# High efficiency Cr (VI) photoreduction by using synthetic hydroxyapatite as photocatalyst

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Journal: EChE

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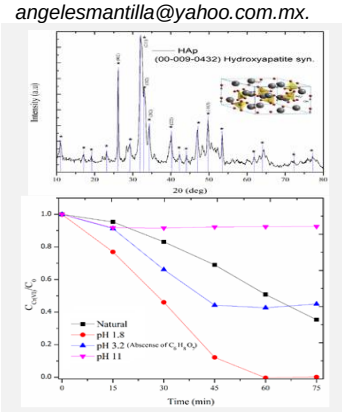


Hydroxyapatite was synthesized using a green chemistry route and low energy cost. Chemical, morphological and textural properties of the synthesized hydroxyapatite were analysed by scanning electron microscopy (SEM), UV-Vis spectroscopy and nitrogen adsorption-desorption (BET); the photocatalytic behaviour was evaluated for the chromium (VI) photoreduction in aqueous phase (40 ppm) using UV light as the source of irradiation. Commercial $TiO_2$ was employed as the reference for these tests..

## Introduction

Nowadays the removal of heavy metals from wastewater is a very concern topic in the field of the science and technological development. [1].

Chromium, as all the transition metals, has various oxidation states[2], being the most stable and frequent species trivalent and hexavalent chromium. Chromium (VI) is considered a very toxic and carcinogenic compound [2].

Several methods to remove chromium (VI) from wastewater have been reported, being the photocatalytic reduction to chromium (III) using semiconductor materials an interesting, green, and low cost alternative [3].

Calcium hydroxyapatite (HAp) is a material widely used in biomedicine, for bone implants manufacture, due to its biocompatibility, but in the last years, hydroxyapatite has been reported as an effective photocatalyst for organic compounds degradation in aqueous phase [4]. In this work the results of Cr(VI) photoreduction using hydroxyapatite synthesized as photocatalyst in presence of UV light are presented.

## Material and Methods

Hydroxyapatite was synthesized by a novel variant of the sol-gel method, where a tetrahydrate calcium nitrate solution ($Ca(NO_3)_2{\cdot}4H_2O$) 1M was prepared and labeled as "A" solution, and a second solution of orthophosphate trisodium ($Na_3PO_4{\cdot}12H_2O$) 1M was marked as solution 'B'. Under slow conditions, solution A was incorporated into solution B using a calculated ratio capable to get a hypo-stoichiometric hydroxyapatite, with the formula $Ca_5(PO_4)_3(OH)$; the pH of the resulting solution was maintained at 10, keeping under constant stirring for 24 hours at room temperature.

Synthesized hydroxyapatite was characterized by X-ray diffraction (XRD), The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method and the band gap values were obtained from the dates of Diffuse reflectance spectra (DRS). The photocatalytic behavior of HAp was evaluated in the photoreduction of Cr (VI) in aqueous solution (40 ppm).

The reaction was carried out using 200 mg of photocatalyst in 200 mL of a previously prepared solution of potassium dichromate, which was irradiated with a Hg lamp with a maximum wavelength emission at 254 nm (4.2 mW) placed in the center of the reactor into a Pyrex cylindrical. The advance of the reaction was follow taking aliquots (4 mL) every 15 minutes. The content of Cr (VI) in the solution was determined following the signal at 236 nm, using an UV Vis spectrophotometer.

## Results and Discussion

From the XRD analysis, the main peak of the hydroxyapatite, with the greatest intensity at 2θ = 31.5 corresponding to the plane (211), accompanied by portions of lower intensity at 2θ = 32 and 2θ = 33 corresponding to the planes (112) and (300) respectively and some secondary peaks at 2θ = 25.5 corresponding to the plane (002), 2θ = 34 corresponding to the plane (202), 2θ = 39.5 corresponding to the plane (-380), 2θ = 41.5 corresponding to the plane (222) and 2θ = 49.5 corresponding to the plane (-163); characterizing this phosphate as a pure hydroxyapatite. (Fig 1).

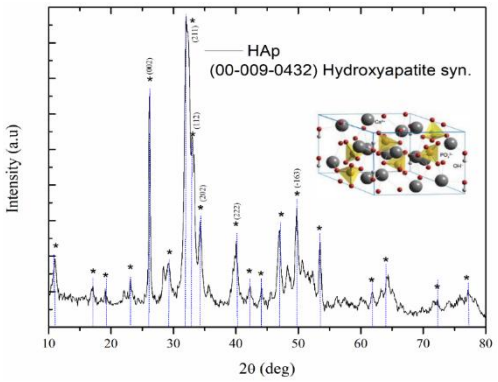


**Figure 1.** X-ray diffraction of of the synthesized sample HAp and simulated structure HAp CoS materials.

In Figure 2 is possible to observe that the photoreduction occurs slowly when the reaction was carried out at pH = 4.2 (pH of the natural medium, without any adjust), using only potassium dichromate solution and hydroxyapatite photocatalyst without adding any sacrificial agent, reaching 70% of Cr (VI) photoreduction in 75 min.

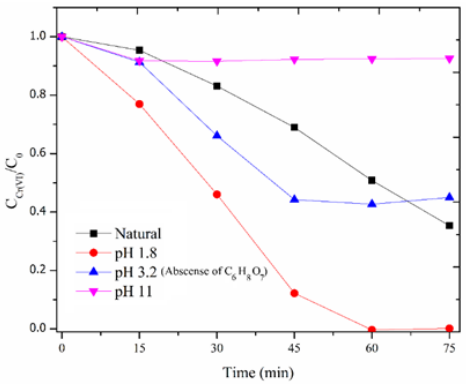


**Figure 2.** Effect of pH in the solution in the Cr(VI) photoreduction using HAp as photocatalyst.

In order to evaluate the stability of HAp as photocatalyst, the material was evaluated by several cycles, and the results were compared with those obtained with commercial Degussa P-25 $TiO_2$, used as a reference photocatalyst, showing HAp photocatalyst an evident superior performance (Fig. 3)

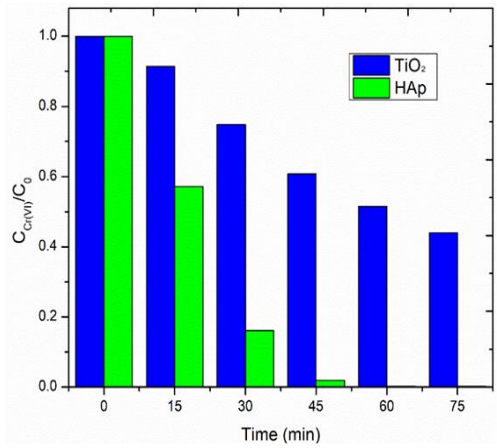


**Figure 3.** Comparison of the performance of HAp as a photocatalyst against commercial Degussa P-25 $TiO_2$ photocatalyst.

## Conclusions

High Cr(VI) photoreduction was reached using synthetic hydroxyapatite obtained by a single sol gel method at mild conditions as photocatalyst. The results were more evident when the pH values were adjusted to acid form. These results of reaction, in addition to the easy, low cost and clean synthesis method, allow us to propone HAp as an excellent material to be used as an active photocatalyst for Cr(VI) photoreduction.

***Acknowledgments***

Authors thank financial support of the IPN SIP 20240548 and CB-285711 projects.

***References***

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