# Organic pollution in water due to gold mining: A preliminar assessment of a possible AOP-based strategy to reduce/mitigate pollution

*P. Vargas Jentzsch[1], C. Ramos[1], J. L. Rivera[1], J. Ruales[1], C. Bernal[1], X. Díaz[1], D. Endara[1], F. Muñoz Bisesti[1], A. Romero Carvajal[2].* (1) Escuela Politécnica Nacional, Ladrón de Guevara E11-253, 170525, Quito, Ecuador, paul.vargas@epn.edu.ec. (2) Escuela de Ciencias Biológicas, Pontificia Universidad Católica del Ecuador (PUCE), Avenida 12 de Octubre 1076 y Vicente Ramón Roca, 170525 Quito, Ecuador.
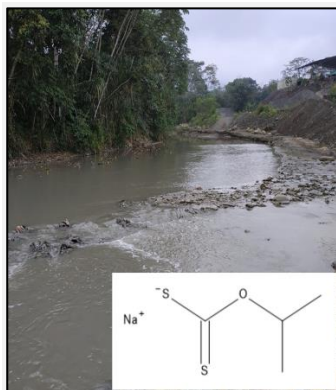


Mining activities are not only responsible for pollution related to inorganic species (e.g., toxic metals) but also for certain organic compounds. Xanthates are organic compounds used in flotation to separate and concentrate metals like gold. These compounds can be released into the environment through effluents of gold processing plants. Advanced oxidation processes (AOPs) were proposed for the removal of xanthates from water. Potential treatments were tested using a commercial sodium isopropyl xanthate (SIPX). Three approaches were considered for the removal of SIPX from water: 1) $H_2O_2$/UVC treatment, 2) a heterogeneous Fenton process with corroded iron (called "iron oxides"), and 3) a heterogeneous Fenton process with iron oxides and UVC radiation. The treatments were tested at two pH values: 7.0 and 5.0. Almost total removal of SIPX was achieved with the treatments carried out at pH 5.0. The use of corroded iron in heterogeneous Fenton processes for the removal of organic pollutants in effluents from mining activities could be a cheap alternative to reduce/mitigate pollution in this sector.

## Introduction

Mining activities were and are essential for the world because they allow the obtention of a variety of critical row materials. Buildings, machinery, vehicles, tools, and any imaginable currently existing technology would not exist without mining. However, there are well-documented environmental impacts associated with non-metallic and metallic mining activities.

Flotation is a method used for the separation and concentration of ores and is widely used to recover gold from pulverized mineral materials. The method requires certain chemical products, of an organic nature, that can pollute water bodies if effluents are not properly treated prior they discharge. This means that pollution due to mining activities is not only related to toxic metals (also known as "heavy metals") but also to certain organic compounds that can negatively affect the quality of water and aquatic ecosystems. "Xanthates" are typically used for the separation and concentration of gold employing flotation. In Ecuador, in the mining district of Ponce Enríquez, the use of sodium isopropyl xanthate (SIPX) and potassium amyl xanthate (PAX) was verified. These substances are toxic. The pollution of rivers was verified at the point that even the characteristic smell of xanthates is easily noticeable in the proximity of the water body. This is the case of the "Siete" river (see the photo of the graphical illustration).

A proper treatment is required to remove xanthates from water before its discharge to a receiving water body. The treatment should be simple and cheap to facilitate its application. Therefore, treatments based on a heterogeneous Fenton process with corroded iron (it simulates scrap) and the process of hydrogen peroxide with ultraviolet radiation C ($H_2O_2$/UVC) were proposed. Results on the removal of a xanthate as a function of time were obtained for the proposed treatments.

## Material and Methods

Commercial sodium isopropyl xanthate (SIPX) applied in the flotation process in a gold processing plant in the mining district of Ponce Enríquez (Ecuador) was used for the experiments.

Solutions of SIPX in distilled water were prepared to simulate the effluent of a gold processing plant. To treat the solutions of SIPX, a batch lab scale system equipped with one UV lamp (Osram, 36W, 254 nm) and a Petri dish with a magnetic stirrer was used. Aqueous solutions of SIPX with an initial concentration of 66.67 mg/L were used for all assays. Two pH values (7.0 and 5.0) were considered.

Corroded iron was obtained by the corrosion of iron filings recovered from a metalworking workshop. Fine particles of the corroded iron, called "iron oxides" for purposes of this work, were separated with a laboratory sieve.

Three approaches were considered for the removal of SIPX from water: 1) $H_2O_2$/UVC treatment (different $H_2O_2$ concentrations were tested), 2) a heterogeneous Fenton process with iron oxides (20 mg of iron oxides was added and a concentration of $H_2O_2$ of 91.6 mM was used), and 3) a heterogeneous Fenton process with corroded iron and application of UVC radiation (20 mg of iron oxides was added and a concentration of $H_2O_2$ of 91.6 mM was used, plus the exposition to UVC radiation). The third approach was applied only for the pH value that allowed the higher removal of SIPX with the previous approaches.

The concentrations of SIPX in the aqueous solutions at different times of treatment were determined by measuring the absorbance of the solutions with a UV-VIS spectrophotometer (Hitachi U-1900) at a wavelength of 301 nm. Since each assay was carried out with a small volume of solution, the absorbance measurements were made with the total volume of solution for each time of

reaction after filtration through a PVDF syringe filter (diameter 25 mm and pore size 0.45 µm). To rule out any interference related to degradation products or any substance occurring in the solutions, the measured concentrations with the spectrophotometric method of some samples were contrasted with HPLC measurements, and no significant differences were observed.

## Results and Discussion

At a pH value of 7.0, SIPX is stable in an aqueous solution for several hours. On the other hand, a remarkable decrease in the concentration of SIPX (around 40%) can be observed in aqueous solutions regulated to pH 5.0 by the addition of a strong acid. This is in good agreement with a previous report in which it was demonstrated that xanthates hydrolyze, in an acidic medium, leading to the formation of carbon disulfide and an alcohol [1]. Also, this explains why xanthates can be found in rivers in the mining district of Ponce Enríquez; the measured pH of water in these rivers is slightly higher than 7.

Figure 1 shows the results of the tested treatments for the removal of SIPX from water carried out with an initial pH value of 7.0. $H_2O_2$ alone, as the oxidizing agent it is, can promote certain degradation of SIPX and this effect is improved by the application of UVC radiation. The heterogeneous Fenton process shows better results than the process $H_2O_2$/UVC, however, the percentage removal of SIPX is only around 65% after 60 min of reaction.
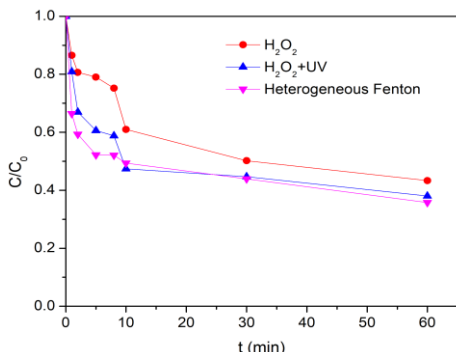


**Figure 1.** Degradation of SIPX as a function of time at pH 7.0 for the treatments with $H_2O_2$, the process $H_2O_2$/UVC, and the heterogeneous Fenton process with iron oxides.

Since the treatments at a pH value of 7.0 showed limited effectiveness in terms of SIPX removal, treatments at a pH value of 5.0 were also tested. Although this implies the use of a strong acid to reach the desired pH for the solution,

there is also the possibility of taking advantage of the acid hydrolysis of the xanthate mentioned before. Figure 2 shows the results of the tested treatments for the removal of SIPX from water carried out with an initial pH value of 5.0.
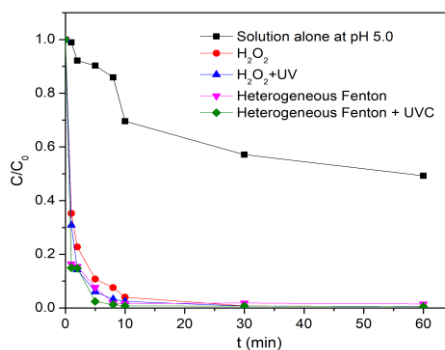


**Figure 2.** Degradation of SIPX as a function of time at pH 5.0 for the treatments with $H_2O_2$, the process $H_2O_2$/UVC, the heterogeneous Fenton process with iron oxides, and the heterogeneous Fenton process with iron oxides plus UVC radiation.

After 60 min of reaction, the removal of approx. 50% of SIPX can be achieved only due to hydrolysis of the compound. However, it should be pointed out that carbon sulfide shows toxicity in aquatic organisms as well as inhibits the nitrification process [2]. Therefore, hydrolysis alone cannot be used to remove SIPX from water. An oxidative process capable of eliminating the carbon sulfide is necessary to avoid the mentioned adverse effects in the receiving water bodies, i.e., rivers. Then, when $H_2O_2$ alone, the process $H_2O_2$/UVC, the heterogeneous Fenton process, and the heterogeneous Fenton process plus UVC radiation were applied, almost the total removal of SIPX was reached in 60 min of reaction.

Certain aspects should be considered to selecting the best treatment among the treatments working at pH 5.0. For the processes involving the iron oxides, the removal of SIPX due to adsorption, to some degree, cannot be ruled out. The extent of the contribution of adsorption to the total removal of SIPX from water must be estimated.

SIPX was almost removed with all the treatments that took place at pH 5, however, the remaining degradation products may exhibit toxic effects on living organisms. Therefore, (eco)toxicological tests for the treated waters are needed to complement the SIPX removal experiments.

## Conclusions

Xantates can be released into the environment through the effluents of gold processing plants, therefore, a simple and cheap water treatment is required. The effective removal of SIPX was possible with the $H_2O_2$/UVC treatment, a heterogeneous Fenton process with iron oxides, and a heterogeneous Fenton process with iron oxides and UVC radiation, in all cases, at a pH value of 5.0. (Eco)toxicological considerations may be important in selecting the best treatment.

*References*
[1] X-h. Chen, Y-h. Hu, H. Peng, X-f. Cao, *Journal of Central South University*, 22 (2015) 495-501.
[2] Y. Avnimelech, *Aquaculture*, 220 (2003) 549.