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DEPARTMENT OF CHEMISTRY

Analytical Chemistry Stream
MSc Thesis

APPLICATION OF CHEMOMETRICS METHODS TO RESOLVE INTERMEDIATES FORMED DURING PHOTOCATALYTIC DEGRADATION OF METHYL ORANGE

By
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A thesis submitted to the College of Natural Sciences of Addis Ababa University in partial fulfillment of the requirement for the Degree of Master of Science in Analytical Chemistry.

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As thesis research advisors, we hereby certify that we have read and evaluated this thesis prepared, under our guidance, by Zeyede Aregahegn entitled '*Application of chemometrics methods to resolve intermediates formed during photocatalytic degradation of methyl orange*'. We recommend that it be submitted as fulfilling the thesis requirement.

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As member of the Board of Examiners of the M.Sc. Thesis Open Defense Examination, we certify that we have read, evaluated the Thesis prepared by Zeyede Aregahegn and examined the candidate. We recommended that the Thesis be accepted as fulfilling the Thesis requirement for the Degree of Master of Science in Chemistry (Analytical Chemistry).

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Declaration

I, the undersigned, declare that this thesis is my original work and has been submitted in partial fulfillment of the requirements for the degree of masters of Science at Addis Ababa University. All sources of materials used for this thesis have been duly acknowledged. This paper has never been submitted to and/or presented in any other University, college or institution in candidature of any other degree, diploma, or certificate.

Name: Zeyede Aregahegn

Signature: ______________
Date: ______________

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List of abbreviations and acronyms

MO	Methyl orange
PCA	Principal component analysis
FA	Factor analysis
MCR-ALS	Multivariate curve resolution alternative least square
UV/Vis	Ultraviolet Visible
VB	Valence band
CB	Conduction band
MO	Methyl orange
PCA	Principal component analysis
FA	Factor analysis
MCR-ALS	Multivariate curve resolution alternative least square

Abstract

Application of chemometrics methods to resolve intermediates formed during photocatalytic degradation of methyl orange

Zeyede Aregahegn
Addis Ababa University, June 2016

The efficiency of two catalysts (TiO_2 and TiO_2 supported on zeolite) for the photocatalytic degradation of MO dye has been evaluated by means of chemometrics methods by using UV/Vis spectroscopic data of the degraded dye. This study provides clear evidence about the catalytic efficiency of the two catalysts under UV light irradiation for the degradation of MO dye. MCR-ALS statistical method was used for the catalytic efficiency evaluation. MO photodegradation at pH 3 using TiO_2 catalyst shows better decolorization efficiency than at pH 8 and using TiO_2 supported on zeolite catalyst but the kinetics of MO degradation is quicker at pH 8. For the degradation using TiO_2 at pH = 3, after 150 min of photocatalysis reaction, the species that shows the concentration profile of MO disappears. The kinetics data reveals that the reaction is first order with respect methyl orange in any case.

Key words: Chemometrics, Photodegradation, MCR-ALS, MO and TiO_2.

1. Introduction

1.1. Photocatalytic degradation of dyes

1.1.1. Dyes

Dyes are organic compounds with aromatic ring structures, which have delocalized electron system. Dyes are classified according to their application and chemical structure, and are composed of a group of atoms known as chromophores which are responsible for the color of the dye. These chromophores are parts of a molecule that have electronic bands with energy differences comparable to the energies of the UV-visible light which is then absorbed by them. These chromophore-containing compounds are based on the functional groups, such as azo, anthraquinone, methine, carboxyl, nitro, arylmethane, carbonyl and others. In addition, they contain electrons withdrawing or donating substituent's so as to generate or intensify the color of the chromophores known by their auxochromes. The most common auxochromes are amine, chloride and hydroxyl groups.

It is estimated that more than 100,000 commercial dyes are available to textile industries with over 700,000 tons of commercial dye being produced annually (Jafari *et al.*, 2012), from these more than 90% of reactive dyes can remain untreated and about 10-15% of the synthetic dyes are discharged into wastewater as effluent which carries the potential toxic organic compounds to cause environmental damage. Disposal of the colored wastewater from textile industries into receiving water streams generally may be toxic to aquatic life, they also cause a problem because they may be mutagenic and carcinogenic and can cause severe damage to human beings, such as dysfunction of kidney, reproductive system, liver, brain and central nervous system (Elkady *et al*, 2015).

Textile wastewater contains a large amount of such different dyes and chemicals that make a difficult environmental challenge because of the complexity of chemical composition makes it difficult to be treated (Beyene, 2014). Even though some textile industries treat their wastewater before discharging, the dyes will not completely degrade since these dyes have many aromatic rings in the structure so that it is difficult to degrade easily or they may be changed into another toxic substance during the degradation process. The technologies for color removal can be divided into three categories: biological, chemical and physical (Sahu and Karthikeyan, 2013). All of them have advantages and drawbacks. Traditional physical techniques include activated carbon, adsorption, reverse osmosis and ultrafiltration among others; however, these physical processes simply transfer the pollutants from one to another medium causing secondary pollution. This generally requires further treatment of solid-wastes and regeneration of the adsorbent, which adds more cost to the process. Biological processes involving microbiological or enzymatic decomposition and biodegradation can be used for dye removal (Ajmal *et al.*, 2014). However due to the large group of aromatic rings present in the dye molecules and the stability of the synthetic dyes, such biological degradation processes are not effective for the removal of these dyes from the textile wastewater (Río *et al.*, 2012). Chemical process include chlorination, ozonation, adsorption on organic or inorganic matrices, precipitation, chemical oxidation processes and advanced oxidation processes such as Fenton and photo-Fenton catalytic reactions, H_2O_2/UV processes, and photodegradation through photocatalysis processes. From these techniques photocatalysis is becoming increasingly important since it has a great potential to solve such environmental problems. In recent time, photocatalysis has been investigated by different researchers as this is a very efficient method for wastewater treatment process especially at the textile industries. There are a lot of catalysts used in the photocatalysis process. Among these catalysts titanium dioxide (TiO_2) is the most common and efficient catalyst. It is relatively inexpensive and provides photo-generated holes with high oxidizing power due to their wide band gap energy (Wen-Hsin *et al.*, 2012). Titanium dioxide (TiO_2)-based photocatalytic materials have been used for the decomposition of undesired and harmful organic compounds in the air and water (Kamegawa *et al.*, 2014).

In general, elimination or decoloration of colored wastewaters has been a big challenge over the last decades, and up to now there is no single and economically attractive treatment that can effectively decolorize dyes (Andre, 2007). To solve this problem appropriate and efficient method of degradation must be used in the textile industries and at the same time, control of the dye concentration in effluents and intermediates from degradation needs to be carried out to ensure the efficiency of the wastewater treatment.

1.1.2. The health effects of dyes

Many of the synthetic dyestuffs are chemically stable and difficult to remove by conventional wastewater treatment process, in many cases, textile wastewater is above unacceptable limit, hinders light penetration, damages the quality of the receiving streams and agricultural fields, affect the life of organism. Disposal of the colored wastewater from textile industries into receiving water streams generally may be toxic to aquatic life, they also cause a problem because they may be mutagenic, carcinogenic and can cause severe damage to human beings, such as dysfunction of kidney, reproductive system, liver, brain and central nervous system (Elkady *et al.*, 2015). It is estimated that more than 100,000 commercial dyes are available to textile industries with over 700,000 tons of commercial dye being produced annually (Jafari *et al.*, 2012), from these as more than 90% of reactive dyes can remain untreated and about 10-15% of the synthetic dyes are discharged into wastewater as effluent which carries the potential toxic organic compounds to cause environmental damage.

1.1.3. Mechanisms for photocatalytic dye degradation processes

There are two basic photocatalytic dye degradation mechanisms. These are direct dye degradation mechanism and indirect dye degradation mechanism (Ajmal *et al.*, 2014). But indirect dye degradation mechanism is the most common and efficient whereas direct dye degradation mechanism is a far slowest mechanism.

Semiconductors like TiO_2 are often used as catalytic agents (Šíma *et al.*, 2013) because of their high stability, low costs, and exhibits higher catalytic activity under the UV light irradiation as a result high degradation efficiency and negligible toxicity. TiO_2 is the most investigated photocatalyst and has been found to be capable of decomposing a wide variety of organic and inorganic compounds in both liquid and gas phases (Su *et al.*, 2013).

Direct dye degradation mechanism involves the dye excitation under visible light photon (Hosseinnia *et al.*, 2010; Ajmal *et al.*, 2014). This excited state dye species is further converted into a semi-oxidized radial cation (Dye^+) by an electron injection into the conduction band of TiO_2. The trapped electron then reacted with oxygen to form superoxide radical anions ($O_2^{-\cdot}$) which in turn result the formation of hydroxyl radicals ($OH\cdot$) which is responsible for the oxidation of the organic compounds (Ajmal *et al.*, 2014).

$$\text{Dye} + h\nu \ \square\ \text{dye}^* \qquad (1)$$

$Dye^{*} + TiO_2 \rightarrow dye^{+} + TiO_2$ (2)

Indirect photocatalytic dye degradation process mainly involves four basic steps (Ajmal *et al.*, 2014; Sahu and Karthikeyan, 2013). The photocatalytic dye degradation mechanism is shown in Figure 1.

1. Photoexcitation step. When the UV-Vis radiation is applied to the sample that contains the catalyst, the photoelectron is promoted from the filled valence band of the semiconductor photocatalyst (TiO_2) surface to the empty conduction band as a result of irradiation which absorbs a photon (*hv*). Then the excitation process leaves a photogenerated hole (h^{+}**)** on the valance band of the semiconductor which is active reaction surface.

$TiO_2 + hv\ (UV) \rightarrow TiO_2\ (e^{-}(CB) + h^{+}\ (VB))$ (3)

The photo-generated holes and electrons can migrate to the surface of TiO_2 particles and serve as redox sources that react with adsorbed reactants, leading to the formation of superoxide radical anions, hydrogen peroxide and hydroxyl radicals involved in the oxidation of dye pollution (Su *et al.*, 2013)

2. Ionization of water. In this step, the photogenerated hole at the valance band of the catalyst surface reacts with water or hydroxide ion to produce hydroxyl radical which is a strong oxidizing agent that can attack a dye molecule especially those which is near to the catalyst surface.

$TiO_2\ (h^{+}VB) + H_2O \rightarrow TiO_2 + OH\cdot + H^{+}$ (4)

$TiO_2\ (h^{+}VB) + HO^{-} \rightarrow TiO_2 + OH\cdot$ (5)

3. Oxygen ionosorption. In this step the excited electron in the conduction band $e^{-}(CB)$ is taken up by oxygen and produces anionic superoxide radical ($O_2^{-\cdot}$).

$O_2 + e^{-}(CB) \rightarrow O_2^{-\cdot}$ (6)

4. Protonation of the generated superoxide radical. In this step the superoxide radical is being protonated to form hydroperoxy radical (HOO·) and then subsequently H_2O_2 which further dissociates into highly reactive hydroxyl radicals (OH·).

$O_2^{-\cdot} + H^+ \leftrightarrow HOO\cdot$ (7)

$2HOO\cdot \rightarrow H_2O_2 + O_2$ (8)

$H_2O_2 \rightarrow 2OH\cdot$ (9)

Dye + OH· → degradation products (10)

Dye + h^+(VB) → oxidation products (11)

Dye + e^-(CB) → reduction products (12)

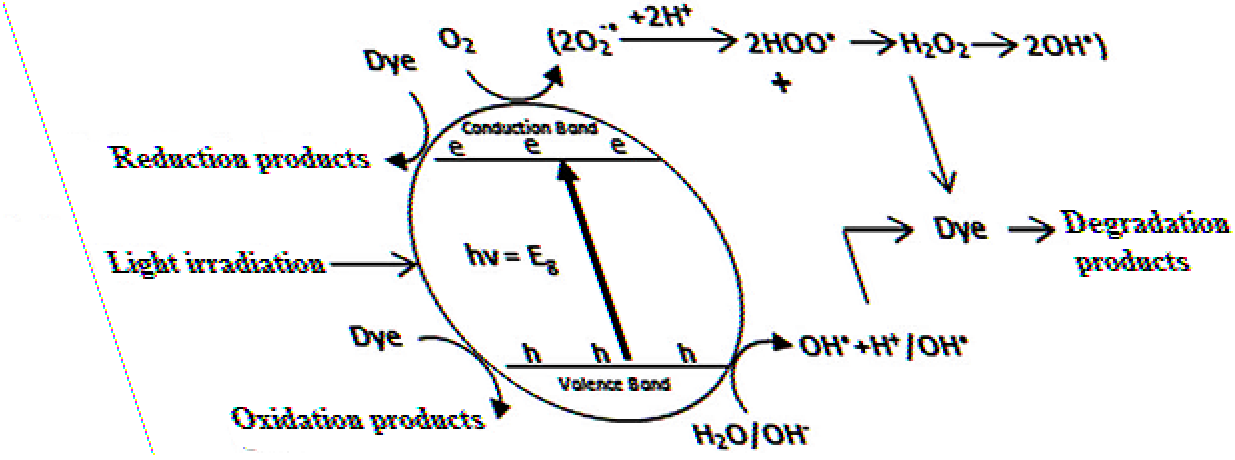


Figure 1: Pictorial representation of indirect dye degradation mechanism (Ajmal *et al.*, 2014).

Under visible light the semiconductor is not excited as its adsorption threshold is in visible region; only the chemisorbed dyes are excited at wavelengths longer than 420 nm to produce singlet and triplet states (Hosseinnia *et al*., 2010). Indirect mechanism generally has advantage over direct mechanism because, direct mechanism is believed to be a far slower reaction compared to indirect mechanism (Ajmal *et al.*, 2014).

There are factors affecting TiO_2/UV light degradation process, some of these factors are, initial load of the sample, amount of catalyst (in which the use of excessive amounts of catalyst may reduce the amount of energy being transferred), UV irradiation time, solution's pH (pH of the solution has a complex effect on photocatalytic oxidation rates, reaction rates are generally different if the molecule of colorant is in its acidic or alkaline) and temperature (Stasinakis, 2008; Shin *et al.*, 2015).

In different reports the synthesis and degradation efficiency of TiO_2 and TiO_2 supported on zeolite catalysts were investigated by using spectral measurements. But there is no report in the literature to study the efficiency of these catalysts by applying chemometrics methods. In this research we apply chemometrics methods like MCR-ALS to study the efficiency of the two catalysts in two different pH media (pH 3 and pH 8).

1.1.4. Methyl orange (MO)

Methyl orange is an azo dye frequently used as a pH indicator for titrating most mineral acids, strong bases (Funar-Timofei, 2010), and estimating alkalinity of waters and also employed as reagent for detection of bromine. In a solution becoming less acidic at pH > 4.4, methyl orange changes color from red to orange and finally to yellow and with increasing in acidity of the solution at pH < 3.1, methyl orange can change color from orange to red, which is both color changes occur in acidic conditions. In addition to this methyl orange is used largely in textile industries. It is an example of the widely spread azo dies, which are resistant to complete biodegradation (Shih *et al.*, 2010). For these reasons, methyl orange is commonly used as a model dye to study in environmental cleanup. Hence it selected for the present study. The structure of methyl orange is shown in Figure 2.

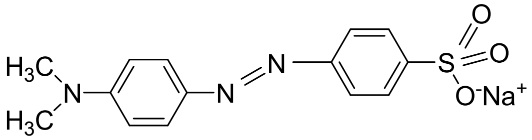


Figure 2: Chemical structure of methyl orange (*p*-dimethylamino-azobenzenesulfonic acid sodium salt).

1.2. Chemometrics

Chemometrics is the chemical discipline that uses mathematical and statistical methods to design or select optimal experimental procedures, to provide maximum relevant chemical information by analyzing chemical data, and to obtain knowledge about chemical systems (Rodionova and Pomerantsev, 2006). It is statistical method which helps as how to get chemically relevant information from measured chemical data, how to represent and display this data and how to get useful information from data (Wold, 1995). The scientific world today uses the data package for large quantity of numbers generated by modern analytical instrumentation to understand, quantify and interpret complex data. The chemometrics application of statistical and mathematical methods for analytical data to permit maximum collection and extraction of useful information is an interdisciplinary science suitable for solving diverse applications. Nowadays various analytical techniques like high performance liquid chromatography (HPLC), near infrared (NIR), UV/Vis, and Fourier transform infrared (FT-IR) spectroscopic instruments are being combined with various chemometrics models like multivariate analysis methods for the evaluation of different analytical data (Pawar and Kamat, 2014). The use of chemometric tools in data analysis, together with recent advances in computer technology which simplify complex mathematical calculations, leads to the development of multivariate data analysis as a powerful tool in the evaluation of food quality (Lee *et al*., 2009). Every scientist nowadays uses software related to mathematical and statistical methods for processing and distribution of knowledge to the scientific community. A deeper understanding of these methods and tools for viewing all data simultaneously is needed. In chemistry, chemometrics is used as an important area to be able to help work with many data obtained in the analysis.

There are different methods of statistical analysis for different chemical data interpretations. The number of variability sources related to the number of chemical species present in the reaction can be analyzed using singular value decomposition (SVD) and evolving factor analysis (EFA) of the UV–Visible spectra recorded during the photocatalytic reaction process to obtain information about the spectral profiles of each compound (Fernández *et al.*, 2011). Multivariate curve resolution-alternating least-squares (MCR-ALS) is one of the most powerful chemometrics tools for obtaining chemical information from measured experimental data to extract qualitative and quantitative information of the reactants, reaction intermediates, and products present in a chemical reaction from a UV-Vis spectroscopy data (Teglia *et al.*, 2016). This method is useful specifically to study the photooxidative reaction of textile dyes. Chemometrics techniques also used to discriminate between very similar chemical components from which several groups could ideally be determined and the method is particularly suited for working with large data sets and may be used to classify different components into distinct groups by the correlation of measurement data (Lee *et al.*, 2009). Multivariate curve resolution-alternative least square (MCR-ALS), can be applied to study the photocatalytic degradation of dyes since it has allowed for the simultaneous determination of the adsorption and rate constants and to study the effect of several factors on the process of interest (Fernández *et al.*, 2012; Fernández *et al.*, 2013). Principal component analysis can be applied to study the polarity effect of solvents and concentration effect of the sample on the spectra of FT-IR measurement.

1.2.1. Historical background of chemometrics

The notation chemometrics was introduced in 1971 by the Swedish scientist, Svante Wold, and after invention of chemometrics for a grant application, and then Wold joined with the American scientist Kowalski in 1974 to create the International Chemometrics Society (Brereton, 2014) shortly thereafter by the two pioneers in the field. Wold was a professor of organic chemistry at Umeå University, Sweden, and Kowalski was a professor of analytical chemistry at University of Washington, Seattle. Although Wold and Kowalski are credited for creating chemometrics, but in practice one could argue that even the earliest analytical experiments in chemistry involved a form of chemometrics, the field is generally recognized to have emerged in the 1970s as computers became increasingly exploited for scientific investigation. Since then, chemometrics has been developing and is now widely applied to different fields of chemistry, especially in analytical chemistry. In the analytical chemistry field, the application of chemometrics mainly being useful for qualitative and quantitative analysis, process analytical chemistry and design of experiments (Rodionova and Pomerantsev, 2006).

1.2.2. Types of chemometrics

There are different types of chemometrics methods which can be applied differently for the chemical analysis based on the type of data and the analytical method in which they are being interpreted. Principal component analysis (PCA), factor analysis (FA) and multivariate curve resolution alternative least square (MCR-ALS) are some of these chemometrics methods. Factor analysis (FA) is a multivariate statistical approach which is an important tool that can be used in the development, refinement, and evaluation of tests, scales, and measures that can be used in different disciplines (Williams *et al*., 2010). FA and PCA are similar methods used for reduction of multivariate data; the difference between them is FA assumes that the existence of a few common factors during the variation in the data while PCA does not make such an assumption. FA tries to explain the maximum amount of common variance in a correlation matrix using the smallest number of explanatory constructs, whereas, PCA tries to explain the maximum amount of total variance in a correlation matrix. But most of the time PCA is the most commonly used procedure. Multivariate curve resolution (MCR) technique can be helpful to analyze spectral data, which decomposes the set of spectra into the product of the constituent pure spectral components and their corresponding relative composition matrices without any reference spectra and it allows to analyze different spectral data even when the multiple spectra overlap with one another (Muto *et al*., 2009). In this study only the applications about PCA is given since the method is best applied to the large spectroscopic data analysis by reducing the dimension of the data set and MCR since it helps to analyze multiple spectral data.

1.2.3. Multivariate curve resolution alternative least square (MCR-ALS)

Multivariate curve resolution (MCR) is suitable technique to decompose large number of spectral signals into individual components by using alternating least square algorithm. MCR is aimed the extraction of concentration profiles and pure component spectra with as few assumptions about the data as possible (Muto *et al*., 2009). The assumption is based on the fact that spectral response is linearly proportional to the concentration of a chemical compound in a mixture

(Beer's Law) at given wavelength-dependent absorbances (Muto, *et al.*, 2009; Fernández *et al.*, 2012; Fernández *et al.*, 2013).

If we have matrixes X, C and S, then

$$\mathbf{X} = \mathbf{C}\mathbf{S}^{\mathbf{T}} + \mathbf{E} \tag{13}$$

Where, **X** is the measured data matrix (**m × n**), **C** is the matrix containing the pure concentration profiles (**m × k**), **S** contains the pure spectra (**n × k**) where **k** is the number of components obtained from MCR-ALS optimization, **m** is the number of data (frequencies) of the measured spectrum, **n** is number of spectra, superscript **T** denotes the transpose of the matrix and **E** is an error matrix due to noise. The solving method follows an iterative algorithm that minimizes **E**.

To study the photocatalytic degradation of dyes, MCR-ALS method can be applied for the simultaneous determination of the adsorption and rate constants and to study the effect of several factors on the photocatalysis process (Fernández *et al*., 2012).

2. Objectives

2.1. General objective

Determining intermediate compounds formed during photocatalytic degradation of textile dye with TiO_2 and TiO_2 supported on zeolite catalysts using chemometrics methods

2.2. Specific objectives

(i) To study the efficiency of TiO_2 and TiO_2 supported on zeolite catalysts for the photocatalytic degradation of dyes.

(ii) To study the kinetics of photodegradation of dyes using TiO_2 and TiO_2 supported on zeolite catalysts using chemometric methods.

(iii) To apply statistical methods for the analytical data to get maximum information and interpret the spectral data.

3. Experimental

3.1. Photodegradation of methyl orange

3.1.1. Samples and reagents

Methyl orange (reagent grade, BDH Chemicals Limited, Poole, England) was used as a dye sample. Commercial nano-size TiO_2 and TiO_2 supported on zeolite (prepared in the laboratory) were used as catalysts for the photocatalytic reaction.

3.1.2. Apparatus

Photocatalytic reactor. Figure 3 shows an image of the photocatalytic reactor used in this study. The batch reactor is a cylindrical vessel made up of quartz glass with a capacity of 0.75 liter. The reactor is continuously stirred by a magnetic stirrer and it has an outlet to sample the reacting mixture at different times. The source of light is a Heraeus medium pressure mercury lamp (150 watt) that is surrounded by a cooling jacket that has the double function of isolation the lamp from the solution and dissipating the heat generated by the lamp by means of water circulation. The lamp and cooling jacket are immersed into the reacting solution.

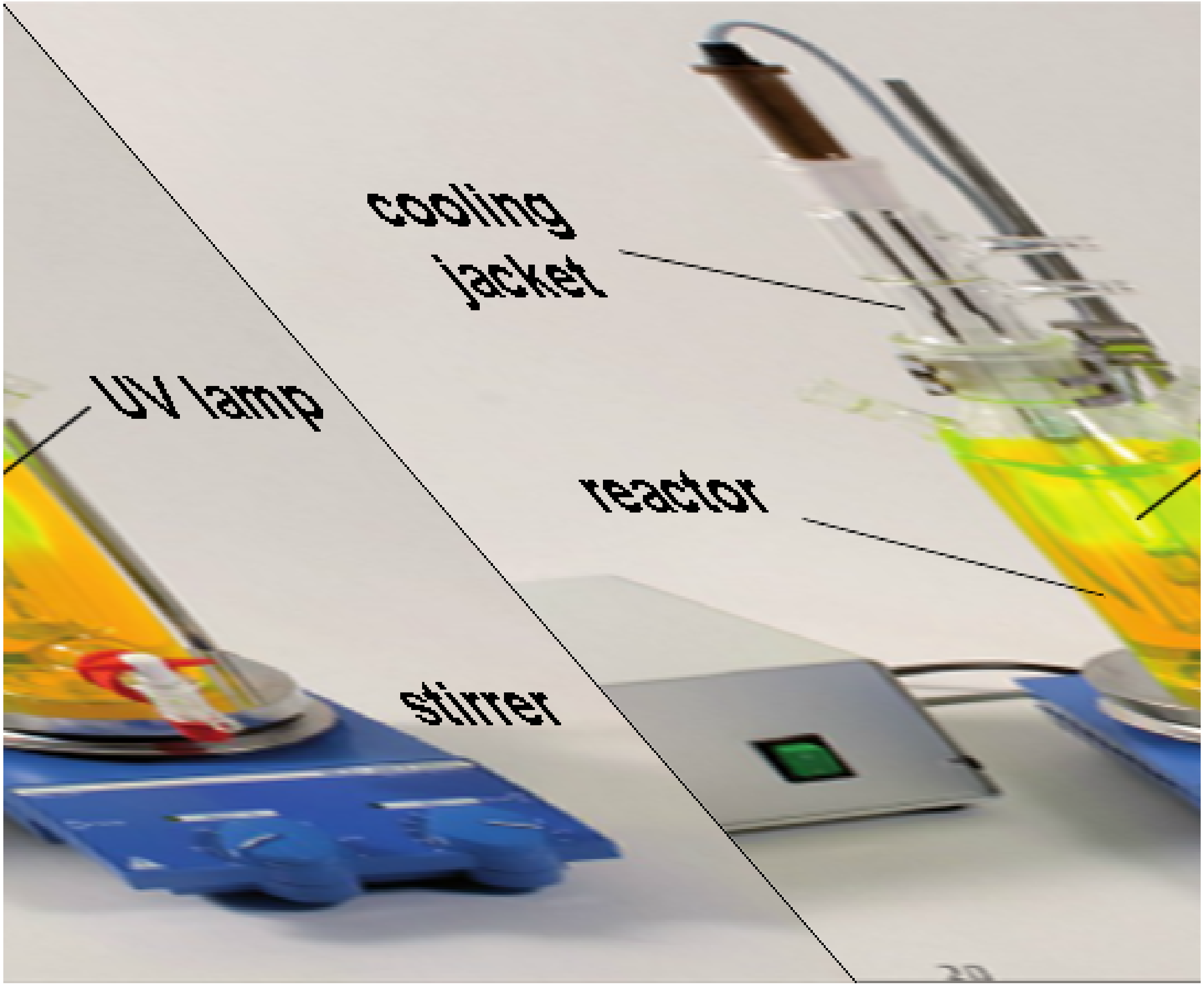


Figure 3: Photochemical reactor.

UV/Vis/NIR spectrophotometer. Spectra of the reacting mixtures dye were measured using Perkin-Elmer spectrum 65 UV/Vis/NIR double beam spectrometer with photomultiplier tube detector and recorded with Perkin-Elmer winlab software of the instrument.

3.1.3. Methods and procedures

Concentration of methyl orange (MO) was chosen as 20 mg/L. Degradation of MO was done at two different pHs (pH = 3 and pH = 8) because MO have different structures at these pHs that may affect the degradation mechanism.

Preparation of supported catalyst: TiO_2 supported on zeolite (8.5% TiO_2) catalyst was prepared by suspending the zeolite in a solution of titanium (IV) butoxide ($Ti(OBut)_4$) dissolved in a mixture of 2-propanaol ($CH_3CHOHCH_3$) and water (H_2O) with volume ratio of 1:10:2 ($Ti(OBut)_4$: $CH_3CHOHCH_3$: H_2O) then calcined in air at 400 ^{0}C for 3 h (Guesh *et al.*, 2016).

Preparation of the reactive mixture: A solution of 20 mg/L of MO was initially prepared and adjusted to pH 3 or 8 using 0.1 M H_2SO_4 or 0.1 M NaOH solutions respectively. 750 mL of solution were loaded into the reactor and then the corresponding amount of phortocatalyst was added. Under stirring a suspension is formed. When using Zeolite/TiO_2 as catalyst, 0.5 g of solid were added and in order to keep constant the amount of TiO_2, 0.045 g were added for the reactions using pure TiO_2.

Experimental procedure: Samples were taken before applying the UV radiation and after applying the UV radiation separately. The suspension was irradiated with a 150 W UV lamp (Heraeus medium pressure mercury lamp) and samples were withdrawn in frequent/regular time intervals during the photocatalysis process. The withdrawn samples were centrifuged and the supernatant was analyzed by UV-Vis spectrometer. The sample was stirred for 30 min before the irradiation is applied. The first sample was taken immediately before the lamp was immersed and after at different time intervals (within each 10 min interval up to 60 min and 20 min interval after 60 min) during the photocatalysis process. The withdrawn samples were centrifuged for 20 min and the supernatant was carefully separated from the precipitate and analyzed. UV-Vis spectra were recorded in between 227 and 800 nm wavelength using 1.0 cm path length quartz cell for each sample. The baseline was taken with distilled water in the same cell.

4. Result and discussion

4.1. Photodegradation of methyl orange

Decolorization of methyl orange during the photocatalysis process using TiO_2 catalyst was effectively performed within the first hour. Figure 4 show different samples of the reaction at times up to 30 min. Observe that by that time, the solution has lost a significant intensity of orange color.

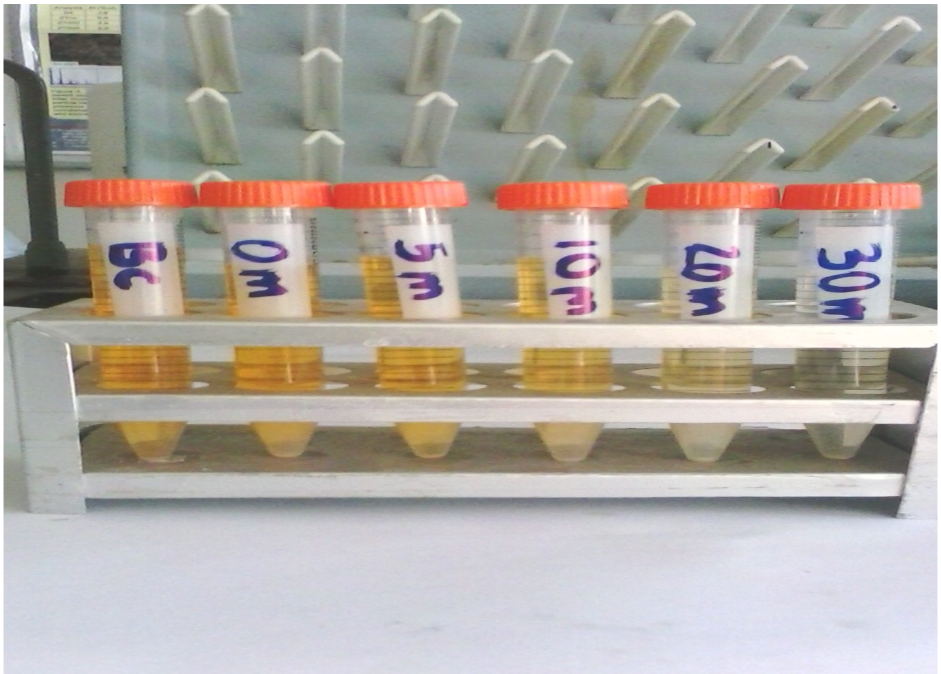
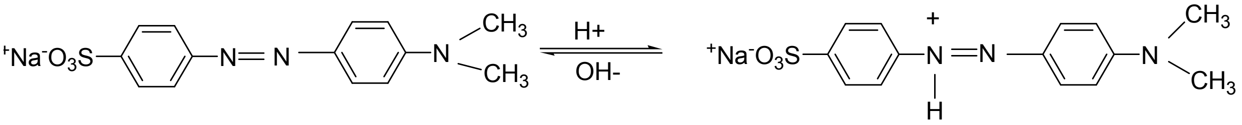


Figure 4: Samples during the photocatalysis degradation of methyl orange with TiO_2 catalyst.

The UV-Vis spectra of the samples also reveal MO decomposition in the presence of TiO_2 photocatalyst under UV irradiation. Figure 5 shows the UV-Vis spectra of MO degradation at different times of reaction using TiO_2 at pH 3 and 8. The spectrum ranges from 227 nm to 800 nm. It can be seen that the characteristic absorption peak intensity for the sample decreases with increasing degradation time. After 240 min of UV irradiation, the absorption peak is totally removed in both cases. For the photocatalysis of MO at pH = 3, (Figure 5a) a peak at the wavelength characteristic of MO at 488 nm is observed whereas at pH = 8 (Figure 5b) the maximum is at 464 nm. That is expected since MO has different structures (Scheme 1) and hence different colors at pH acidic and basic.

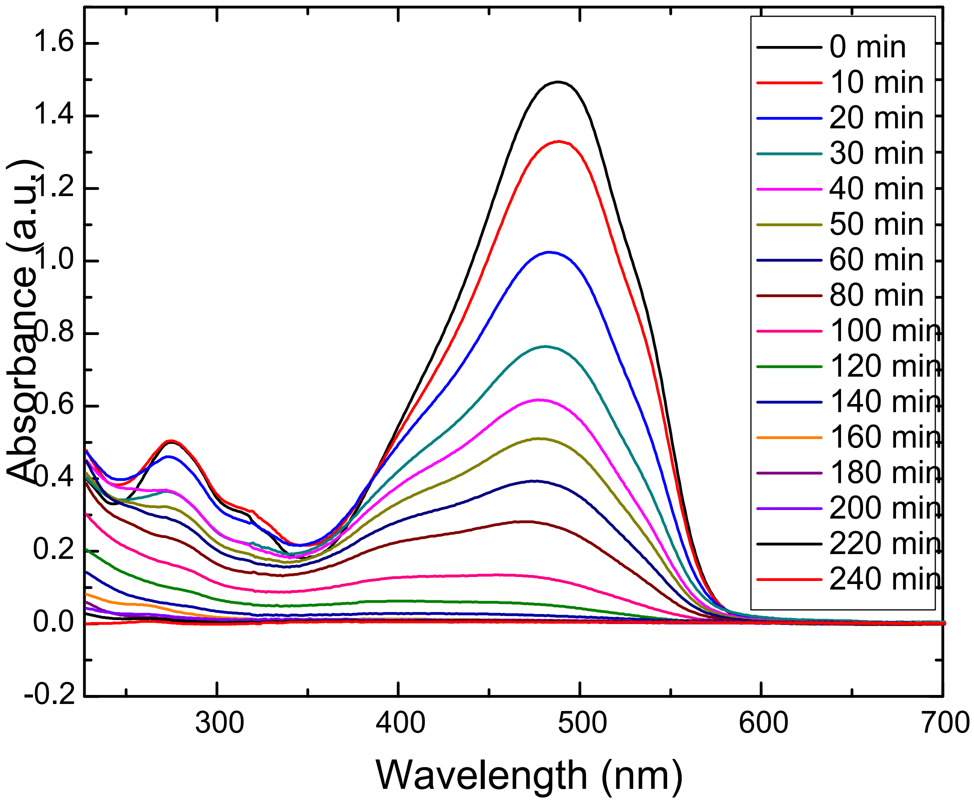


Yellow form of methyl orange

Red form of methyl orange

Scheme 1: Structure of methyl orange in acidic (red form) and basic media (yellow form).

a)


Absorbance (a.u.)
Wavelength (nm)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
300
400
500
600
700
0 min
10 min
20 min
30 min
40 min
50 min
60 min
80 min
100 min
120 min
140 min
160 min
180 min
200 min
220 min
240 min

b)

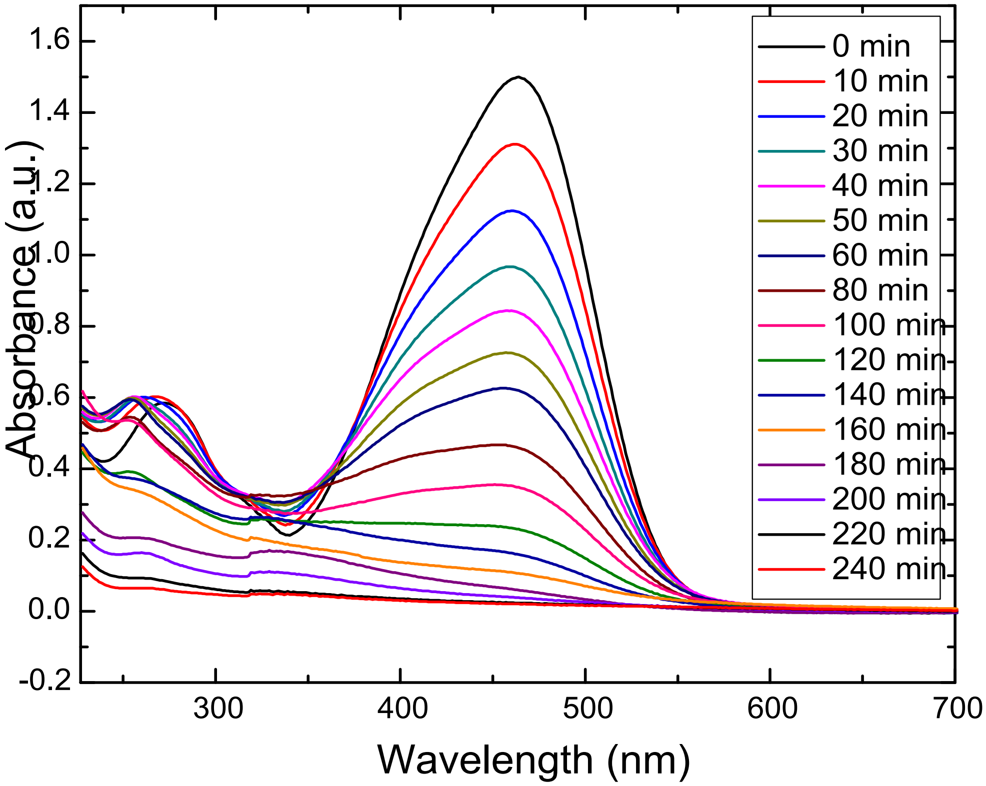


Figure 5: Photocatalytic degradation of 20 mg/L methyl orange a) at pH 3 with commercial TiO_2 catalyst and b) at pH 8 with commercial TiO_2 catalyst.

For the photocatalysis of 20 mg/L MO at pH 8 (Figure 5b), the photodegradation is apparently slightly slower compared to pH = 3 solution. However, monitoring the absorbance at the maximum of the peak is not a rigorous method to study the kinetics of degradation because the spectra measured consists of a mixture of intermediates apart from the starting MO; these intermediates may absorb at similar frequencies with MO and bias the absorbance value for the neat MO. For that reason MCR-ALS is applied to these data. Figure 6 shows the UV-Vis spectra of MO degradation at different times of reaction using TiO_2 supported in zeolite at pH 3. As it can be observed, the rate of decrease of the intensity for the UV-Vis spectra is slower than the degradation of the same solution using TiO_2 catalyst at either pH 3 or pH 8. However, the absorbance at t = 0 min is significantly lower than the absorbance when using the same solution with TiO_2 catalyst. This may be due to the adsorption capacity of zeolite. The porous surface of the zeolites speeds up the adsorption of MO since their higher surface area (Guesh *et al*., 2016).

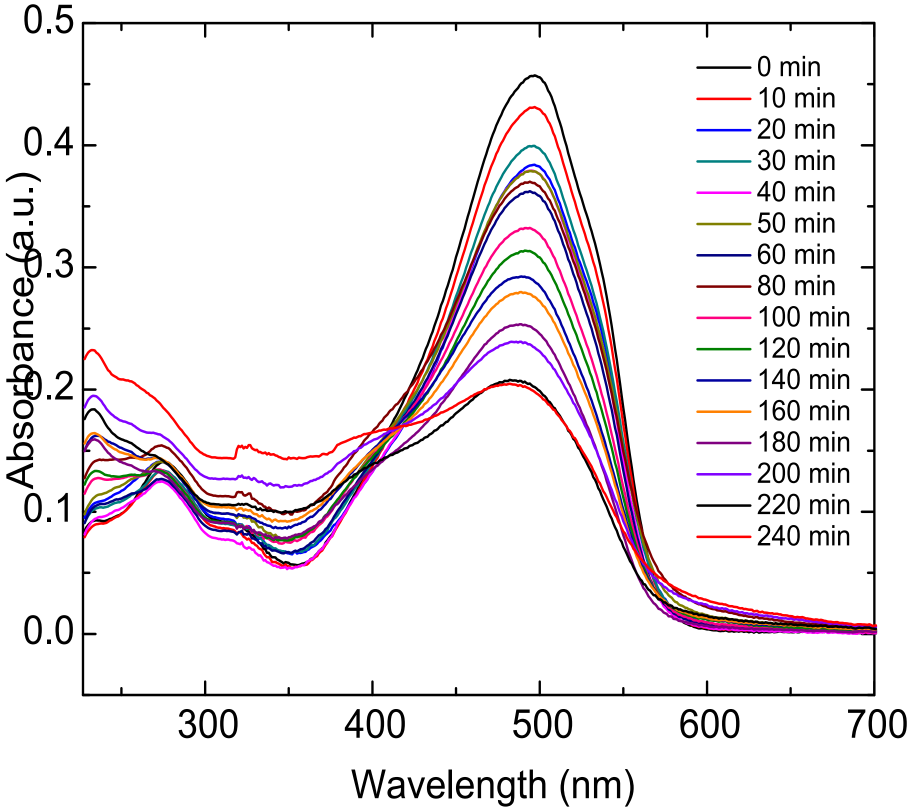


Figure 6: Photocatalytic degradation of 20 mg/L methyl orange at pH 3 with TiO_2 supported on zeolite catalyst.

4.1.1. Statistical analysis

A data matrix was constructed with a column representing absorbance (573 points) and rows corresponding to degradation time interval (16 variables). The data was treated by chemometrics tools with MATLAB 7.8 (MATLAB R2009a). MCR optimization was carried out to decompose spectral signals into individual components by using alternating least square algorithm.

The profiles shown in Figures 7-9, the black line shows that the concentration of MO, the red, green and blue colors show that the intermediate compounds formed during the photocatalysis reaction.

The concentration profile for the MO show at the beginning was high and decreases through time when the photocatalysis reaction was going. Intermediate 1 (red line) is the component that appears at higher concentrations at shorter times, followed by intermediates 2 and 3 (lines blue and green respectively), indicating that the reaction path may follow such sequence.

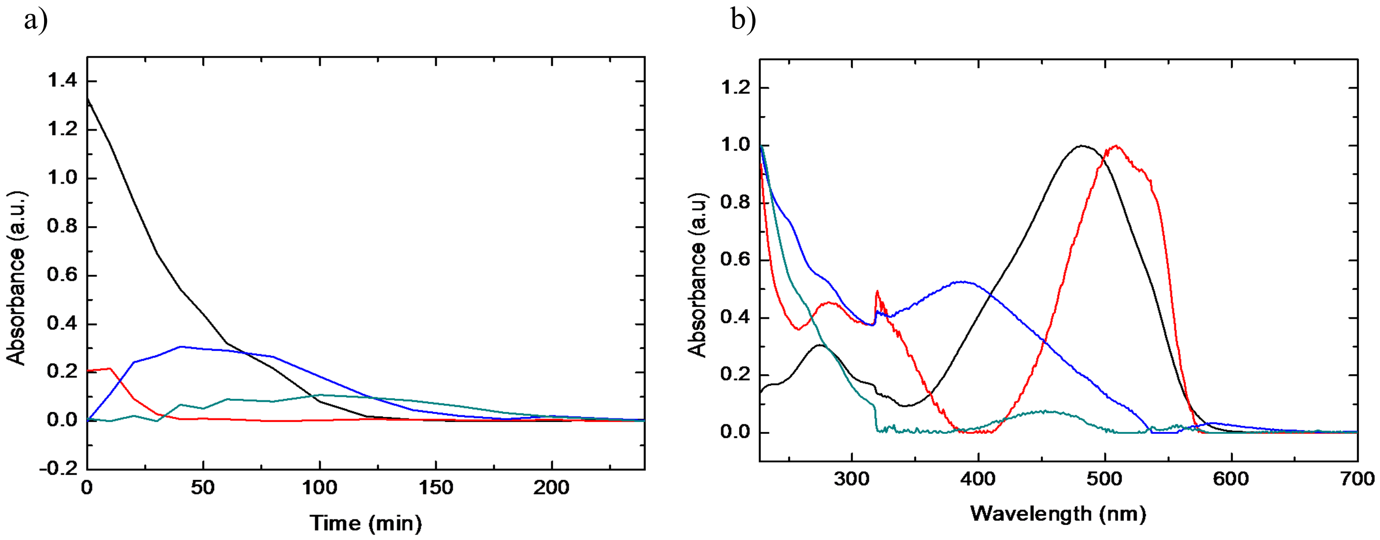


Figure 7: Profiles of the chemical species involved in the photooxidative degradation process of MO pH 3 solution using TiO_2 catalyst obtained by MCR-ALS, a) concentration profile and b) spectral profile. (—): MO; (—): Intermediate 1; (—): Intermediate 2; (—): Intermediate 3.

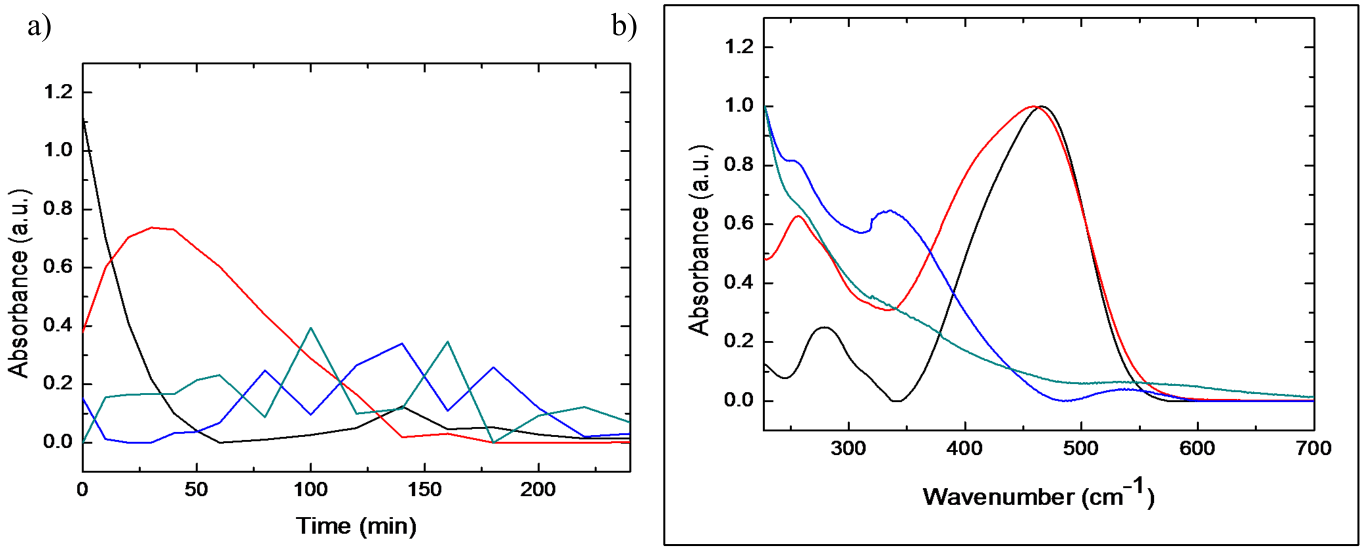
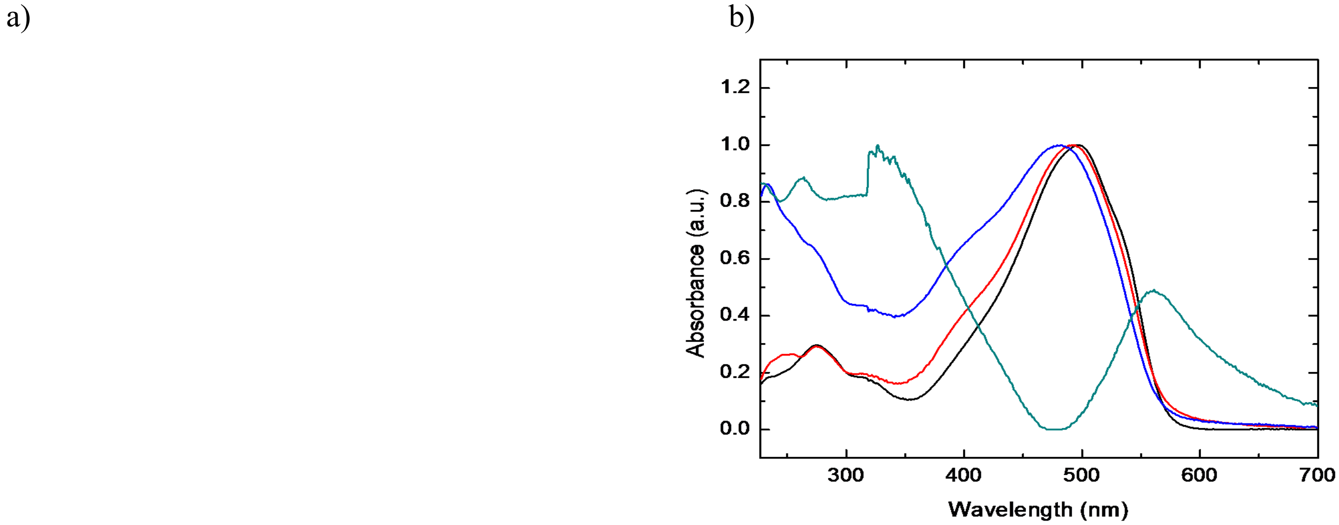


Figure 8: Profiles of the chemical species involved in the photooxidative degradation process of MO pH 8 solution by using TiO_2 catalyst obtained by MCR-ALS. a) concentration profile and b) spectral profile. (—): MO; (—): Intermediate 1; (—): Intermediate 2; (—): Intermediate 3.



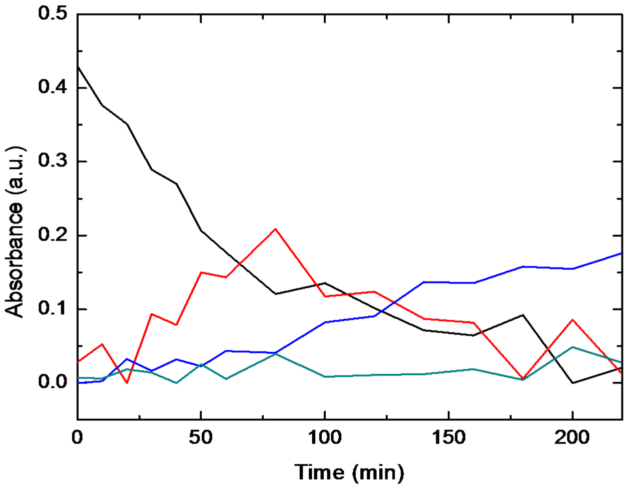


Figure 9: Profiles of the chemical species involved in the photooxidative degradation process of MO pH 8 solution by using TiO_2 supported on zeolite as catalyst obtained by MCR-ALS. a) concentration profile and b) spectral profile. (—): MO; (—): Intermediate 1; (—): Intermediate 2; (—): Intermediate 3.

According to the spectral profiles (Figures 7b-9b), intermediate 1 and 2 have their maxima in the visible region so they can be assigned to different fragments from MO during the degradation process. Intermediate 1 has similar UV-Vis spectra with MO, but with the maximum slightly shifted. That behavior is typical of the azoic colorants; the first fragments are very similar to the starting reactant. Intermediate 2, however has a UV-Vis profile significantly different than MO (except in Figure 9), which may indicate fragments that keep a certain degree of aromaticity but with very different structure (may be fragments from the breaking of the azo bond). Finally, intermediate 4 absorbs only in the region of UV, which is typical of final free radical from the last degradation fragments.

For the degradation using TiO_2 at pH = 3 (Figure 6), after 150 min of photocatalysis reaction, the species that shows the concentration profile of MO disappears. Notice that in Figure 4a, at 120 min, the spectra show certain absorption, but in that case it does not correspond to MO but to intermediates 2 and 3.

When comparing Figures 8a and 9a, the rate of degradation of MO is actually higher for the latter (pH = 8) even though in Figure 4 seem to be the opposite. At pH = 3, MO degrades to intermediate 1, but this intermediate seem to be instable because degrades quickly at 30 min; apparently to intermediate 2 and this to intermediate 3.

At pH = 8 the MO quickly degrades to intermediate 1 that reaches a maximum of intensity at 30 min. This intermediate further degrades into intermediates 4 and 5, however in this case the MCR analysis cannot provide a defined concentration profile for them. From the concentration profile, the degradation process is completed with shorter time by using TiO_2 catalyst than using TiO_2 supported on zeolite catalyst (Figure 9). The species that shows the concentration profile of MO does not disappear until 220 min when using TiO_2 supported on zeolite (black line). Intermediate 1 shows a maximum at t = 80 min and then gradually decreases. Intermediate 2 increases the concentration when the degradation time increases. It seems that the reaction time was not sufficient to start degrading intermediate 2 to intermediate 3 since the concentration of the latter stays at very low values.

4.1.2. Kinetic study

Once the contribution of the reactant and intermediates to the UV-Vis spectra has been distinguished, 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 and using the same proportionality constant for that using the composite TiO_2/zeolite. Results are sown in Figure 10.

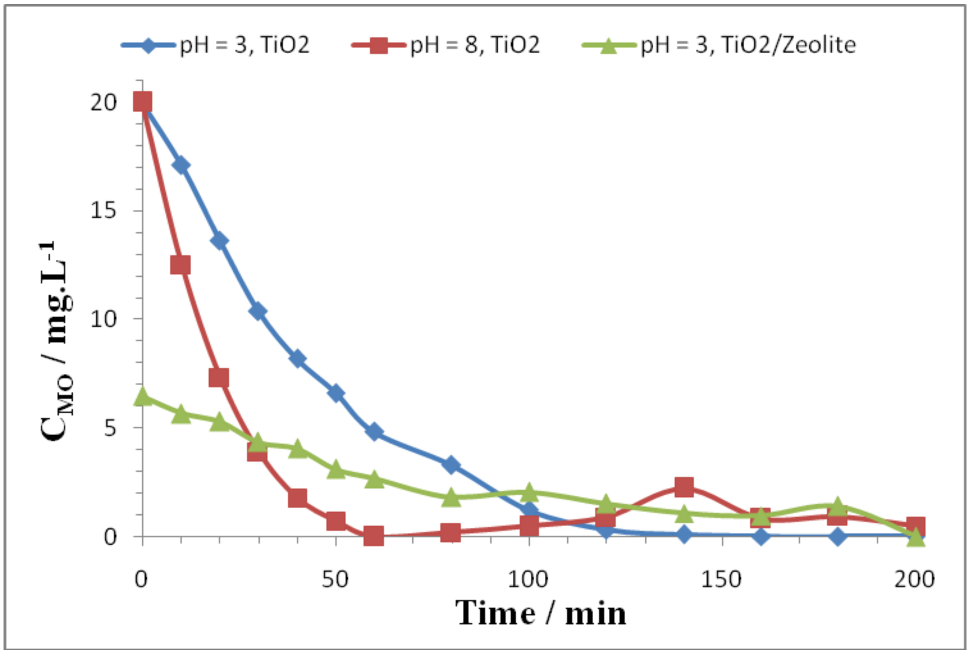


Figure 10: Kinetics for the photodegradation of MO using TiO_2 at pH 3.

As discussed before, a simplified mechanism for the reaction path can be sequencial as shown in Scheme 2.

$$\text{MO} \rightarrow \text{Intermediate 1} \rightarrow \text{Intermediate 2} \rightarrow \text{Intermediate 3}$$

Scheme 2: Photodegradation reaction sequence.

Then, the kinetic equation for the first step (degradation of MO) can be proposed to be:

$$-\frac{dC_{MO}}{dt} = kC_{MO}^{n} \qquad (14)$$

Where k is the rate constant and n, the order of reaction respect the concentration of MO. Then the integrated equation will have a different shape depending on the value of n:

$$\begin{aligned} &\ln C_{MO} = -kt + const && \text{for } n = 1 \\ &\frac{1}{C_{MO}} = kt + const && \text{for } n = 2 \\ &\frac{1}{C_{MO}^{2}} = 2kt + const && \text{for } n = 3 \end{aligned} \qquad (15)$$

By trying to fit the different expression of C_{MO} (as shown in equation 15) against time, the value of n can be obtained from the best fit. Take as sample the reaction at pH = 3 for TiO_2.

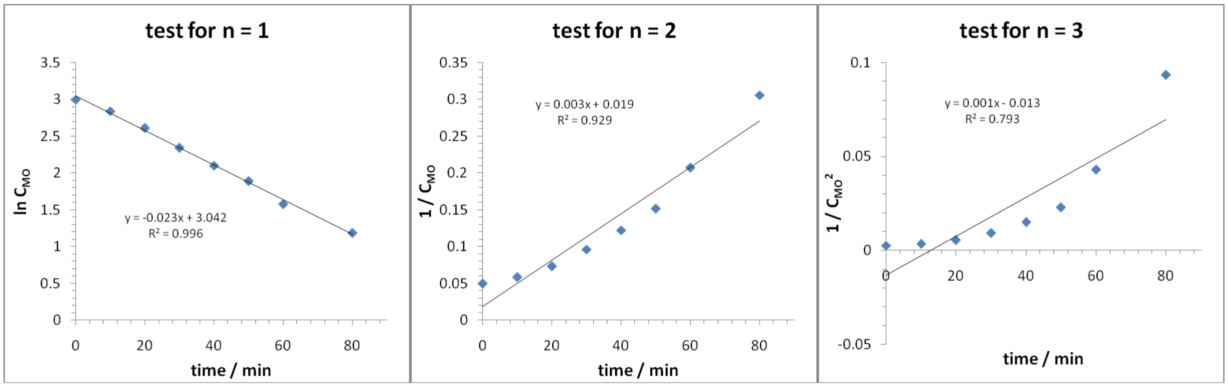


Figure 11: Kinetic analysis of pseudo rate orders for the photodegradation of MO using TiO_2 at pH 3.

As one can see in Figure 11, the experimental data fit better to a plot ln C_{MO} vs time, therefore the reaction is first order respect methyl orange. The same thing happens with the rest of the reactions. From the slope of the kinetic constant Table 1 can be extracted.

Table 1: Rate constants for the degradation of MO using TiO_2 at pH 3 and 8 and using TiO_2 supported on zeolite catalysts.

Reaction	k / min^{-1}
pH = 3, TiO_2	0.023
pH = 8, TiO_2	0.061
pH = 3, TiO_2/Zeolite	0.015

5. Conclusion

MCR-ALS method was applied to evaluate the photocatalytic activities of TiO_2 and TiO_2 supported on zeolite catalysts. MO photodegradation at pH 3 using TiO_2 catalyst shows better decoloring efficiency than at pH 8 and using TiO_2 supported on zeolite catalyst. In terms of kinetics for MO degradation, it is quicker at pH 8 for 60 min and then when the degradation time increasing the kinetics becomes slow. The degradation process is completed with shorter time by using TiO_2 catalyst than using TiO_2 supported on zeolite catalyst. The photocatalytic degradation of MO using TiO_2 supported on zeolite at pH 3 shows low efficiency but, the maximum UV/Vis absorbance at 0 min was is low because of the adsorption capacity of zeolite at the beginning decrease the adsorption peak.

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