

# Electrochemical Degradation of Phenol in Aqueous Solution on Pbo<sub>2</sub>- Clay/Polyaniline Nanocomposites

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#### Abstract

In this work a novel electrode was successfully prepared using in-situ oxidation of Pb - montmorillonite in ammonium solution.  $PbO_2$ -clay/polyaniline nanocomposite anodes have small crystallites of  $PbO_2$  which indicates that are much more amorphous than those of chemical  $PbO_2$ . When cycling this novel electrode in sulfuric acid solution, higher capacity is obtained. In addition,  $PbO_2$ -clay/ polyaniline anode has faster and higher phenol removal efficiency than that of chemical  $PbO_2$ .

Keywords: Montmorillonite, nanocomposites, lead dioxide, phenol degradation.

# Introduction

Many of the world's water ways and water sources are polluted and contaminated by heavy metals and organic materials such as pesticides and herbicides, dyes, phenols and phenolic compounds. Thus water purification is a process of extreme importance. Hydration and swelling are the main properties of clays with respect to their role played in landfill sites [1-4]. Clay minerals are alumino-silicates that are very reactive materials due to their small grain size, large surface area and adsorption properties. As they are able to retain inorganic and organic contaminants, clays as raw or composite materials were widely applied in many industrial fields [5-12]. To date many environmental scientists have focused on the development of stable anodes for removal of persistent organic pollutants by electrochemical oxidation [13].Traditional electrodes, such as graphite and nickel, show poor current efficiency in organic degradation [14]. Phenols can be oxidized rapidly at the Pt anode but they can inactivate the Pt anode due to the deposition of oligomers on the anode.

PbO<sub>2</sub> was regarded as an excellent metal oxide electrode and was widely used in electrochemical oxidation because of its lower cost compared to noble metals, good conductivity, chemical stability in corrosive media, as well as high over-potential for oxygen evolution reaction [15,16]. The aim of this work is a comparative study of the electrochemical degradation of phenol in aqueous solution on chemical lead dioxide and PbO<sub>2</sub>- clay/polyaniline nanocomposite anodes.

#### Eperimental

## **Preparation of Pb-MMt**

Na-MMt was treated with 100 ml of 1M  $Pb(NO_3)_2$  solution at room temperature for 24 h under vigorous stirring. The products were washed with deionized water thoroughly and the supernatants were separated by centrifugation. The solid parts were filtered off, washed with deionized water repeatedly until a negative nitrate test was obtained.

#### **Preparation of PbO<sub>2</sub>-MMt**

The (Pb-MMt) was treated with 100 ml of a stirred solution containing a mixture of ammonium persulfate, sodium hydroxide and ammonia at room temperature for 24 h. The solid parts (PbO<sub>2</sub>-MMT) obtained were filtered off, washed with deionized water and overnight dried at 105°C.

#### **Preparation of PbO<sub>2</sub>-clay/polyaniline**

 $PbO_2$ -MMT was dipped in a solution of 0.1 M of aniline and 0.5 M of HCl at room temperature and stirred. The composite material is separated by centrifugation and filtered off. Then bathed in an oxydizing solution of ammonium persulfate, sodium hydroxide and ammonia at room temperature for 24 h. The chemical polymerizaztion occurs and a  $PbO_2$ -clay/polyaniline nanocomposite powder is obtained.

Chemically lead dioxide, as reference sample was prepared following the same method. An appropriate amount of lead acetate is used as starting material instead of (Pb-MMt). The

solution was stirred at room temperature for 24 h. The brown-black powder obtained was filtered off, washed repeatedly with deionized water then overnight dried at 105°C.

## **Electrochemical Activity Measurements**

The electrochemical measurements were carried out in a three electrode cell. The working powder electrode is at 1 cm distance from a large platinum rectangular-shaped counter electrode. An Hg/Hg<sub>2</sub>SO<sub>4</sub>/saturated K<sub>2</sub>SO<sub>4</sub> reference electrode was used. The potential-current curves were recorded after cycling the electrodes in 1.28 s.g. H<sub>2</sub>SO<sub>4</sub> solution in the potential range 1.8 to 0.5 V at a sweep rate of  $20mVs^{-1}$ . The capacity expressed in mAh cm<sup>-2</sup> is determined by integrating the surface area of the cathodic peak corresponding to the reduction of PbO<sub>2</sub> to PbSO<sub>4</sub>.

## **Electrochemical Removal of Phenol**

The electrolysis of aqueous solutions containing phenol was carried out in a 100-mL onecompartment Pyrex glass cell. The anode was supported vertically and parallel to the Platinum cathode. The distance between the cathode and the anode was 3 cm. 50mL of sample solution was used in each experiment. The electrolysis was conducted under constant potential in aqueous solution containing 20 mM of phenol and 0.08 M HClO<sub>4</sub> in Acetonitrile.

## **Results and Discussions**

Fig.1 shows the average crystallite size at FWHM (full width at half maximum) versus distance for PbO<sub>2</sub>-MMt and chemical PbO<sub>2</sub>. The average crystallite size of PbO<sub>2</sub> particles for PbO<sub>2</sub>-MMt and chemical lead dioxide was calculated using Sherrer equation. The  $(2\ 2\ 1)$ ,  $(0\ 02)$ ,  $(1\ 1\ 1)$  and (110) orientations for the PbO<sub>2</sub> phase are selected. From Fig. 1, it is clearly seen that PbO<sub>2</sub> particles in the PbO<sub>2</sub>-MMt sample are much smaller than those prepared by the chemical route in aqueous solution.



Figure1: Average crystallite size at FWHM versus distance for PbO2-MMt and chemical PbO2.

Figs.2 and 3 show respectively the electrochemical capacities of chemical  $PbO_2$  and  $PbO_2$ clay/polyaniline expressed in mc/cm<sup>2</sup> versus the number of cycles. It is clearly seen that nanoparticles of  $PbO_2$ -clay composite are much more active than those of chemical  $PbO_2$ . This may explained but the fact that  $PbO_2$ -clay particles are much more amorphous and are more hydrated than those of chemical  $PbO_2$  which exhibit a small increase in the capacity during the first three cycles. After the third cycle the surface of the anode is covered with a layer of PbSO4 reputed as non conductor product and therefore a decrease in the electrical activity is observed.



Figure 2: Capacity of chemical PbO<sub>2</sub> versus number of cycles



Figure 3: Capacity of PbO<sub>2</sub>-clay Composite Versus Number of Cycles

The cyclic voltammetric response of a solution containing 20 mM phenol and 0.08 M HClO<sub>4</sub> on PbO<sub>2</sub>-clay composite surface is plotted in Fig. 4. The phenol oxidation peak appeared around 1.5 V versus Hg/Hg<sub>2</sub>SO<sub>4</sub>. The data indicates that phenol oxidation peak current increased with cycling. Electrolyses were carried from the solution mentioned above at this potential for one hour by using PbO<sub>2</sub> anodes. The UV spectra of the three solutions before electrolysis and after electrolyses on chemical PbO<sub>2</sub> and PbO<sub>2</sub>-clay composite surfaces are represented respectively in Fig.5. The characteristic peak of phenol appears at 270 nm. In

addition, it is clearly seen that PbO<sub>2</sub>-clay/ polyaniline anode has faster and higher phenol removal efficiency than that of chemical PbO<sub>2</sub>.



**Figure 4**: Cyclic voltametric response of a solution containing 20 mM phenol and 0.08 M HClO<sub>4</sub> on PbO<sub>2</sub>-clay/ polyaniline anode (scan rate is 20 mV s<sup>-1</sup>).



Figure 5: UV absorption spectra of the phenol degradation solution: 1):before electrolysis, 2):after electrolysis on chemical PbO<sub>2</sub> anode. 3):after electrolysis on PbO<sub>2</sub>-clay/ polyaniline anode.

## CONCLUSION

Phenol degradation was achieved on two types of  $PbO_2$  anodes at room temperature. It has been proven that crystallite size of  $PbO_2$  has a profound effect on the electrochemical degradation of phenol.  $PbO_2$  surfaces with high amorphous parts provided faster aromatic ring opening and decreased the electrolysis time for phenol degradation. In addition, has faster and higher phenol removal efficiency than that of chemical  $PbO_2$ , which exhibits high crystallinity.

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