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Review

Recent developments of electro-oxidation in water treatment — A review

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ABSTRACT

Industrial processes generate huge amounts of hazardous effluents every day. Conventional purification techniques, such as biological methods (aerobic and anaerobic treatment) and chemical coagulation, are commonly applied to purify wastewaters. Tertiary treatment methods e.g., ultrafiltration, ozonation, adsorption and UV light disinfection have also been examined for the purpose. However, these techniques are not capable of removing all harmful compounds and pathogenic microbes from wastewater. Therefore, novel methods should be developed for using together with these techniques to improve the purification results.

Interest in water treatment by electrochemical methods has grown in recent years. Electrochemical oxidation has been applied successfully to degrade different organic pollutants and disinfect drinking water and municipal wastewaters. Also many industrial wastewaters, such as textile, olive oil, pulp and paper mill and tannery effluents have been treated successfully by this technique.

This review article shows that electrochemical oxidation can be used to treat effluents from different sources and also to disinfect different microbes present in wastewaters and drinking water. It also gives an overview of the recent developments in electrode preparation and configurations. Coupling this technique together with other methods has also increased purification results in a remarkable way.

Contents

1. Introduction

Industrial processes consume a huge amount of raw water for various purposes [1] which consequently results in the generation of large amounts of wastewater. Wastewaters are a very complex mixture of different organic and inorganic compounds and some of them can be toxic and difficult to degrade. Effluents are mainly treated by conventional technologies such as aerobic and anaerobic treatment and chemical coagulation [1]. However, these techniques are not capable of removing all harmful compounds from wastewater or generate a large amount of toxic sludge. Therefore, other methods have been applied together with these techniques to improve purification results. These include membrane technologies [2–4], photocatalysis [5], adsorption [6], advanced oxidation processes [7,8] and ozonation [9–11], which, however, have also their own drawbacks.

Electrochemical technologies, such as electro-oxidation (EO), electrochemical coagulation (EC) and electrochemical flotation (EF) have

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also received major attention in recent years [12]. Electrochemical techniques are rather simple to operate and can degrade many harmful pollutants completely before they reach to the receiving aquatic environment. They could also be called "green technology" methods because little or no chemicals are needed to facilitate water treatment. Development of novel electrode materials has great potential to improve treatment efficiency. Electrochemical techniques can offer a more efficient means of treating wastewaters, industrial process waters and disinfecting drinking water.

Electrochemical techniques have been applied extensively to treat various wastewaters, disinfect drinking water or enhance the remediation of polluted soils [12–19]. Especially EO treatment has received a great deal of interest in wastewater treatment and organic pollutants oxidation in recent years [20–23]. The technique is rather simple in which, oxidants are produced during the treatment in situ either directly at the electrodes surface or indirectly from chemical compounds in the treated water. EO treatment in the removal of various organic pollutants and disinfection of waters is discussed in detail in this article. Recent development trends in EO treatment are also reviewed critically.

2. Electro-oxidation

2.1. Mechanisms

Electro-oxidation may occur either by direct oxidation by hydroxyl radicals produced on anode's surface [24] or by an indirect process where oxidants like chlorine, hypochlorous acid and hypochlorite [25–31] or hydrogen peroxide/ozone [32–35] are formed at electrodes by following reactions (1)–(7):

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (1)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (2)$$

$$HOCl \rightarrow H^+ + OCl^- \quad (3)$$

$$H_2O \rightarrow {}^*OH + H^+ + e^- \quad (4)$$

$$2\,{}^*OH \rightarrow H_2O_2 \quad (5)$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \quad (6)$$

$$O_2 + {}^*O \rightarrow O_3. \quad (7)$$

Indirect oxidation occurs when e.g., active chlorine species are generated from chloride ions anodically to destroy pollutants. In so-called mediated electro-oxidation e.g., metal ions are oxidized on an anode from a stable state to a reactive high valence state which in turn attack pollutants directly and may also produce hydroxyl free radicals to promote degradation [12]. In direct electro-oxidation (anodic oxidation) oxidation of pollutants in the electrolytic cell occurs at the electrode surface or by direct electron transfer to the anode [20]. Also, powerful oxidants called reactive oxygen species (ROS) can be formed from water discharge at the anode. These are e.g., hydroxyl radicals and oxygen in the oxide lattice [20]. Anodic oxidation has some benefits over indirect oxidation such as no need to add chemicals to treated solution and producing less secondary pollution.

2.2. Electrode Materials

Several electrodes have been used for water treatment by electrochemical oxidation. Traditionally anode materials used for water and wastewater treatment include lead and lead dioxide [36–39], dimensionally stable anode (DSA) electrodes [40–43], graphite [44–46] and boron-doped diamond (BDD) electrodes [47–54]. Lead and lead dioxide have been used as anodes because of their stability, low cost and high oxygen evolution potential which delays O_2 evolution in favor of Cl_2 evolution [36]. Hamza et al. [37] reported the complete mineralization of 1,3,5-trimethoxybenzene in acid media at a Ta/PbO_2 anode. They found that all oxidation products were finally oxidized to CO_2 by the intermediary of carboxylic acids. Awad and Abo Galwa [38] found out that the electrocatalytic activity of a lead dioxide electrode depends on the conductive electrolyte. They concluded that in the presence of H_2SO_4 electrolyte electrode poisoning occurred, since an adherent film formed on the anode surface. The dissolution of toxic Pb^{2+} ions also hinders the use of lead and lead dioxide as anodes [12].

Recently novel Fe doped PbO_2 electrodes with a high oxygen evolution potential (OEP) and excellent electrochemical oxidation performance were prepared by Jiang et al. [55]. Electrodes were Ti/TiO_2 nanotube arrays electrodeposited by different $Fe(NO_3)_3$ concentrations including also 0.5 M $Pb(NO_3)_2$. Fe doping on PbO_2 electrode improved OEP and thus, the degradation efficiency of *p*-nitrophenol reached 100% in 90 min oxidation. It was also noticed that energy consumption (0.28 kWh g^{-1} for Fe-0.02 doped PbO_2 electrode) was reasonable during the treatment. In another study by Chen et al. [56], traditional Ti/SnO_2–Sb/PbO_2 electrode was compared to the constructed PbO_2 electrode which had a more regular and compact morphology with better oriented crystals of lower size. Electrochemical degradation of nitrobenzene was improved by enhanced mass transport at the developed electrode. It was also observed that constructed PbO_2 electrode had higher oxygen evolution overpotential and higher accumulated hydroxyl radical concentration than traditional electrode. Similar behavior was also attained in the degradation of a real textile wastewater using β-PbO_2 and DSA® anodes [57]. Use of the Ti–Pt/β-PbO_2 electrode led to higher chemical oxygen demand (COD) removal rates than with DSA electrodes (20% more at pH 3 and 25 °C). These observations confirm that development of novel electrode materials can enhance the EO treatment efficiency and decrease the operational costs.

DSA are catalytic oxide electrodes which can effectively generate active chlorine species because of their low Cl_2 overpotential [20]. Efficient degradation of paper mill wastewater was achieved by using three-dimensional electrodes (Ti/Co/SnO_2–Sb_2O_5) combined with activated carbon treatment [41]. This was mainly due to the fact that the conversion rate within an electrochemical reactor can be increased substantially due to its large specific surface area in comparison to conventional two-dimensional electrodes. So-called "non-active" DSA 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 [43]. However, SnO_2 electrodes are not stable. With "active electrodes", such as RuO_2 and IrO_2, only selective oxidation of the organic species in the solution occurs. In a review article by Wu et al. [58], it is stated that surface modification of mixed metal oxide (MMO) anodes will increase their efficiency in organic compound degradation. Modification of surface of MMO anodes by nano- and microstructures will increase the surface area, and hence the reaction rates.

Recently the potential of conducting diamond films for water treatment has been recognized. They 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 [48,50]. They also have the highest oxygen evolution overpotential value (2.7 V for Ti/BDD) [12] 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 [49]. It is also known that besides hydroxyl radical formation on the electrode surface, diamond electrodes also increase mediated oxidation by other electrochemically formed compounds such as persulfate, perphosphate or hypochlorite depending on the electrolyte used.

The low pressure conversion of carbon to diamond crystals has made it possible to grow a thin layer of diamond film on suitable substrates such as silicon, niobium, tungsten, molybdenum, and titanium [51].