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PRELIMINARY STUDIES ON DIVERSE THEMES

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TREATMENT OF EFFLUENTS THROUGH CONJUGATED USE OF HYDROGEN PEROXIDE AND UV RADIATION

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Abstract

At present several technologies of treatment of effluents with hydrogen peroxide are in use which aim to kill the organic compounds; cyanides; arsenic; nitrous oxides; and sulfides. However satisfactory they may be, there is scope for their development, whose trends are: to improve operational aspects and to widen the spectrum of pollutants to be slaughtered. The process of photo-activation of hydrogen peroxide with ultraviolet radiation (H_2O_2 / UV process) for oxidative treatment of effluents gained momentum after 1992, and is promising due to the maintenance of the characteristics of high environmental compatibility. A series of experiments were carried out with synthetic solutions containing free cyanide. The photo activation process proved to be efficient and environmentally compatible.

Keywords: peroxide; ultraviolet; environmental; hydrogen; pollutant; cyanide

I - Introduction

At present several technologies of treatment of effluents with hydrogen peroxide are in use which aim to kill the organic compounds; cyanides; arsenic; nitrous oxides; and sulfides.

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However satisfactory these processes are, the practice of use shows that there is space for their development, whose tendencies are to improve operational aspects and to widen the spectrum of pollutants to be slaughtered.

The process of photoactivation of hydrogen peroxide with ultraviolet radiation (H_2O_2 / UV process) for oxidative treatment of effluents gained momentum since 1992. This is because the characteristics of the process are the maintenance of the characteristics of high environmental compatibility typical of the treatments conventional with peroxide (because when the H_2O_2 decomposes leaves only water and oxygen as waste); Ultraviolet radiation besides the known microbicidal action, induces the decomposition of several chemical compounds; And there is no introduction of contaminants into the medium being treated.

In this technology, the main oxidants in the system are hydroxyl radicals, produced by direct photolysis of hydrogen peroxide by UV radiation according to the reaction:

H_2O_2 + UV fótons = 2OH•

II - Photochemical production of free radicals

Some chemical reactions proceed quickly when their reagents are exposed to light. The reactions of this species are called photochemical, such as: the darkening of a photographic film when exposed to light; the gradual decay of the colors of the tissues in the presence of light; the process of photosynthesis in which the CO_2 and H_2O present in the atmosphere, in the presence of chlorophyll, are transformed into carbohydrates and O_2.

It is part of the current knowledge that the light of a given frequency can only be absorbed or emitted by a molecule if it can donate or receive an energy equal to the product of its frequency by its wavelength ($E = h\nu$) where ν is the frequency and h is Planck's constant, a relation which can also be expressed in the form:

$$E\ (cal/mol) = (2{,}8579 \times 10^8) / (wavelength\ in\ A)$$

As light is a form of energy, upon reaching a molecule or polyatomic ion it will be absorbed, raising the internal energy level of the structure. This excitement may be of character: rotational; vibrational; or electronic.

As a result, on some occasions the breakage of one or more covalent bonds will occur, which results in the formation of atoms or groups of atoms that have one or more unpaired electrons, called free radicals (Table 1).

This chemical entity may exist for a sufficient time to take part in a chemical reaction step.

Although the use of peroxides as photo-initiators of a polymerization has been described, there is an obstacle to absorb only wavelengths less than 3200 Å, which makes it difficult to use them efficiently in ordinary glass equipment.

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Table 1: Comparison between the type of chemical bond, its dissociation energy, wavelength for the breakdown of the chemical bonds and the absorbed wavelength.

Connections	Dissociation energy	Wavelenght for connection breaks	If absorbed the light will break this connection	
	KCAL/GMOL	Nm	253,7 nm	184,9 nm
C-C	82,62	346,1	YES	YES
C=C	145,8	196,1	NO	YES
C-Cl	81,0	353,0	YES	YES
C-F	116,0	246,5	NO	YES
2C-H	98,7	289,7	YES	YES
C-N	72,8	382,7	YES	YES
C=N	147,0	194,5	NO	YES
C-O	85,5	334,4	YES	YES
C-S	65,0	439,9	YES	YES
O-O	119,1	240,1	NO	YES
-O-O-	47,0	608,3	YES	YES
-O-H	117,5	243,3	NO	YES
C Ξ C	199,6	143,2	NO	NO
CN	212,6	134,5	NO	NO
C=O(aldehyde)	176,0	162,4	NO	NO
C=O (ketone)	179,0	159,7	NO	NO
C=S	166,0	172,2	NO	NO

III - Technological Aspects

The equipment necessary for the treatment of effluents by this process consists of: an oxidation unit; hydrogen peroxide feed module; acid feed module; base power module; UV light generation module; and control panel.

The system architecture consists of: its oxidation units are arranged in series; The UV light generating modules are mounted inside these units so that they are surrounded by the effluent flow; Cleaners that must be assembled in order to remove any solids that may accumulate on the UV generation units.

IV - Example

A study carried out at PUC-Rio: destruction of cyanides by the combined use of hydrogen peroxide and solar UV light.

This study shows that the natural degradation of effluents in tailings dams, reinforced with the oxidizing chemical treatment, significantly increases the speed of the process (HERMANN, 1993).

A mechanism was presented according to the reactions (Figure 1):

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$$H_2O_2 \xrightarrow{UV} 2OH\cdot \quad (1)$$

$$OH\cdot + CN^- \rightarrow OH\cdot + CN \quad (2)$$

$$CN^{\cdot} + OH^{\cdot} \rightarrow HOCN \quad (3)$$

$$HOCN \rightarrow H^+ + OCN^- \quad (4)$$

$$CN^{\cdot} + CN^{\cdot} \rightarrow (CN)_2 \quad (5)$$

$$(CN)_2 + OH^- \rightarrow HCN + OCN^- \quad (6)$$

$$HCN \rightarrow H^+ + CN^- \quad (7)$$

$$CN^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \quad (8)$$

$$OH^{\cdot} + H_2O_2 \rightarrow H\,O_2^{\cdot} + H_2O \quad (9)$$

$$2OH_2^{\cdot} \rightarrow H_2O_2 + O_2 \quad (10)$$

Figure 1: Mechanism of oxidation reactions from hydrogen peroxide (Journal of Photochemistry, 1987).

In this test were used synthetic solutions (aiming to study the degradation rate of free cyanide); All experiments started from the same initial concentration of 26 mg / l at 25 ºC, following a two-level statistical factorial plan (to verify the effect of pH, H_2O_2%, and UV wavelength).

The results of this study can be partially illustrated (Figure 2) by the curves [CN] versus time:

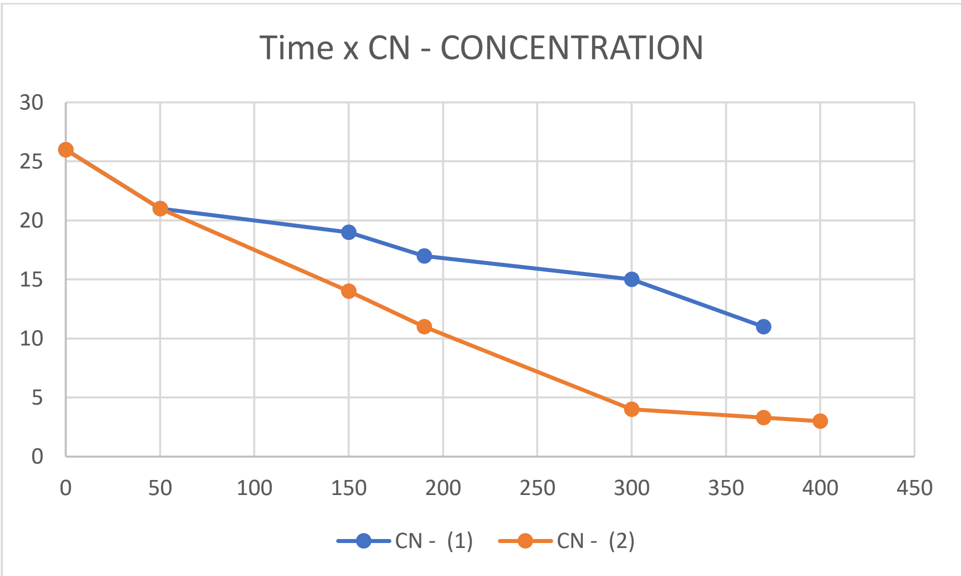

Figure 2: Effect of UV and H2O2 on the destruction of CN- in water at Ph = 9 and T = 25ºC

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V - Conclusions

The H_2O_2 / UV process stands out as a new generation of oxidative treatment of effluents. Its main characteristics reveal:

- a powerful oxidation system. At 25 ° C and Ph = 0, the redox potential of the OH · radical is approximately 2.8 V, versus 1.8 V of H_2O_2 (both referred to the standard hydrogen electrode);

- high environmental compatibility. The use of this oxidative system leaves as final residue only water and oxygen.

- The equipment required to operate the process is relatively simple, easy to assemble, operate and maintain.

VI - References

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