

Evaluation of the Discoloration of Methyl Orange Using Black Sand as Semiconductor through Photocatalytic Oxidation and Reduction

P. Acosta-Santamaría, A. Ibatá-Soto, A. López-Vásquez

Abstract—Organic compounds in wastewaters coming from textile and pharmaceutical industry generated multiple harmful effects on the environment and the human health. One of them is the methyl orange (MeO), an azoic dye considered to be a recalcitrant compound. The heterogeneous photocatalysis emerges as an alternative for treating this type of hazardous compounds, through the generation of OH radicals using radiation and a semiconductor oxide. According to the author's knowledge, catalysts such as TiO₂ doped with metals show high efficiency in degrading MeO; however, this presents economic limitations on industrial scale. Black sand can be considered as a naturally doped catalyst because in its structure is common to find compounds such as titanium, iron and aluminum oxides, also elements such as zircon, cadmium, manganese, etc. This study reports the photocatalytic activity of the mineral black sand used as semiconductor in the discoloration of MeO by oxidation and reduction photocatalytic techniques. For this, magnetic composites from the mineral were prepared (RM, M1, M2 and NM) and their activity were tested through MeO discoloration while TiO₂ was used as reference. For the fractions, chemical, morphological and structural characterizations were performed using Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX), X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) analysis. M2 fraction showed higher MeO discoloration (93%) in oxidation conditions at pH 2 and it could be due to the presence of ferric oxides. However, the best result to reduction process was using M1 fraction (20%) at pH 2, which contains a higher titanium percentage. In the first process, hydrogen peroxide (H₂O₂) was used as electron donor agent. According to the results, black sand mineral can be used as natural semiconductor in photocatalytic process. It could be considered as a photocatalyst precursor in such processes, due to its low cost and easy access.

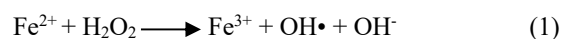
Keywords—Black sand mineral, methyl orange, oxidation, photocatalysis, reduction.

I. INTRODUCTION

NOWADAYS, there is an incremental concern about the damages produced by the industry to the environment, because of the fact that they added recalcitrant and harmful compounds to water streams which can produce several illness to human health. One of them is the MeO. It is used to prepare pharmaceutical products and dyes in textile industry as well. Nevertheless, these dyes are known as hazardous compounds owing to their high stability in environment. Therefore, conventional processes of treating wastewater are not efficient

because they do not remove organic compounds completely or they can generate secondary pollutants and need an additional treatment [1]. Advanced oxidation processes (heterogeneous photocatalysis) could be an alternative to treat recalcitrant compounds through the generation of •OH radicals, they are capable of oxidizing many organic compounds using radiation and a semiconductor oxide.

In order to obtain an increase in the degradation rate of anionic organic substances [2]-[4], TiO₂ is mixed with Fe(III) salts. This is due to the generation of hydroxyl radicals which help reduce Fe(III) to Fe(II)[5]-[7]. Also, the addition of an electron donor agent such as H₂O₂ through its oxidation can form the Fe(III) ion (1) [8]:



Doping TiO₂ structure with different metals also could improve its photocatalytic performance by effective charge transfer from the doping metal-ions to Ti ions [9]-[11]. The photocatalytic reduction of MeO on Au/ TiO₂ semiconductor was carried out with different gold contents with good results [12]. Nevertheless, the preparation of the photocatalyst presents economic limitations on industrial scale, although the solar energy represents a good economic alternative [13].

An alternative to doped catalyst is the application of geocatalysis or heterogeneous catalysis on mineral surfaces as an option to degrade contaminant compounds present in water sources [14]. For instance, minerals such as sphalerite and ilmenite are capable of degrading chlorinated carbon compounds [15], [16], and the volcanic soil could be the base of TiO₂, because it showed a high percentage of degradation of organic compounds [13].

Black sand mineral recovered from Colombian beaches (Santa Marta) has, in its structure, different compounds (Al₂O₃, TiO₂, Fe₂O₃, SiO₂, etc.) that can help to improve the photocatalytic reduction or oxidation of organic compounds [17], [18]. So, in this study, the photocatalytic activity of the MeO using black sand mineral as semiconductor, under artificial UV-Vis light, through photocatalytic oxidation and reduction was evaluated.

II. EXPERIMENTAL

A. Semiconductor Preparation

Black sand was separated in several composites using two different magnetic fields in order to obtain M1, M2, and NM

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(non-magnetic) fractions. The fraction which was not attracted by any magnetic field was called raw material (RM).

B. Black Sand Characterization

The analysis for black sand and its fractions were carried out by chemical, morphological, and structural characterization. The morphology was studied by SEM, the crystalline phases through XRD while the chemical composition was determined by XRF and Energy Dispersive X-Ray Analysis (EDX). Optical characterization was carried out by UV-Vis DRS and the determination of the gap band energy means of Tauc plot.

C. Photocatalytic Oxidation of MeO

Black sand mineral as semiconductor was evaluated in the photocatalytic oxidation of MeO in aqueous suspension containing 20 ppm of MeO and pH=2. The heterogeneous reaction was carried out in an immersed well quartz photoreactor (Ace Glass Inc.) equipped with a cooling tube, with 150 mL and 1 g/L of dosage of catalyst and 10 mmol of H₂O₂ was added after 30 minutes of treatment to improve the photocatalytic activity of the mineral [8], [15], [19]. The treatment was carried out during three hours under UV-Vis irradiation ($\lambda=310$ nm) in magnetic stirring with 30 minutes without light at the beginning of the reaction owing to reach adsorption/desorption equilibrium. The reaction was carried out at acid conditions so pH of the solution was adjusted with HCl solution [20]. MeO samples were withdrawn from the reactor with the semiconductor based mineral being removed from the liquid phase by centrifugation. The degradation kinetic was evaluated by measuring the disappearance of the signal of MeO at $\lambda=507$ nm every half hour with a UV-Vis Shimadzu 2600 spectrophotometer.

D. Photocatalytic Reduction of MeO

Black sand mineral semiconductor was evaluated in the photocatalytic reduction of MeO in aqueous suspension containing 20 ppm of MeO and pH=2 in an immersed well quartz photoreactor (Ace Glass Inc.) equipped with a cooling tube, with 150 mL and 1 g/L of dosage of catalyst.

Photoreduction reactions were carried out under bubbling of nitrogen supplied at a constant rate of 100 mL/min by means of a mass flow controller to remain the photocatalyst in suspension. The treatment was carried out during three hours under UV-Vis irradiation ($\lambda=310$ nm) in magnetic stirring.

The concentration of the substrate after equilibration was measured and taken as the initial concentration (C_0) and at the end of the treatment (C_f). MeO samples were withdrawn the upper part of the reactor with the photocatalyst based mineral being removed from the liquid phase by centrifugation. The photoreduction of the reaction was determined by measuring the disappearance of the signal of MeO at 507 nm as a function of time with a UV-2600 Shimadzu spectrophotometer in the aqueous solution.

III. RESULTS AND DISCUSSION

A. Chemical Characterization

According to XRF analysis, the principal components present in black sand were Fe₂O₃, TiO₂, SiO₂ and Al₂O₃, in their order. Iron oxide is the most representative compound in almost all fractions and in all cases, it exceeds the amount of titanium dioxide present in the samples being common in these kind of "black sands" [13], [17]. NM fraction has high percentage of silica and aluminum oxides. The fraction M2 has high percentages of iron and titanium oxide (higher than the other fractions), which could explain the discoloration's degree obtained. On the other hand, M1 fraction is characterized by a very high presence of iron oxides (87%) in contrast to a very low presence of other compounds like TiO₂ (4%).

The elemental composition by weight percent and atomic percent was determined by EDX analysis, confirming the above results, thus, the black sand, is composed by iron, titanium, silica and oxygen. The relationship between these elements is different for all fractions, thus, M1 is mostly composed by iron, M2, by iron and titanium and NM by silicon and zircon.

B. Morphological and Superficial Characterization

Likewise, based on SEM micrographs, the mineral fractions were composed by irregular grain sizes between 50-200 μ m. These were marked by sharp edges, likely created by sedimentary processes during many time when there were dragged to the beach. The raw material is a heterogeneous mixture of diverse textures like rounded grains and rough structures.

C. Structural Characterization

Crystalline phases confirmed the presence of silicates (quartz and cristobalite), titanium dioxide like rutile, and several iron oxides such as magnetite, ilmenite, and hematite. For example, at M2 fraction there are large amounts of iron oxides as the ilmenite phase and the RM fraction have most representation of ilmenite, minimal phase intensity in M1.

Tauc plot was used to determine the band gap (direct and indirect transition ($n=1/2$ and $n=2$, respectively)). In general, for all fractions the band gap was between 2.95 and 3.0 eV. Based on literature, these values were according to ilmenite (2.90 eV), wustite (1.0 eV) and Fe₃O₄ (0.1 eV) [16], [21].

D. MeO Photocatalytic Oxidation

The discoloration's degree due to change of dye concentration was determined quantitatively by measuring absorbance using UV-vis spectrophotometer (Shimadzu 2600, Japan) using a calibration curve (linear, $R^2 = 0.999$) of the dye solution from standard synthetic dye at several concentrations. UV-Vis absorption spectra showed an absorption band at 507 nm to the discoloration of MeO using black sand mineral as catalyst in oxidation technique. Under acidic conditions, appear a new peak about 247 nm assigned to hydrazine derivate [12]. Fig. 1 showed the discoloration of MeO using

M2 fraction with which best percentage of discoloration was obtained with 91.22%.

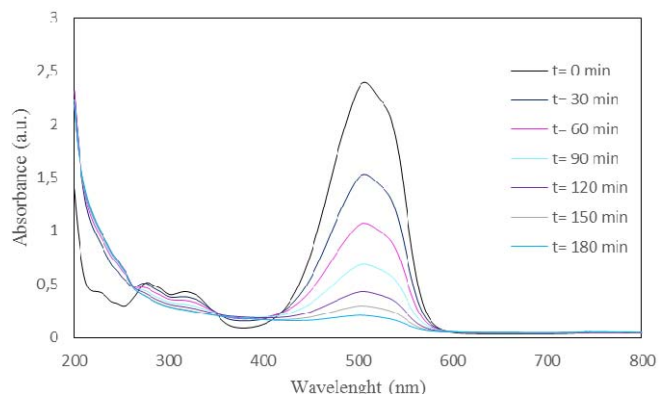


Fig. 1 UV-Vis spectra as a function on time for discoloration of MeO at 20 ppm with M2 fraction (pH=2, $\lambda=507$ nm)

The photolysis of MeO was made with the same conditions than the others fractions but without catalyst and no significant discoloration was observed in the absorption band with 12.65% (Fig. 2). As well as photolysis of MeO adding H_2O_2 with 25% (Fig. 3) which may indicate that de discoloration is achieving by the photocatalyst. The reaction of MeO without UV-Vis was carried out and no discoloration was observed either.

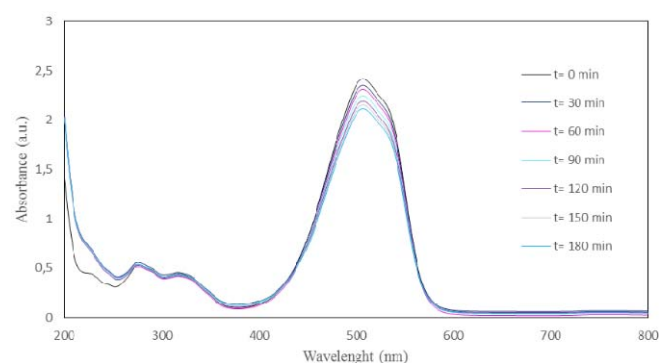


Fig. 2 UV-Vis spectra of MeO without catalyst or H_2O_2 (Photolysis) (pH=2, $\lambda=507$ nm)

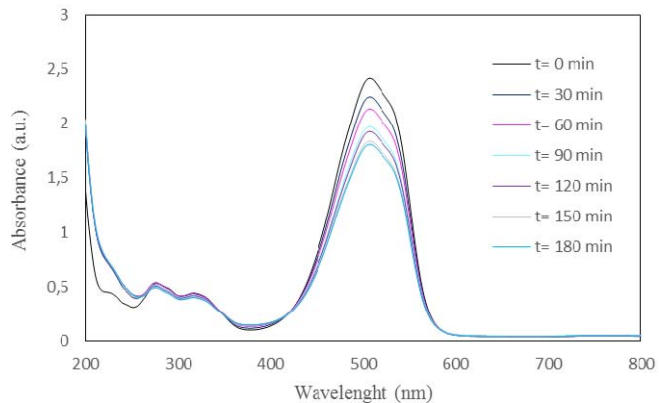


Fig. 3 UV-Vis without catalyst, with H_2O_2 (pH=2, $\lambda=507$ nm)

The photocatalytic oxidation of MeO was carried out with TiO_2 as semiconductor to evaluate the photocatalytic activity of black sand mineral as an option of catalyst in the photocatalytic oxidation of MeO (Fig. 4). Thus, the discoloration achieved with M2 fraction was very close to commercial TiO_2 .

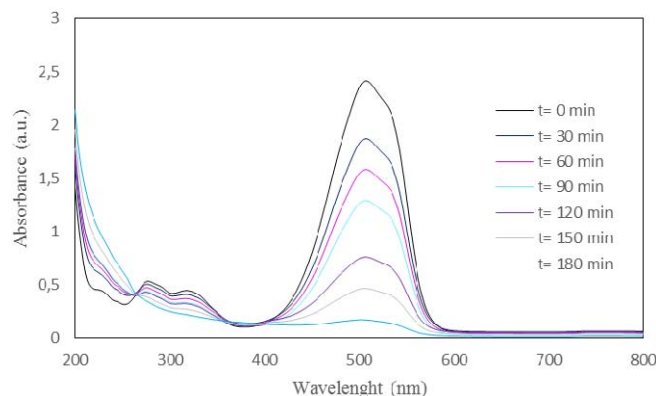


Fig. 4 UV-Vis spectra with TiO_2 semiconductor (pH=2, $\lambda=507$ nm)

Accordingly, the results of the photocatalytic oxidation of MeO with all the fractions and TiO_2 catalyst are shown in Table I.

TABLE I
 DEGRADATION PERCENTAGES OF THE BLACK SAND SAMPLES IN
 PHOTOCATALYTIC OXIDATION

Mineral Fraction	Degradation percentages (%)
M2	91,22
M1	83,61
NM	88,09
RM	82,81
Photolysis with H_2O_2	25,0
Photolysis	12,65
TiO_2	95,2

E. MeO Photocatalytic Reduction

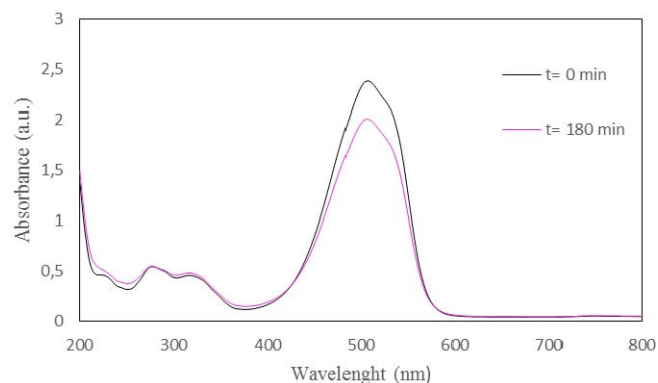


Fig. 5 UV-Vis spectra as a function on time for discoloration of MeO at 20 ppm with M1 semiconductor (pH =2, $\lambda= 507$ nm)

The degradation kinetic for photocatalytic reduction was also evaluated as a function of time of the signal disappearance at the initial concentration and at the end of the treatment by UV-Vis Shimadzu 2600 spectrophotometer. UV-

Vis absorption spectra showed an absorption band at 507 nm to the discoloration of MeO using black sand catalyst. Fig. 5 shows the discoloration of MeO with the M1 fraction, this spectrum corresponds to the best result in reduction with a percentage of 20.02%. Fig. 6 shows the UV-Vis spectra using M2 Fraction with which was obtained a discoloration percentage of 15%. No significant discoloration was obtained from the other fractions of the mineral with this technique RM (8.7%), NM (12.05%).

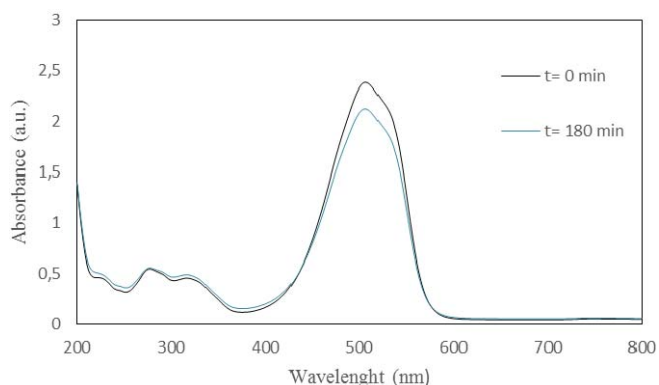


Fig. 6 UV-Vis spectra with M2 semiconductor (pH =2, λ = 507 nm)

The discoloration with TiO₂ as semiconductor showed a similar behavior than the oxidation treatment showed in the Fig. 7. Nevertheless, the degradation percentages of the photocatalytic reduction of MeO with each fraction are shown in Table II.

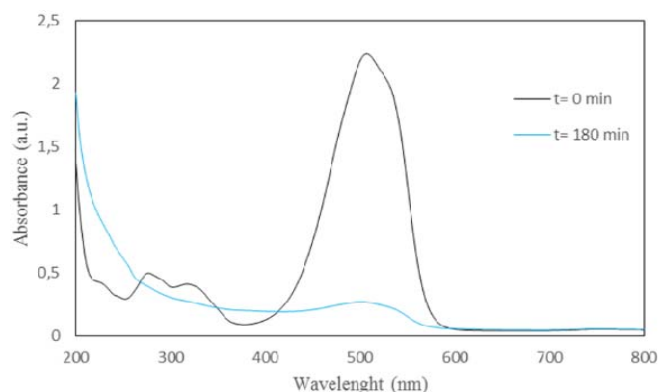


Fig. 7 UV-Vis spectra with TiO₂ semiconductor (pH=2, λ = 507 nm)

TABLE II
DEGRADATION PERCENTAGES OF THE BLACK SAND SAMPLES IN
PHOTOREDUCTION

Mineral Fraction	Degradation percentages (%)
M1	20,02
M2	15,15
NM	12,05
RM	8,7
TiO ₂	94,57

IV. CONCLUSION

These evaluations show the significant contribution of mineral black sand, specifically M2 fraction in the

photocatalytic oxidation of MeO removing hazardous pollutants in different effluents. Giving the importance to the mineral in degradation processes due to its lower costs and a high accessibility of this material in countries like Colombia.

As an acid pH is used and the material black sand has the presence of iron oxides, it is valid to think that there is a photo-Fenton process joined to a heterogeneous photocatalysis because the mineral is not dissolved in the solution in both, oxidation and reduction processes. Also, the photocatalytic oxidation treatment in acidic pH's with the addition of H₂O₂ showed more efficiency in the discoloration of MeO than the treatment of reduction without any electron donor. In both cases, RM fraction corresponding to the part of black sand that was not attracted by any magnetic field was the one that less percentage of discoloration generated, this indicate that the metal compounds present in the sand, has a great influence on the discoloration of MeO and its contribution is significant in contrast to the nonmetallic compounds. Thus, the need for the magnetic separation is checked in order to purge the sand to get higher concentrations of interest photocatalytic materials.

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