

## Study of sunlight degradation of methyl orange in wastewater using the CuCrO<sub>2</sub>/ TiO<sub>2</sub> heterosystem

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### Abstract

*CuCrO<sub>2</sub> is prepared by sol-gel method. The powder as prepared was characterized by X-ray diffraction, scanning electron microscopy and UV-Vis diffuse reflectance. The microstructure is fairly homogeneous with an average crystallite size. The optical deviation (1.87 eV), determined from the diffuse reflectance, is well suited for its use as a photocatalyst. In application, the photo-degradation of an orange methyl dye (12 mg / L) is carried out successfully in a suspension of CuCrO<sub>2</sub> / TiO<sub>2</sub> (1/1). CuCrO<sub>2</sub> is photoactivated by visible light and the electrons of the conduction band are injected into TiO<sub>2</sub>. In the presence of oxalic acid as a hole sensor, a total degradation of methyl orange MO is obtained under optimal conditions (pH 6 and T = 25 °C).*

**Key Words:** CuCrO<sub>2</sub> /TiO<sub>2</sub>, Photo-degradation, methyl orange, Sol-gel process

### Etude de la dégradation de méthyle orange dans les eaux usées par la lumière solaire à l'aide de l'hétérosystème CuCrO<sub>2</sub> /TiO<sub>2</sub>

### Résumé

*CuCrO<sub>2</sub> est un délaftisite élaboré par la méthode sol-gel. La poudre telle que préparée a été caractérisée par diffraction des rayons X, microscopie électronique à balayage et réflectance diffuse UV-Vis. La microstructure est assez homogène avec une taille moyenne de cristallite. L'écart optique (1,87 eV), déterminé à partir de la réflectance diffuse, est bien adapté pour son utilisation comme photocatalyseur. En application, la photo-dégradation d'un colorant de méthyle orange (12 mg /L) est réalisée avec succès dans une suspension de CuCrO<sub>2</sub> / TiO<sub>2</sub> (1/1). CuCrO<sub>2</sub> est photoactivé par la lumière visible et les électrons de la bande de conduction sont injectés au TiO<sub>2</sub>. En présence d'acide oxalique comme capteur de trou, une dégradation total de méthyle orange (MO) est obtenue dans des conditions optimales (pH 6 et T=25 °C).*

**Mots clés :** CuCrO<sub>2</sub>/TiO<sub>2</sub>, Photo-dégradation, méthyle orange, méthode sol-gel).

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## INTRODUCTION

CO<sub>2</sub> emissions have been identified as the main cause of current climate change [1], emissions due to the increasing consumption of "fossil" energy sources such as coal, oil or natural gas. In addition, in order to respond to this major concern regarding the emission of greenhouse gases, a large number of research studies have been aimed for several years at developing the use of energy sources making it possible to produce less CO<sub>2</sub>, or even to stop this production. Drug residues released into our excreta (urine feces) are most likely the main source for most of the products. The concentration in urban wastewater entering the treatment plant correspond substantially to the one which is measured in the urine multiplied by the ratio between the daily volume of urine and the total volume of water discharged. These discharges are purified and some of the active molecules can be stopped at the treatment plant, but not all [2].

Industrial rejection seems to be very difficult to achieve in drug production facilities (process water, wash or drain water, etc.). Even if the losses are minimal, the large quantity of products manufactured or which is handled leads to significant losses to the environment. On a global scale, this contribution is probably small, but the effects can be very significant in aquatic environments immediately downstream of the facilities [3]. Methyl orange is a solution for cutaneous application but the rejection of this drug in the environment likely to have undesirable effects, by its very strong visible color [4].

The photocatalytic process is based on the excitation of a semiconductor (SC) by light radiation, corresponding to an energy greater than or equal to the width of its forbidden band, under light excitation, the electrons (e-) of the valence band (BV) of the SC pass to the conduction band (BC), leaving a positive charge or hole (noted h+) in the BV. These electron / hole pairs can recombine by releasing heat, or react separately with other molecules present in the medium.

Heterogeneous photocatalysis is based on absorption, by a semiconductor, photons of equal energy or greater than the width of the forbidden band (Ec-Ev), which allows electrons to pass from the valence band (Ev) to the conduction band (Ec). Gaps electronic, commonly called holes (or "holes", h+) are thus generated in the valence band and a redox system is created. If their lifespan allows, electrons can be transferred to electron acceptors, while the holes can be fulfilled by electron donors [5, 6]. Provided that the resulting chemical species react before reverse electronic transfers do not take place, generate so-called photocatalytic chemical transformations canthus.

Since molecular oxygen O<sub>2</sub> is the electron acceptor more likely, it can be reduced to a superoxide anion radical O<sub>2</sub><sup>•-</sup> or, depending on the pH, in its protonated form, the radical hydroperoxyl HO<sub>2</sub><sup>•</sup> (pKa = 4.7). These radicals are less reactive than the HO<sup>•</sup> radical with respect to compounds organic. However, they can react to each other to form hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>, or the radical hydroxyl HO<sup>•</sup> by successive reductions. However, the most direct way of formation of the radical HO<sup>•</sup> is hole oxidation of adsorbed H<sub>2</sub>O or OH<sup>-</sup> ion. This radical, one of the most reactive and least selective [7], attacks most molecules by providing other radicals, which react with O<sub>2</sub>. In addition, the organic compounds, P, which have an oxidation-reduction potential greater than EV, can behave as electron donors, which generally leads to the formation of a P<sup>•+</sup> cation radical. The latter is likely to react then, eg with H<sub>2</sub>O, O<sub>2</sub><sup>•-</sup> and O<sub>2</sub>, or even to deprotonate itself if it is very acidic. Finally, cations (aqueous solution) and some organic compounds like CCl<sub>4</sub> or others halomethanes can be reduced if their potential redox is less than EC.

Photocatalytic treatment is therefore a technology of choice for the depollution and integration of this wastewater because it is a powerful system, simple and economical. These different attractive features have generated as a great deal of interest from researchers for the understanding, optimization and industrial application of this process [8]. This research project aims to study the efficiencies of the photocatalytic process to treat methyl orange -contaminated wastewater by using a new CuCrO<sub>2</sub> / TiO<sub>2</sub> heterosystem irradiated with photons of natural light.

## MATERIALS AND METHODS

CuCrO<sub>2</sub> is synthesized by sol-gel method according to the following reaction path:

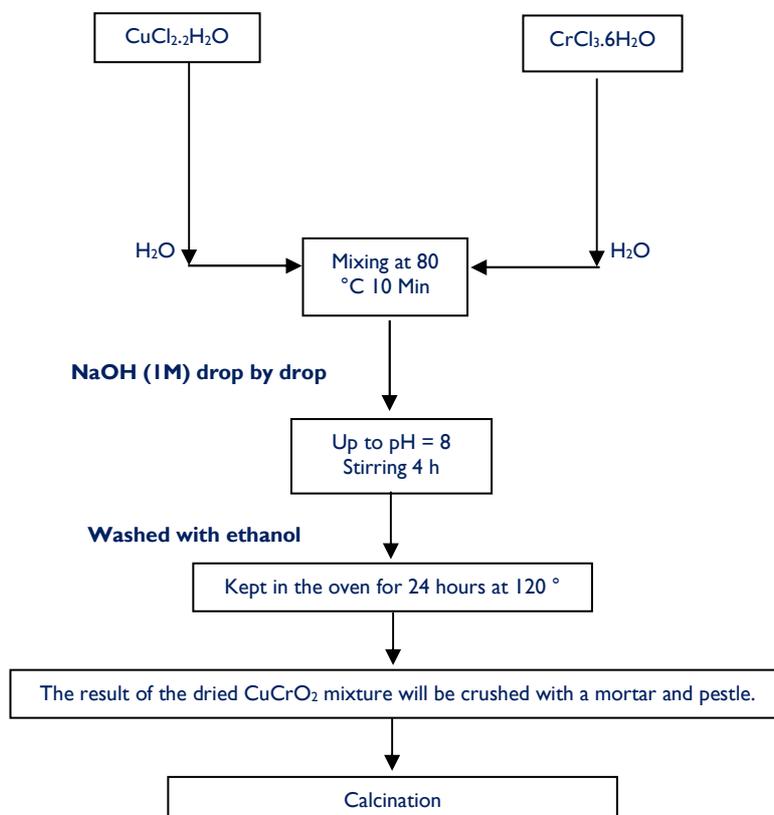
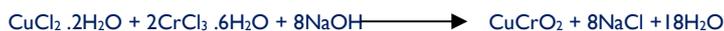


Fig. 1 – Elaboration of CuCrO<sub>2</sub> by sol-gel method.

Copper (II) and Chrome (III) chloride are dissolved in water with adequate amounts. The mixture is left with magnetic stirring at a temperature of 80 ° C for 10 min, after adding sodium hydroxide (1M) dropwise until a pH = 8, leaving stirring until the formation of a gel. After rinsing with ethanol, the gel will be dried in the oven, in order to obtain an amorphous powder. At the end, the calcination will be carried out in ( 750 °C / 3h) to get the finished product. However, for TiO<sub>2</sub> we will use a commercial product in this experiment.

X-ray powder diffraction (XRD) data were collected at room temperature (RT) using a Brüker D8 Advance diffractometer working in Bragg-Brentano reflection geometry with a Cu anode X-ray source, a focusing Ge(111) primary monochromator (selecting the Cu K $\alpha_1$  radiation) and a 1-D position-sensitive detector ("Vantec" detector). Data were collected in the range 2 $\theta$  =20-90°, with a 0.02° step and a 10 s counting time per step.

The diffuse reflectance spectrum is recorded with a UV-VIS spectrophotometer (Specord 210 Plus) equipped with an integrating sphere, PTFE is used as standard. The Scanning Electron Microscopy (SEM) was performed on a FEG-SEM JEOL 7600 in order to evaluate the size distribution as well as the morphology of the nanoparticles.

## RESULTS AND DISCUSSION

### Characterisation

X-ray powder diffraction (XRD) data were collected at room temperature (RT), the pure phase (Fig.2.a) is confirmed in an agreement with the literature [9].

The width of the forbidden band ( $E_g$ ) (Fig.2.b) is determined from the abscissa of the point of inflection ( $\lambda_0$ ) of the diffuse reflectance curve as a function of the wavelength.

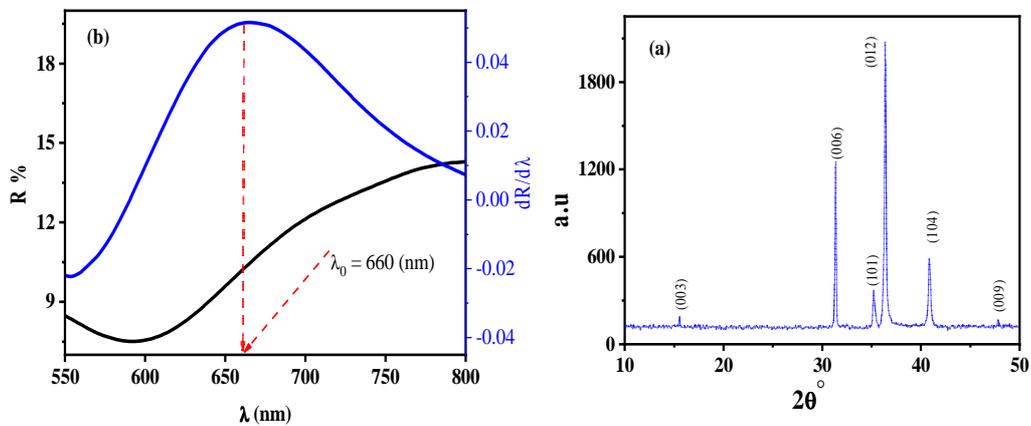


Fig. 2 – a) X-ray diffraction of  $\text{CuCrO}_2$ ; b) The diffuse reflectance spectrum of  $\text{CuCrO}_2$ ;

The width of the forbidden band ( $E_g$ ) is deduced from the coordinates of the point of inflection of the curve. This point corresponds to the maximum of the derivative of this curve. The inflection point is located at  $\lambda_0 = 660$  (nm), which gives  $E_g = hc/\lambda_0 = 1.87$  (eV).

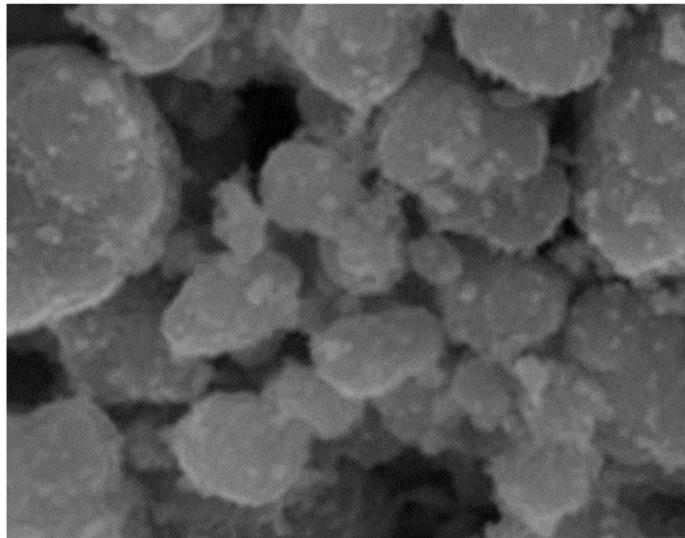


Fig. 3 – Scanning Electron Microscopy of  $\text{CuCrO}_2$

Fig 3. Shows the FEG-SEM images of the  $\text{CuCrO}_2$  powder. The images obtained of  $\text{CuCrO}_2$ , produced by the sol-gel method show particles formed from homogeneous and uniform grains.

### Photo catalysis

The reaction mechanism of photo-catalytic degradation of methyl orange catalyzed by the hétérosystème  $\text{CuCrO}_2/\text{TiO}_2$  shows that the electrons of the conduction band ( $e^-$ ) and the holes of the valence band ( $h^+$ ) are generated when the suspension of the latter is irradiated with a higher luminous energy than its energy of band gap ( $E_g = 1.87 \text{ eV}$ ). The photo-generation of electrons from  $\text{CuCr}_2\text{O-CB}$  may reduce the dye or react with acceptor electrons such as  $\text{O}_2$  adsorbed on the surface of the catalyst or dissolved in water by reducing it to a superoxide radical  $\text{O}_2^-$  anion (Fig. 4).

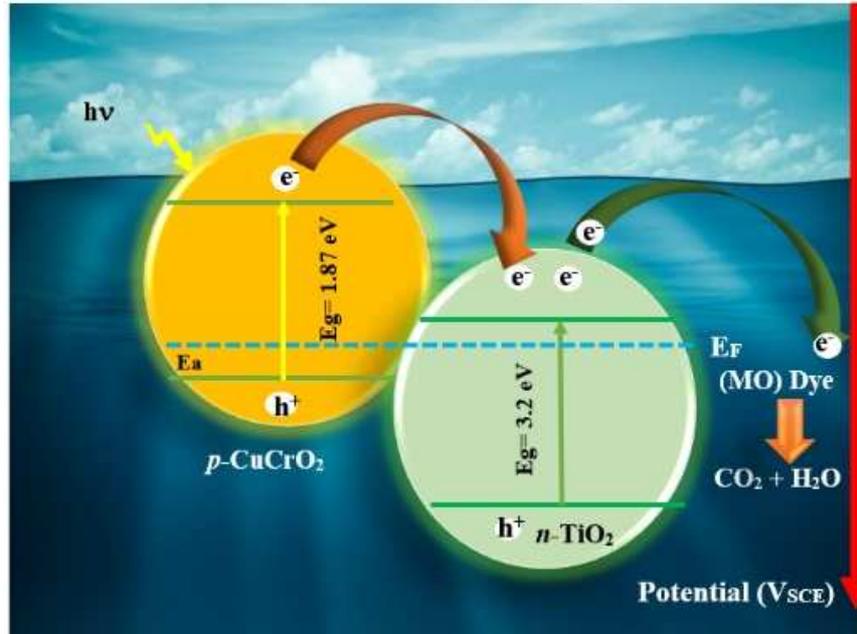


Fig. 4 – The energy band diagram of the hetero-system  $\text{CuCrO}_2/\text{TiO}_2/\text{MO}$  electrolyte

The relevant reactions at the surface of our catalyze causing the degradation of the methyl orange dye can be expressed as follows:



The results of treatment (Fig. 5) of MO were followed by UV-visible on a Shimatzu 1800-type device using quartz cells. Absorbance measurements are made at ( $\lambda_{\text{max}} = 464 \text{ nm}$ ).

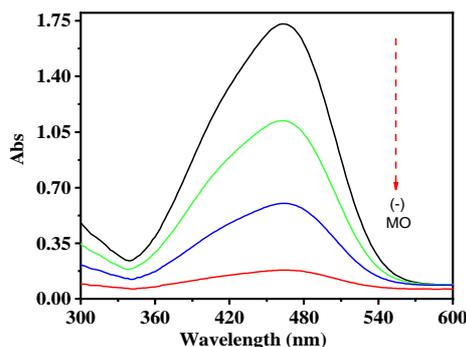


Fig. 5– Photo catalytic degradation of MO (12 mg / L) under CuCrO<sub>2</sub> / TiO<sub>2</sub>

## CONCLUSION

The main objective of this work is the sensitization of CuCrO<sub>2</sub> in the visible domain with a view to the realization of heterogeneous photocatalysis in this spectral domain for the purification of water loaded with organic compounds, in this case dyes. In order to achieve this objective, XRD analysis shows single phase formation. An E<sub>g</sub> value of 1.87 eV was obtained with a direct optical transition. CuCrO<sub>2</sub> was used as a photocatalyst for the detoxification of Methylene orange which was used as a model compound. It can be concluded that the degradation of MO is not directly related to the intensity of solar radiation, but to the presence of catalyst, a total degradation of 12 mg / L as the initial concentration of this model compound was observed at pH = 6 and a temperature of 25 ° C after 4 hours of irradiation.

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