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Review

Natural organic matter (NOM) removal by electrochemical methods — A review

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ABSTRACT

Electrochemical techniques such as electrocoagulation (EC) and electro-oxidation (EO) have proved their efficiency in humic acid, coliform and algae removal from surface waters. Many investigations have also been conducted with synthetic wastewaters. Electrocoagulation combined with membrane filtration hybrid systems can increase natural organic matter (NOM) removal rates remarkably. In EO technology, electrolysis efficiency is strongly linked to electrode composition. Efficiency could be increased by changing the reactor design, using commercial electrodes and exploring the semiconducting properties of oxide mixtures. Electrochemical methods may present an attractive alternative to other NOM removal techniques, such as conventional coagulation and chemical oxidation methods, for natural waters. Surface water treatment with electrocoagulation can produce high quality water, for either potable or industrial use. This technology appears to remove some toxic pollutants from wastewater and could be used as a pretreatment in combination with some other purification technology. Boron-doped diamond (BDD) anodes have proved effective in humic acid removal from aqueous solutions and potentially their total mineralization.

Contents

1. Introduction

Natural organic matter (NOM) is a complex matrix of organic materials (humic substances such as humic acids (HA or HAs), fulvic acids (FA or FAs) and humin) and a key component in aquatic environments [1]. The amount, character and properties of NOM vary considerably according to the origins of the waters. NOM is ubiquitous in waters, sediments and soils. Aquatic NOM is derived both from the breakdown of terrestrial plants and as the by-product of bacteria, algae and aquatic plants. NOM has a significant impact on many aspects of water treatment, including the performance of unit processes, necessity for and application of water treatment chemicals and the biological stability of the water. Changes in NOM quantity and quality have a significant influence on the selection, design and operation of water treatment processes. These changes also cause operational difficulties in water utilities. High seasonal variability and the trend towards elevated NOM concentration levels pose challenges to water treatment facilities in terms of operational optimization and proper process control. It is also essential to be able to understand and predict the reactivity of NOM or its fractions during different phases of the treatment. Once the composition and quantity of NOM in the water source have been examined, suitable methods for efficient NOM removal can be applied. No single process alone can be used to treat NOM due to its high variability. The most common and economically feasible processes available are coagulation and flocculation followed by sedimentation/flotation and filtration.

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Other treatment options for NOM removal include magnetic ion exchange resin (MIEX®) techniques, activated carbon filtration, membrane filtration methods, and advanced oxidation processes.

Electrochemical technologies for water purification and disinfection have been the subject of growing interest in recent years [2]. Techniques such as electrocoagulation (also known as electroflocculation, EC), electroflotation (EF) and electro-oxidation (EO) can easily be distributed [3]. Conventional water purification techniques, such as chemical coagulation, biological treatment or UV oxidation, are not effective against some toxic and refractory organic pollutants, and electrochemical techniques can provide a more efficient means of treating these. Electrochemical methods are innovative, inexpensive and effective in purifying industrial wastewaters before discharge into water systems or circulation back into processes [3–5]. They could also be called "green technologies" because little or no chemicals are needed to facilitate water treatment.

In the EC system multiple electrochemical reactions occur simultaneously at the anodes and cathodes. These can be divided into the main mechanisms that cause the destabilization of pollutants, and side reactions, such as hydrogen formation. Electrodes which produce coagulants in water are made from either iron or aluminum. In addition, there can be inert electrodes, typically cathodes, which are sometimes used in the system as counter-electrodes. Iron and aluminum cations dissolve from the anodes according to Eqs. (1) and (2):

$$Fe(s) \rightarrow Fe^{n+}(aq) + ne- \quad (1)$$

$$Al(s) \rightarrow Al^{3+}(aq) + 3e-. \quad (2)$$

In typical aqueous environments and conditions of the EC process, iron can dissolve in divalent Fe(II) and trivalent Fe(III) forms, whereas aluminum dissolves only in trivalent form Al(III). Fe(II) can further oxidize to Fe(III) if oxidation reduction potential (ORP) and pH conditions are suitable. Oxygen has to be present and pH has to be neutral or alkaline to achieve a reasonable reaction rate [6].

A relatively new technology, used especially for the disinfection of drinking water or treatment of wastewaters, is the electrochemical mineralization of organic compounds [2,7,8]. An electrochemical oxidation mechanism involves the production of ·OH-radicals at the active sites of the anode. The activity of these electrogenerated •OH radicals is strongly linked to their interaction with the anode surface [8].

Electrochemical oxidation may also occur indirectly through the formation of oxidants such as chlorine, hypochlorous acid and hypochlorite [9–15] or hydrogen peroxide/ozone [16–19] at the electrodes by the following reactions (3)–(9):

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (3)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (4)$$

$$HOCl \rightarrow H^+ + OCl^- \quad (5)$$

$$H_2O \rightarrow \bullet OH + H^+ + e^- \quad (6)$$

$$2\ \bullet OH \rightarrow H_2O_2 \quad (7)$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \quad (8)$$

$$O_2 + \bullet O \rightarrow O_3. \quad (9)$$

Several electrodes have been used for water and wastewater treatment by electrochemical oxidation. Anodes used include lead and lead dioxide [20–23], dimensional stable anode (DSA) electrodes [24–27], graphite [28–30] and BDD electrodes [23,31–38].

Lead and lead dioxide are effective anodes due to their stability, low cost and high oxygen evolution potential which delays O_2 evolution in favor of Cl_2 evolution [20]. Hamza et al. [22] completely mineralized 1,3,5-trimethoxybenzene in acid media at a Ta/PbO_2 anode. They discovered that carboxylic acids finally oxidized all oxidation products to CO_2. Awad and Abo Galwa [21] found that the electrocatalytic activity of a lead dioxide electrode depends on the conductive electrolyte. They concluded that electrode poisoning occurred in the presence of an H_2SO_4 electrolyte, since an adherent film was formed on the anode surface. The dissolution of toxic Pb^{2+} ions also hinders the use of lead and lead dioxide as anodes [2].

DSA electrodes are catalytic oxide electrodes which can effectively generate active hydroxyl radicals and active chloride species [25]. They also have a relatively high overpotential for oxygen evolution. Efficient degradation of paper mill wastewater has been achieved using three-dimensional electrodes (Ti/Co/SnO_2–Sb_2O_5) combined with activated carbon treatment [25]. This was mainly due to the fact that their large specific surface area in comparison to conventional two-dimensional electrodes can substantially increase the conversion rate within an electrochemical reactor. "Non-active" electrodes, such as SnO_2, form hydroxyl radicals on their surface more easily, which can result in the complete oxidation of the organic molecules to CO_2 [27]. With "active electrodes", such as RuO_2 and IrO_2, only selective oxidation of the organic species in the solution occurs.

Effective removal of chemical oxygen demand (COD) (>96%) was achieved when the electrochemical degradation process was catalyzed by transition metals [29] or molybdenum and phosphate (Mo–P) modified kaolin with graphite as the anode and cathode [30]. Pollutants were adsorbed on the surface of the kaolin, where they were oxidized by hydroxyl radicals produced at the graphite cathode by the reaction of hydrogen peroxide and transition metals [29]. This process is similar to the electro-Fenton process.

The potential of conducting diamond films for water treatment has recently been recognized. These have an inert surface with low adsorption properties, remarkable corrosion stability even in strong acidic media and an extremely wide potential window in aqueous and non-aqueous media [32,34]. They also have the highest oxygen evolution overpotential value [2,32] meaning that more hydroxyl radicals are formed on the anode surface during treatment. BDD electrodes can also degrade refractory organic pollutants completely and the nature of the pollutant does not affect the efficiency of the process significantly [33]. Furthermore, besides hydroxyl radical formation on the electrode surface, diamond electrodes also increase mediated oxidation by other electrochemically formed compounds such as persulfate, perphosphate, percarbonate or hypochlorite, depending on the electrolyte used.

The main advantages and disadvantages of different electrodes in EO treatment are presented in Table 1.

The simplest electrooxidation reactor design is the tank cell where electrodes can be arranged in mono-polar or bi-polar mode. Besides plane electrodes, the cylindrical electrodes can also be employed [2]. It is also easy to scale up or down depending on the load of a process. Typical reactor design for EO treatment is presented in Fig. 1. It includes a tank, a pump, a DC power supply and an electrochemical reactor with electrodes [39].

2. EC and EO technologies in NOM removal

2.1. EC in NOM removal

EC has been proposed as a promising alternative to chemical coagulation for removing various pollutants from freshwaters and wastewater [40–42]. When iron or aluminum is used as a sacrificial anode, it dissolves and produces Al^{+3}, Fe^{+2} and Fe^{+3} ions in the solution. These ions form metal hydroxides, which dissolve less readily, such as