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Ozone Effect on Wastewater Containing Lead Compounds

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ABSTRACT

Removing heavy metals from water has been a subject of high interest in the recent decades. The global concern aimed at identifying efficient and inexpensive methods for wastewaters depollution. Ozonation is one of the successful methods, due to the ozone strong oxidative attributes. The present paper is a study on decreasing the concentration of lead ions through ozone barbotage. The study was made at two different temperatures and different exposure time intervals, as means to creating optimal conditions for lead removal from wastewaters through ozonation.

KEYWORDS: ozonation, lead, cyclic voltammetry

Introduction

Heavy metals are to be found in soil usually as minerals combined with oxygen and sulphate and are dragged along by soil erosion or by volcanic activity. Due to anthropic activities like metallurgical or chemical industry, mining, agriculture and also due to landfills (industrial and household), the heavy metals concentration in soil and water has increased alarmingly (Shi, Shao, Li, Shao & Du, 2009; Cao, Chen, Zhang, Zhang, Qiao & Men, 2010; Yi, Yang, & Zhang, 2011; Bird, Macklin, Brewer, Zaharia, Balteanu, Driga & Serban, 2009). Lead is one of the most frequent metals to be found in wastewaters.

Removing lead from wastewaters usually involves expensive technologies, as a series of operations are needed, combining mechanical, biological, physical and chemical methods. One of the methods used in water depollution is treating water with ozone.

The aim of this study is to investigate the effect of ozone on the Pb2+ ions in the waters resulted from industrial activities, using cyclical voltammetry. This electro-chemical method is one of the most convenient for the heavy metals determination in a solution, due to its inexpensive cost and easy operation, as compared to other methods (Lanez, Rebiai, Saha & Alia, 2011). Lead is among the most frequent contaminants in the industrial wastewaters (Serrano et al., 2010), and very harmful for the human health (Serrano et al., 2010; Kaplan, Yildirim, Yildirim & Tayhan, 2011). Ingesting it leads to liver and kidney failure, infertility and fetal malformations (Serrano, N. et al., 2010), anemia or central nervous system problems (Zhao, Xia, Fan, Zhao & Shen, 2012).

The literature provides multiple examples of ozonation of wastewaters containing heavy metals. The best results were obtained in removing Fe and Mn through ozone precipitation (Majumdar & Sproul, 1973; Shammas & Wang, 2005; El Araby, Hawash & El Diwani, 2009). Vanadium oxidation using the same method (Danilov & Karpov, 2000) and treating it with sulphuric acid resulted in getting V^{5+}, a filterable polymeric compound. The effect of ozone on zinc and cadmium is also mentioned in the literature. When zinc and cadmium were found in organic complexes (Zn-EDTA, Cd-EDTA), ozone has been discovered to have a stronger effect than in the case of uncomplexed metals, as zinc and cadmium have a reduced oxidation state (Zn^{2+}, Cd^{2+}) (Poon, 1984). Neamtu et. all studied the ozone effect on aluminium in a sollution in various temperatures and exposure time intervals. The results showed that temperature directly influences the ozone effect on the decreasing of the aluminium ions concentration (Neamtu, Bolundut & Pica, 2013).

Research methodology

The study presents an attempt to decrease lead ions concentration from simulated wastewater using ozonation. Two samples of distilled water polluted with $Pb(CH_3COO)_2$ of 0.01M (standard solutions), have been exposed to ozone by barbotage at 5 °C and 25 °C, at four different timeframes: 30, 60, 90, 120 minutes.

The determinations of metallic ions were made by cyclic voltammetry, using a VersaSTAT 3 (Princeton Applied Research) potentiostat, on a -4 to +4 V potential range and a 0.1 V/s scanning rate. The thermostatic cell comprising a glassy carbon working electrode, a platinum counter electrode and a calomel reference electrode, was connected to the potentiostat.

The lead peaks were determined by cyclic voltammetry before and after each of the four ozonation timeframes, aiming to establish the variation of the peaks. The treatment was performed using an EDO – 05 equipment (Inventica LTD Bistrita, Romania), with a 500 mg O_3/h ozone concentration emission.

Results and discussions

The experimental results are presented in Figure 1 and Table 1 for the temperature of 5 °C and in Figure 2 and Table 1 for the temperature of 25 °C. There is an important amount of organic compounds in the studied solution, due to the fact that the experiments were made on lead acetate [$Pb(CH_3COO)_2$].

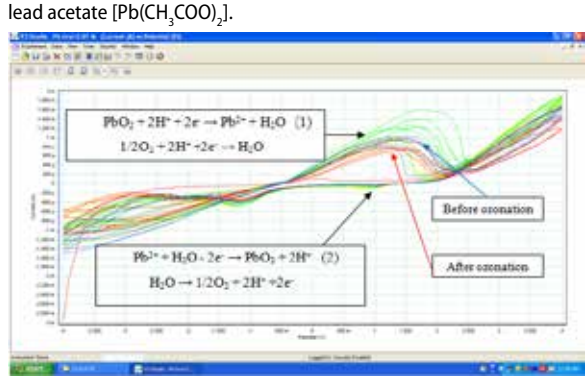

Figure 1. Overlapped voltammograms obtained in the determination of lead ion at 5 °C

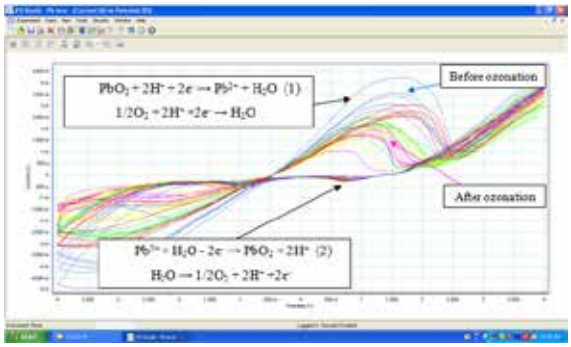

Figure 2. Overlapped voltammograms obtained in the determination of lead ion at 25 °C

Table 1. $Pb(CH_3COO)_2$ at 5 °C and 25 °C

Substance	Standard sample	Ozonated 30 min	Ozonated 60 min	Ozonated 90 min	Ozonated 120 min	Normal potential in standard conditions	Measured potential
$Pb(CH_3COO)_2$ 5 °C	blue	red	green	yellow	-	+1.8 V +0.84 V	+1.7 V +0.8 V
$Pb(CH_3COO)_2$ 25 °C	blue	red	green	yellow	pink	+1.8 V +0.84 V	+1.7 V +0.8 V

The reactions that could occur are:
$Pb^{4+} + 2e^- \rightarrow Pb^{2+}$ and
$Pb^{4+} + 4e^- \rightarrow Pb^0$.

After the voltammetric measurements, it was observed that the lead peaks in the standard solution, before the ozone treatment (blue line) are located around (+0.8V) – (+1.7V), very close to the ones in the literature (+0.84V and +1.8V) (Niac, Voiculescu, Baldea & Preda, 1984). In the peaks value identification, the potential value of the calomel electrode was considered (ESC) in relation to the hydrogen electrode at 25 °C, which is 0.244V.

The cyclic voltammetry curve is complex due to multiple reaction possibilities of lead ion in aqueous solution. There is a possibility that lead dioxide (PbO_2) will form on the surface of the glassy carbon.

The appearance of a hysteresis loop is noted, probably due to an oxidation reaction of Pb^{2+} to Pb^{4+}, as a result of lead oxide formation (PbO_2) (reaction 2 on the Figure 1 and Figure 2). Because of the existence of an acid environment in the solution, the oxidation reaction of the oxygen ions from (H_2O) to (O_2^0) is also possible (Niac et al., 1984).

Next in the the catodic voltammetry cycle, the formed PbO_2 electrode might decompose into Pb^{2+}; the oxygen also might be reduced to H_2O (reaction 1 on the Figure 1 and Figure 2).

In the cathodic domain of the voltammogram, it can be noticed that at 5 °C there is no decrease in lead ion concentration, compared to 25 °C, where there is a descending trend (the current value decreases from approximately 3.5mA to approximately 2mA). The highest efficiency is noted after 120 minutes of ozone exposure (pink line). A decrease of the lead peak amplitude means a decrease in lead ions concentration, due to the fact that the cathodic current is directly proportional to the metallic ions concentration (Kounaves, 1997; Zanello, 2003). This is due to the fact that certain compounds can be more stable at lower temperatures, being more difficult to remove by ozonation, but less stable as temperature increases, which makes them easier to remove.

Conclusions and personal considerations

The results of the experiments show that lead ions are less stable at 25 °C, which makes ozonation more efficient at this temperature. The reduction of the peak amplitude starts after 30 minutes and continues to decrease as the exposure time increases. The best results are achieved after 120 minutes when the current values decrease from approximately 3.5mA to approximately 2mA.

No significant decrease in peak amplitude is noticed at 5 °C, regardless of the exposure time.

The redox reactions that occured during the experimental determinations may be considered quasireversible processes, due to the low amplitude of the peaks and the large distance between them. The peak potential also moves with the scanning rate. This shows the effectiveness of the ozonation on lead ions concentration decreasing in an aqueous solution.

Two main factors were considered to ensure the optimal conditions in the removal of lead from wastewaters through ozonation: the time of exposure to ozone and the temperature of the studied sollution.

Even if the ozonation is not considered to be the most efficient method of treating lead containing wastewater, it contributes successfully in reducing the metallic ions concentration level, by converting them into less harmful compounds or into compounds that can be easily removed by a subsequent method.

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