

In-situ Photocatalytic Reduction of Hexavalent Chromium in Contaminated Soil

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Abstract— The photocatalytic reduction of hexavalent chromium was conducted in laboratory environment in order to evaluate the alternative use of this technology for in-situ decontamination. The soil samples used had initial concentrations of Cr(VI) of 651.0, 308.0 and 112.0 mg kg⁻¹, with loads of catalyst TiO₂ which were exposed to UV irradiation through black light. Different loads of catalyst of 0.1-2% (w/w) were tested in soil contaminated by hexavalent chromium with a concentration of 651 mg kg⁻¹ for a period of 88 hours of exposure. In addition, we examined the effect of alkalinity Ca(OH)₂ (10% w/w). The rise in the pH due to Ca(OH)₂ addition shows no measurable effect on the chromium reduction. The photocatalytic remediation using TiO₂ combined with UV light showed their effectiveness in the reduction of Cr(VI) at 2, 4 and 6 cm of depth of contaminated soil, moreover also showed mobility of the contaminant towards to surface.

Index Terms— Chromium (VI) reduction, Photocatalytic in-situ soil decontamination.

I. INTRODUCTION

Over time, variations in global temperature have caused climatic changes. These increased rainfall levels what causes alterations in river channels leading to flooding in the lower grounds causing environmental disaster. One of these disasters occurred in the Sabana de Bogotá-Colombia, where the river exceeded the levels flood affecting great land extensions principally productive sectors as flower crops, livestock and grass. These problems are enhanced due to human activities over side causes raise river pollution levels. In this sector, the main pollution activities are related with waste disposal and are discharged to environment, especially in the aquatic ecosystem [1]. In the upper part of the Bogotá river (Villapinzón-Colombia), it develops the bigger leather tannery industry. This condition require great amounts of water to develop its industrial activities and therefore produces important levels of waste affecting the

natural sources, principally the river because wastewater are disposal in the Bogota river. A lot of industrial dumping is discharged without any type of treatment into the river Bogota increasing the pollution levels due principally to organic pollutants and chromium (permissible limit 0.01 mg L⁻¹) [2].

Wet-blue process is the main technique used by the producers, generating discharges with high levels of chromium. This is the most representative metallic specie on the river which causes pollution problems when the river floods lands nearby to riverbed. When this occurs, the chromium suffers a phase change, depositing into the ground and altering the metal natural concentrations. This generates raise in permissible levels according to environmental regulations [3]. In this sense, has been founded that soils contaminated with metals such as arsenic, barium, beryllium, cadmium, hexavalent chromium, mercury, nickel, silver, lead, selenium, thallium and vanadium, prevents the normal development of plants and crops causing decreasing in productivity levels.

Cr(VI) has particular interest to scientist due to its toxicity and mobility therefore, is a great challenge its removal from wastewater. It is a strong oxidizing agent which is carcinogenic, mutagenic and diffuses easily through soil and aquatic environments. Cr(VI) does not form insoluble compounds in aqueous solutions therefore its separation is not feasible. Some oxyanions are very mobile and toxic in the environment, Cr(III) cations are not. Like many metal cations, Cr(III) forms insoluble precipitates. Thus, reducing Cr(VI) to Cr(III) simplifies its removal from effluent and also reduces its toxicity and mobility [4].

The chromium toxicity depends of its oxidation states. Hexavalent ions are highly mobile, soluble and bioavailable however trivalent form exhibits other properties. For example, Cr(III) exists in precipitates or is strongly adsorbed by inorganic and organic colloids in soils, and is one of the micronutrient elements in humans. Thus, many methods have been explored to utilize reductants or cause the transformation of Cr(VI) to Cr(III) in Cr(VI)-contaminated soils [5]. Because it is only weakly sorbed onto inorganic surfaces, Cr(VI) is mobile in nature. On the other hand, Cr(III) is readily precipitated or sorbed on a variety of inorganic and organic substrates at neutral or alkaline pH.

Due to the great number of sources and environmentally hazardous chemical composition of these contaminants, implementation of innovative treatment processes for contaminated soil remediation is a matter of pressing concern. Numerous potential technologies exist for soil remediation and degradation processes. These include biological, physical and chemical treatments.

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Advanced oxidation processes are promising techniques for degrading an extensive variety of hazardous compounds in remediation of soil at waste disposal and spill sites. Photocatalytic processes can be applied both *in situ* (to soil in place) and *ex situ* (after soil excavation). Matching the remedial oxidant and technology of delivery to the contaminant of concern and site conditions is an extremely important step in the successful remediation of contaminated soil.

The use of advanced oxidation process in the treatment of contaminated soil has been demonstrated recently [6]. From these methods, photocatalytic reaction, using TiO_2/UV , can simultaneously treat organic compounds and heavy metals, as well as transform non-degradable to biodegradable organic compounds. Titanium dioxide (TiO_2) semiconductor has the ability to reflect radiation visible and absorbs the electromagnetic radiation that is close to the UV region [7]. It's the most used photocatalytic semiconductor in environmental applications. Parameters like the pH ($\text{pzc} \sim 7.0$), which must be above or below this value to the catalyst was negative or positively charged, catalysts loading and contaminant concentration must be considered to specific treatment. Heterogeneous photocatalysis of organic pollutants using TiO_2 under UV irradiation and/or solar light has demonstrated successful performance in various remediation systems of polluted soil. The addition of small amounts of TiO_2 enhanced the photodegradation on soil surfaces significantly [8].

The TiO_2 photocatalytic reduction has been reported to be effective for the removal of Cr(VI) . Besides TiO_2 , the use of ZnO and CdS in the photocatalytic reduction of Cr(VI) to Cr(III) has also been reported. Cr(VI) has a toxicity one hundred times higher than that of Cr(III) .

In this study, a series of batch experiments at lab scale were carried out to investigate the effect of soil types on Cr(VI) reduction with or without irradiation. The effects of chromium concentration, catalyst loading, pH and soil depth were considered based on previous methodologies.

II. METHODS AND MATERIALS

A. Materials

Titanium dioxide (Degussa, AEROXIDE P25) was used as received. Calcium hydroxide Ca(OH)_2 , diphenylcarbazide, hydrogen peroxide and nitric, sulphuric and phosphoric acid were reagent grade.

Three types of soils from Chia (Cundinamarca) –Colombia were selected for this study (Figure 1). The soils (0–40 cm) were sampled, dried in air, disaggregated by hand to reduce clumping, and sieved. The fraction less than 100 mesh size, which was mixed and split several times to obtain representative homogenized sample, was used in the experiments. The selected properties in Suba–Cota, Hato Grande and La Chavela are listed in Table 1.

B. Irradiation experiments to contaminated soil

Soil samples were taken directly from Chia (Cundinamarca) influence Bogotá river zone. The experiments were carried out to lab scale conditions, where 10 grams of soil located in Petri dishes and adjusted to experimental conditions. The plates were exposed to UV artificial light during 88 h, so all graphs showing the

irradiation time refers to the amount of exposure to black light in sequential time.

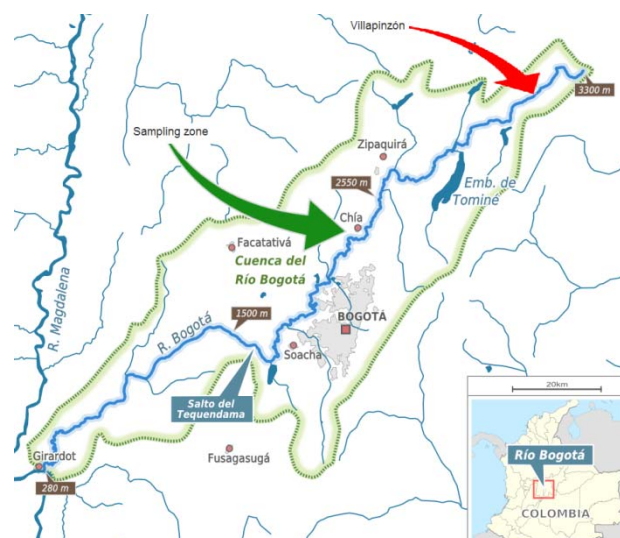


Fig. 1. Influence Zone River. Affected areas by flooding of contaminated Bogotá river (Chía zone – sampling). Disposal of waste from tannery industry (Villapinzón). Adapted from [9].

TABLE I
CHEMICAL AND PHYSICAL CHARACTERISTICS SOILS

Item	Suba-Cota	Hato Grande	La Chavela
Organic matter, %	16.55	13.18	14.25
Real density, g	1.73	2.23	1.68
pH	7.0	4.38	7.73
Elec. conductivity, ds cm^{-1}	1.14	1.58	1.43
Zn, mg kg^{-1}	973	896	516
Fe, mg kg^{-1}	488	269	345
Mn, mg kg^{-1}	63	260	36
Cu, mg kg^{-1}	345	62	32
Cr(VI) , mg kg^{-1}	651	308	112
Total Cr, mg kg^{-1}	883	525	251

To Cr(VI) determination, 0.5 grams of soil were taken after 16, 24, 40, 48, 64, 72 and 88 hours of artificial irradiation and analyzed by digestion for Cr(VI) . The catalyst loading was made by adding the studied amount of TiO_2 in the soil, followed by manual shaking for 30 minutes in a glass vessel.

To study the optimum concentration on the reduction of Cr(VI) , three plates were prepared with contaminated soil samples. In each plate 0.0, 0.1 and 2.0% TiO_2 (w/w) were incorporated into the soil and submitted to photocatalytic treatment. The influence of metal concentration was also evaluated by means of samples Suba–Cota, Hato Grande and La Chavela, followed by the addition of 1.0% (w/w) catalyst.

The influence of soil alkalinity by Ca(OH)_2 in photocatalytic degradation was also assessed for Cr(VI) reduction. The addition of Ca(OH)_2 is performed to adjust the pH to alkaline conditions, was made by weighing of the amount of reagent and mixing to the soil.

Considering that the artificial radiation penetrates only a few centimeters of the soil surface, we assume that the photocatalytic treatment is effective only in the top of soil.

For these reason one experiment was carried out, to evaluate the reduction rate and mobility of Cr(VI) as a function of soli depth. Two plastic cylinder (3.5 cm in diameter and 10 cm high) containing soil contaminated with 1.0% TiO₂ (w/w) and humidity (30% w/w) were irradiated with artificial UV light on a 24 and 48 hours period. Each cylinder was cutted at intervals of 2.0 cm down from top until cylinder bottom (three slices in total). Each slice was analyzed for Cr(VI).

c. Hexavalent chromium analysis

The metal ion present on soil surfaces were extracted by 0.5M HNO₃, hydrogen peroxide and distilled water. The suspension was mixed in a shaker bath at 60±2 °C for 30 min. and was filtered. Cr(VI) concentration was measured using the 1,5 diphenylcarbazide colorimetric method, using phosphoric acid buffer to control pH for the color development. The absorbance at 540 nm was measured in a 1.0 cm cell on a UV-Pharo 3000 spectrophotometer (Merck). A 781 Methrom pH/Ion, after two-point calibration, was used to determine pH values [10].

III. RESULTS AND DISCUSSION

A. Effect of the hexavalent chromium concentration

Figure 2 shows the results obtained for the reduction when the concentration of Cr(VI) in the soil varied among 651.0, 308.0 and 112.0 mg kg⁻¹ using 1.0 % (w/w) of TiO₂ and exposed to artificial UV radiation. Reduction follows a pseudo first order kinetics with a half-life about 24 hours to all Cr(VI) concentration levels. In the absence of catalyst, there is photolysis effect after 10.0 hours of treatment until 88 hours of irradiation being more noticeable at higher loads of pollutant. Cr(VI) reduction in the absence of the catalyst may be due to both photolysis and the presence of iron species which promote the ion conversion. The results shows that for these levels of pollution, soil loaded with 1.0% of catalyst is enough to reach an efficiency about 50.0 % for Cr(VI) reduction.

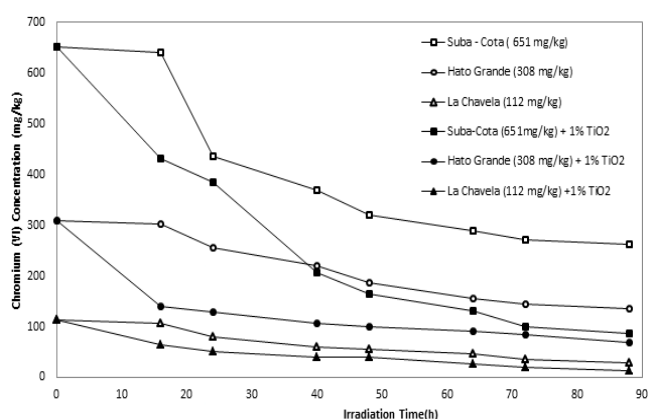


Fig. 2. Influence of Cr(VI) concentration on the photocatalytic reduction in soil after flooding in presence and absence of TiO₂ to three different soils.

B. Effect of load catalyst in Cr(VI) reduction in soil

The studies were development with Suba-Cota soil (651.0 mg kg⁻¹). Changes in the concentration of TiO₂ from 0.1 to

2.0 % (w/w) have not significant effect in the chromium reduction after 24 hour, as shows Figure 3.

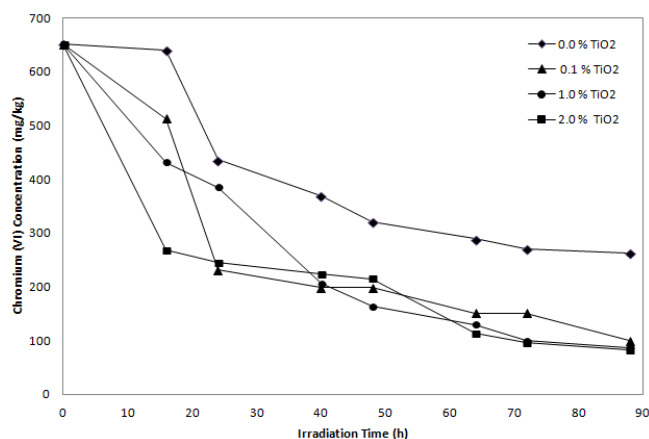


Fig. 3. Catalyst loading effect on the reduction of Cr(VI) in Suba-Cota soil after flooding (651.0 mg kg⁻¹).

The results show that with catalyst loading of 2.0 % promotes maximum rates reduction of Cr(VI), but not a result showing a significant difference. It is clear that before 24 hours there is a significant degradation in both soils about 70.0% less contamination.

Again, was presented the reduction of Cr(VI) in absence of photocatalyst. According to Figure 3, catalyst load was selected as 1.0 % for the others experiments.

C. Effect of alkalinity with and without the presence of load catalyst.

Figure 4 shows that alkaline conditions by adding Ca(OH)₂ to the soil does not significant effect in Cr(VI) photoreduction when compared to natural soil.

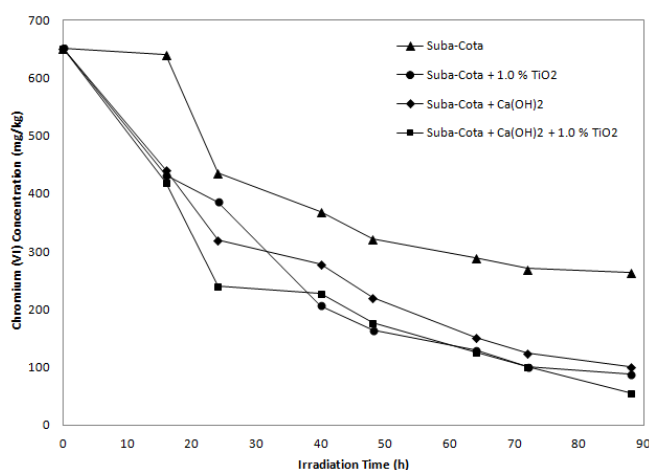


Fig. 4. Influence of alkalinity on the photocatalytic reduction of Cr(VI) in soil after flooding in the presence and absence of TiO₂.

This results shows that, the limitant mechanism for hexavalent chromium reduction using heterogeneous photocatalysis is more related to suitable conditions of mobility the metal ion to the catalyst surface, or increasing the transport of the pollutant. It's remarkable that the experiments in soil where carried out at lab scale using in situ decontamination.

D. Depth soil effect

One of photocatalytic process limitants is the optical thickness. In the soil case, the process has a limited application, since it acts only in the uppermost lawyer. As shows in Figure 5, in the profile of Cr(VI) reduction in soil contaminated (Suba-Cota) illuminated by UV radiation after 48 h of illumination, the concentration of the Cr(VI) in the top 2.0 cm of soil was about 200 mg/kg (60.0 % reduction), with a decrease through soil depth.

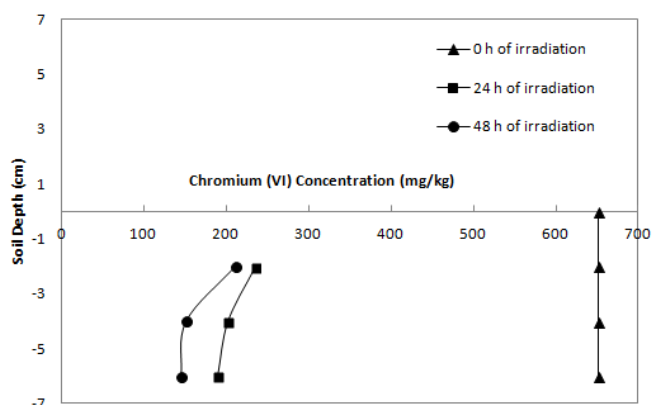


Fig. 5. Photocatalytic reduction of Cr(VI) in soil after flooding at different depths.

At 4.0 cm depth, chromium reduction reached values around 80.0 % of natural concentration in contaminated soil.

IV. CONCLUSION

The aim of this work was to assess the feasibility of using TiO_2 for in-situ soil remediation. To evaluate the Influence of Cr(VI) concentration on the photocatalytic reduction in soil after flooding in presence and absence of TiO_2 , different soils were used (Suba-Cota, Hato Grande and La Chavela). However to evaluate the effect of load catalyst, pH and depth soil in Cr(VI) reduction, just Suba-Cota zone soil sample was tested.

The major conclusions of this study are as follows: The results shows at these levels of Cr(VI), loading the contaminated soil with 1.0 % of catalyst was enough to reach efficiencies about 50.0 % for the reduction. In-situ process was easy and the Cr(VI) half life don't exceed 20 h under best conditions. The results show that with catalyst loading of 2.0 % promotes maximum rates reduction of Cr(VI), but not a result showing a significant difference. It is clear that before 24 hours there is a significant degradation in both soils about 70.0 % less contamination.

Alkaline conditions by adding $\text{Ca}(\text{OH})_2$ to the soil does not significant effect in Cr(VI) photoreduction when compared to natural soil. On the other hand, after 48 h of illumination the concentration of the Cr(VI) in the top 2.0 cm of soil was about 200 mg/kg (or around 60.0 % reduction), with a sharp increase in the reduction process in the soil column. At 4.0 cm depth, chromium reduction reached values around 80.0 % of natural concentration in flooding soil. At greater depths there is a remarkable transport effect, which can refer to hexavalent chromium mobility towards the surface.

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