

Electrochemical Incineration of Oxalic Acid at Manganese Dioxide Rotating Cylinder Anode: Role of Operative Parameters in the Presence of NaCl

Ali H. Abbar,^{a,z} Rasha H. Salman,^b and Ammar S. Abbas^b

^aChemical Engineering Department, University of Al-Qadisiyah, Diwaniya 58002, Iraq ^bChemical Engineering Department, University of Baghdad, Baghdad 10071, Iraq

A detailed experimental study was devoted to the anodic oxidation of oxalic acid using manganese dioxide rotating cylinder anode with the objective to evaluate in a systematic way the effect on the oxalic acid oxidation process of several relevant parameters, including the presence of sodium chloride, the current density (J), the rotation speed, the temperature, and the initial concentration of oxalic acid. Thin manganese dioxide film on graphite substrate has been prepared by electrochemical oxidation from MnSO₄-H₂SO₄ electrolyte. The morphology of this electrode was investigated by XRD, SEM, EDS and AFM techniques. The results show that a firm γ -structure of MnO₂ film on graphite rod can be obtained successfully. The results indicate that the presence of NaCl has a vital role on the performance of the oxalic acid incineration process. Also current density has the major effect on the removal and current efficiencies. Positive effect of temperature on the removal and current efficiencies and negative effect of rotation speed were observed. The best adopted operative conditions were $T = 50^{\circ}$ C, J = 40 mA/cm² and 200 rpm in the presence of 1g/l NaCl where a conversion of about 97% and a current efficiency close to 55% with energy consumption less than 28 kWh(kg of COD)⁻¹ were obtained after four hours of electrolysis time. The findings of the present research validate that incineration of oxalic acid can be carried out successfully on MnO₂ anode.

© 2016 The Electrochemical Society. [DOI: 10.1149/2.0551613jes] All rights reserved.

Manuscript submitted July 5, 2016; revised manuscript received September 9, 2016. Published September 20, 2016.

Discharging of industrial wastewater containing toxic organic compounds presents a major risk to the environment and must be prevented. Some of these organic compounds are called "recalcitrant" because they are resistant to biological treatment. Therefore, they are toxic to microorganisms and should be degraded before discharge.^{1,2}

Oxalic acid (OA) is one of these types of organic compounds. It has several various manufacturing and industrial uses including use in fabric printing and dyeing; bleaching straw hats; removing paint; varnish; rust or ink stains; and cleaning wood. After these industrial applications this compound is discharged in the water effluents. OA also is the main and final intermediate for the catalytic and electrochemical oxidation of several other organic compounds.³ Recent works have confirmed that electrochemical methods offer an attractive alternative to traditional routes for treating oxalic acid.^{4,5} The effectiveness of the electrochemical oxidation depends on many factors including the material of the electrode and the nature of the organic substrate.^{6–8}

Several anodic materials have been tested, but most of them presented important disadvantages such as a rapid loss of activity (graphite), high cost (Si-boron-doped diamond (BDD)), release of toxic ions (PbO₂), limited service life (SnO₂) and not complete oxidation (IrO₂).^{6,7} Therefore, a great effort is devoted to investigate cheaper anode materials with comparable performances to be used in the treatment of wastewater containing organic compounds. Among these, manganese oxides (MnOx) materials represent an exciting family for electrode manufacture. These oxides display good electrocatalytic properties, low cost and availability, environmental compatibility and chemical stability. Up to now, they are primarily used as cathodes in alkaline batteries,⁹ in lithium-ion batteries¹⁰ and super capacitors,¹¹ while fewer applications are reported concerning the electrochemical treatment of toxic compounds.¹²⁻¹⁵ No previous works have been conducted to electrochemical incineration of OA using MnO2 as anode material. On other hand, manganese dioxide due to its electrocatalytic properties presents low overpotential for chlorine evolution thus representing a potentially promising electrode material for the treatment of effluents containing a high chloride load, such as textile wastewaters where chloride is added specifically to increase the ionic strength of the bath.¹⁴

Electrodes based on manganese oxide thin films may be obtained by different methods such as sol–gel,¹⁶ physical vapor deposition,¹⁷ electrostatic spray deposition,¹⁸ electrochemical deposition,¹⁹ and chemical bath deposition.^{20,21} The low costs of equipment and accurate control of deposited thickness make electrodeposition method very widely used in the synthesis of manganese dioxide.¹⁹

Recently the rotating cylinder electrode (RCE) electrochemical reactor has become a good alternative design in wastewater treatment due to the high rate of mass transfer and uniform distribution of current and potential. It has found successful applications in metal removal from dilute solutions. However, using it in the electrochemical oxidation was limited to few uses.²²

The present work will be studied the effect of the main operative parameters, such as the presence of chloride ions, the current density, the speed of electrode rotation, the initial OA concentration, and the temperature on the anodic incineration of OA at manganese dioxide rotating cylinder electrode, with the aim to obtain the best operative conditions of the process and to evaluate if it is possible to achieve the total incineration of OA with high current efficiency and lower energy consumption as possible as by using MnO_2 plated on graphite as anode.

Experimental

All chemicals used in the experiments were of reagent grade and there was no need for further purification, $MnSO_4.H_2O$ (Thomas Baker), H_2SO_4 (Riedel-deHaën), oxalic acid (LOBA Chemie), NaCl (Thomas Baker), and distilled water were used in the preparation of all aqueous solutions.

MnO₂ electrode preparation.—Manganese dioxide was electroplated on graphite rod of 1.98 cm diameter and 32.3 cm² active surface area by anodic deposition in acidified sulfate bath (100g/l MnSO₄-90 g/l H₂SO₄) with a total volume of 0.6 L. The graphite rod was first polished with SiC paper of 600 grit, degreased with acetone and washed with water then treated by immersion in boiling water until evolution of gas ceased followed by activating as anode in an electrolyte with 90g/l of H₂SO₄ using a current density of 14 mA/cm² for 30 minutes and finally washed with pure water in an ultrasonic bath. During electrodeposition, the graphite rod was held as anode and hollow concentric graphite cylinder of 8cm inner diameter with 326.7cm² inside surface area as the counter electrode. Anodic deposition was performed under constant applied current (galvanostatic conditions) using DC power supply (UNI-T: UTP3315TF-L) with a current density of 6 mA/cm² for two hours at 80-85°C. This procedure gave a deposit with 7.0 millimole of total manganese. The MnO₂ electrode was washed thoroughly with distilled water then stored in a container