Degradation of Cyanide from Gold Mining Wastewater Using Photocatalysis

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Abstract: In recent years, water quality issues related with hazardous wastewater and toxic substances have attracted worldwide attention. Cyanide is a major toxin in wastewater resulting from a diversity of industries, including gold mining. Cyanide has adverse health effects on people as well as other living organisms. The toxic effects of cyanide are so important to cause nerve damage and thyroid glands malfunctioning. In this paper, the degradation of cyanide in waters resulting from gold mining activity was carried out in a batch system with two catalysts TiO2 Degussa P-25 and TiO2 doped with copper heteropolyimolybdate, that was synthesized in laboratory and characterized by FTIR and XRD. Assays showed a degradation of 98.55% with a concentration of 0.3 g/L of TiO2 and 97.17% with TiO2 doped with 1% of Cu heteropolyimolybdate (1 g/L) in 50 min of reaction. A real mining sample showed a cyanide degradation of 55.76% with TiO2 in 240 min of reaction. All the assays were made applying photodegradation using a 125-Watt mercury lamp as source. These results are encouraging to use this technology for the removal of cyanide coming from highly contaminated aqueous effluents.

1. Introduction
The presence of dangerous chemical compounds in the environment is the result of anthropogenic activity. In the last years, environmental legislation has focused on demanding the protection of water bodies, due to the lack of it and the dramatic increase of diseases and dysfunctions of the nervous system in animals and humans [3]. Cyanide is one of the most prevalent toxic environmental pollutants, resulting from industrial processes such as coking plants, oil refineries, and several chemical industries processing resins, plastics, dyes, varnishes, pharmaceuticals and pesticides, etc. Cyanide is also present in chemicals that are used to reveal photographs. Cyanide salts are used for galvanization, metal cleaning and recovery of gold from mining activities [6,7]. Previous studies [11], showed the presence of cyanides at low concentrations in water that are of environmental and toxicological interest, because this may cause lethal effects on plants, animals and humans [12, 13]. In human health, cyanide avoids the body cells from receiving oxygen, causing tissue hypoxia and cyanosis. Cyanide enters the human body through inhalation, ingestion or absorption through the skin [14, 15]. Cyanide in acid water streams produces hydrocyanic acid (HCN), which is a highly toxic chemical; if the water pH is basic, it is maintained as cyanide. Due to this is necessary to reduce the cyanide levels in wastewater before discharging it into the water bodies, because of the social and public health problems that these involve [8]. In mines, gold containing waste is recovered using activated carbon. Once extracted from activated carbon, gold is concentrated by precipitation or galvanization [9]. Since gold is a noble metal, it is not soluble in water. To dissolve it, a substance like cyanide is needed, because it may form complexes and stabilize gold in solutions [10]. In Colombia, gold exploitation is done legally and illegally in rural conflict zones where authorities are not capable to protect the environment from these dangerous effluents. Most of the studies reviewed in the literature perform a quantification of cyanides present in water, others postulate absorbers that could recover or trap cyanide but would be transferring the problem of a pollutant in an aqueous effluent to a solid waste contaminated not giving a true solution [16]. So, the aim of this project is to remediate through Photocatalysis real mining water samples to provide a method to minimize cyanide effluents in conflict zones.
2. Experimental

2.1 Preparation of Copper heteropolyimolybdate
Copper heteropolyimolybdate synthesis was carried out by wet coprecipitation. The solutions of copper sulfate (CuSO$_4$) and ammonium heptamolybdate (NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O, were previously heated at 80 °C for 10 min., Mixed and then boiled in a Borosilicate glass reactor (at approximately 94 °C), forming a precipitate that after a certain time was filtered, washed and dried in an oven at 100 °C. The initial precipitate was a by-product of the synthesis where the copper heteropolyimolybdate was obtained. Copper heteropolyimolybdate ([NH$_4$]$_4$[CuH$_6$Mo$_6$O$_{24}$].5H$_2$O,) was precipitated from the mother liquor which was obtained from the above filtration with an excess of acetonitrile.

2.2 Collection and conservation of samples.
The aim of the sampling procedure was to obtain representative samples of the parameters to be analysed, conserving the relative concentrations of all the components present in the original material. At each sampling site, enough water was taken at different times. For storage, a time of 8 hours was taken, due to the collection of the sample that took place on working days, from 8 a.m., because it is the time when the mining activity begins and ended at 4 p.m. approximately. Individual portions of the water under study were taken and mixed in a single bottle [17].

2.3 Photodegradation experiments of cyanide.
The cyanide photodegradation experiments were carried out in the reaction system at room temperature (30 ± 2 °C) and at atmospheric pressure by bubbling air into the system, to avoid recombination of the electron-hole pairs (see figure 1). The temperature of the system was measured by a thermocouple and regulated by cooling water that removes the heat generated by the UV lamp. In order to optimize the photocatalytic degradation of cyanide, the following factors were taken into account, taking as a reference the work carried out by Sarla et al. (2004) [18]: Concentration of TiO$_2$ catalyst (0.2 - 3 g / L), Type of catalyst (TiO$_2$; TiO$_2$ doped with HPMoCu), Initial cyanide concentration (100 ppm), Reaction time (50 minutes) and pH (10.8 - 12),

![Photoreactor and its components](image)

**Figure 1.** Photoreactor and its components

The above was done to obtain the optimum concentration of the catalyst. With this catalyst concentration, the initial pH was varied between 10.8 and 12, in order to obtain the value that maximized the percentage of degradation. The levels of catalyst concentration and pH were selected based on the literature review [19, 20]. The initial cyanide concentration was set taking into account the concentration of total cyanide present in the effluents of the mining area and the time of reaction in relation to a series of preliminary tests.

The degradation study of the real samples was carried out taking as reference a research done by Augugliaro et al. (1997) [21] in the reaction system taking into account the optimal fixed concentration of catalyst (TiO$_2$ and TiO$_2$ doped with copper heteropolyimolybdate) and pH. The residual water from the mining area of southern Bolívar, had an initial concentration of 75.62 ppm of total cyanides and a pH 6.8, and were preserved with NaOH, because the cyanide in Residual water is in a very complex matrix.

As the initial concentration of this effluent was 75.62 ppm than that fixed in the previous kinetic studies, a degradation test of a synthetic mixture with an initial concentration of 72.64 ppm of CN- was previously carried out, adding the concentrations of the compounds found in the respective physical-chemical analysis of the water, very similar to the real sample, with the same concentration of catalyst and adjusting the pH of
the initial solution to 10.8 adding NaOH, which allowed to estimate the reaction time necessary to degrade a solution with this initial concentration and have a reference study. For these tests, a time of 360 min was set and 4 mL of sample was taken at 1-hour intervals. The chemical oxygen demand (COD), total organic carbon (TOC) was analyzed for the corresponding samples from the mining area of southern Bolivar "Barranco de loba" at 60, 120, 180, 240, 300 and 360 minutes.

2.4 Determination of cyanide.

The samples taken from the reaction system were centrifuged for 7 minutes at 4200 rpm, then the potentiometric method was used to determine the final concentration in each of the samples, following the Standard Methods for the Examination of Water and Wastewater, 23rd Edition of the 2017 [17], using a cyanide selective ion electrode potentiometer, which allows us to measure the potential of the specific ion in the solution.

2.5 Physicochemical characterization of mining water.

Water samples from the mining area of Barranco de Loba, south of Bolivar (Colombian Caribbean), were subjected to physical-chemical tests for COD and TOC in accordance with the Standard Methods for the Examination of Water and Wastewater, 23rd Edition of 2017 [17].

3. Results and Discussion

3.1 Characterization of the catalyst

IR spectrum of TiO2 doped with (NH4)4 [CuH6Mo6O24].5H2O is shown in figure 1, where a wide band between 3200-3400 cm⁻¹ is observed which is attributed to the stretching vibrations of the hydroxyl groups from the hydration waters.

The typical region of absorption of TiO2 between 1200-1700 cm⁻¹ is shown and they are physically assigned to water adsorbed on the surface, this behavior is similar to that reported by (Dvoranová D. et al., 2002). The signal at 862.0 cm⁻¹ can be assigned to the Cu-O-H and MoO4 binding vibrations. The peak at 1118.2 cm⁻¹ is due to asymmetric Ti-O stretches and octahedral Mo = O terminal oxygens.

The XRD pattern of titanium dioxide doped with 1% copper heteropolyimolybdate is depicted In Figure 3. The diffractographic analysis was performed based on the cards N ° 83-2243, 78-2485, and 22-0504 respectively, (XRD patterns).
The results showed a higher proportion in the phase of anatase-TiO2 (■) which showed a peak at 3.2468 Å, 1.8911 Å, 1.6657 Å which confirm the presence of TiO2 in all samples. Meanwhile, the rutile phase-TiO2 (▲) showed peaks at 3.2468 Å, 2.4855 Å, 1.6910 Å, 1.3605 Å, and the phase (NH4)4 [CuH6Mo6O24].5H2O (◆) showed a typical distance of 5.0680 Å.

3.2 Cyanide Photodegradation experiments.

The percentages of cyanide degradation obtained by varying the catalyst concentration (TiO2 Degussa P-25) between 0.1 and 3 g / L are shown in Figure 1. The initial concentration of cyanide was 100 ppm, pH was 10.8 and reaction time was 50 min. Results showed an increase in degradation from 0.1 to 0.3 g / L, possibly due to the greater number of photons absorbed by the photocatalyst, which provides a high concentration of charge per volume unit. From 0.3 to 3.0 g / L there is a degradation reduction, since the penetration of the UV photons decreases, therefore, less TiO2 particles may be activated. Therefore, the optimum catalyst point is 0.3 g / L with a degradation percentage of 98.55%. This was the selected concentration of TiO2 catalyst used for the subsequent degradation tests.

Study of the influence of TiO2 catalyst concentration doped with copper heteropolimolybdate Vs % Degradation of cyanide for the reaction system.

Percentages of degradation obtained from cyanide using doped catalyst are depicted in Figure 2. The concentration of the TiO2 degussa P-25 catalyst were 0.3 and 1.0 g/L, and Cu heteropolimolybdate concentration varied between 0.1% and 10% during 50 min of reaction. The best results were obtained with 1 g/L of TiO2 and a doping of 1%, showing a degradation percentage of 97.17%. It may be seen that for the same catalyst concentration of 0.3 g/L of TiO2 and doped TiO2 there is a pronounced decrease in the degradation percentage for the case of modified TiO2. The negative effect of the photooxidation of cyanide due to the presence of Cu (1) -CN- which are species that are formed in competition reactions with the hydroxyl radicals produced on the surface of TiO2 under UV radiation.
Influence of doped TiO$_2$ catalyst concentration on cyanide degradation

Figure 5.

Influence of the catalyst TiO$_2$ and TiO$_2$ doped with heteropolimolybdate of Cu Vs% degradation of the cyanide for the reaction system.

In order to increase the uptake of the electrons and decrease the recombination of the electron - hollow pairs, strategies were followed in the modification of the structure and composition of the catalyst. These approaches include modifying the TiO$_2$ surface doped with metal ions and adding compounds that transfer charge to the semiconductor [22]. Table 1 shows the percentages of degradation obtained from cyanide of 98.55% and 97.16% in a time of 50 minutes, using TiO$_2$ and TiO$_2$ doped with copper heteropolimolybdate, respectively in which it was observed that the modified catalyst decreases the cyanide degradation in compared to the unmodified one, this can be attributed to the fact that during the preparation surface area has been lost.

| Time (min) | TiO$_2$ (%) | (TiO$_2$ – Cu) (%) | Without catalyst (%) |
|------------|-------------|--------------------|----------------------|
| 0          | 0           | 0                  | 0.00                 |
| 10         | 35.94       | 33.02              | 2.25                 |
| 20         | 65.85       | 44.84              | 8.54                 |
| 30         | 87.91       | 58.82              | 10.12                |
| 40         | 97.97       | 77.37              | 12.91                |
| 50         | 98.55       | 97.16              | 15.32                |

Study of the influence on the pH variation in the photocatalytic degradation of cyanide

Figure 3 shows the percentages of degradation of cyanide obtained by varying the pH between 10.8 and 12.0, starting from an initial concentration of cyanide 100 ppm and a concentration of catalyst 0.3 g / L, during 50 min of reaction. The results showed an increase in the degradation of cyanide by decreasing the pH, because at high pH values the adsorption of cyanide ions with negative charge by the hydroxide groups absorbed on the TiO$_2$ surface is not favourable, allowing the permanence of free cyanide in solution. Therefore, the optimum point of pH is 10.8 with a degradation percentage of 98.55%, since the pH cannot be lowered below the pka of hydrogen cyanide which is equal to 9.21 at 25 °C.
Figure 6. Influence of pH on the photocatalytic degradation of cyanide in the presence of 0.3 g/L TiO2, Co = 100 ppm

3.3 Characterization of mining water.
Generally, cyanides in industrial wastewater are found together with other contaminants that interfere with the photocatalytic degradation process. For this reason, the degradation of cyanide compounds presents in an industrial discharge of the mining area Barranco de Loba, Santa Cruz mine, Colombia was studied. DQO and TOC were applied to real samples and were analysed in laboratory according to the standard methods for water and wastewater analysis.

3.4 Chemical oxygen demand (COD)
The initial cyanide concentration of the sample was 75.62 mg/L and COD was 3911.6 mg/L, the behaviour of CDO and cyanide degradation process are shown in Figure 4. COD decreased 76.36%, while for the cyanide was 55.76% in 240 min of reaction, indicating the non-selectivity of the photocatalysis towards the destruction of other organic compounds present in the sample, which are also water pollutants.

Figure 7. Curves of photocatalytic degradation of total cyanide and COD of mining water

3.5 Total organic carbon (TOC)
Curves of the photocatalytic degradation of the total cyanide and the total organic carbon of the real sample are depicted in figure 5. Initial concentration of TOC was 224 mg/L and experiments showed a decrease of the total organic carbon in 94.01 mg/L and a degradation of CN- in 55.76%, indicating that part the organic matter was also photodegraded confirming once again the non-selectivity of photocatalytic degradation.
Figure 8. Curves of the photocatalytic degradation of total cyanide and the TOC of mining sample

4. Conclusions

According to the review of the bibliography, the results and their discussion can be concluded that: (i) The degradation system showed us that the total cyanides, present in the aqueous residual discharges, coming from the mining sector, may be degraded through heterogeneous photocatalysis, providing a viable alternative for the destruction of contaminants in mining effluents. (ii) In the photodegradation of the cyanide (75.62 ppm), there was a reduction of 76.36% of the COD, while for the cyanide it was 55.76% in 240 min. This means that cyanide was photodegraded and also another series of organic compounds that were present in the degradation, showing the non-selectivity of the photocatalytic process in the destruction of the organic contaminants. (iii) Cyanide compounds present in the real sample were degraded by heterogeneous photocatalysis in 55.76% with TiO$_2$, while the simulated synthetic sample reached 98.41% with TiO$_2$ %, which showed the effect of the interferences generated by the compounds present in the residual sample competing with the cyanides for the OH$^-$ radicals produced by the excitation of the catalyst.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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