Degradation of Cyanides in Wastewater from Gold Mining: A Review of Literature

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Abstract: Among the persistent chemical compounds in the residual discharges are the highly toxic cyanides used in the industrial sector and in particular the mining industry for the extraction of gold, frequently appearing in low concentrations in the water, deteriorating its quality. Being of vital importance the treatment of the cyanide effluent, to reduce the concentration of cyanide before its final discharge, thus producing less toxic effluents, to achieve this several studies have been carried out and developed methods for its treatment, chemical, physical and biological An alternative to improve the quality of wastewater is the heterogeneous photocatalysis mediated by different semiconductors such as TiO_2, considering this a simple technology and economical in relation to bioremediation treatments, effective and innovative in our environment for aqueous effluents.

Key words: Cyanized waters, environmental pollution, gold mining, liquid spills, quality, toxic effluents

INTRODUCTION

The chemical industry and other industries related to it generate residual waste in the form of water streams which in many cases contain organic matter in concentrations too low without significant environmental impact, or high becoming a source of pollution which represents an important burden for the conservation of the environment (Garcia-Ochoa and Santos 2001; Yeddou et al., 2011, Olivero-Verbel et al., 2011, Barrios et al., 2017).

In the last three decades the world environmental legislation has focused on demanding the protection of bodies of water, because the shortage of water and the dramatic increase of diseases and dysfunctions of the nervous system in animals and in man have given voice alert to take measures on the need for the preservation of this natural resource (Moussavi et al., 2018; Anonymous, 1984).

Among the organic compounds and groups of persistent pollutants in the residual discharges are cyanides that are highly toxic (Chiang et al., 2003;

Guadalima and Monteros, 2018) are used in the industrial sector to produce study, textiles and plastics. They are also, present in the chemicals that are used to reveal photographs. Cyanide salts are used in metallurgy for galvanization, metal cleaning and recovery of gold from the rest of the material removed and cyanide gas is used to exterminate pests and insects in ships and buildings (Sarla et al., 2004; Pirmoradi et al., 2017).

The cyanide present in streams of acidulated water form HCN that is highly toxic if the water has a basic pH is maintained as cyanide, being necessary to reduce the levels of cyanide in the wastewater before being discharged to the natural channels, for the problems social and public health issues (Irfan et al., 2017; Dash et al., 2009a, b).

Studies carried out by Final Evaluation Report of the Regional Corporation of Southern Bolivar, 2003 show the presence of cyanides that are of environmental and toxicological interest at low concentrations which can cause effects on plant, animal and human organisms (Garcia-Ochoa and Santos 2001; Pala et al., 2015). In

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human health, it prevents the cells of the body from receiving oxygen causing tissue hypoxia and cyanosis, whose symptoms are: rapid, deep breathing, convulsions, loss of consciousness and asphyxia through inhalation ingestion or absorption through the skin (Kuyucak and Akcil, 2013).

Most of the studies quantify the cyanides present in the waters, others post absorbent that could recover or trap the cyanide but they would be transferring the problem of a pollutant in an aqueous effluent to a solid waste contaminated, not giving a true solution. In Colombia, the discharge regulations in decree 1594 of 1984 under Article 38, establishes that the concentration of cyanide admissible for human and domestic consumption is 0.2 mg/L in accordance with Resolution 1074 of October 28, 1997 issued by the DAMA, the allowed values of cyanide to be conducted to a body of water are 1.0 mg/L and the EPA established a maximum contamination level of 0.2 mg/L in drinking water.

Considering the treatment or purification of wastewater, the development of new technologies has been promoted such as heterogeneous photocatalysis mediated by different semiconductors, one of which is TiO_2, considering it a simple, economical technology in relation to bioremediation treatments, efficient and innovative in our means for aqueous effluents (Jaramillo *et al.*, 2002; Dwivedi *et al.*, 2016).

One of the advantages of this technology may lie in profitability and the possibility of using solar radiation as an energy source. Currently there are solar collectors for the degradation of organic compounds (Plataforma Solar de Almeria), using TiO_2 as a photocatalyst in which satisfactory results have been found (Malato *et al.*, 2002; Vidal *et al.*, 1999; Ray, 1999). Heterogeneous photocatalysis, unlike most physicochemical processes is not selective and can be used to treat complex mixtures of contaminants (Jaramillo *et al.*, 2002; Mesa, 1998; Gebresemati *et al.*, 2017).

MATERIALS AND METHODS

Generalities of cyanide: It is a highly dangerous and poisonous chemical that contains carbon and nitrogen is usually found combined with other chemicals forming compounds. For example, simple compounds of cyanide are hydrogen cyanide, sodium cyanide and potassium cyanide. Due to its properties, cyanide is used in the manufacture of metal parts and in numerous organic products such as plastics, synthetic fabrics, fertilizers, herbicides, dyes and pharmaceuticals. It is also, used in

Table 1: Physicochemical properties of cyanide compounds

Properties	Sodium cyanide	Hydrogen cyanide
Fusion point (°C)	563.7	-13.4
Boiling point (°C)	1496	25.70
Solubility (g/100 g of H₂O) at 10°C	48	Miscible
(Organic solvents)	Ethanol, formaldehyde	Ethanol, ether
Ka	It has no data	5.1×10^{-2}
Vapor pressure (mm Hg)	0.76 (at 800°C)	630 (at 20°C)
Density (g/cm³)	1.60	0.6884 (Liquid at 20°C)
Molecular mass	49.01	27.03
Color	White	Transparent
Physical state	solid	Gas or liquid
Odor	Odorless	Almond

Own elaboration

the chemical industry due to its composition and the ease with which it reacts with other compounds (Acheampong and Lens, 2014).

The signs and symptoms of the CNS (Central Nervous System) are typical and progressive: hypoxia includes headaches, agitation confusion, seizures, lethargy, coma and death. Initially there is a tachypnea of central origin followed by bradypnea, hypotension and bradycardia. Cardiogenic and non-cardiogenic pulmonary edema and gastrointestinal disorders (not frequent) may occur: abdominal pain, nausea and vomiting. The time of onset of symptoms is rapid (10-15 min) with gaseous and inorganic forms, usually minutes and if the exposure is to organic cyanogenetic substances can take hours because they must be metabolized. It has a smell of almonds, it does not occur as long as it is present, it is not detectable in 40% of cases (Razanamhandry *et al.*, 2016).

The cutaneous manifestations are variable: a cherry red color of the skin is traditionally described due to the increase in the saturation of Hb (Hemoglobin) with O_2 in venous blood due to the decrease in the use of O_2 in the tissues. Blood in arteries and veins is the same color. Cyanosis has also, been described. If there is recovery of the acute picture, there are sequelae such as personality changes, memory deficits and extrapyramidal syndromes. It is described for chronic exposure: dermatitis, hypokinesia, mental deterioration, thyroid disease, visual disorders, optic atrophy (Gordo, 2018).

Physical-chemical properties of cyanide compounds: Table 1 shows the most important physicochemical properties of cyanide compounds.

Mechanism of toxicological action: Cyanide has great affinity for Fe as Ferric ion (+++). After being absorbed, it reacts rapidly with the trivalent Fe of mitochondrial Cytochrome P 450 and in this way inhibits cellular respiration. Thus, cyanide efficiently blocks the production of ATP (Adenosine Triphosphate) and among

other metabolic abnormalities, lactic acidosis and the decrease in the use of O_2 by the cell that is cytotoxic hypoxia, can occur. The clinical and histopathological manifestations of the CNS are due to the inhibition in the use of O_2 (Quintero *et al.*, 2017).

The exact mechanism is not defined but it would be due to the inhibition of antioxidant enzymes such as catalases, glutathione dehydrogenase, glutathione reductase or superoxide dismutase. The interaction of cyanide with cytochrome oxidase is reversible through endogenous detoxification pathways including sulfurotransferases. These routes are the research bases for effective antidotes. Among the sulfurotransferases is the kinase which is a mitochondrial enzyme that transforms cyanide into thiocyanate by binding it to a sulfide group. The thiocyanate thus formed has little toxicity. This reaction can be hastened by the administration of sodium thiosulfate that adds sulfur molecules (Agudelo *et al.*, 2010).

Generalities of the cyanate: The Cyanate (CON-) has an interest in the analysis of industrial wastewater due to the alkaline chlorination process used to oxidize cyanide which produces cyanate in the second reaction. The cyanate is unstable at neutral or low pH, therefore, the sample should be stabilized as soon as it is obtained by the addition of sodium hydroxide until pH >12, the cyanate around 7 can continue to be oxidized with chlorine to produce CO_2 and N_2 in addition, it can be hydrolyzed in ammonia when heated to a low pH (Quispe *et al.*, 2011).

RESULTS AND DISCUSSION

Conventional treatments: Remediation of cyanide: there are several procedures for the treatment of cyanides and they include several physical methods, adsorption, complexation and oxidation. These methods predominantly include separation or destruction processes and can occur naturally. The separation processes that include physical methods, adsorption and complexation are used to concentrate and thus recover the cyanide by recycling. On the other hand, destruction processes are used to vary the carbon-nitrogen triple bond and thus destroy cyanide and produce non-toxic or less toxic species that are commonly required as oxidation methods (Garica, 2015).

Within oxidation processes, the most recent applications are photocatalytic methods. Photolysis can increase the redox reaction by supplying electromagnetic radiation energy to catalyze electron transfer processes. Electromagnetic radiation is absorbed, causing in an

electron of the absorbent compound the passage from an internal state to an excited state, possibly separating pairs of electrons from one to another. Electrons are more susceptible and therefore more apt to participate in redox reactions (Fajardo *et al.*, 2010).

Photoreduction occurs when the absorbing species donates the electron to other species. Photooxidation occurs when the absorbing species accepts an electron of another species in order to fill these vacant electrons. Excited electrons eventually relax to internal states of the reaction products. The energy needed to promote electrons from a basal state to the excited state is usually equivalent to that possessed by Ultraviolet (UV) radiation (Quiroga and Olmos, 2009).

Many redox reactions can be catalyzed by exposure to artificial currents such as arc, lamp and laser or by sunlight. High sources of energy such as gamma radiation and low as visible light can be used but are limited. Photolytic reactions can be induced directly if the absorbent compound is the species that is remediated or indirectly if the absorbent compound is available to transfer photo energy to the remediated species (Sancho *et al.*, 2011).

Photolysis can be carried out in the absence of photosensitizers (direct photolysis) or in the presence of aqueous species (homogeneous photolysis and photocatalysis) or solid semiconductors (heterogeneous photocatalysis). These photochemical methods are relatively new technologies and are known as advanced oxidation processes. Homogeneous photocatalysis is rarely practiced due to the difficulty in the separation of aqueous species by recycling. Heterogeneous photocatalysis is more viable because solid-liquid separation processes are standard and can use a fixed-bed system (Garces Giraldo *et al.*, 2004).

Advanced oxidation processes for the elimination of pollutants: contaminated water can generally be processed by biological treatment plants by absorption with activated carbon or other adsorbents or by conventional chemical treatments (thermal oxidation, chlorination, ozonation, potassium permanganate, etc.). However in some cases these procedures are inadequate to achieve the degree of purity required by law or for the subsequent use of the treated effluent which has led to the development of new wastewater purification technologies (Domenech *et al.*, 2001; Alrousan *et al.*, 2012).

These new technologies are within Advanced Oxidation Processes or Advanced Oxidation Technologies (PAOs or TAOs) that are based on physicochemical processes capable of producing profound changes in the chemical structure of pollutants.

The concept was initially established by Glaze and his collaborators (Carey *et al.*, 1976) who defined the PAOs as processes that involve the generation and use of powerful transient species, mainly the Hydroxyl radical (OH°). This radical can be generated by photochemical means (including sunlight) or non-photochemical and have high effectiveness for the oxidation of organic matter (Domenech *et al.*, 2001).

Classification of advanced oxidation technologies: No Photochemistry; these originate powerful reactive species, mainly the hydroxyl radical, through the transformation of chemical species or through the use of different forms of energy with the exception of light radiation. Within these technologies are (Domenech *et al.*, 2001; Kopytko *et al.*, 2017)

- Ozonation in an alkaline medium
- Ozonization in hydrogen peroxide
- The Fenton (Fe_2+/H_2O_2) and related processes
- Electrochemical oxidation

Photochemicals: These processes are important for compounds that react slowly with the hydroxyl radical. Avoid the use of O_3 or reduce its proportion with the consequent reduction of costs, health risks and environmental concerns. Within these technologies are (Domenech *et al.*, 2001; Lopez and Sierra, 2012):

- Photolysis of water in the vacuum ultraviolet
- UV/ozone
- The heterogeneous photocatalysis

Advantages of advanced oxidation technologies: Some advantages are (Domenech *et al.*, 2001; Duran *et al.*, 2009). Not only do they change the phase to the pollutant (as in the case of air entrainment or activated carbon treatment) but they also chemically transform it. Complete mineralization (destruction) of the contaminant is generally achieved. On the other hand, conventional technologies that do not use highly oxidizing species do not completely oxidise organic matter. They are very useful for refractory contaminants that resist other treatment methods, mainly biological. They serve to treat pollutants at a very low concentration (for example, ppb). They are ideal to reduce the concentration of compounds formed by alternative pretreatments such as disinfection. They consume much less energy than other methods (for example incineration).

Heterogeneous photocatalysis: The process of solar detoxification by photocatalysis consists of the use of the most energetic part of the solar spectrum (wavelength less than 400 nm (nanometers)) to cause an oxidation reaction.
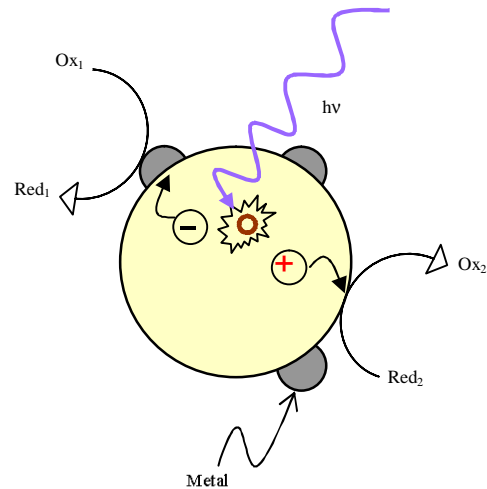

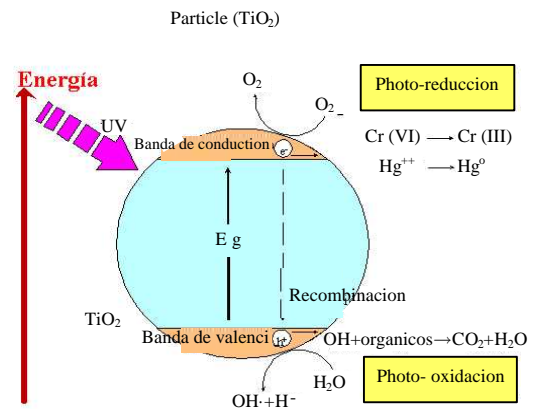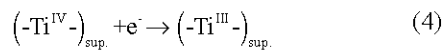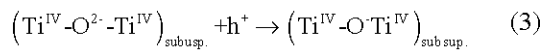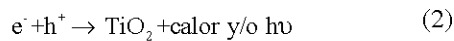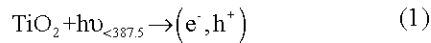Fig. 1: Schematic representation of the reaction of electron transfer to the semiconductor

Fig. 2: Schematic representation of electron-hole pair formation in a semiconductor particle

This occurs when ultraviolet radiation activates a semiconductor such as Titanium dioxide (TiO_2) (Mesa, 1998). The process is heterogeneous because there are two active phases, solid and liquid (Cardona, 2001, Laliberte, 2015).

When the titanium dioxide is irradiated with light, the electrons (e-) are excited from the valence band to the conduction band, generating electronic voids in the valence band called hollows (hb+) (Eq. 1 and Fig. 1 and 2). The two carriers (e-, h+) can recombine (Eq. 2) and be placed quickly on the surface of the oxide where they are trapped in intrinsic subsurface energy traps (Ti IV-O_2-Ti IV) for the holes and surface traps (-TiIV-) for the electrons (Eq. 3 and 4). The carriers (e- and h+) being on the surface of the oxide can perform interfacial electron transfers with Donors (D) such as OH-, H_2O and

Acceptors (A) such as oxygen, adsorbed on the surface of titanium dioxide, carrying out redox reactions (Eq. 5 and 6). The low quantum yield of photocatalytic reactions is due to the speed of recombination. Recombination is not carried out or is carried out in small quantity when the carriers interact rapidly with the donors and acceptors but it is essential that the donors and acceptors are preabsorbed before the luminous excitation of the TiO_2. Because titanium dioxide lacks continuous interband states (those that facilitate recombination), the carriers (e- and h+) have sufficiently long half-life times to allow them to perform the interfacial transfer of electrons (Mesa, 1998; Serpone, 1997; Osathaphan *et al.*, 2008).

$$TiO_2 + h\upsilon_{<387.5} \rightarrow (e^-, h^+) \qquad (1)$$

$$e^- + h^+ \rightarrow TiO_2 + calor\ y/o\ h\upsilon \qquad (2)$$

$$\left(Ti^{IV} - O^{2-} - Ti^{IV}\right)_{sub\,susp.} + h^+ \rightarrow \left(Ti^{IV} - O^- Ti^{IV}\right)_{sub\,sup.} \qquad (3)$$

$$\left(-Ti^{IV}-\right)_{sup.} + e^- \rightarrow \left(-Ti^{III}-\right)_{sup.} \qquad (4)$$

$$h^+ + D \rightarrow D^+ \qquad (5)$$

$$e^- + A \rightarrow A^- \qquad (6)$$

The speed and efficiency of photocatalysis are significantly improved in the presence of molecular oxygen or inorganic oxidizing species such as peroxydisulfate, periodate and peroxides. Molecular oxygen decreases the recombination between the two carriers (e- and h+) because when it is adsorbed on the surface of the semiconductor it is phototransformed to the peroxide anion O_2-, remaining adsorbed. Peroxide O_2- is an effective oxidizing agent that can attack adsorbed and non-adsorbed organic compounds or can be reduced with the electrons generated in the irradiation of TiO_2 by forming the divalent anion peroxide, O_2. In this way the h+ do not run the risk of recombining with the electrons and on the contrary they participate in the generation of the hydroxyl free radical (Mesa, 1998; Gomez *et al.*, 2000; Parmon *et al.*, 2002; Feng *et al.*, 2018).

Parameters that influence the process: Many parameters influence qualitatively and quantitatively in the photocatalytic oxidation-reduction process and as a consequence, are decisive in the overall efficiency of the process. The most important are (Gomez *et al.*, 2000; Mekuto *et al.*, 2016; Yu *et al.*, 2016).

pH: Normally, the photocatalysis process is more efficient in an acid medium ($3 \leq pH \leq 5$). The pH affects the surface properties of the catalyst and the chemical form of the compound to be degraded and this manifests itself in alterations in the rate of degradation and in the tendency to flocculate the catalyst. In the case of cyanides, it is important to maintain the basic pH because the formation of hydrocyanic acid occurs in acid.

Catalyst: In heterogeneous photocatalysis, multiple semiconductors have been used, such as Al_2O_3, ZnO, Fe_2O_3 and TiO_2 However, the most widely used is titanium dioxide because it has a greater photocatalytic activity, it is not toxic, it is stable in aqueous solutions and it is not very expensive. The anatase crystalline form of TiO_2 seems to be the crystalline form with better photocatalytic properties and this has been attributed, among other reasons, to the greater capacity of photoadsorption of anatase by molecular oxygen and its ionized forms and its low relative speed of pair recombination hollow-electron. The optimal concentration of catalyst that provides a total adsorption of the efficient photons for the TiO_2 Degussa P-25 varies from 0.1-5.0 g/L (Gimenez *et al.*, 1999; Percherancier *et al.*, 1995; Fortuna *et al.*, 2015).

In order to increase its photocatalytic efficiency, TiO_2 has been subjected to doping with various metal ions (Pozzo *et al.*, 1997; Cardona, 2001; Liu *et al.*, 2013) it has also been tried to sensitize the catalyst to wavelengths. greater, (visible light) using dyes or colorants, both organic and organometallic. So, far, positive results have not been obtained. The titanium dioxide produced by Degussa under the trade name of P25 is the unsupported catalyst most used for having shown greater effectiveness. It is a semiconductor that exists in three crystalline forms: anatase, rutile and brokite; the most common forms are anatase and rutile since they are the most effective in the treatment of wastewater, the band gap energy for the anatase form is approximately 3.0 eV and for the rutile phase 3.0 eV. The TiO_2 Degussa P-25 is produced by flame hydrolysis of titanium tetrachloride at high temperatures (greater than 12000C) in the presence of hydrogen and oxygen. The powder TiO_2 P-25 has a surface area of 50 ± 15 m^2/g and an average particle diameter of 21 nm. The product is cubic particles with rounded edges, non-porous and has a 99.5% purity (anatase ratio: rutile 70:30).

Primary studies of photocatalytic degradation of cyanide: The first publication on the process of degradation by heterogeneous photocatalysis of pollutants in both aqueous and gaseous phases is due to Carey *et al.* (1976),

Since then, a historical analysis of the evolution of the development of the photocatalytic process for water purification allows the identification of four clearly different stages. In the first stage with scarce publications, roughly between 1976 and 1985, only a few scientific groups worked on the subject-no specific application was yet visible. The second stage, from the mid-1980 s to the first years of the 1990 s, coincided with a growing concern and concern of the international scientific community on environmental issues. In it, the possibility of applying this process to the treatment of pollutants in water was raised (Al-Ekabi and Serpone 1988, Arias-Lafargue *et al.*, 2017).

The success of the first experiences gave rise to a massive incorporation at the end of the 80s and as results of very optimistic extrapolations of the results obtained until then, came to be considered the photocatalytic process as a possible universal method for the degradation of organic pollutants (Mesa, 1998; Kim *et al.*, 2018).

In the first stage that can be framed between the mid and late 90's there was a proliferation of contradictory results which is why the basic research studies and their applications generated a debate about the real possibilities of application of the process. Emphasis was placed on the drawbacks of the limitations to produce large quantities of hydroxyl radicals and the slowness of the global degradation process. Encouraging results were obtained when studying almost real systems, simultaneously with other negative or doubtful results, generating much confusion in the perception of the non-scientific public (Mesa, 1998; Donato *et al.*, 2007, Baeissa, 2015).

The fourth stage in which we are currently is characterized by a more conservative and realistic view of the possibilities of associated technology, focused on those specific and specific applications in which technology, properly developed can be viable and competitive (Johnson, 2015).

Within the investigations, Peral *et al.* (1990) studied the oxidation of cyanide catalyzed by TiO_2 under UV illumination. The research was carried out by determining the production of photo-oxidized cyanide using different concentrations, irradiation time, light intensity, pH and temperature values. They observed that during the first minutes of irradiation the main product of the oxidation was OCN-but in long times all the cyanide was converted to CO_{3-2}. From the kinetic analyzes carried out, it was deduced that the oxidation constant of the cyanide by photo generated holes is 70% of the corresponding water oxidation constant.

Hidaka *et al.* (1992) studied heterogeneous photocatalytic degradation of cyanide on TiO_2 surface.

They built a large-scale photoreactor that was an excellent resource for the decomposition of large amounts of cyanide and quantitatively determined the disappearance of CN-, the consumption of O_2, the intermediate formation of OCN- and the mineralization last to CO_2 and N_2.

Bravo *et al.* investigated the photocatalytic oxidation of cyanide to nitrate with TiO_2. They established that the photocatalytic oxidation of cyanate ions in aqueous solution and in the presence of TiO_2 takes place by two different reaction routes, depending on the pH of the solution. For pH lower than 10, the main product of oxidation is nitrate instead of N_2, NH_4^+ is formed by hydrolysis of OCN- and this photo-oxidation produces nitrate and nitrite; the proportion of the hydrolysis controls the reaction speed of the whole process. The photo-oxidation of OCN- to N_2 occurs in a strongly basic medium. For pH values lower than 5, NH_4^+ is difficult to oxidize, remaining stable in solution.

Choi *et al.* (1994) analyzed the effect of doping nanoparticles of TiO_2 with 21 metals, improving in some cases the oxidative capacity and in others the reductive capacity of TiO_2, due to the nature, concentration and distribution of the dopant.

Ahmed and Attia (1995) studied airgel materials by detoxifying cyanide in wastewater. They used ultraviolet radiation and (TiO_2-SiO_2) airgel as a photocatalyst to oxidize and degrade aqueous cyanide species to CO_2 and N_2; prepared the photocatalyst airgel by sol-gel technique and supercritical drying with different contents of SiO2 (TiO_2 SiO_2, molar ratio 1:1.3, 1:2.6 and 1:3.9) and observed that by increasing the SiO_2 content it apparently decreases the density and translucency increases. They compared the high photocatalytic activity by oxidation of CN- in diluted solutions (1000 and 522 ppm) of ferric cyanide with titanium powder and proved that the airgel with a high content of SiO_2 (TiO_2: SiO_2 molar ratio 1:3.9) had high efficiency in photocatalytic oxidation of CN-species under experimental conditions.

Augugliaro *et al.* (1997) investigated the photocatalytic oxidation of cyanides in aqueous suspension of TiO_2 irradiated in the UV-Near region. They studied the proportion of photo-oxidized cyanide by variation of parameters: initial concentration of cyanide, Catalyst concentration initial pH, power of radiation and concentration of chloride ions in the reaction mixture. They observed that the photo-oxidation of cyanide is affected by the concentration of the catalyst, the concentration of the chloride ions and the power of irradiation which was independent of the initial concentration of the cyanide and the pH; they used the kinetic model of Langmuir-Hinshelwood. They also, investigated the reaction path where cyanide, nitrate and carbonate were the main products.

Chiang *et al.* (2002) investigated the photocatalytic degradation of cyanide using TiO_2 modified with copper oxide. The copper content on the TiO_2 surface was varied from 0.05-10.0% and found that the CuO deposits in nanoparticles were present on the TiO_2 surface. They also, found that the photo-oxidation path of the cyanide with the doped catalyst was slightly improved at 0.1% Cu, also, decreasing the photocatalytic degradation of the CN-, explained in terms of the ion competition reaction of Cu cyanide complexes. By the superficial hydroxyl radicals and as a final product the cyanide was oxidized to cyanate.
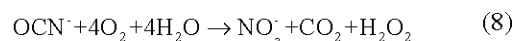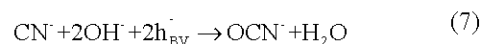
Hernandez-Alonso *et al.* (2002) studied the increased activity by ozone of aqueous suspensions of titanium dioxide for the photocatalytic oxidation of CN-free. They used a batch-type photoreactor with immersed lamp to treat aqueous and irradiated suspensions in the near UV region, using air or ozone-air mixtures as oxidation reagents, producing measurable speeds up to low cyanide concentration values. In the presence of ozone, the rate of oxidation of cyanide by the heterogeneous photocatalytic mechanism is increased for their results they took into account the Langmuir-Hinshelwood equations and reached that ozone strongly interacts with TiO_2 leading mainly to the formation of ozonide radicals.

Amal *et al.* found the kinetics and mechanisms of photocatalytic oxidation of cyanide in the presence of the TiO_2 catalyst. Where the quantum efficiency of oxidation was low (0.1-0.2%) due to 11-Low absorption of cyanide ions on the surface of TiO_2. Absence of homogenous reaction between cyanide ions and diffused hydroxyl radicals. High recombination speed of hollow electron in the photocatalyst TiO_2. They developed a kinetic model to describe the mechanism involved in the photocatalytic oxidation of cyanide and concluded that the only oxidation product detected was cyanate type and they followed the direct oxidation of cyanate by photo generated holes.

Davit *et al.* (2003) investigated the photocatalytic absorption and degradation of acetonitrile with FT-IR (Infrared spectrometers with Fourier Transform). In the degradation they used a Batch type reactor with 2 types of commercial TiO_2 powder (Merck and Degussa P-25) as photocatalyst and obtained the initial conversion rate of the highest acetonitrile with Merck TiO_2 than with TiO_2 Degussa P-25. They used the (FT-IR) to investigate the molecular aspects of the absorption and photo-oxidation of acetonitrile on the two powders of TiO_2 whose surfaces were completely hydrated. They found that the absorption of acetonitrile is reversible only for the Merck TiO_2 and the stable photo acetamido species formed on TiO_2 could poison some photocatalytic sites evidenced by the initial conversion rate loss of acetonitrile.

Oh and Jenks (2004) studied the photocatalytic degradation of a cyanuric acid in R recalcitrant species. This degradation occurred in aqueous suspensions with TiO_2 (Degussa P25) by addition of the fluoride ion at low pH, subjecting itself to the formation of hydroxyl radicals in homogeneous phase, for this hypothesis took into account the degradations of 4-t-butylpyrazine and other compounds organics provided with TiO_2.
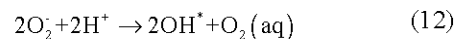
Photocatalytic degradation of cyanides: The photocatalytic degradation of cyanides is another interesting application, since, this technique does not produce sludge or highly toxic compounds, such as cyanogen chloride, it avoids the use of products difficult to handle such as chlorine and does not It is necessary to store chemical reagents. Another additional advantage is the possible recovery of the metal normally complexed to cyanide. Photocatalytic oxidation is capable of transforming CN- into products such as cyanate, OCN- (about 1000 times less toxic) with a careful choice of reaction conditions. Once this conversion is achieved, the OCN- is completely oxidized and the final products are mainly CO_2 and NO_3 (Mesa, 1998; Bruger *et al.*, 2018).

$$CN^- + 2OH^- + 2h_{BV}^\cdot \rightarrow OCN^- + H_2O \qquad (7)$$

$$OCN^- + 4O_2 + 4H_2O \rightarrow NO_3^- + CO_2 + H_2O_2 \qquad (8)$$

Mechanism for oxidation of cyanide: The heterogeneous photocatalysis has been used for oxidation of cyanide and three mechanisms are proposed. The first mechanism produces hydroxyl radicals via reduction of adsorbed water or hydroxide adsorbed by gaps in the valence band:

$$H_2O + h + OH^* + H+ \qquad (9)$$

$$OH- + h + OH^* \qquad (10)$$

On the other hand, hydroxyl radicals are produced by the second mechanism by reaction of dissolved oxygen with excited electrons and in the conduction band through an intermediate superoxide (O^{-2}):

$$O_2(aq) + e^- \rightarrow O_2^- \qquad (11)$$

$$2O_2^- + 2H^+ \rightarrow 2OH^* + O_2(aq) \qquad (12)$$

The two reaction mechanisms show that the final products are cyanide oxidized to cyanate, nitrogen gas,

Chiang *et al.* (2002) investigated the photocatalytic degradation of cyanide using TiO_2 modified with copper oxide. The copper content on the TiO_2 surface was varied from 0.05-10.0% and found that the CuO deposits in nanoparticles were present on the TiO_2 surface. They also, found that the photo-oxidation path of the cyanide with the doped catalyst was slightly improved at 0.1% Cu, also, decreasing the photocatalytic degradation of the CN-, explained in terms of the ion competition reaction of Cu cyanide complexes. By the superficial hydroxyl radicals and as a final product the cyanide was oxidized to cyanate.
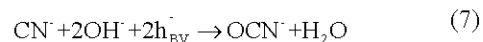
Hernandez-Alonso *et al.* (2002) studied the increased activity by ozone of aqueous suspensions of titanium dioxide for the photocatalytic oxidation of CN-free. They used a batch-type photoreactor with immersed lamp to treat aqueous and irradiated suspensions in the near UV region, using air or ozone-air mixtures as oxidation reagents, producing measurable speeds up to low cyanide concentration values. In the presence of ozone, the rate of oxidation of cyanide by the heterogeneous photocatalytic mechanism is increased for their results they took into account the Langmuir-Hinshelwood equations and reached that ozone strongly interacts with TiO_2 leading mainly to the formation of ozonide radicals.

Amal *et al.* found the kinetics and mechanisms of photocatalytic oxidation of cyanide in the presence of the TiO_2 catalyst. Where the quantum efficiency of oxidation was low (0.1-0.2%) due to 11-Low absorption of cyanide ions on the surface of TiO_2. Absence of homogenous reaction between cyanide ions and diffused hydroxyl radicals. High recombination speed of hollow electron in the photocatalyst TiO_2. They developed a kinetic model to describe the mechanism involved in the photocatalytic oxidation of cyanide and concluded that the only oxidation product detected was cyanate type and they followed the direct oxidation of cyanate by photo generated holes.

Davit *et al.* (2003) investigated the photocatalytic absorption and degradation of acetonitrile with FT-IR (Infrared spectrometers with Fourier Transform). In the degradation they used a Batch type reactor with 2 types of commercial TiO_2 powder (Merck and Degussa P-25) as photocatalyst and obtained the initial conversion rate of the highest acetonitrile with Merck TiO_2 than with TiO_2 Degussa P-25. They used the (FT-IR) to investigate the molecular aspects of the absorption and photo-oxidation of acetonitrile on the two powders of TiO_2 whose surfaces were completely hydrated. They found that the absorption of acetonitrile is reversible only for the Merck TiO_2 and the stable photo acetamido species formed on TiO_2 could poison some photocatalytic sites evidenced by the initial conversion rate loss of acetonitrile.

Oh and Jenks (2004) studied the photocatalytic degradation of a cyanuric acid in R recalcitrant species. This degradation occurred in aqueous suspensions with TiO_2 (Degussa P25) by addition of the fluoride ion at low pH, subjecting itself to the formation of hydroxyl radicals in homogeneous phase, for this hypothesis took into account the degradations of 4-t-butylpyrazine and other compounds organics provided with TiO_2.
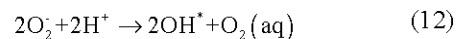
Photocatalytic degradation of cyanides: The photocatalytic degradation of cyanides is another interesting application, since, this technique does not produce sludge or highly toxic compounds, such as cyanogen chloride, it avoids the use of products difficult to handle such as chlorine and does not It is necessary to store chemical reagents. Another additional advantage is the possible recovery of the metal normally complexed to cyanide. Photocatalytic oxidation is capable of transforming CN- into products such as cyanate, OCN- (about 1000 times less toxic) with a careful choice of reaction conditions. Once this conversion is achieved, the OCN- is completely oxidized and the final products are mainly CO_2 and NO_3 (Mesa, 1998; Bruger *et al.*, 2018).

$$CN^- + 2OH^- + 2h_{BV}^{\cdot} \rightarrow OCN^- + H_2O \qquad (7)$$

$$OCN^- + 4O_2 + 4H_2O \rightarrow NO_3^- + CO_2 + H_2O_2 \qquad (8)$$

Mechanism for oxidation of cyanide: The heterogeneous photocatalysis has been used for oxidation of cyanide and three mechanisms are proposed. The first mechanism produces hydroxyl radicals via reduction of adsorbed water or hydroxide adsorbed by gaps in the valence band:

$$H_2O + h + OH^* + H+ \qquad (9)$$

$$OH- + h + OH^* \qquad (10)$$

On the other hand, hydroxyl radicals are produced by the second mechanism by reaction of dissolved oxygen with excited electrons and in the conduction band through an intermediate superoxide (O^{-2}):

$$O_2(aq) + e^- \rightarrow O_2^- \qquad (11)$$

$$2O_2^- + 2H^+ \rightarrow 2OH^* + O_2(aq) \qquad (12)$$

The two reaction mechanisms show that the final products are cyanide oxidized to cyanate, nitrogen gas,

nitrite and nitrate by the hydroxyl radicals and are also, effective for the remediation of thiocyanate, (INADs) and SADs. The third mechanism involves the reduction of cyanide by voids in the valence band to produce Cianil CN* radicals:

$$CN^- + h^+ \rightarrow CN^* \qquad (13)$$

Hydroxyl radicals produced according to the above reactions that react with the Cyanyl radicals:

$$CN^* + OH^* \rightarrow OCN^- + H^+ \qquad (15)$$
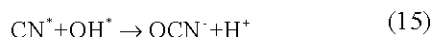
Resulting cyanate that additionally reacts with hydroxyl radicals (Barakat *et al.*, 2004).

CONCLUSION

The review of the literature shows that in the reaction systems it is allowed to show a high percentage of degradation of cyanide in aqueous medium which indicates the use of photocatalytic technology in the treatment of persistent compounds, such as cyanide using TiO_2 and TiO_2. Doped with copper heteropolyolyb date as a catalyst. It is also, well known that the factors that most influence the photocatalytic degradation are: type of catalyst, reaction time initial concentration of cyanide, catalyst concentration and air flow. Likewise, the degradation system shows that the total cyanides, present in the aqueous residual discharges, coming from the mining sector, can be degraded by means of the heterogeneous photocatalysis, providing a viable alternative for the destruction of contaminants that are in effluents watery. Finally, the photocatalytic degradation when air is supplied is higher than that obtained when it is absent, therefore, the supply of oxygen is important because it increases the rate of degradation of the substrate, since when it is not supplied, it tends to exhaust the oxygen that is dissolved in water.

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