

Sonochemical Enhancement of Cyanide Ion Degradation from Wastewater in the Presence of Hydrogen Peroxide

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Abstract

This paper presents a comparative study on the capacity of some oxidizing agents: hydrogen peroxide, atmospheric oxygen and barium peroxide to destroy cyanide ions under ultrasound irradiation. Special attention was directed towards hydrogen peroxide activity with or without sonication.

Keywords: cyanide ions, hydrogen peroxide, wastewater, ultrasound, acoustical cavitation, sonochemical degradation

Introduction

Wastewater quality has become a serious problem for the environment and for human health. This explains researchers' preoccupation to develop new methods and to improve the efficiency of classical methods of wastewater treatment.

Cyanide (CN⁻) is a species of high toxicity found mostly in industrial effluents. Inorganic cyanide salts are often used in metallurgical industry activities such as metal surface treatment, but also in mining industry (e.g. for gold extraction). All these activities consume large amounts of water and water effluents always contain cyanide that must be treated before disposal to the natural environment.

A large number of procedures have been proposed for treatment of cyanides: physical (dilution, membranes, hydrolysis/distillation) adsorption (minerals, activated carbon, resins) complexation (acidification/volatilisation,

metal addition, flotation, solvent extraction) and/or oxidation (bio-oxidation, catalytic, electrolytic, chemical, photolytic) methods. There are several methods in which chemical oxidants (oxygen, ozone, hydrogen peroxide, chlorine, sodium hypochlorite, and sulphur dioxide) are used, with or without catalysts and each method has its advantages and disadvantages. [1]

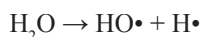
The use of hydrogen peroxide (H₂O₂) is the basis of one of the most effective methods for cyanide destruction. Hydrogen peroxide is easy to handle, it does not form insoluble salts (which create their own waste disposal problems) and the residual hydrogen peroxide degrades to water and oxygen.

Since the beginning of the investigation on sonochemistry processes a lot of works have appeared on ultrasound treatment of wastewater. Now, thanks to a large number of practical applications, ultrasound treatment has become more common, especially for wastewater processing in order to clean it from non-biodegradable pollutants. [2] Sonication has proven to be an efficient method for treatment of hydrocarbon contaminated water, being suc-

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cessfully applied for degradation of aliphatic, aromatic or halogenated hydrocarbons and for some pesticide components as well [3-10].

The mechanism proposed for the sonochemical degradation of organic pollutants is usually based on the formation of short-lived radicals generated in violent cavitation events. [11-16].



It is already known that ultrasonic irradiation of liquids causes acoustic cavitations: the formation, growth and implosive collapse of bubbles. The cavitation generates sites of locally high temperatures and pressures for short periods of time, which are responsible for unusual sonochemical effects. [17- 19]

Therefore, the goal of this work was to study the degradation of cyanide in aqueous solution by the hydrogen peroxide under sonication. The influence of the sonochemical processes and the influence of the initial concentration of hydrogen peroxide on the rate of cyanide degradation were also studied, with the use of different oxidising agents (oxygen, barium peroxide).

Materials and Methods

The experiments were performed in CFT:IUS-30 apparatus produced by Romanian National Institute of Technical Physics, with 37 kHz working frequency. The cyanide concentration was measured following the international standard ISO 6703 recommendation. Hydrogen peroxide (30%) and potassium cyanide (99.99%) were purchased from Merck. The experiments were made on 100 ml bidistilled water (0.5 mS conductivity) samples with initial cyanide concentration 0.1 mg CN⁻/mL at working temperatures between 30°C and 35°C.

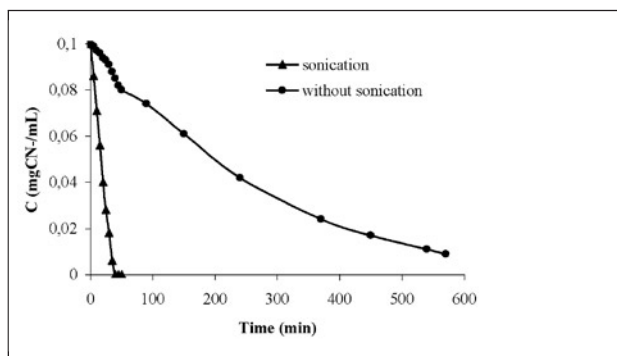


Fig. 1. The change in CN⁻ ions concentration vs. time, with and without sonication.

($f=37$ KHz, $C_{\text{CN}^-}=0,1$ mg/mL, $T=30-35$ °C, $\text{CN}^-/\text{H}_2\text{O}_2: 1/30$)
Where: f = working frequency [KHz]; C_{CN^-} = initial cyanide ions concentration [mg/mL]; T = working temperature [°C]; $\text{CN}^-/\text{H}_2\text{O}_2$ = initial ratio cyanide ions/hydrogen peroxide [gram/gram].

Results and Discussion

As a result of sonication the cyanide degradation was almost fifteen times faster than without it. After 40 minutes of ultrasound irradiation the cyanide ions were completely removed from the water treated while in the non-irradiated sample after 570 minutes the concentration of cyanide was 0.009 mg CN⁻/mL.

The plot in Fig. 1 shows the cyanide degradation time for two contaminated water samples, with the same initial ratio $\text{CN}^-/\text{H}_2\text{O}_2: 1/30$ (gram/gram), with and without sonication.

By varying the amount of hydrogen peroxide added to similar samples of cyanide-contaminated water (0,1 mg CN⁻/mL) the influence of initial ratio $\text{CN}^-/\text{H}_2\text{O}_2$ on the reaction rate was evidenced. Four samples of water with different initial ratio $\text{CN}^-/\text{H}_2\text{O}_2$ (gram/gram): 1/30 (a), 1/15 (b), 1/3(c) and 1/1 (d) were sonicated (Fig 2).

As a result of a decrease in the initial hydrogen peroxide amount the time needed for complete cyanide degra-

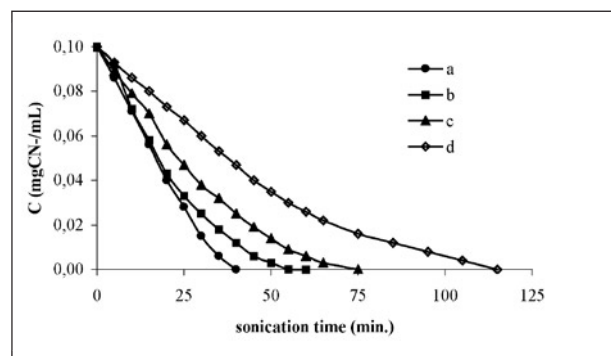


Fig. 2. The influence of the initial ratio $\text{CN}^-/\text{H}_2\text{O}_2$ on the sonication time.

($f=37$ [KHz], $C_{\text{CN}^-}=0,1$ [mg/mL], $T=30-35$ [°C], $\text{CN}^-/\text{H}_2\text{O}_2$ [g/g] = a: 1/30; b: 1/15; c: 1/3; d: 1/1)

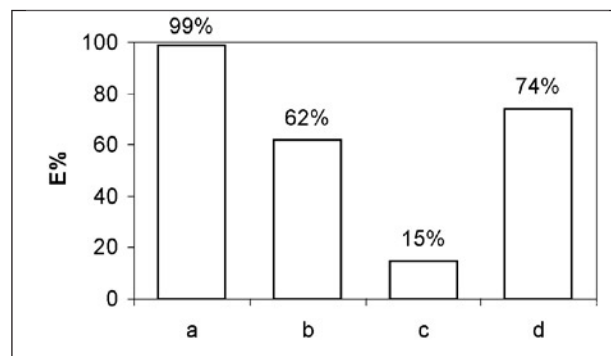


Fig. 3. The influence of the oxidising agent on the sonication efficiency after 30 minutes of ultrasound irradiation.

(a – H_2O_2 , $[\text{CN}^-/\text{H}_2\text{O}_2] = 1/23$ [mol/mol]; b – H_2O_2 , $[\text{CN}^-/\text{H}_2\text{O}_2] = 1/2,3$ [mol/mol]; c – BaO_2 , $[\text{CN}^-/\text{BaO}_2] = 1/2,3$ [mol/mol]; d – O_2 air bubbled)

degradation increased from 40 minutes at CN⁻/H₂O₂: 1/30 ratio to 115 minutes at CN⁻/H₂O₂: 1/1 ratio.

The plot in Fig. 3 presents the efficiency of ultrasound irradiation in cyanide degradation in different conditions, after 30 minutes of sonication.

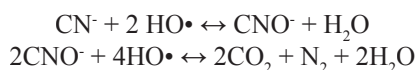
The unexpected high efficiency of oxygen (74%) could be explained by the formation of hydrogen peroxide during acoustical cavitation, which is already a very well-known phenomenon. [12, 13, 15] At the same initial molar ratio of cyanide (1/2,3) hydrogen peroxide is much more efficient (64%) than barium peroxide (15%).

The efficiency of water decontamination (E%) was calculated from the formula:

$$E\% = [(C^i - C^f)/C^i] \times 100$$

where: Cⁱ = initial cyanide concentration; C^f = cyanide concentration after 30 minutes of sonication.

The reaction steps, which characterize the overall process, with or without initial hydrogen peroxide, are:



Conclusions

The capacity of ultrasound treatment to enhance the degradation of cyanide ions in the presence of hydrogen peroxide was proved. The efficiency of the process at constant values of ultrasound frequency (37 KHz) depends upon the initial quantity of hydrogen peroxide. In the same conditions and at the same initial molar ratio of cyanide, hydrogen peroxide is more efficient than barium peroxide, in cyanide degradation. The oxygen presence in the solution during sonication is favorable for HO[•] radical formation, hence cyanide degradation occurs without hydrogen peroxide addition.

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