

APPLICATION OF CHEMOMETRIC METHODS TO RESOLVE INTERMEDIATES FORMED DURING PHOTOCATALYTIC DEGRADATION OF METHYL ORANGE AND TEXTILE WASTEWATER FROM ETHIOPIA

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ABSTRACT. The efficiency of two catalysts (TiO₂ and TiO₂ supported on zeolite) for the photocatalytic degradation of methyl orange dye and wastewaters from Ethiopian textile industry was evaluated by chemometric methods from UV/Vis data of the reaction mixtures at different times. Multivariate curve resolution statistical analysis combined with an alternating least squares algorithm (MCR-ALS) proved to be an efficient method to resolve the different intermediates present during the photocatalytic degradation of the pollutants and to provide information about their evolution with time. Methyl orange photodegradation at pH = 3 showed different intermediate and concentration profiles than at pH = 6. The evolution of intermediates from textile wastewater photodegradation could also be resolved by this method. From the concentration profile or the reactants, a kinetic study was done. Results revealed that all the photodegradation reactions followed a first order kinetics. When TiO₂ supported in Zeolite is used, reactions are in general slower, probably due to a mechanism of adsorption/desorption.

KEY WORDS: Chemometrics, Dye photodegradation, Wastewater, MCR-ALS, Methyl Orange

INTRODUCTION

It is estimated that more than 700,000 tons of commercial dyes are produced annually [1], from these more than 90% can remain untreated and about 10-15% of them are discharged into wastewater. These effluents carry the potential toxic organic compounds to cause environmental damage. Moreover, they can hinder light penetration and damage the quality of the receiving streams and agricultural fields. In Ethiopia, textile industry is increasingly growing; only in 2011 its consumption of dyes and other chemicals was higher than 14,000 tones [2]. Therefore, there must be an equally growing concern about treatment of the wastewater originated [3].

The technologies used for colour removal can be divided into three categories: biological, chemical and physical [4]. Traditional physical techniques include adsorption, reverse osmosis and ultrafiltration among others; however, these physical processes simply transfer the pollutants from one to another medium causing secondary pollution. Biological processes [5] involving microbiological or enzymatic decomposition and biodegradation are not effective due to the stability of dye molecules [6]. Chemical processes include precipitation, chemical oxidation processes and heterogeneous photocatalytic oxidation. From these techniques, the latter are proposed as an interesting alternative to conventional methods [7, 8].

Among the catalysts used in photocatalysis of dyes, titanium dioxide (TiO₂) is the most common and efficient catalyst. It is relatively inexpensive, non-hazardous and stable [8, 9]. Moreover, it can be easily supported onto other solid matrixes to increase the reusability [2, 10]. Photodegradation mechanism is complex [11]. When the UV-Vis radiation is applied, the

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photoelectron is promoted from the filled valence band of TiO₂ to the empty conduction band. Then the excitation process leaves a photogenerated hole (h⁺) on the valence band. Holes and electrons can migrate to the surface of TiO₂ particles and serve as redox sources that react with adsorbed reactants such as H₂O, O₂ and dye molecules, leading to the formation of superoxide radical anions, hydrogen peroxide and hydroxyl radicals that can oxidize the dye molecules. There are many factors affecting TiO₂ catalyzed photodegradation processes, such as initial load of the sample, amount of catalyst or temperature. pH of the solution has a complex effect on photocatalytic oxidation rates [11-13]. Reaction rates are generally different if the molecule of colorant is in its acidic or alkaline form.

The evolution of dye concentration as a function of reaction time is usually evaluated by UV-Vis adsorption since as reaction proceeds, the colour of the sample disappears. However, discolouration does not mean complete degradation. Dyes generally are formed by chemically stable moieties (aromatic rings). Some fragments obtained from incomplete degradation can still be toxic and they may not absorb within the visible range so, the absence of colour is not a good criterion to consider the treated water free of pollutants. In order to ensure the efficiency of the wastewater treatment it is necessary to design a method to determine the progress of the reaction and to analyze the intermediates formed. Such method must be easy, non-expensive and rapid enough to allow a real-time monitorization. Chromatography coupled with mass spectrometry has been proved to be a powerful technique to determine the intermediates during photocatalytic degradation of different dyes [14-17] but these techniques are time consuming and samples usually require pretreatment. A quicker and easier approach is to record UV-Vis spectra and resolve the intermediates using chemometric methods such as multivariate curve resolution-alternating least-squares (MCR-ALS), and evolving factor analysis (EFA) [17-19].

MCR-ALS has been successfully applied to study the photocatalytic degradation of model dyes and mixtures. It has allowed for example to resolve the time evolution of different intermediates during degradation of Acid Yellow 9 [17] and the effect of several factors on the degradation kinetics [18]. However, we have found no reports in literature about application of such methods in real wastewaters. In this paper, MCR-ALS treatment was applied to UV-Vis spectra to study the efficiency and reaction path of two TiO₂-based catalysts in two different pH media for the photodegradation of Methyl Orange (MO) and wastewaters from a tannery in Ethiopia.

EXPERIMENTAL

Methyl Orange (reagent grade, BDH Chemicals Limited, Poole, England) was used as a dye sample. Commercial nano-size TiO₂ and TiO₂ supported on zeolite were used as catalysts for the photocatalytic reaction. Solutions of 0.1 M H₂SO₄ and 0.1 M NaOH were used to adjust the pH. TiO₂ supported on zeolite (8.5% TiO₂) catalyst was prepared in our laboratory by suspending the zeolite in a solution of titanium(IV) butoxide dissolved in a mixture of 2-propanol and water with volume ratio of 1:10:2 (Ti(OBut)₄ : CH₃CHOHCH₃ : H₂O) then calcined in air at 400 °C for 3 h. Details of the synthesis and full characterization were published elsewhere [2, 20].

The batch reactor is a cylindrical vessel made of quartz glass with a capacity of 0.75 L. It is continuously stirred by a magnetic stirrer and it has an outlet to sample the reacting mixture and to purge the oxygen flow. The source of light is a 150 W UV lamp (Heraeus medium pressure mercury lamp) that is surrounded by a cooling jacket by water recirculation. The lamp and jacket are immersed into the reacting solution.

A solution of 20 mg/L of Methyl Orange (MO) was initially prepared and adjusted to a value of pH such that upon addition of catalyst the final pH was either 3 or 6. MO has a transition pH interval of 3.1-4.4 so pH was chosen to explore the reactivity of MO in the acidic and the basic form.

In a typical experiment 0.045 g of TiO₂ was suspended into 750 mL of MO solution in the reactor. When TiO₂/Zeo is used, 0.5 g was added instead in order to keep constant the amount of

active TiO_2 . A small flow of O_2 was bubbled into the solution. The suspension was stirred for 30 min before irradiation is applied to let any adsorption process to occur. The first sample was taken immediately before the lamp was immersed and then at different time intervals. Sampling volume was ca. 10 mL. The samples were centrifuged for 20 min, the supernatant was carefully separated from the precipitate and the UV-Vis spectra was recorded using a Perkin-Elmer spectrum 65 UV/Vis/NIR double beam spectrophotometer using 1 cm path length quartz cells. Degradation experiments of wastewaters were conducted in a similar way [2] but concentration is difficult to determine since the composition of the water is not known. Total organic carbon for the starting wastewater had been previously determined as 34.2 mg/L [2].

The statistical treatment was done by MCR-ALS algorithm using MATLAB 7.8. In first place, an estimation of the number of components is done using an evolving factor analysis [21] that analyses the evolution of the different factors with reaction time. The number of significant components was estimated visually and set to 4.

The data matrix \mathbf{D} ($m \times 573$) was constructed with columns representing absorbances between 228 and 400 nm inclusive. Rows correspond to spectra at the different time intervals (m). MCR-ALS consists on decomposing the matrix \mathbf{D} as:

$$\mathbf{D} = \mathbf{C} \cdot \mathbf{S}^T + \mathbf{E} \quad (1)$$

Matrix \mathbf{S} (573×4) contains information about the spectra profiles, i.e. for each component. \mathbf{C} ($m \times 4$) is the profile of concentration, that is the concentration of each component in every sample taken at different times. Equation 1 is resolved iteratively to minimize the residual matrix \mathbf{E} . Initial estimation for \mathbf{C} was taken as the EFA profiles. The MCR-ALS algorithm was applied constrained to non-negativity for the concentration and spectral profiles. For reactions of wastewater the number of components resolved was 3.

RESULTS AND DISCUSSION

Degradation of Methyl Orange

Discolouration of MO during the photocatalysis process using TiO_2 catalyst was effectively performed within the first hour since the solution had lost a significant intensity of orange colour. Figure 1 shows the UV-Vis spectra of MO degradation at different times of reaction using TiO_2 at pH = 3 and 6 and TiO_2/Zeo at pH = 3. The characteristic absorption peak intensity for the sample decreases with increasing reaction time. After 240 min of UV irradiation, the absorption peak is totally removed when pure TiO_2 is used as catalyst. However, when using TiO_2/Zeo the decrease of the intensity for the UV-Vis spectra is slower than when using pure TiO_2 catalyst. It must be taken into account that the absorbance at $t = 0$ min is significantly lower when using the supported catalyst. That is because the zeolite is a porous structure with a high surface area. Then, it adsorbs part of the MO within its structure decreasing its concentration in solution [2].

Figure 2 to 4 show the concentration and spectral profiles for the species involved in MO photodegradation resolved by MCR-ALS. They display the typical behaviour of a reaction in different steps. Concentration of MO (black lines) decreases while several intermediate compounds appear at different times and degrade at different rates. Intermediate 1 and Intermediate 2 (red and blue lines, respectively) appear at shorter times, followed by Intermediate 3 (green line) that appears at a longer time. Spectrum of intermediate 1 has a similar shape than MO with their maxima in the visible region but shifted to lower wavelengths. Intermediate 1 then will contribute to the colour of the sample. Intermediates 2 and 3 absorb mainly in the region of UV.

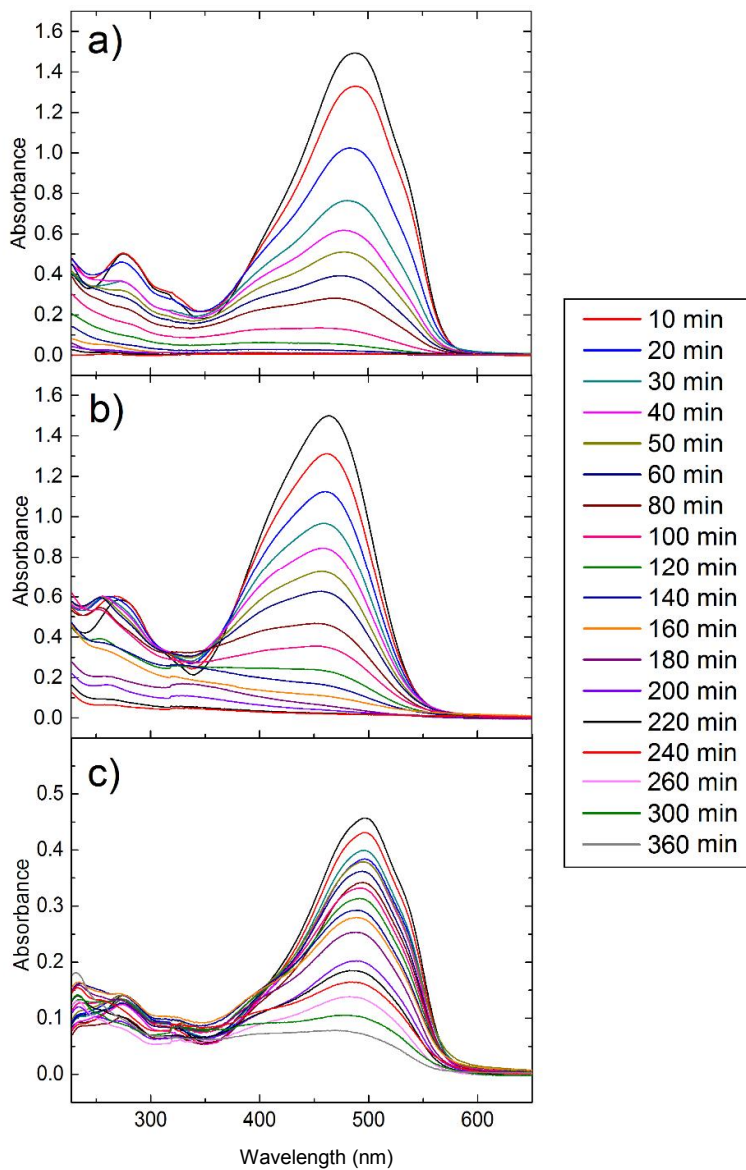


Figure 1. UV-Vis spectra for the photocatalytic degradation of 20 mg/L MO solution at a) pH = 3 with commercial TiO_2 catalyst, b) pH = 6 with commercial TiO_2 catalyst, c) pH = 3 with TiO_2 supported on zeolite catalyst.

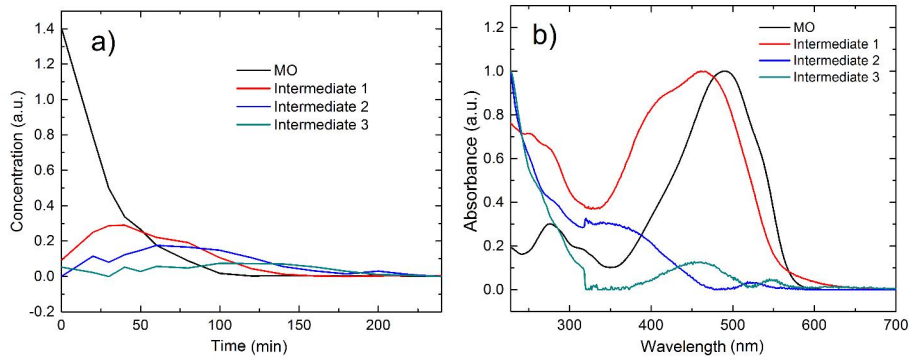


Figure 2. Profiles of the chemical species involved in the photooxidative degradation of MO at pH = 3 using TiO_2 catalyst obtained by MCR-ALS. a) concentration profile and b) spectral profile.

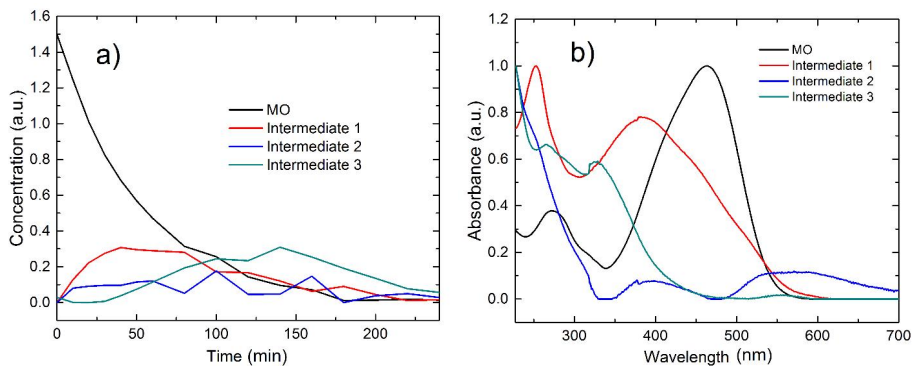


Figure 3. Profiles of the chemical species involved in the photooxidative degradation of MO at pH = 6 using TiO_2 catalyst obtained by MCR-ALS. a) concentration profile and b) spectral profile.

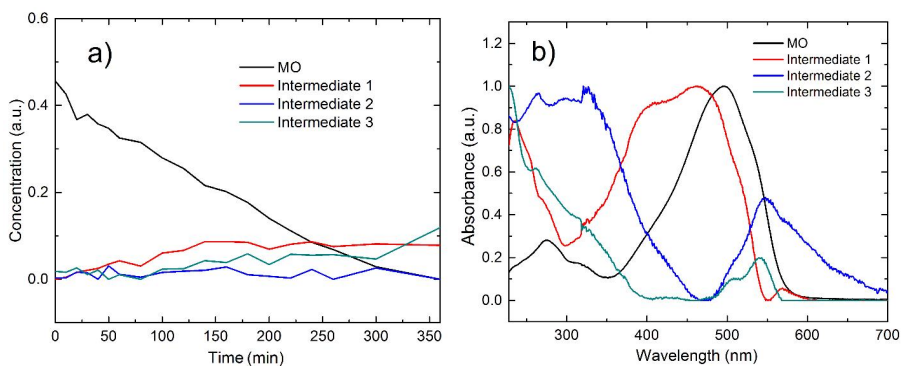


Figure 4. Profiles of the chemical species involved in the photooxidative degradation of MO at pH = 3 using TiO_2 supported on zeolite as catalyst obtained by MCR-ALS. a) concentration profile and b) spectral profile.

However, some differences are observed depending on the reaction conditions. Spectral profiles for Intermediate 1 at pH = 6 show absorbance at lower wavelengths than pH = 3 indicating that photodegradation 3 follows a different path because the reactant and the first intermediate have different structures. Spectral profiles for Intermediate 2 show also significant differences, at pH = 6 it absorbs preferentially in the UV region.

From the concentration profile, the degradation process is completed within shorter time when using TiO₂ catalyst than TiO₂ supported on zeolite (Figure 4). The concentration profile for MO does not disappear until ca. 300 min when using TiO₂/Zeo while concentration of Intermediates 1 to 3 gradually increases with time. It seems that the reaction time was not sufficient to start degrading them since their concentration stay at low values.

The results obtained in this work agree to other reports found in literature. GC-MS analysis of the photodegradation of MO [14, 15] showed that in the first steps, oxidation intermediates similar to MO are detected, and they absorb UV-Vis at lower wavelengths. These intermediates are originated from two possible mechanisms: demethylation of the -N(CH₃)₂ moiety of MO and ·OH attack to an aromatic ring. If the MO is originally in its red form (pH > 4.4), quinonoid intermediates are also possible [15]. Three intermediates from the photodegradation of Acid Yellow 9 were also detected by UV-Vis and MCR-ALS statistical treatment and their concentration and spectral profiles follow behaviour similar to those in this work [17]. According to them, Acid Yellow 9 is oxidized to an intermediate of similar structure that is subsequently split into two smaller aromatic compounds (fragments from the breaking of the azo bond). The same seems to be happening in our case. Intermediate 1 seems to be a molecule that has a similar structure than the starting reactant. Intermediates 2 and 3, however have a UV-Vis profile significantly different to MO, which may indicate fragments that keep a certain degree of aromaticity but with very different structure [17].

Degradation of wastewater

Photocatalytic degradation of a wastewater from a textile industry in Ethiopia using TiO₂ and TiO₂/Zeo was reported previously [2, 20]. Discolouration of wastewaters was evaluated by monitoring the maximum in the UV-Vis spectra. In this work, the spectra were analysed in more detail by applying MCR-ALS algorithm. UV-Vis spectra of the reacting mixture at different times using TiO₂ and TiO₂/Zeo are shown in Figure 5a and 6a, respectively. A MCR-ALS treatment was done to these spectra to resolve them into different intermediates. Figures 5b and 6b show the corresponding concentration profiles. Again, the behaviour is typical of a reaction in different stages as the degradation of MO. Wastewater concentration (black line) decreases quickly with time while a first intermediate appears (red line) in the first minutes of the reaction that starts to decrease again after 240 min of reaction, presumably to a second intermediate (blue line). Concentration for this latter intermediate increases with time and does not reach a maximum. These results, displayed in figures 5b and 6b, suggest a reaction path MO → Intermediate 1 → Intermediate 2.

The concentration profiles obtained when using TiO₂ supported in zeolite as catalyst show a very similar profile but the first stage (MO → Intermediate 1) seems to be slightly slower whereas the second stage (Intermediate 1 → Intermediate 2) goes faster.

These results show that it is possible to analyze the progress of a degradation reaction of wastewaters using a UV-Vis spectrophotometry data coupled to MCR-ALS statistical treatment. This procedure is quick and inexpensive, because as it can be adapted so that the energy is obtained from solar light and it does not require costly facilities. Due to these advantages, new possibilities are opened for real-time monitorization in photocatalytic degradation of wastewater coming from textile industries in Ethiopia.

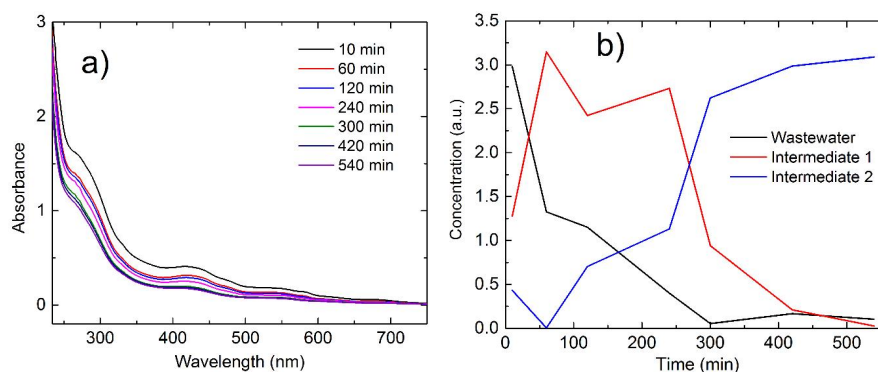


Figure 5. a) UV-Vis spectra for the photocatalytic degradation of real wastewater using TiO_2 . b) Concentration profile of the components resolved by MCR-ALS.

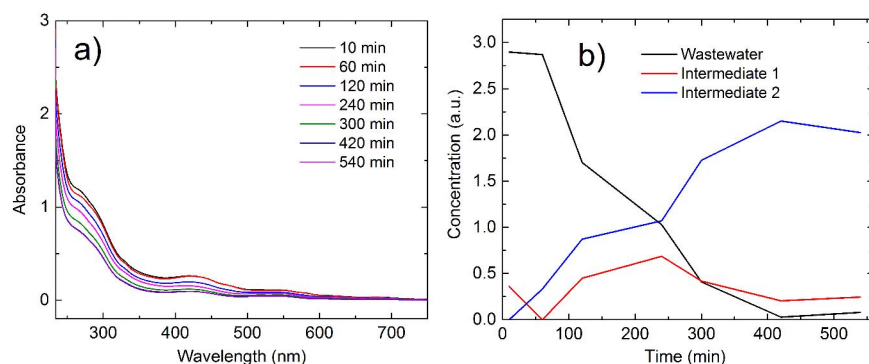


Figure 6. a) UV-Vis spectra for the photocatalytic degradation of real wastewater using TiO_2/Zeo . b) Concentration profile of the components resolved by MCR-ALS.

Kinetic study

Monitoring the absorbance at the maximum of the peak is not a rigorous method to study the kinetics of any degradation because the spectra measured consists of a mixture of intermediates including the starting reactant; these intermediates may absorb at similar wavelengths and bias the absorbance value for the reactant. However, once the contribution of the different components to the UV-Vis spectra has been resolved, it is possible to carry out a rigorous study of the kinetics of reaction for the photodegradation of MO. The evolution of the concentration of MO with respect to time can be obtained from the concentration profiles obtained by MCR-ALS; assuming the absorbance at $t = 0$ corresponds to 20 mg/L for the reactions using pure TiO_2 . Data are displayed in Figure 7.

For the first stage ($\text{MO} \rightarrow \text{Intermediate}$), since there are no other reactants involved and the rest of the parameters that can affect the reaction (irradiation, catalyst concentration, etc) do not vary, the MO degradation can be postulated to follow a general pseudo n -degree kinetics equation:

$$-\frac{dC_{MO}}{dt} = k_n C_{MO}^n \quad (2)$$

Plots of $\ln C_{MO}$ vs t followed a linear trend so the order of the kinetics was $n = 1$ for the three MO degradations. Figure 7 shows the MO concentration obtained from the concentration profiles of MCR-ALS and the fitting to a 1st order kinetics equation. For the degradation of wastewater, the concentration of the dye cannot be determined in absolute units but k_l can be obtained from concentration in arbitrary units by fitting $\ln C/C_0$ vs t . The calculated kinetic constants are shown in Table 1.

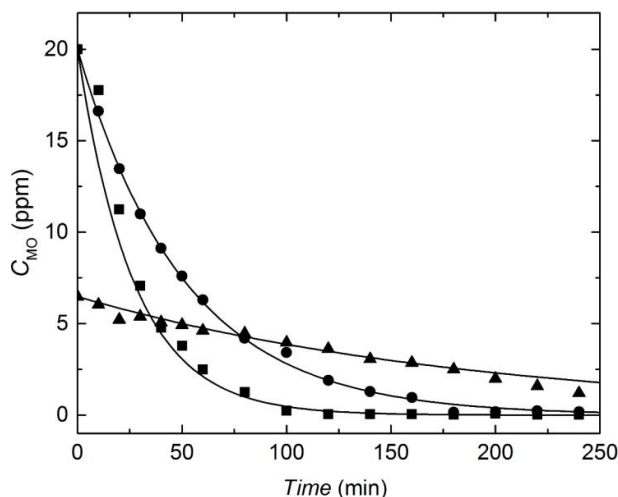


Figure 7. Kinetics for the photodegradation of MO using (—■—): TiO_2 at pH = 3; (—●—): TiO_2 at pH = 6; (—▲—): TiO_2/Zeo at pH = 3.

Table 1. Rate constants for the degradation of MO and wastewater.

Reactant	Catalyst	pH	k_1 (min^{-1})
MO	TiO_2	3	0.0375
MO	TiO_2	6	0.0196
MO	TiO_2/Zeo	3	0.0052
Wastewater	TiO_2	Not measured	0.0068
Wastewater	TiO_2/Zeo	Not measured	0.0062

The reaction for the step $\text{MO} \rightarrow \text{Intermediate 1}$ at pH = 3 is faster as shown in Table 1. Comparing the reaction of degradation of MO at pH = 3 using different catalysts the supported catalyst degrades MO slower than the neat TiO_2 . One must take into account however that there is a first stage of adsorption that decreases significantly the initial concentration of MO. Also, the equilibrium of adsorption/desorption of MO onto zeolite may affect the speed of reaction. Degradation of wastewater is generally slower than degradation of MO probably because the dyes in the wastewater are more stable to photodegradation than MO. The kinetic constant for the degradation of wastewater using supported catalyst is slightly lower than using TiO_2 , unlike what it is observed if only absorbance is monitored [2]. This is consistent to the concentration

profile shown in Figure 6 where the concentration of Intermediate 1 is significantly lower when using TiO₂/Zeo and this intermediate also absorbs in UV-Vis.

CONCLUSION

Multivariate curve resolution-alternating least-squares method (MCR-ALS) was successfully applied to resolve the intermediates of the photocatalytic degradation of methyl orange and real wastewaters of a textile industry in Ethiopia using TiO₂ and TiO₂ supported on zeolite as catalysts. pH values of 3 and 6 were evaluated for comparison. The concentration profiles are typical of a reaction in steps. For the MO degradation, the spectral profiles suggest that the first step yields an intermediate with a similar structure than MO followed by intermediates with a certain degree of aromaticity but much less coloured. Probably fragments from breaking the azo bond. The photodegradation follows a different mechanism depending on the pH. A kinetic study was done from the concentration profile of the reactants. All the reactions followed a pseudo 1st order kinetics. Reactions using TiO₂/Zeo are generally slower but the zeolite support contributes with an adsorption/desorption mechanism.

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