Kinetic Study of Cyanide Degradation from Gold mining wastewater Using Photocatalysis

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Abstract—Highly toxic cyanides are among the most persistent chemical compounds in effluents, these chemicals are used in several industrial sectors and particularly in mining industry for the extraction of gold. Cyanides frequently appear at low levels in water, deteriorating its quality. In this paper a degradation of 55.76% and 62.99% was obtained using TiO₂ catalyst and TiO₂ doped with Cu heteropolybdate respectively in 360 min of reaction, applying photodegradation with a 125 watt mercury lamp source. Most of the trials showed that the degraded compound kinetics may be adjusted to a pseudo first order model.

1. Introduction

Industrial growth, agricultural exploitation and demographic expansion lead to the appearance of emissions and waste [1]. The presence of these wastes into the environment in quantities greater than their capacity to eliminate them, implies an imbalance in the biosystem. These changes may affect the quality and health of living beings that inhabit the environment and may even become impossible the life of existing species [2]. This situation demands an urgent study of the polluting forms in the environment that affect the habitat, and also the application of techniques and procedures for its monitoring, prevention and remediation [3].

The protection of is essential because it is vital for the development of life and for its scarcity [4]. Although about 70% of the Earth's surface is covered by water, only 2.5% of the planet's water is fresh, of which more than 99.5% is found as frozen water (polar ice caps, glaciers) or underground [5]. Due to the difficult access and the enormous technological and economic cost involved in the extraction of this fraction of water, man has historically resorted to the use and exploitation of rivers and surface lakes, which represent a low 0.01% of total water [6].

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Cyanide is a chemical group made up of an atom of carbon bonded to a nitrogen atom by triple bonding [7].

Most cyanides, whether of natural or industrial origin, are powerful, fast-acting poisons [8]. The main cause of water contamination by cyanide is the industrial activity and includes activities such as: mining and chemical industry, wastewater treatment, incineration of municipal waste, use of pesticides, etc [9]. Water has the capacity to transport a large amount of substances either in dissolved form or as suspended material. Thanks to this characteristic, the contamination of a water source, even if it occurs in a specific location, has repercussions over long distances and therefore affects regions of great extension [10].

Exposure to cyanide for a short period may cause damage to the brain, heart, produce coma and finally death [11]. In aquatic ecosystems, the presence of cyanide concentrations above 5 and 7.2 μg/L reduce the swimming capacity and inhibit reproduction of many fish species [12].

Due to the high complexing capacity that cyanide ion possesses, it is able, for example, to form stable compounds with almost any heavy metal at low concentrations, while its compounds may fix chemical substances that are present in nature and materials produced by man [13]. In this way, there are more than 2,000 natural sources of cyanide, (different species of arthropods, insects, bacteria, algae, fungi and higher plants contain it), as well as numerous common organic products such as plastics, synthetic textiles, fertilizers, herbicides, dyes and pharmaceutical products [6, 10]. All this puts man in permanent contact with a large number of cyanide compounds, including food, that are removed from human body by the liver, not reaching in this way harmful concentrations to health [14].

Of all the processes to obtain and purify gold in operation, the cyanide leaching method developed at the end of the 19th century, is the most effective one [3, 9]. Although its application involves the use of cyanide compounds and the generation of by-products derived from said compounds that are dangerous for the environment and humans, the percentages of extraction of the precious metal are so high that they have converted it into the more used process today in different gold mining operations [12].

In recent years, there has been an increase in foreign investment in the mining sector in Colombia. The participation of this sector has increased its presence in the Gross Domestic Product and State policies are increasingly side by side with the exploitation of minerals through concession figures. According to the Ministry of Mines and Energy (MME), in 2014 the GDP of the mining sector without hydrocarbons represented 2.10% of the total GDP of the economy. Likewise, the sector received 43% of the direct foreign investment that arrived in the country [15]. Environmentally, the forms of free cyanide (HCN and CN⁻) are not generally detectable in mining effluents. The concern for the toxicity of effluents lies in the complex forms of cyanide and the possibility of breaking down and generating free cyanide in the new system [16].

On the other hand, photo-catalysis is a useful process in the treatment and / or purification of water. Currently, this topic is of great interest to scientific community, as it has proven to be an adequate alternative treatment for the purification of waters with contaminant content of difficult removal like cyanide. The heterogeneous photo-catalysis, unlike most photochemical processes, is not selective and may be used to treat complex mixtures of pollutants [12]. Nowadays the methods used for dissolved cyanides removal are: physical, chemical, biological or mixed.

The photocatalytic degradation of cyanides is another interesting application since this technique does not produce sludge or highly toxic compounds, such as cyanogen chloride. The use of hazardous products such as chlorine is avoided and it is not necessary to store chemical reagents. Another additional advantage is the possible recovery of the metal normally complexed to cyanide [5]. 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 CO2 and NO3 [6, 12].

The physical methods are based on the ion exchange, the absorption on activated carbon and separation by flotation. Biological treatments (bio-remediation) are limited to low concentrations of
cyanides. Chemical methods generally involve oxidation of cyanide with reagents such as SO2, air, chlorine, potassium permanganate, hydrogen peroxide and ozone, among others [13].

Some of the advantages of photo-catalysis are that the process may be carried out with solar energy, besides the organic pollutant is completely destroyed, solving the problem of subsequent disposal of industrial process waste. Additionally, it uses as basic input a relatively unexpensive and non-toxic substance that theoretically might be recovered in its entirety: titanium dioxide (TiO2), which is used in crystalline form as a photocatalyst.[14].

An alternative to improve the quality of wastewater, is the heterogeneous photocatalysis mediated by different semiconductors such as TiO2, considering this an effective, simple, and economical technology in relation to bioremediation treatments [11]. The aim of this work was to evaluate the kinetic of the degradation of cyanide in wastewater of gold mining.

2. Materials And Methods
Kinetic studies of cyanide degradation in this system were performed at an initial contaminant concentration of 100 ppm, with pH and catalyst concentration obtained in previous experiments, during 50 min of reaction, taking 1 mL of sample at intervals of 10 min, under the following experimental conditions: Air, TiO2, UV radiation, Air + TiO2, UV Radiation + Air, UV radiation + TiO2 and UV radiation + Air + TiO2.

To observe the effect of O2, the intensity of radiation and the catalyst on the photocatalytic degradation, assays were made combining these parameters in order to make a more detailed analysis in the photocatalytic reaction. The conditions of pH and concentration of the catalyst were optimized. Table 1 shows the reaction targets. Tests with TiO2 and TiO2 doped with heteropolybdate were made under the same experimental conditions, taken as a model to compare the results. Figure 1 show the set up.

| Name                        | Air (O2) | Light | pH | Catalyst concentration (TiO2 g/L) | Catalyst concentration TiO2 with copper heteropolybdate |
|-----------------------------|----------|-------|----|-----------------------------------|--------------------------------------------------------|
| Aeration                    | X        | X     |    |                                   |                                                        |
| Balance of adsorption and desorption | X        | X     | X  |                                   |                                                        |
| Adsorption and aeration     | X        | X     | X  |                                   |                                                        |
| Photolysis                  | X        | X     |    |                                   |                                                        |
| Photochemistry              | X        | X     |    |                                   |                                                        |
| Photocatalytic with air     | X        | X     | X  |                                   | X                                                      |
| Photocatalytic              | X        | X     |    |                                   |                                                        |

The degradation study of real samples was carried out in the reaction system taking into account the optimal concentration of catalyst (TiO2, TiO2 doped with copper heteropolybdate) and pH. The residual water from Gambote and the mining area of the South of Bolívar, had an initial concentration of 0.025 and 75.62 ppm of total cyanides respectively and a pH of 6.4 and 6.8 respectively, and they were conserved with NaOH, because the residual cyanide is in a very complex matrix, an analysis of the state of the samples was carried out, in order to eliminate interferences.
3. Results And Discussions

*Kinetic study of cyanide degradation*

The kinetic study of the degradation of cyanide under different experimental conditions is depicted in Figure 2, showing the contribution of the catalyst (TiO$_2$), air and type of radiation in the photocatalytic reaction.

In the CN$^-$ + Cat curve, the equilibrium of adsorption - desorption of the cyanide on the catalyst is shown, observing a small adsorption of 0.33% on the catalyst since the concentration decreased by 4.11% in 50 min, due to the low adsorption of the cyanide ions on the surface of titanium dioxide. These data are in agreement with those reported in the literature by Chiang et al. 2002 [17] and Chiang et al. 2003 [18], reported an adsorption of 0.35% up to 3.71% with respect to the initial concentration of solutions. In the photolysis curve when only light is supplied, a concentration decrease was observed in 14.42% in 50 minutes, due to the lack of oxygen [19].

![Figure 1. Photoreactor and its components](image)

![Figure 2. Kinetic study of the degradation of cyanide under different experimental conditions. Co Cat. = 0.3 g/L TiO2 and Co cyanide = 100 ppm](image)
When only air was supplied to the solution, it was observed that the concentration of cyanide decreased to 0.17% in 50 min, due to the lack of formation of C-radicals centered by absence of oxygen.

The curve CN + light + air, showed that the photolytic degradation of cyanide in the presence of air reaches 15.32% in 50 minutes of reaction, this degradation is contributed due to the presence of air in the system by the formation of species such as organic peroxides that contribute to the oxidation process, in the CN- + light + Cat curve, it was observed that photocatalytic degradation of airless cyanide is 27.78% in 50 min, although water dissolved oxygen was not enough due to the presence of the catalyst, that increases the degradation rate when irradiation provided to the system activated the catalyst generating electron-hole pairs.

The curve of CN- + Light + Cat + air, showed better results with a degradation of cyanide to 98.55% in 50 minutes, this evidenced that the presence of oxygen is essential for effective oxidation because the oxygen provided by the air acts as an acceptor of the electrons generated in the semiconductor when it absorbs the radiant energy, avoiding the recombination of the pair in the surface of the same, making the photocatalytic reaction more efficient [20].

The above is verified by the kinetic analysis shown in Figure 3, where the reaction constant is determined.

![Figure 3. Kinetic adjustment of pseudo-first order for the photocatalytic degradation of cyanide](image)

**Kinetic study of the degradation of the real sample**

When comparing the degradation of the stock solution with the synthetic one, it showed that there is an increase in time for cyanide degradation, which indicates that aggregated compounds produce interference.

Figures 4 and 5 show the variations in the concentration of total cyanides as a function of time for the real and synthetic samples, using as catalyst TiO₂ and TiO₂ doped with 1% copper heteropololybdate. Noting that the percentage of degradation is of 55.76% for the real sample and 98.08% for the synthetic with TiO₂ and 62.99% for the real one, 98.53% in the synthetic with TiO₂ doped with HPMoCu 1% in 390 minutes respectively, in which the real sample presents a slower kinetics of degradation, because not only are the interferences added to the synthetic sample, but a series of metal complexes with cyanide M (CN-) xy- that inhibit the photodegradation of cyanide in the presence of TiO₂ by the competition between M (CN-) xy-complexes and free cyanides by the surface of the active sites of *OH-TiO₂. These results are in accordance with those reported by Chiang et al. (2003) [18], and Carp et al. (2004) [21].
Figure 4. Photocatalytic degradation of cyanide in real and synthetic sample. Cat: 0.3 g / L TiO$_2$ and Co CN$-$ total 75.62 ppm and 72.64 ppm of real and synthetic sample respectively.

Figure 5. Photocatalytic degradation of cyanide in real and synthetic sample. Cat: 0.3 g / L TiO$_2$ doped with HPMoCu 1% and Co CN$-$ total 75.35 ppm and 72.64 ppm of real and synthetic sample respectively.

In Figure 6, the influence of the type of catalyst on the degradation of cyanide in the real sample is shown, observing a small difference in the kinetics of degradation where the doped TiO$_2$ reaches 62.99%, while the TiO$_2$ 55.76%. The degradation of cyanide reported, may be analyzed in terms of the langmuir-hinshelwood model:

$$ r = - \frac{dc}{dt} = K_2 \theta_o2 \theta_{CN^-} $$

Where $r$ is the reaction rate for cyanide oxidation in units mM / s and $K_2$ (mM / s) is the kinetic constant of second order, the terms $\theta_o2$ and $\theta_{CN^-}$ refer to the surface fraction covered by oxygen and cyanate respectively.

The term $\theta_o2$ can be assumed constant, considering the continuous bubbling of air to the reaction system, reducing the equation to:

$$ r = - \frac{dc}{dt} = K_1 \theta_{CN^-} $$

Where the kinetic constant of first order $K_1$ is equal to $K_1 = K2002$, the coated surface $\theta_{CN^-}$ can be expressed as: $\theta_{CN^-} = K \ast CCN^- / 1 + K \ast CCN^-$, replacing in the equation we have that:
\[ r = - \frac{dc}{dt} = K_1 K^* C_{CN^-} / (1 + K^* C_{CN^-}) \]

**Figure 6.** Kinetic photocatalytic degradation of cyanide present in real sample with respect to the influence of the catalyst 0.3g/L TiO$_2$ and 1g/L TiO$_2$ doped with HPMoCu 1%

A plot of the reciprocal of the initial cyanide photo-oxidation ratio \( r \) versus the reciprocal of the initial cyanide concentration shows a straight line as can be seen in Figure 7, with a value of \( r^2 = 0.9607 \), which indicates a good approximation between the prediction of the equation and the experimental results.

**Figure 7.** Reciprocal plot of the proportion of initial cyanide photo-oxidation (1/r) versus reciprocal of cyanide initial concentration (1/Ci)

In Figures 8 and 9, variations in the concentration of cyanide and cyanate during the photoreaction of cyanide degradation (75.72 mg / L) which is equivalent to 2.91 mM in real water, using TiO$_2$ and TiO$_2$ doped with HPMoCu 1% as catalyst are shown. In several photocatalytic oxidation studies of cyanide solutions, cyanate was the main oxidation product for both TiO$_2$ and doped copper modified TiO$_2$ [22, 23]. It may be observed that during the cyanide oxidation, the cyanate concentration increases in the same way as the cyanide concentration decreases. The non oxidation of cyanate was detected during the experimental assays, which is in agreement with the works of [22, 23]. Many
reported results show that the percentage of CN- reaction with OH * are two orders of magnitude higher between the CON- and OH * reaction [24, 25, 26, 27].

4. Conclusion

According to the review of the bibliography, the results and their discussion can be concluded that: The photocatalytic degradation when air was supplied was higher than that obtained when it was absent, therefore the oxygen supply is important because it increases the degradation rate of the substrate, since the lack of supply tends to deplete the dissolved oxygen in water.

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