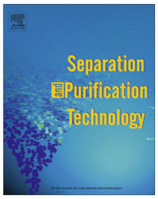
Separation and Purification Technology 154 (2015) 281–289

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur



# Activity of Pt/$MnO_2$ electrode in the electrochemical degradation of methylene blue in aqueous solution

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## ARTICLE INFO

*Article history:*
Received 28 April 2015
Received in revised form 3 August 2015
Accepted 23 September 2015
Available online 26 September 2015

*Keywords:*
Electrochemical degradation
Pt/$MnO_2$ anode
Direct oxidation of methylene blue
Response surface methodology
Optimization

## ABSTRACT

The electrochemical oxidation of methylene blue (MB) in aqueous solution was studied by galvanostatic electrolysis using $MnO_2$ electrode as anode. The $MnO_2$ electrode was prepared by electroplating method, and was characterized by X-ray diffraction (XRD), the cyclic voltammetry (CV) and amperometry $j = f(t)$. This study has been done in synthetic media using sulfate sodium as electrolyte and thus only the contribution of the direct effect of electrolysis has been put into evidence. The electrochemical oxidation performance of the prepared electrode was investigated using MB as a model pollutant. UV spectroscopy and chemical oxygen demand (COD) measurements were conducted to study the kinetics of MB electrochemical degradation and the mineralization under different operating conditions. An experimental design methodology (Box–Behnken design) has been applied to determine the optimal experimental condition in term of effectiveness. The best conditions have been found after 120 min of electrolysis with Pt/$MnO_2$ operated at pH $\approx$ 8 with a current density of 7 mA $cm^{-2}$ in presence of <0.1 mol $L^{-1}$ of sodium sulfate. In these conditions, higher than 90% of MB removal can be obtained with an abatement of slightly over 70% of COD. These results indicate that the suggested modified electrode was highly efficient in the treatment of effluents containing methylene blue dye with very slight effect of matrix.

## 1. Introduction

Electrochemistry is a promising method for the water and wastewater treatment and has received considerable attention recently. Electrochemical method applied in water treatment has been investigated by many researchers [1–7]. Toxic organics can be effectively oxidized by the electrochemical method [8,2,5,9–14], demonstrating that this approach may be feasible for largest group of dyes, which are widely used in the textile industry [15,16]. Because of the simply in structure and operation, it is possible that the electrochemical method can be developed as a cost-effective technology for the treatment of aromatic pollutants [9].

The efficiency and selectivity of electrochemical oxidation of organic compounds are mainly effected by the nature of the electrodes that are used in the process [10,11]. Dimensionally stable anode (DSA), made by the deposition of a thin layer of metal oxides on a base metal, usually titanium, have been proved to be effective in organic degradation [2,9–11,14]. Suitable anode should exhibit high activity toward organic oxidation and low activity toward secondary reactions (e.g. oxygen evolution) coupled with high current efficiency [17,18].

On traditional electrode materials, such as Au, Pt, and C whilst the oxidation reaction by oxygen transfer is spontaneous, it is characterized by low reaction rate constant [19,20]. Oxygen transfer is usually favored on an anode material with high oxygen evolution over-potential. Otherwise, most of the supplied current will be wasted in oxygen evolution reaction. Moreover, polymerization reactions that could take place inactivate the anode [21,22]. Thus, anodic material with a very high oxygen overvoltage is essential [23,24].

It is a relatively new trend in dye waste water treatment and various electrode materials have been tested, such as boron-doped diamond (BDD) [25–27], $PbO_2$ [28,29], $SnO_2$ [28,30,31], and mixed metal oxide ($RuO_2$) [32], which are robust and efficient water oxidation catalysts that exhibit high turnover frequencies under mild conditions. However, the high cost and scarcity of noble metals severely limit the widespread use of these catalysts as (DSA) for oxygen evolution reaction (OER). Thus, a distinct need

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http://dx.doi.org/10.1016/j.seppur.2015.09.049
1383-5866/

exists for more abundant materials that can serve as efficient catalysts in such systems [33–40].

Numerous studies have examined the electrochemical oxidation of $H_2O$ by Mn-containing materials, particularly manganese oxides, such as the simple oxides $MnO_2$, $Mn_2O_3$, and MnOOH and complex oxides $MnFe_2O_4$ and Mo- or W-doped MnO [41–45].

Layered manganese oxides, in particular birnessite ($\delta$-$MnO_2$), have recently received widespread attention because of their unique adsorptive, catalytic, ion-exchange, and electrochemical properties. So far, a number of procedures have been developed for the synthesis of birnessite-type manganese oxides. Particularly, the electrodeposition technique was looked upon as a low-cost, clean, and simple technique for the production of novel electroactive materials.

In this present study, electrochemical oxidation of methylene blue (MB) has been investigated using Pt/$MnO_2$ as anode electrode. The anodic electrodeposition was made galvanostatically from an electrolyte consisting of a 0.01 mol $L^{-1}$ $MnSO_4$ with $Na_2SO_4$ as supporting electrolyte. The details for the $MnO_2$ films electrodeposition process are described in section Materials and Methods. The first part of this work evaluates the behavior of electrode in the presence of MB solution using cyclic voltamperometry and chrono-potentiometry study. The second part concerns the use of a statistical methodology for a rational analysis of the combination of operational factors that led to the best treatment of electro-oxidation process for MB removal. A Box–Behnken experimental Design (BBD) design was used to optimize MB degradation in term of effectiveness.

## 2. Materials and methods

### 2.1. Reagents

Analytical grade MB ($C_{16}H_{18}N_3SCl{\cdot}2H_2O$) was purchased from Sigma–Aldrich. Sodium hydroxide (NaOH) and sulfuric acid ($H_2SO_4$) were obtained from Fluka. Sodium sulfate ($Na_2SO_4$) was used as support electrolyte. Water used in the experiments was distilled. The pH of solution was adjusted to desired range by using diluted sulfuric acid ($H_2SO_4$) or NaOH.

### 2.2. Preparation of Pt/$MnO_2$ electrode

Electrolysis tests were performed in an open, undivided and cylindrical electrochemical cell of 250 mL capacity. $MnO_2$ was deposited glvanostatically on the platinum substrate (5 cm × 3 cm) by electrochemical anodization of manganese at a current density of 4 mA $cm^{-2}$, in aqueous solution $10^{-2}$ mol $L^{-1}$ $MnSO_4$ containing $Na_2SO_4$ at a concentration of $10^{-1}$ mol $L^{-1}$. Electrolysis experiments of aforesaid Pt/$MnO_2$ anode was performed at pH = 1.0 (adjusted by adding $H_2SO_4$), at 25 °C, during 30 min. A stainless steel plate of 15 $cm^2$ (6 cm × 2.5 cm) area electrode was used as cathode, and $Hg/Hg_2SO_4/K_2SO_4$ saturated (electrode REF621 Radiometer Analytical, $E$ = 0.651 V/ENH) electrode was selected as reference electrode. A magnetic stirrer (DELTA LABO) with a rotational speed of 250 rpm was used to maintain the electrolytic homogeneity of the solutions. The applied voltage was supplied by an electrochemical analytical instrument (Radiometer Analytical, VoltaLab 21).

### 2.3. Analytical methods

Analytical parameters were measured to evaluate the electro catalytic oxidation efficiency of above-mentioned organic compound dye, these parameters were:

A UV–vis spectrophotometer (Hach DR-5000) was used to monitor the MB concentration at 662 nm. The equation used to calculate the color removal efficiency in the treatment experiments is:

$$MB_{removal}\% = \left(\frac{C_0 - C}{C_0}\right) \times 100 \qquad (1)$$

where $C_0$ and $C$ were initial and present concentrations of the MB in solution (mg $L^{-1}$), respectively.

COD was determined with the aid of ECO25 Thermo reactor and 10 μL precision digital burette using closed-refluxed titrimetric method according to standard procedure as described by other authors [46]. The COD values obtained from the two methods were matched with each other. The equation used to calculate the COD removal efficiency in the experiments is:

$$COD_{removal}\% = \left(\frac{COD_0 - COD}{COD}\right) \times 100 \qquad (2)$$

where $COD_0$ (initial) and COD (final) of the dye solutions are calculated in mg $L^{-1}$.

## 3. Results and discussion

### 3.1. Physicochemical characterization

The X-ray diffraction (XRD) determination of the structure present in the electrode was carried out by an X'Pert Pro powder diffractometer with a vertical configuration using a power of 45 kV and a current of 40 mA. XRD pattern of the manganese oxide film prepared by electrodeposition, under electrochemical conditions cited above, is shown in Fig. 1. The diffraction peaks observed at $2\theta$ = 37.5, 42.5, 55, 60, and 67 are assigned to the (1 0 1), (1 1 1), (2 1 1), (2 2 0), and (3 1 0) planes of ($\delta$-$MnO_2$).

### 3.2. Electrochemical measurement

Chrono potentiometry was used to estimate the anodic potential imposed for $MnO_2$ formed. A current density of 4 mA $cm^{-2}$ was imposed during the tests (Fig. 2). The Pt/$MnO_2$ anode showed relatively high potential (≈2.1 V/ESM). A higher anodic potential is believed to imply greater energy consumption, which can be unfavorable while increasing the current intensity. However, a high potential is seen as important symbol of a better electro-catalytic activity at the fresh surface.

The oxygen evolution reaction (OER) is taken place when the current densities abruptly increase in the linear polarization curve. Anodes with high over-potential for OER have high electrocatalytic activity for the organics oxidation [47,48]. The mechanism for the anodic oxidation of organic compounds can be detailed shown as below for a Pt/$MnO_2$ electrode, which is a typical active electrode [47].

$$\equiv MnO_2() + H_2O_{ads} \rightarrow \equiv MnO_2({}^{\cdot}OH_{ads}) + H^+ + e^- \qquad (3)$$

$$\equiv MnO_2({}^{\cdot}OH_{ads}) + R \rightarrow \equiv MnO_2() + RO + H^+ + e^- \qquad (4)$$

where $\equiv MnO_2()$ represents the electro-active sites of the electrode, and RO represents organic oxidation products. The oxidation of organics is mediated by adsorbed ${}^{\cdot}OH$. An inevitable but undesirable concomitant reaction is oxygen evolution (Eq. (5)).

$$\equiv MnO_2({}^{\cdot}OH_{ads}) \rightarrow \equiv MnO_2() + 0.5O_2 + H^+ + e^- \qquad (5)$$

As shown in Fig. 3, the OER potentials were 1.25 V and 1.50 V (vs. ESM) for the (Pt) electrode and the (Pt/$MnO_2$) electrode, respectively. Obviously, manganese oxide layer enhanced the overpotential for OER of electrode (Pt). This could be explained by the