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Desalination 223 (2008) 187–193

DESALINATION

www.elsevier.com/locate/desal

# The use of the advanced oxidation process in the ozone + hydrogen peroxide system for the removal of cyanide from water

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Received 20 December 2006; accepted 3 January 2007

#### Abstract

The results of laboratory tests are presented in this paper, which demonstrate a possibility of using the advanced oxidation process for the removal of cyanide from the water. A comparative analysis was carried out for the processes of ozonation, oxidation with hydrogen peroxide and advanced oxidation in the  $O_3 + H_2O_2$  system.

The paper presents experimental test results that indicate a very clear effect of the value of pH on the efficiency of the ozonation process. The performed tests have confirmed an increase in cyanide reduction with increasing reaction of water treated. This may suggest a higher susceptibility of cyanide to indirect oxidation by hydroxyl radicals than to direct oxidation by ozone. In this connection, tests were carried out on the use of advanced oxidation methods for the removal of cyanide. These methods are based on the generation of hydroxyl radicals being the most active reagents. In most processes, 'OH radicals are produced with the help of an oxidant added. In view of the fact that hydrogen peroxide is used for waste-water treatment, the tests were carried out for the  $O_3 + H_2O_2$  system. The paper gives optimal ozone doses in conjunction with hydrogen peroxide for water prepared with a cyanide solution. The effect of oxidizer dosing order of on the reduction of cyanide is described.

Keywords: Advanced oxidation process; Ozonation; Hydroxyl radicals; Cyanide

### 1. Introduction

Cyanide belong to substances posing the greatest threat to the quality of water intended

for consumption by humans. They may occur in natural water in the case, where the water is contaminated with industrial wastes. Cyanides can penetrate to underground water with effluents from granulated slag stockyards in iron metallurgy, or as a result of contamination with waste

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Presented at the conference on Desalination and the Environment. Sponsored by the European Desalination Society and Center for Research and Technology Hellas (CERTH), Sani Resort, Halkidiki, Greece, April 22–25, 2007.

water forming in nonferrous metal foundries; copper, zinc and cadmium processing plants; electroplating plants, etc.

This type of contamination occurs in underground water in the region of the city of Częstochowa in Poland. Increased concentrations of cyanide were observed at the Mirów water intake in the early 60s, and they have remained essentially at the same level do date. Cyanide can penetrate to underground water as a result of being washed out from blast-furnace slag stockyards located on the premises of the Plate Mill of the Częstochowa Steelworks. Contaminated water occurs in several deep wells, with the cyanide concentrations ranging from 0.01 do 0.11 mg/L, depending on the location of the well hole.

Literature describes numerous methods of removing cyanide from waste water [1-4]. However, there are no data available on methods possible to be used in water treatment in the case, where it is necessary to remove contamination to a very low level of 0.05 mg/L. Based on available literature and operational experiments on a water treatment station it has been determined that a method possible to be utilized in this case is ozonation and oxidation with hydrogen peroxide. Other methods used in waste water treatment cannot be applied either due to the formation of harmful products or in view of high initial cyanide concentration required for the reaction to proceed fast.

# 2. Purpose and scope of the study

The purpose of the study was to determine the effect of the combined use of ozone and hydrogen peroxide on the degradation of cyanides present in water. Obtained results were used for comparing the effectiveness of processes conducted with the use of the  $O_3/H_2O_2$ ,  $H_2O_2/O_3$  systems and the process of ozonation and oxidation with hydrogen peroxide. This article presents results obtained from laboratory tests.

The scope of the study covered:

- preliminary tests, in which effective ozone doses for different initial cyanide concentrations in the ozonation process and the effect of the reaction value on process efficiency were determined;
- (2) principal tests, in which the removal of cyanides was determined for two systems of advanced oxidation, i.e. O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>, and for the use of hydrogen peroxide alone.

## 3. Laboratory testing methodology

Model water was used in the tests. The preparation of water samples involved the addition of a specified amount of the standard cyanide solution.

The ozonation process was accomplished using an IMPOZ MINI 2 ozonizer. This is a device designed for producing an ozone and air mixture of a concentration of up to  $12 \text{ gO}_3/\text{m}^3$ . The ozonation process was conducted at a constant flow of ozoned air of 10 dm<sup>3</sup>/h. The variable process parameter, being dependant on the ozone dose, was the contact time. The oxidation process was run in a glass column of a capacity of 1800 cm<sup>3</sup> and a diameter of 3.5 cm. An overpressure system of introducing the air-ozone mixture to the water was used.

The oxidation of cyanides with hydrogen peroxide was conducted using a 30% solution of  $H_2O_2$ . The advanced chemical oxidation process was run using two oxidation systems:  $O_3/H_2O_2$  and  $H_2O_2/O_3$ . In the first case, hydrogen peroxide was dosed at the end of the ozoning process, and in the second case, before the starting of the process. According to the literature, the moment of introducing  $H_2O_2$  to the water has a great influence on the final oxidation result achieved. The best results are obtained by dosing hydrogen peroxide after  $4 \div 8$  min from the start of ozonation. Hydrogen peroxide was dosed to the glass column.

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