonia removal.

The ammonia electrolysis technology is also being evaluated by the Department of Defense (DoD) for energy efficient water reuse.\textsuperscript{87,88}

**Outlook**

Electrochemical technologies offer multiple advantages for water treatment, management, and efficiency:

- **Tolerant to variability of the waste streams.** The processes can be designed to withstand the variability of waste streams and they can be combined effectively with other unit operations.
- **Effective treatment at point of use.** Advanced electrochemical reactors for water treatment are compact, modular, and portable.
- **Easy to operate.** The water treatment process can be completely automated and its performance can be monitored and controlled via the cloud.
- **Easy to install.** The systems can be plugged into wastewater treatment facilities as an electrical appliance (minimum plumbing, no heavy concrete construction needed) for complete removal of pollutants or to increase capacity of the water treatment facility (retrofit).
- **Enable decentralized treatment of water.** This minimizes risks of water contamination during storms and decreases energy consumption.
- **Easy integration with renewable energy (electricity) sources.** This has a significant impact in municipal wastewater treatment plants. Current processes for municipal water treatment are based on biological alternatives and are not efficient to be coupled with renewable energy sources. The incorporation of electrochemical technologies would enable the direct use of electricity to remove contaminants.
- **Enable recovery of resources.** Depending on the composition of the waste stream, electrochemical technologies can be used to recover chemicals, metals, or energy.
- **Lower emission limits.** Electrochemical technologies provide opportunities to remove contaminants at levels that cannot be achieved with biological processes.

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About the Author

GERARDINE (GERR) BOTTE is a university distinguished professor and Russ professor of chemical and biomolecular engineering at Ohio University, the founder and director of Ohio University’s Center for Electrochemical Engineering Research, and the founder and director of the National Science Foundation I/UCRC Center for Electrochemical Processes and Technology. She and members of her research group are working on projects in the areas of electrochemical engineering, electrolysis, batteries, electrolyzers, sensors, fuel cells, mathematical modeling, and electrocatalysis. She has 140 publications (including 22 granted patents). She is a fellow of The Electrochemical Society, charter fellow of the National Academy of Inventors, and a fellow of the World Technology Network. Botte served as past chair, vice chair, and secretary/treasurer of the IEEE Division. She received her BS in chemical engineering from Universidad de Carabobo (Venezuela) in 1994. Prior to graduate school, she worked as a process engineer in a petrochemical plant (Petroquimica de Venezuela) where she was involved in the production of fertilizers and polymers. She received her PhD in 2000 (under the direction of Ralph E. White) and ME in 1998, both in chemical engineering, from the University of South Carolina. She may be reached at botte@ohio.edu.

http://orcid.org/0000-0002-5678-6669

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