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SYNTHESIS AND CHARACTERIZATION OF PHOTOCATALYST

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بسم الله الرحمن الرحيم

(قالوا سبحانك لا علم لنا إلا ما علمتنا إنك أنت العليم
الحكيم)

صدق الله العظيم

سورة البقرة الآية (31)

إهداء

إلى روح المرحوم الدكتور محمد الطاهر المحبس نسأل الله أن يرحمه ويغفر له ويجعل جنات
الخلد مستقرا له . طيبته وطابته ذكراك حيا أو ميتا .

إلى من لا أوفى قدرا و أرتقي لمكانتها حتى و لو صعدت أعلى الجبال قمما....

((أمي و أبي))

إلى من لا تفارقكم عيناى نظرا و أسترد طفولتي معهم في أجمل صوراً...

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إلى من التقطت لي الأيام معهم أروع صوراً و لن يقف لسانى عن حبي لهم ذكراً...

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF PHOTOCATALYST

The study describes the basics of photocatalysis of methylene blue (MB) dye on semiconductors, mainly on nanocrystalline MnTiO_3 and mixer of $\text{MnTiO}_3/\text{TiO}_2$ assisted with sunlight irradiation.

The semiconducting nano-materials, MnTiO_3 and mixer of $\text{MnTiO}_3/\text{TiO}_2$ were prepared by sol-gel chemical method and characterized by the experimental *techniques* such as XRD, IR-ATR, Raman spectroscopies, TG-TD thermal analyses and TEM microscopy. The effect of various process parameters such as initial concentration, contact time, loading of photocatalyst and initial pH value on the degradation of the MB dye were investigated. Results show that the percentage removal of MB dye increase with an increase in exposure time. The effects of the variation of light source and intensity on the degradation of MB dye were studied. In this research there was clear that the degradation of methylene blue using solar light irradiation was more effective and efficient than of artificial UV light irradiation. The percent degradation of methylene blue was significantly improved with use of UV-C radiation compared to UV-A radiation. The experimental data was analyzed to fit the specific order of reaction kinetics and Langmuir-Hinshelwood to determine adsorption rate constant. It was demonstrated that the photodegradation of MB follows a pseudo first-order kinetic with the correlation coefficient $R^2 > 0.97$.

الملخص

تحضير ووصف المحفزات الضوئية

هذه الدراسة توضح أساسيات التفكك الضوئي المحفز لصبغة الميثيلين الأزرق MB علي سطح المركبات البلورية بحجم النانومتر مثل $MnTiO_3$ والمختلطة $MnTiO_3/TiO_2$. تم تحضير هذه المواد شبه الموصلية $MnTiO_3$ والمختلطة $MnTiO_3/TiO_2$ بالطريقة المعروفة طريقة السائل الهلامي (Sol-gel)، كما تم التعرف عليها وتصنيفها بواسطة طرق التحليل الكيميائية الاتية : طيف أشعة اكس والأشعة تحت الحمراء وطيف رامان والتفكك الحراري والميكروسكوب الإلكتروني.

XRD , IR ,Raman spectroscopies , TG-TD thermal analyses and TEM microscopy .

وكما تمت دراسة تأثير بعض العوامل المختلفة علي مدى كفاءة إزالة وتكسير صبغة الميثيلين الأزرق MB من المحاليل المائية. ومن بين هذه العوامل : التركيز الابتدائي للصبغة 1×10^{-5} optimum at, وزمن التلامس solar light irradiation 4h, ووزن المادة المحفزة $MnTiO_3, = 0.005g/50ml$ والرقم الهيدروجيني $pH=6$. أوضحت نتائج هذه الدراسة أن النسبة المئوية % لإزالة الصبغة MB من المحاليل المائية تزيد بزيادة زمن التلامس كما أنها تزيد بزيادة فترة التحفيز (التعرض للأشعة) .

تمت دراسة تأثير زمن التحفيز والرقم الهيدروجيني علي مدى إزالة الصبغة عند $pH = 6$ ولقد تبين من خلال النتائج إن النسبة المئوية لإزالة الصبغة تزيد بزيادة زمن التحفيز . كذلك تمت دراسة تأثير التحفيز باستعمال مصادر أشعة مختلفة (الشمس والأشعة فوق البنفسجية) علي النسبة المئوية % لإزالة الصبغة . أثبتت النتائج إن صبغة الميثيلين الأزرق باستعمال أشعة الشمس كمصدر للتحفيز أكثر فعالية من استعمال الأشعة فوق البنفسجية الصناعية بنوعها (UV-A و UV-C) .

وان استعمال UV-C, 10W كان أكثر فعالية من نظيرتها UV-A, 100W وتوضح نتائج هذا البحث أنه يمكن إزالة الصبغات بطريقة التفكك الحفز الضوئي باستعمال شبه الموصلات النانوية . وكذلك دراسة ميكانيكيات التفاعل الحفزي علي الأسطح النانوية والمدعم بالتشيع الضوئي . تحليل النتائج ومطابقتها لميكانيكيات رتبة التفاعل ونموذج طريقة الادمصاص (Langmuir-Hinshelwood) . كان بهدف تحديد معدل سرعة التفاعل K كما تم تحليل النتائج بتطبيق نموذج ميكانيكيات رتبة التفاعل الأولي First order علي النتائج العملية وذلك لحساب العوامل الميكانيكية K_1 و n من خلال النتائج نلاحظ مطابقة تفاعل الصبغة علي سطح العامل الحفاز الصلب ويتبع نموذج لانجوميير وميكانيكية الرتبة الأولى بمعامل ارتباط احصائي

$$(R^2 > 0.98)$$

Contaminants from industrial effluents often pose a major environmental problem. Semiconductor photocatalysis is one of the techniques, that has great potential control aqueous organic as well as inorganic contaminants or air pollutants [1].

The photocatalysis has focused on the use of nanosized semiconductor materials as photocatalysts for the removal of ambient concentration of organic and inorganic species from aqueous or gas phase systems in environmental clean-up, drinking water treatment, industrial and health applications [2]. Photocatalysis, i.e. using semiconductor particles under sufficient irradiation energy for the simultaneous reduction and oxidation of different redox system, has been intensively studied during the last 30 years [3, 4]. Dyes usually have complex aromatic molecular structure which makes them more stable and difficult to biodegrade. Many dyes are toxic, and may cause destruction or inhibiting of their catalytic capabilities [5]. To reduce the risk of environmental pollution from such waste it is necessary to treat them before discharging to the receiving environment [6]. Due to their low biodegradability, a conventional biological treatment process is not very effective in treating dye wastewater [7, 8]. Photocatalytic degradation has a great potential to control aqueous contaminants or pollutants [9]. There are various methods for removal of organic and inorganic compounds from the wastewater as filtration, electrolysis, precipitation, ion exchange and adsorption process [10]. Most of these methods require high capital and recurring expenditure and consequently they are not suitable for small scale industries [11]. The photocatalysis is new, fast, convenient and less expensive method for degradation of methylene blue (MB) was applied [12]. Among the various oxides semiconducting photocatalysts TiO_2 and ZnO are important

photocatalysts, because they are very effective due to high band gap, safe, inexpensive, stable to photocorrosion, and maximum removal of the dyes [13]. It holds several advantages over conventional oxidation processes, such as complete mineralization of the pollutants [14], use of near-UV or solar light [15] no addition of other chemicals, and could be operated at near room temperature [16].

1.1. Photocatalysis

The word photocatalysis is composed of two parts:

- 1- The prefix photo, defined as "light".
- 2- Catalysis is the process where a substance participation in modifying the rate of a chemical transformation of the reactants without being changed in the end.

Hence, photocatalysis is a reaction which uses light to activate a substance that could help to modify the rate of a chemical reaction without being involved itself. Moreover, when a solid material is used as the photocatalyst the definition of heterogeneous photocatalysis is preferred [17].

1.2. Semiconductor photocatalysis

The most commonly used photocatalysts are semiconductor materials (most of them metal oxides) which, unlike metals, possess a void energy region (band-energy structure), where no energy levels are available (Figure 1.1). The void region which extends from the top of the filled valence band to the bottom of the vacant conduction band is called band

gap, Eg. Activation of a semiconductor photocatalyst is achieved through the absorption of a photon of ultra-band gap energy, which results in the promotion of an electron from the valence band into the conduction band e^-_{CB} and in the concomitant generation of a hole in the valence band, h^+_{VB} . The reaction of either the photo promoted electron with a reducible adsorbed substrate (usually oxygen in aerated system) and/or the hole with an oxidatizable adsorbed species can subsequently occur.

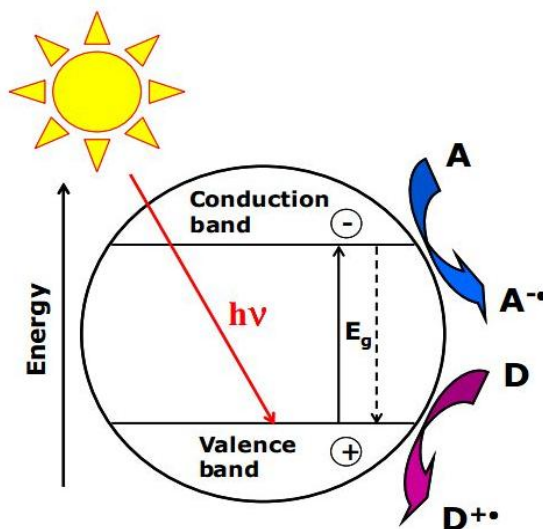


Figure 1.1: Simplified scheme of semiconductor activation.

The probability and the rate of such charge transfer processes depend on the position of the conduction and valence band edges and on the redox potentials of the adsorbed species. For example, when a semiconductor is used as a photocatalyst in the environmental remediation, usually involving the photodecomposition or complete mineralization of organic pollutants, it should be capable to generate a valence band hole (VB) with a redox potential that is positive enough to oxidize the organic pollutant. At the same time the photogenerated electron in the conduction band (CB) should be negative enough to reduce adsorbed O_2 to superoxide radical anion [18].

Figure 1.2 shows the band gap of several semiconductors and standard redox potentials of water. The ability of a semiconductor to undergo photo induced electron transfer to an adsorbed particle is governed by the band energy positions of the semiconductor and the redox potential of the absorbates.

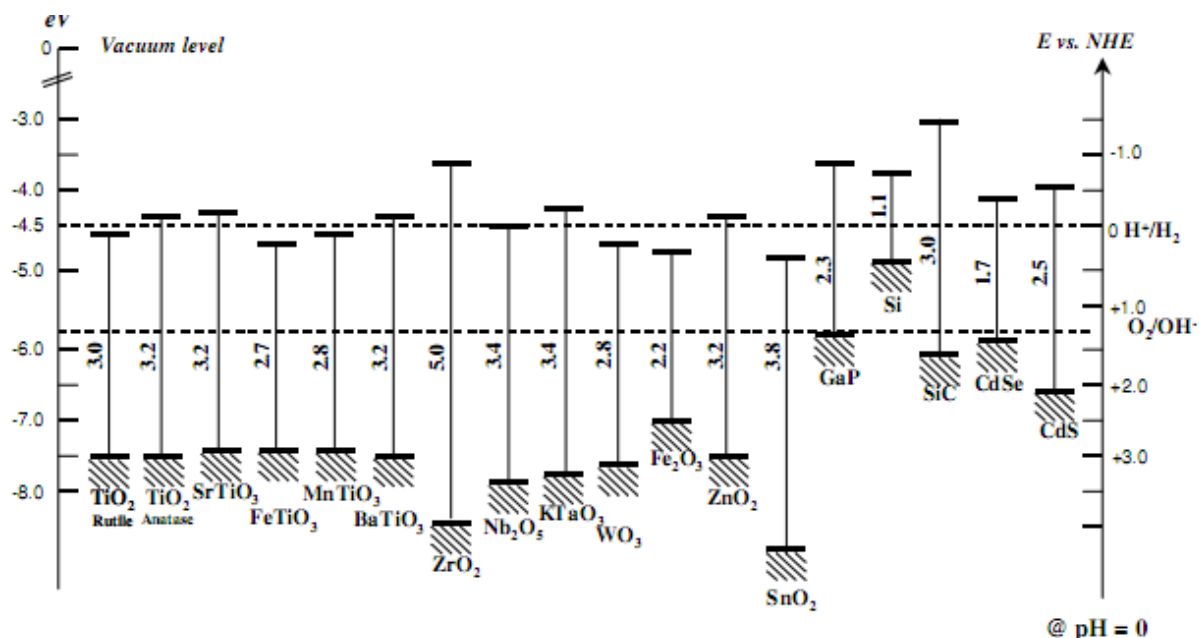


Figure 1.2: Band gap position (top of valence band and bottom of conduction band) in various semiconductors [19].

Recombination of electron-hole pairs can occur, in competition with charge transfer to adsorbed species, in the volume of the semiconductor particle or in its surface with the release of heat. This phenomenon represents the major deactivation path which could significantly decrease the overall photocatalytic efficiency.

The detrimental process of back-donation to the semiconductor after charge transfer to the adsorbed species can also occur. Thus, by

considering titanium oxide (TiO_2) as an example of semiconductor with photocatalytic properties, the main reaction scheme of a photocatalytic process can be mainly summarized in the following equations and depicted in Figure 1.3.

- Charge separation : $\text{TiO}_2 + h\nu \rightarrow e^-_{\text{CB}} + h^+_{\text{VB}}$
- Bulk/surface recombination : $e^-_{\text{CB}} + h^+_{\text{VB}} \rightarrow \text{heat}$
- Surface trapping : $h^+_{\text{VB}} + \equiv \text{Ti-OH} \rightarrow \equiv \text{Ti-O}^\bullet + \text{H}^+$
 $e^-_{\text{CB}} + \equiv \text{Ti-OH} \rightarrow \equiv \text{Ti}^\bullet + \text{OH}^-$
- Surface recombination : $e^-_{\text{CB}} + \equiv \text{Ti-O}^\bullet + \text{H}^+ \rightarrow \equiv \text{Ti-OH}$
 $h^+_{\text{VB}} + \equiv \text{Ti}^\bullet + \text{OH}^- \rightarrow \equiv \text{Ti-OH}$
- Interfacial charge transfer : $\text{Red}_1 + \equiv \text{Ti-O}^\bullet \rightarrow \text{Ox}_1 + \equiv \text{Ti-OH}$
 $\text{Ox}_2 + \text{H}_2\text{O} + \equiv \text{Ti}^\bullet \rightarrow \text{Red}_2 + \equiv \text{Ti-OH}$
- Back reaction : $\text{Red}_2 + \equiv \text{Ti-O}^\bullet \rightarrow \text{Ox}_2 + \equiv \text{Ti-OH}$
 $\text{Ox}_1 + \equiv \text{Ti}^\bullet \rightarrow \text{Red}_1 + \equiv \text{Ti-OH}$

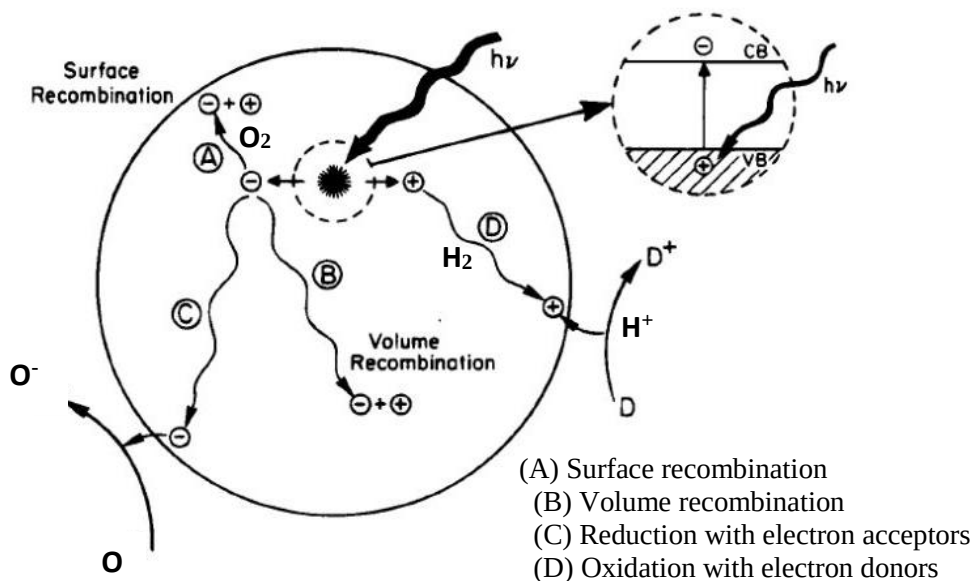


Figure 1.3: Schematic photoexcitation in a solid followed by de-excitation events [20].

1.3. Nanocrystalline photocatalysts

Nanocrystalline photocatalysts are ultrasmall semi-conductor particles which are a few nanometers in size. The interest in these small semiconductor particles, with diameters ranging between 1 and 100 nm, originates from their unique photophysical and photocatalytic properties [21, 22].

Generally, for all catalyst materials, a high surface area is an advantage in terms of a greater concentration of active sites per square meter and this generally leads to higher reactivity [23]. This can be explained in terms of an increase in the number of active sites per square meter as well as greater absorbance of the pollutant on the catalyst surface [24]. The increase in crystallite size and changes in the microstructure with a decrease in surface area greatly influence the photocatalytic property of the catalyst [25, 26] since the physical and chemical properties depends on of the synthesis route .

The rate of photocatalytic degradation of organic pollutant depends on the size of the catalyst, cristanility, surface morphology and the preparation methods. Nanoparticles of catalyst show distinguished changes in their optical properties compared to those of bulk materials as macro size. So particle size and surface area are the effective parameters of photocatalytic activity of nanomaterials. Higher reduction activity and smaller band gap energy occur for two reasons, firstly there is more radiation intensity and secondly shorter wavelengths are needed to excite electrons in nanomaterials.

Nanosize particles absorb more radiation, due to their higher surface areas. Effect of size on the photo-degradation efficiency can be ascribed to following

reasons: when the size of photocatalyst crystals decreases, the amount of the dispersion particles per volume in the solution will increase, resulting the enhancement of the photon absorbance, at the same time, the surface area of nano-particles photocatalyst will increase, which will promote the adsorption of more dyes molecules on the surface [27].

Nanoparticles also exhibit blue shift (shorter wavelengths) as the particle size is reduced [28]. Nanosized catalysts exhibited higher reaction rates due to low mass-transfer limitations [29]. Therefore, the increased surface area of nanosized particles and high absorptivity may prove beneficial for the decomposition of dyes in aqueous media.

1.4. MnTiO₃ Photocatalysts

The titanium-based oxides, such as barium titanate [30], cadmium titanate [31], bismuth titanate [32], cobalt titanate [33] and lead titanate [34], can be referred to as smart family owing to their excellent dielectric and photostrictive properties. Manganese ion in oxides is a well-known activator used mainly for producing tunable solid state laser media, holographic recording and optical data as storage as well as thermoluminescent detectors [35, 36]. Recently, manganese titanate MnTiO₃ has attracted much attention for its strong absorption in the visible region which may be propitious to the utilization of solar energy [37] and photocatalysis [38].

Manganese titanate MnTiO₃ adopts the pyrophanite structure with trigonal/rhombohedral R-3 H symmetry (unit cell: $a = 5.1386(0)$, $b = 5.1386(0)$, $c = 14.2857(2)$, $Z = 6$) [39]. The pyrophanite structure is an ordered corundum structure in which the Ti⁴⁺ and M²⁺ ions occupy alternate basal-plane layers of

cationic sites. The structure is based on a polyhedral chain of TiO_6 and MnO_6 (Figure 1.4).

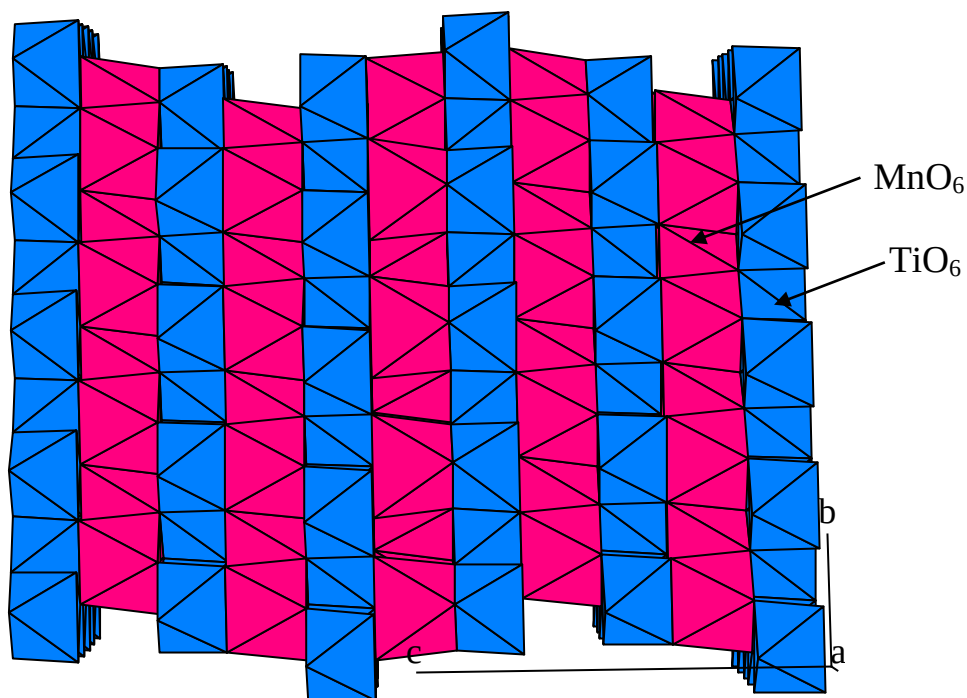


Figure 1.4: Projection along $[100]$ of the pyrophanite MnTiO_3 structure.

The pyrophanite MnTiO_3 , is a humidity sensing material with excellent sensitivity, good selectivity, low temperature coefficient near zero and good stability [40, 41]. MnTiO_3 is a band-gap semiconductor (2.8 eV) and so can extend light absorption to visible light [42].

Presently, the trend for the development of advanced catalyst materials is not directed towards new compositions but mainly towards a better control of the microstructure, resulting in enhanced optical properties of existing materials. With this aim the powder morphology, the particles size and the particles size distribution are of prime importance. Among parameters governing the powders morphology, the method of synthesis has been proved to be decisive. For instance, it is well

established that the sol–gel process provides the possibility to prepare nanocatalyst of high quality with various shapes while controlling their microstructure [43-45].

1.5. Sol-gel synthesis

Sol-gel processes have brought a new view in the domain of glass and ceramics fabrication and they have enlightened the importance if chemistry involves the complete fabrication lines of materials, from initial chemical precursors to the final products. The basic idea is to progressively create an oxide network by polymerization reactions of chemical precursors dissolved in a liquid medium. Sols and gels are two forms of matter that have been known to exist naturally for a long time.

The sol–gel technology started with processing of dense, bulk materials, and great effort has been made to density porous gels into glasses and ceramics (Figure 1.5).

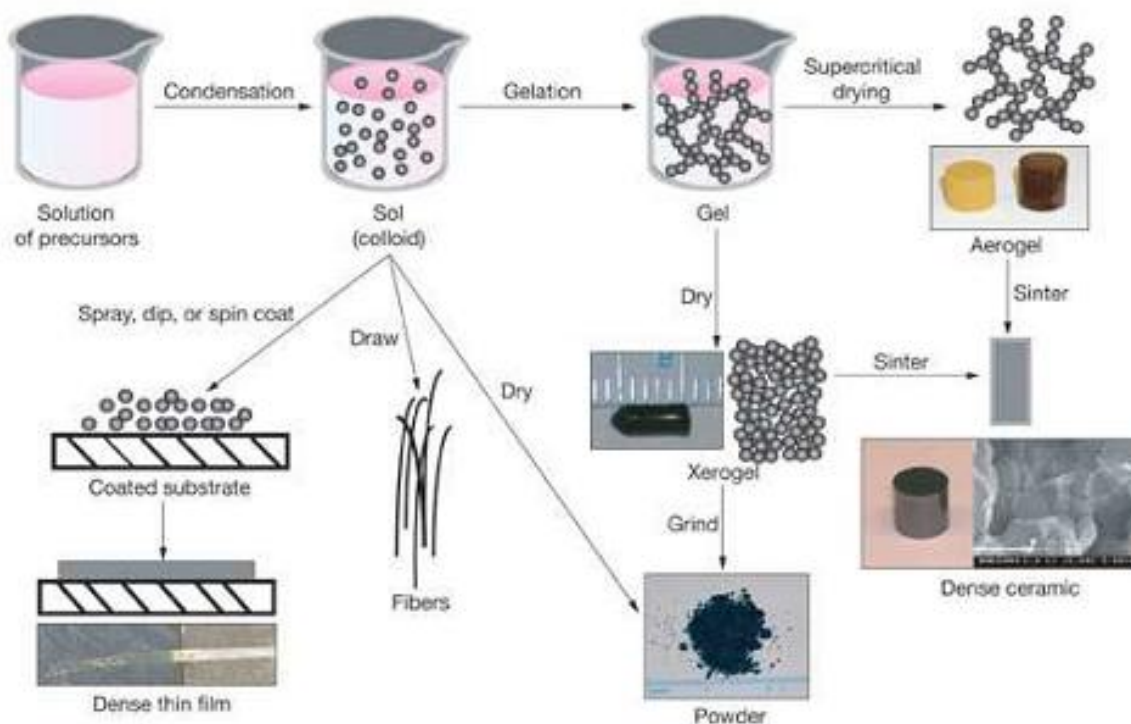


Figure 1.5: Schematic overview of the sol-gel processes [46].

By this method it has been possible to produce submicrometer powders with high purity, nuclear fuel, ionic and electronic conductors and magnetic materials among others

The sol-gel is a very effective and important process when it is required the production of homogeneous complexes ceramics reproducible as the new technologies demand. Though this, sol-gel process is an excellent option for producing high quality and purity materials, since grinding and compression operations are avoided, well below those used in conventional processes. For this reason the sol-gel method has been called "soft chemistry method". Some of the advantages and disadvantages of sol-gel method are presented in Table 1.1.

Table 1.1: Advantages and disadvantages of the sol-gel method [47].

Advantages	Disadvantages
✓ High homogeneity of the products compared with conventional method.	✗ Precursor expensive.
✓ High purity of the products obtained.	✗ Long time of reaction.
✓ Low temperatures of preparation: - Save energy. - Decrease the evaporation losses. - Decrease air pollution - Possibility to control morphology phases.	✗ Fine porous materials.
✓ Preparation of new amorphous materials out of normal range of obtaining temperatures.	✗ Presence of residual hydroxyl groups.
✓ Formation of crystalline phases from amorphous materials.	✗ Residual carbon.

-
- ✓ Better crystalline products from special properties of gels.
 - ✓ Preparation of thin films on different kind of substrate.
-

I.6. Application of photocatalysis

Heterogeneous photocatalysis has been demonstrated as a low cost and sustainable technology for the treatment of a host of pollutants in air and water including organics and heavy metals. As photocatalysis makes use of sunlight or UV radiation, the technology is inexpensive, environmentally friendly and can be applied worldwide.

Conventional technologies for wastewater treatment are in most cases able to meet the current water quality standards. The chances and potential fields of application of photocatalytic systems with artificial UV-sources include new water treatment plants or plants where conventional methods need to be replaced and the treatment of water contaminated with trace contaminants such as estrogens, the treatment of industrial wastewater contaminated with high loads of organic compounds or metals as well as small scale systems [48, 49]. Photocatalysis has been used successfully in many developing countries to destroy pathogens [48] and algal blooms in fresh water supplies. Photodisinfection sensitized by TiO_2 has been used to degrade the green algae, treat humic substances [49] which act as substrates for bacterial growth, inhibit bacterial degradation of impurities in natural water, and aid the transport of metals in the environment. Selected applications of photocatalysis are given in Table 1.2.

Table 1.2: Overview of different photocatalysis applications [48].

Property	Category	Application
Self-cleaning	Materials for residential and office buildings	Exterior tiles, interior furnishings, plastic surfaces, aluminum siding
	Indoor and outdoor lamps	Coatings on fluorescent lamps
Air cleaning	Indoor air cleaners	Photocatalyst-equipped air conditioners
	Outdoor air purifiers	Concrete for highways, roadways and footpaths, tunnel walls
Water purification	Drinking water	River water, ground water, lakes and water-storage tanks
	Others	Fish feeding tanks, drainage water and industrial wastewater
Antitumor	Cancer therapy	Endoscopic-like instruments

1.7. Objectives of present study

Based on the above, further research and development are needed in both upstream process optimization and downstream water quality evaluation in order to implement photocatalytic activity in large-scale of the water treatment system. The

main objective of this of the study is to degrade a model compound methylene blue dye which is a common pollutant in the industrial sewage. The prime objective was to carry out the literature survey on the use of nano-semiconductor materials as photocatalysts for the removal of ambient concentrations of organic and inorganic species from aqueous phase systems in water treatment. Another objective is to optimize the photocatalytic process for different parameters such as pH, UV intensity, use of solar light, nanocatalyst dose (MnTiO_3), initial concentration, volume to area ratio etc. and to study their effect on the degradation and decolorization of methylene blue in terms of change in absorbance of the resulting solution.

The present study organized in the following form: chapter 2 describes the theoretical aspects of the main stages involved in photocatalytic degradation of methylene blue using semiconductor nanoparticles and processes sol-gel synthesis method of photo-catalysts. In chapter 3, describes the experimental procedures used to obtain the nanopowder of MnTiO_3 in detailed. Chapter 4, is a discussion of the results:

- 1- Preparation and characterization of nanosized photocatalyst MnTiO_3 by two routes sol-gel, SG_1 and SG_2 .
- 2- Study on degradation of model compound, methylene blue dye, which is a common pollutant in the industrial swage, using nanosized photocatalyst MnTiO_3 .

This study includes the effect of the following parameters on catalysis process of dye degradation.

- ✓ Effect of contact time.
- ✓ Effect of Initial concentration of MB dye.

- ✓ Effect of photocatalyst loading (pure MnTiO_3 and mixed $\text{MnTiO}_3/\text{TiO}_2$ nanoparticles).
- ✓ Effect of pH on methylene blue removal.
- ✓ Effect of solar/UV light irradiation on the photocatalytic activity.

There are a lot of textile wastewater treatment processes including biodegradation methods, various physical methods such as phase-separation, and chemical methods. Nevertheless, none of them is completely satisfactory, for example, phase-separation process with adsorption on activated carbon does not remove or degrade pollutants from the environment. Biological methods are ineffective to degrade pollutants. It is difficult to destroy contaminants containing large, stable and refractory compounds of dyes. Photocatalysis provides an eco-friendly pathway for degradation of many organic pollutants. This technique is considered as a promising technology for wastewater treatment [50].

Both homogeneous and heterogeneous catalytic reactions usually are carried out under ultraviolet or visible light, many reported publications emphasized that heterogeneous photocatalytic oxidation overcomes homogeneous photooxidation which adding oxidizing solutions. Main disadvantage of homogeneous processes is their oxidants are consumed, whereas heterogeneous photocatalysis may be reused or fixed on some materials for extended periods and for easy gathering [51].

Heterogeneous photocatalytic degradation using semiconductor nanoparticles as catalysts is an effective technique. Applying the concept of nanotechnology to heterogeneous catalysis helps us understand more accurately the transformations occurring on the catalyst's surface at a molecular level. The synthesis of materials with nanometric dimensions will facilitate a better understanding of the reaction mechanisms as well as to design novel useful catalytic systems. Nevertheless,

despite several advances in designing new methods to obtain reproducible materials, there still exist numerous difficulties which need to be overcome. From the point of view of the materials, photocatalysts require a series of characteristic properties depending on their applications, including particle size, specific surface area or space between the electronic levels, among others [52, 53].

2.1. Photocatalysis

Houas *et al.* (2001) [54] investigated photocatalytic degradation pathway of methylene blue in water. The results show that methylene blue could be successfully decolorized and degraded by titania-based photocatalysis at room temperature. A detailed reaction mechanism could be presented from the initial step of adsorption involving the cationic functional group of MB molecule, which is probably adsorbed perpendicularly to the surface down to the final products (CO_2 , SO_4^{2-} , NH_4^+ and NO_3^-). The degradation intermediates originated from the initial opening of the central aromatic ring and their subsequent metabolites were formed in agreement with general rules already put in evidence in the degradation of other complex molecules in water. It can be concluded that photocatalysis can decontaminate colored used waters. Photocatalysis appears as the only sub discipline of heterogeneous catalysis, which is able to convert organic pollutants to CO_2 in water without heating nor using high pressure of oxygen nor requiring chemical reactants or additives.

Neppolian *et al.* (2002) [55] investigated the solar light induced and TiO_2 assisted degradation of textile dye reactive blue 4. The authors found that TiO_2 catalyst photodegradation using solar irradiation is a suitable technique for removal of dyes in wastewater from textile industries. The intermediates formed during the

course of degradation give strong evidence for the destruction of the dye into smaller fragments. The oxidizing agents such as hydrogen peroxide and persulphate ion have major role in the

degradation efficiency of the dye. The additives such as sodium carbonate and sodium chloride are hindering the rate of photocatalytic degradation but it can be removed by diluting the dye solution to appropriate concentration.

Rusmidah and Ooi (2006) [56] investigated the photodegradation of new methylene blue N in aqueous solution using zinc oxide and titanium dioxide as catalyst. The results show that 0.015 g TiO_2 and 0.085 g ZnO (15 : 85) was the optimum ratio of TiO_2 and ZnO mixture to degrade Methylene Blue. Any amount greater or less than the optimum ratio decreased the activity of the catalyst.

Kuo and Ho (2006) [57] studied the solar photocatalytic decolorization of dyes in solution with TiO_2 film. The results show that as compared to solar photocatalytic systems without TiO_2 film, application of TiO_2 film to solar photocatalytic system has successfully improved the color degradation capability of the solutions of organic dyes. It was believed that the improved color degradation capability was due to the fact that the visible region of solar light could excite the dye molecules adsorbed on TiO_2 film, followed by a series of photosensitizing reaction. Furthermore, the UV region of solar irradiation could excite TiO_2 molecules to initiate the photocatalytic degradation by generation of hydroxyl radicals, which further promoted the decolorization efficiency pronouncedly. The decolorizing efficiency was in relation to both the maximum absorbance wavelength of dye and the adsorbability of dye on

TiO₂ film. Within the conditions studied, best decolorizing efficiency was achieved for the solution of Methylene Blue. Accordingly, instead of using

artificial UV light source, the solar photocatalytic process assisted by TiO₂ films showed potential application for the decolorization of wastewater.

Tayade *et al.* (2007) [58] studied photocatalytic degradation of dyes and organic contaminants in water using nanocrystalline anatase and rutile TiO₂. The results show anatase and rutile nanocrystalline TiO₂ have been prepared by hydrolysis of titanium tetraisopropoxide and characterized by different physical techniques. The crystallite sizes of anatase (14 nm) and rutile (32 nm) nanocrystalline TiO₂ are changed because of thermal treatment. Anatase nanocrystalline TiO₂ was mesoporous with 124 m².g⁻¹ surface area. There was a shift in the absorption edge of 11.9 nm observed in rutile, which leads to lower band-gap than anatase nanocrystalline TiO₂ due to increase in particle size. The catalysts have been tested for the photocatalytic degradation of AP, NB, MB and MG, which are found in different industries effluents. Higher photocatalytic activity of anatase nanocrystalline TiO₂ was obtained as compared with rutile TiO₂. Studying the reason for the higher photocatalytic activity of the nanocrystalline TiO₂ catalysts is still under progress.

Ullah and Dutta (2008) [59] studied photocatalytic degradation of organic dyes with manganese-doped ZnO nanoparticles. From results ZnO is a wide and a direct band gap material that has been shown to demonstrate photocatalytic activities. The authors therefore, synthesized Mn-doped ZnO nanocrystals for the first time using wet-chemical precipitation techniques. The newly synthesized ZnO:

Mn^{2+} has been observed as an excellent photocatalyst under visible illumination. ZnO: Mn^{2+} photocatalysts showed promising results for degradation of organic dye with visible light irradiation when used as suspended colloids. From

the results we conclude that the photocatalytic activities of doped ZnO nanoparticles are close to 50 times higher than ZnO under visible light irradiation. These preliminary results suggest that ZnO: Mn^{2+} nanoparticles can be used as immobilized photocatalysts for water and environmental detoxification from organic compounds, inorganic compounds like arsenic and bacteria. The development of such photocatalysts may be considered a breakthrough in large-scale utilization of heterogeneous photocatalysis via visible light to address water contamination and environmental pollution.

Xiao *et al.* (2008) [60] studied the solar photocatalytic degradation of methylene blue in carbon-doped TiO_2 nanoparticles suspension. The results show that carbon-doped TiO_2 nanoparticles were prepared by sol–gel auto-combustion technique. UV vis diffuse reflectance spectra showed that carbon-doped TiO_2 exhibited obvious absorption in the visible light range, which was ascribed to the presence of oxygen vacancy state between the valence and the conduction bands because of the formation of Ti^{3+} species in the as-synthesized carbon-doped titania. The sample calcined at 873 K showed the highest photocatalytic activity under solar light irradiation. At low catalyst loadings, such as 0.5 g/L, the catalyst surface and absorption of light were the limiting factors; thus, an increase in catalyst loading greatly enhances the process efficiency. At high loadings, penetration of the light inside the reaction medium was reduced because of the light scattering and shielding effect by catalyst particles. In addition, a basic pH level and a lower initial

concentration of methylene blue (MB) solution were found to be beneficial for photocatalytic degradation.

Yao and Wang (2010) [61] studied the decolorization of methylene blue with TiO_2 sol via UV irradiation photocatalytic degradation. The results show that TiO_2 sol synthesized via a sol-gel method was used in the photocatalytic degradation of MB under UV light. Also, the particle size of TiO_2 sol was 22.5 nm, which was one cause of the light photocatalytic activity of the sol. The high initial concentration of MB interfered with the penetration of UV light transmission. The activity of TiO_2 sol improved in alkaline media. In acidic media, more electrons reacted to form oxidizing species to increase the degradation.

Mohabansi *et al.* (2011) [62] studied the photo degradation of methylene blue dye effluent by advanced oxidation process by using TiO_2/ZnO photo catalyst. The results obtained this study show the efficiency of AOP's in removing dyes, which resists other conventional treatment processes. Photo oxidative degradation appears to be a promising technology that has many applications in environmental cleanup systems. A detailed feasibility study has been carried out on photo catalytic degradation of MB using TiO_2 and ZnO powder as a photo catalyst under UV radiation. It was observed that pH; catalyst dosages and $\text{H}_2\text{O}_2/\text{COD}$ ratio all significantly affect the photo catalytic degradation of MB. The Results of the study indicate that ZnO is very effective & suitable alternative to TiO_2 . The best reaction dosage of ZnO catalyst is about 50 mg/750ml. The maximum degradation efficiency of dye was achieved with the combination of UV + H_2O_2 + ZnO . The

maximum decolorisation occurred in ≤ 90 min. The photo degradation of MB is 99.99%. It follows the first order kinetics.

Mehra and Sharma (2012) [63] studied Photo catalytic degradation of two commercial dyes in aqueous phase using photo catalyst TiO_2 . It was found that the photocatalytic activity of TiO_2 is greater in the presence of solar light as compared to UV light. Experimental results indicate that the decolorization of dyes is felicitated in the presence of catalyst. The initial rate of photodecolorization increased with increase in catalyst dose up to an optimum loading after that it did not show any effect. As the initial concentration of the dye was increased, the rate of decolorization decreased in each dye. The rate of photo decolorization was found to increase with increase in pH, exhibiting maximum efficiency (98.5%) at pH 8, beyond which the rate of degradation remained constant.

Shrivastava (2012) [64] studied the photocatalytic degradation of Methylene blue dye and Chromium metal from wastewater using nanocrystalline TiO_2 Semiconductor. TiO_2 was selected as the photocatalyst for this study because it is insoluble under most conditions, Photo stable, nontoxic and has higher photocatalytic efficiency and relatively inexpensive. The photocatalytic oxidation using a semiconducting material TiO_2 with UV light was successively applied for the degradation of dye and metal species. TiO_2 can remove the dye and metal from aqueous solution. The degradation rate was increased significantly by increasing the amount of semiconductor, while on increasing substrate concentration decolourisation decreases. The pH condition was found to be affected the degradation of metal as well as dye.

Joshi and Shrivastava (2012) [65] studied removal of methylene blue dye aqueous solution using photocatalysis. They found that the photocatalytic degradation of methylene blue can be achieved by using photocatalysts TiO_2 , and ZnO . From this experiment it is possible to obtain decolorized water in a convenient time scale. The experimental results indicates that the degradation process, TiO_2/UV , ZnO/UV system is very effective compared with different natural and artificial adsorbent available. The rate of degradation of dye is found to be more at 0.5 g/L than in 1.0 g/L. of these two catalysts TiO_2 and ZnO , Titanium dioxide is more efficient catalyst than ZnO in the removal of methylene blue. In this system hundred percent of removal of dye is possible in a practical time scale.

2.2. Nanophotocatalyst

Zhou and Kang (2004) [66] studied synthesis and structural properties of manganese titanate MnTiO_3 nanoparticle. In this study, the nanoparticle of MnTiO_3 was prepared by the reaction of TiO_2 powders (P-25) with transition metal hydroxide in CTAB micelle solutions and followed by calcination. The structural, chemical and light absorption properties of these particles were studied with TEM, XRD, UV–Vis and Raman spectroscopy. The nanoparticles are almost spherical or slight stretched and the sizes are in the range of 40–60 nm. The prepared manganese titanate nanoparticles showed a significant absorption band shift into the visible region of 400–700 nm compared to pure of TiO_2 powder. The Raman absorption peaks at 685, 611, 465, 360, 336, 264, 236, 208 cm^{-1} for MnTiO_3 compared to P-25

show the formation of Ti–O–Mn bonds and not just the mixtures of titanium dioxide with transition metals.

Zhou *et al.* (2005) [67] studied the sol-gel preparation and spectroscopies of the pyrophanite MnTiO_3 nanoparticles. They found that pyrophanite MnTiO_3 nanoparticles can be produced from the reaction of the mixed manganese oxides with titanium dioxide in xerogel, which was prepared by the sol-gel method at 75°C in CTAB/ethanol/ H_2O /HCl micelle solutions, during the decomposition of CTAB at the calcinations temperature of 900°C . The prepared MnTiO_3 nanoparticles are almost spherical or slightly stretched and the average sizes are 50 nm, showing a significant absorption band shifted into the visible region. The new Raman absorption peaks at 684, 610, 462, 360, 336, 263, 235 and 202 cm^{-1} for MnTiO_3 show the formation of Ti-O-Mn bonds at the calcinations temperature of 900°C , not just the mixtures of titanium dioxide with manganese oxides.

Guangneng *et al.* (2005) [68] studied the Synthesis of single-crystal BaTiO_3 nanoparticles via a one-step sol-precipitation route. The authors have successfully synthesized agglomerate-free, single-crystal BaTiO_3 nanoparticules via a one-step sol-precipitation route at a low-temperature of 80°C for 5 h. Inexpensive TiCl_4 was used in this process. The formation of the single-crystal BaTiO_3 nanoparticles occurred through a diffusion mechanism of Ba^{2+} ions into the gel at strong alkaline condition. This method might be extendible to other multi-component materials.

He *et al.* (2010) [69] investigated the photodegradation of aqueous methyl orange on MnTiO_3 powder at different initial pH. MnTiO_3 powder was synthesized at low temperature by a sol–gel method. The powder has excellent photocatalytic activity in the destruction of methyl orange in aqueous solution. Low initial solution

pH results in more efficient decolorization of dependence on irradiation time with sunlight of the concentration of aqueous methyl orange containing H_2O_2 and MnTiO_3 powder aqueous methyl orange on MnTiO_3 . H_2O_2 substantially accelerates decolorization of the aqueous methyl orange solution on MnTiO_3 , especially at low initial pH. This excellent photocatalytic activity shows that MnTiO_3 powder is a promising photocatalyst for use in many applications in heterogeneous catalysis and decontamination of the environment.

Enhessari *et al.* (2012) [70] investigated the synthesis, the characterization and the optical properties of MnTiO_3 nanopowders. The authors have successfully synthesized rhombohedral MnTiO_3 powders via a sol–gel synthetic procedure at 900°C . TEM image showed that the particles are in the size range of 22–30 nm. Particle size has been estimated with Scherrer formula about 28 nm and the results obtained from the two methods are close approximately. SEM image indicated that rhombohedral

MnTiO_3 particles were formed, and the size of particles was homogeneous. The formation of MnTiO_3 is further supported by the FT-IR spectra. EDX spectra confirm that this material consists of essentially titanium–oxygen–metal networks and that transition metal Mn has formed a compound with Ti. Using UV–vis spectrum, it has been concluded that MnTiO_3 has a direct band gap value of 3.18 eV.

In this chapter, we present the reagents and equipments, as well as experimental and analytical methods, specifically elimination of dye technique: photocatalysisdegradation.

3.1. Reagents and materials

In this study, manganese titanate $MnTiO_3$ photocatalyst was synthesized. In the synthesis of the catalyst, Titanium (IV) oxide (Powder P-25: mixture of 70% Rutile and 30% Antase) and Titanium (IV) isopropoxide (TTIP) were used as a starting precursor. Distilled water was used as solvent; Nitric acid and Acetic acid were used as peptized in the sol-gel method. Table 3.1 shows all the chemicals with used their sources, their gross and their purities formulas.

Table 3.1: Properties of materials used in catalyst synthesis.

Product	Formula	Company	Purity
Mangane (II) chloride tetrahydrate	$MnCl_4 \cdot 4H_2O$	SIGMA-ALDRICH	>99%
Titanium (IV) oxide(P-25)	TiO_2	ALDRICH	99.5 %
Titanium (IV) isopropoxide (TTIP)	$Ti[O(C_3H_7)]_4$	Fluka	>99%
Hexadecyl tri methyl ammonium bromide (CTBA)	$C_{19}H_{42}NBr$	SIGMA	$\geq 99\%$
Sodium hydroxide	$NaOH$	Fluka	>97%
Nitric acid	HNO_3	PA Panreac	65%
Acetic acid	CH_3COOH	RECTAPUR	99-100%

The methylene blue dye was obtained from Laboratory Chemicals. Methylene blue is a dark green powder at room temperature and gives a dark blue solution when dissolved in water. Methylene blue is a heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3SCl$ (3,7-bis(Dimethylamino)-phenothiazin-5-ium chloride). The molecular structure of the dye is given in Figure 3.1.

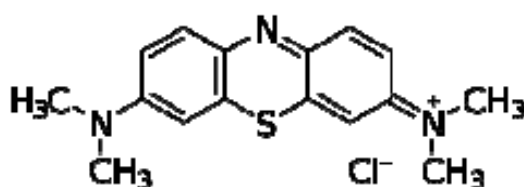


Figure 3.1: Crystal structure of methylene blue [71].

3.2. Instrumentation

3.2.1. X-ray diffraction (XRD)

X-ray diffraction (XRD) measurement was carried out at room temperature using a Philips X-Pert Prodiffractometer (Figure 3.2). The diffractometer consists of a goniometer mounted vertically on an X-ray generator KRISTALLOFLEX 800. This positions the sample goniometer which is rotated at constant angular velocity.



Figure 3.2: Diffractometer Philips X-Pert Pro

The radiation from the X-ray tube is then diffracted by the sample and captured by a detector (scintillation counter NIM kind with which radiation of wavelengths of from 0.01 to 0.27 nm can be measured). We used the copper $K_{\alpha 1}$ radiation ($\lambda = 1.5405 \text{ \AA}$) selected using a rear blade graphite monochromator.

The diffractograms were recorded under the following operating conditions:

- Field angular 2θ : $10^\circ - 70^\circ$.
- Angle increment in 2θ : 0.006° .
- Integration time by counting: 11s.

Based on the XRD data, the crystallite size can be determined from the broadening of corresponding X-ray spectral peaks by Scherrer formula [72].

$$D = k\lambda/\beta\cos\theta$$

Where D is crystallite thickness, k is Scherrer constant ($\sim 0.9-1$), λ is wavelength of the X-ray, β is the broadening of a diffracted peak at the full width at half maximum (FWHM) in terms of radian and θ is diffraction angle in degrees.

3.2.2. Transmission Electron Microscope (TEM)

TEM images have been made by the Centre for Cellular Imaging Health (CICS) located at the Faculty Medicine of Clermont-Ferrand in France. The particle morphology was investigated by means of a Hitachi H-7650 transmission electron

microscope (TEM) operating at 80 kV, in a high resolution mode and combined with
a Hamamatsu AMT HR CCD

camera placed in a side position (Figure 3.3). The samples were deposited on a carbon grid after being dispersed in absolute ethanol.

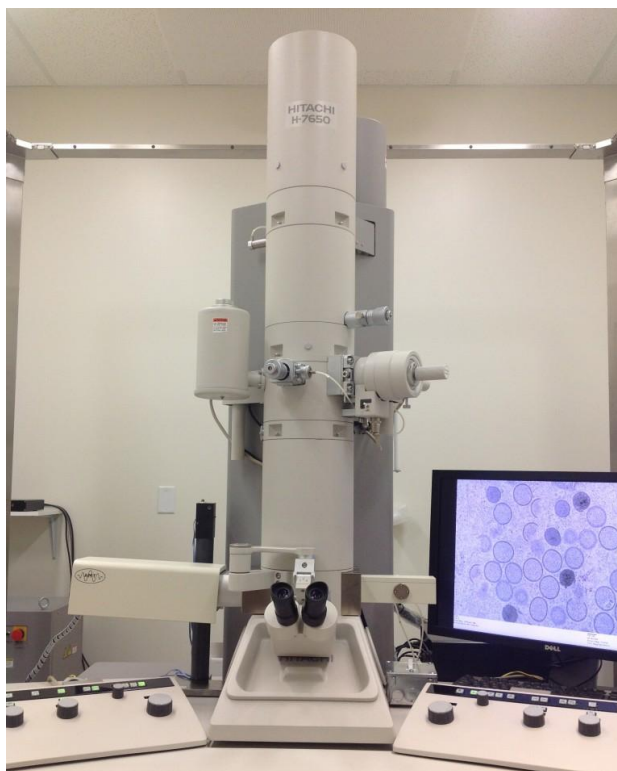


Figure 3.3: Transmission electron microscope Hitachi H-7650

3.2.3. Thermogravimetric and differential thermal analysis

Thermoanalytical measurements (TG-DTA) were performed using a Setaram TG-DTA92 microbalance (Figure 3.4) to operate in a controlled (air, N₂) atmosphere, i.e. air in this case. Thermograms were recorded between 30 and

1200°C with a heating rate of 10°C/min. Measurements were performed on initial quantities of powder of 10 mg to about 15 mg, contained in an alumina crucible.



Figure 3.4: Setaram Microbalance TG-DTA92 used DTA-TGA.

3.2.4. FT-IR instrumentation

The FT-IR spectra of the photocatalysts were recorded using NICOLET 5700 spectrometer (Figure 3.5). Records spectra in the area 400-4000 cm^{-1} were performed under the following conditions:

- Spectral resolution was 8 cm^{-1} .
- The number of accumulations of scans is 32.



Figure 3.5 : Spectrometer NICOLET 5700

3.2.5. Raman Spectrometer

The Raman study was conducted on a micro Raman spectrometer CONFOCAL T64000 Jobin-Yvon OLYMPUS microscope equipped with a CCD detector. The line at 514.53 nm located a coherent laser InnovaAr 70C5 operating at the transmission power of 200 mW was used for electron excitation (Figure 3.6).

The working conditions been selected for recording spectra were as follows:

- The number of scan accumulations is 3, with durations of 60 seconds each.
- The range of frequencies investigated between 200 and 1200 cm^{-1} .

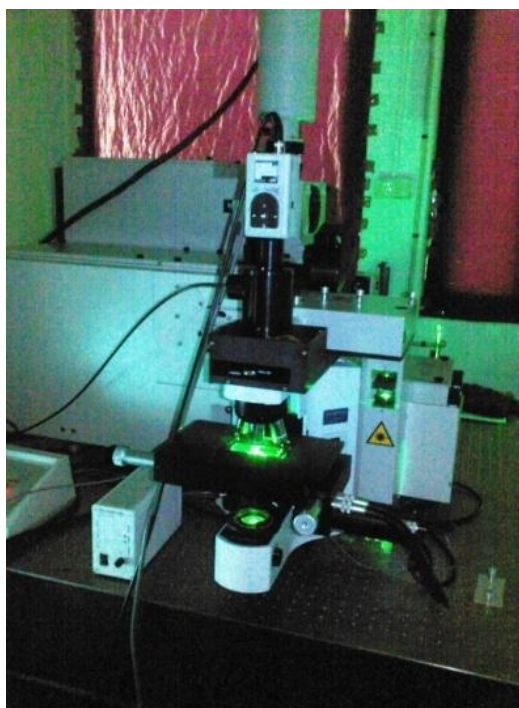


Figure 3.6 : Spectrometer Raman CONFOCAL T64000.

3.2.6. Ultraviolet- visible (UV-vis) Spectroscopy

A OPTIMA UV-vis spectrometer SP-3000 Plus, Figure 3.7, equipped with a cuvette (international labs-type 1 Q 10 mM) was used to measure the absorbance of the samples. The absorbance measurements were taken at fixed wave length 663 nm for methylene blue.



Figure 3.7 : UV-vis spectrometer SP-3000 Plus

3.2.7. Centrifuge

Centrifuge model MULTIFUGE X3 of a maximum speed 9000 RPM was used for complete the separation of the nanosized semiconductor particles used from the sample solution (Figure 3.8).



Figure 3.8: Centrifuge model MULTIFUGE X3

3.2.8. *Electric furnace*

Muffle furnace model Vecster Ltd (FURNACE DIVISION)(Figure 3.9) was used for treatment of the samples. The calcination temperature at 900°C following by heating rate of 10°C/min. The drying gel is made using an ON-02 type stove.

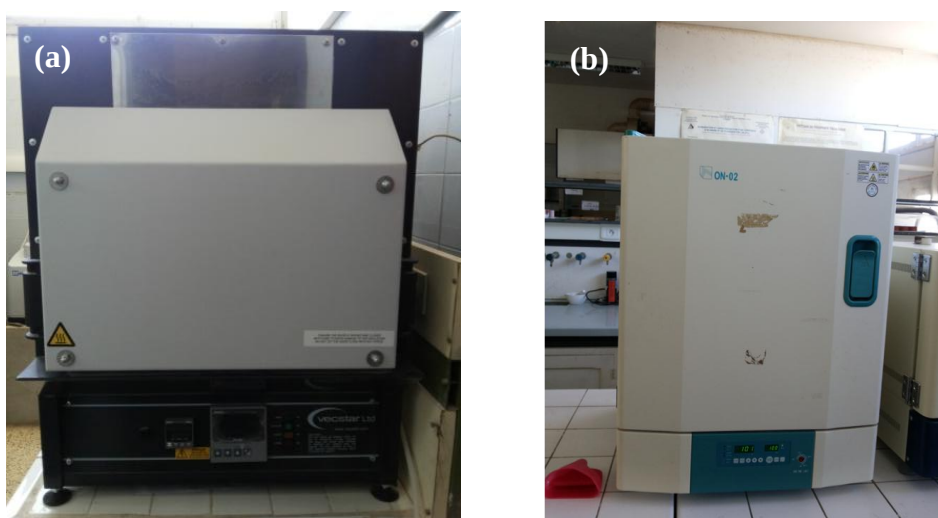


Figure 3.9: (a) Muffle furnace model Vecster Ltd and
(b) Stove model ON-02.

3.2.9. *Magnetic stirrer with hot plate*

The nanosized photocatalysts prepared using a Wisestir MSH-20D magnetic stirrer with hot plate(Figure 3.10), and the stirring capability is 100-1000 r/min.



Figure 3.10: Wisestir MSH-20D magnetic stirrer with hot plate

3.2.10. pH Meter

The pH values during photocatalysts preparation are adjusted using JANWAY 3510 pH Meter (Figure 3.11). The calibration of the apparatus is achieved with buffers standard solutions (pH 4, 7 and 10).



Figure 3.11: JANWAY 3510 pH Meter

3.3. Experimental methods

In this work, the experiments could be categorized into 2 groups.

- Preparation of the MnTiO_3 photocatalyst material
- Photocatalytic activity tests

3.3.1. Preparation of nanosized photocatalyst

The structure of the catalyst which plays a crucial role in substrate binding by the size of its particles. Indeed, the larger the size, the smaller the contact surface will be and this will lead to therefore decrease its holding capacity. Sol-gel process allows synthesizing materials of high purity and homogeneity in a variety of shapes: ultrafine powders with controlled shapes, films, fibers, aerogels, between others. In this research work, MnTiO_3 nanoparticles were prepared by the sol-gel process following two methods of preparation.

3.3.1.1. Sol-gel method (SG-1)

In this work, the synthesis route, 0.01 mol $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was dissolved into 30 ml distilled water, which reacts with 0.02 mol NaOH to produce $\text{Mn}(\text{OH})_2$. Then 0.01 mol of P-25 powder (TiO_2) was added to the above solution. An aqueous micelle solution of CTAB (0.01 mol CTAB in 30 ml distilled water) was added to the mixture. The mixed solution then stirred using under magnetic stirring at 75 °C (Figure 3.12). The mixed solution was further refluxed for 12 h at 75 °C. The supernatant was then decanted, and the solid residue was washed three times with distilled water, dried in air at 100 °C for 12 h and calcined in air at 900 °C for 6 h.

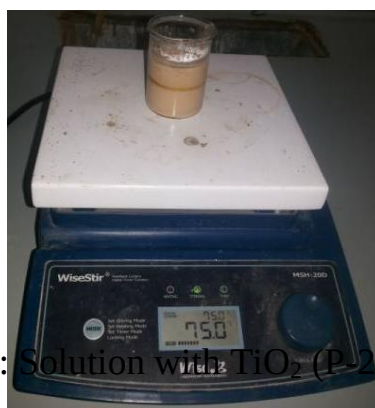


Figure 3.12: Solution with TiO_2 (P-25) starting precursor.

3.3.1.2. Sol-gel method (SG-2)

In this method, An appropriate amount of manganese chlorite tetrahydrate $\text{MnCl}_4 \cdot 4\text{H}_2\text{O}$ (0.6 g) was dissolved in 25 mL of distilled water with addition 0.12 mL of nitric acid HNO_3 , 1.6 mL acetic acid CH_3COOH and then 0.115g of CTAB cationic surfactant. 1 ml of titanium propoxideisopropoxide, $\text{Ti}[\text{O}(\text{C}_3\text{H}_7)]_4$ was added to the above mixture (the molar ratio of Mn to Ti was 1:1 in the reactants) and a white precipitate was formed immediately. The mixture was then stirred for 12h maintaining the temperature at 50°C (Figure 3.13). The resulting semi-transparent colloidal suspension solution was evaporated at 80°C till the formation of powder. The powder was dried and ground and calcined at 900°C for 6 hours.

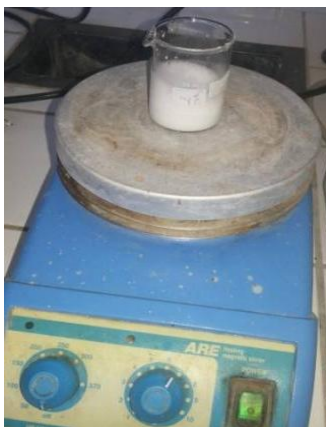


Figure 3.13: Solution with $\text{Ti}[\text{O}(\text{C}_3\text{H}_7)]_4$ (TTIP) starting precursor.

3.3.2. Nanosized photocatalytic experiments

Direct photolysis comprises irradiating the matrix with a light intensity of selected wavelength so that the energy of the photons can be absorbed in the medium, in particular contaminants to be degraded. Indeed, due to their property to absorb the UV light, the molecules were activated using by charge transfer before degraded. Because thus, many studies advised and showed that photolysis was an effective method to oxidize certain compounds.

3.3.2.1. Light Sources

Different light sources were used for photodegradation of organic pollutants like: direct sun light or UV Lamps.

Direct sun light was used for photodegradation experiment with nanoparticle MnTiO_3 powder. Irradiation experiments were carried out in a glass reactor (Figure 3.14). The methylene blue dye solutions with the desired initial concentrations were poured into the glass reactor and MnTiO_3 photocatalysts with different loadings were placed in the pyrex vessel. The experiments were conducted under room temperature (20°C). Samples of the methylene blue dye solution were taken after 1, 2, 3, 4 and 5 hours of different time interval of irradiation.



Figure 3.14: Bottles represent the solution exposed to sun light irradiation for different time interval (1 hr, 2 hrs, 3 hrs, 4 hrs and 5hrs).

UV photo-degradation reactions were conducted in a magnetically stirred. The pyrex vessel was placed in a radiation cabinet equipped with UV fluorescent lights(each UV light having an intensity of 100 or 10W)(Figure 3.15).

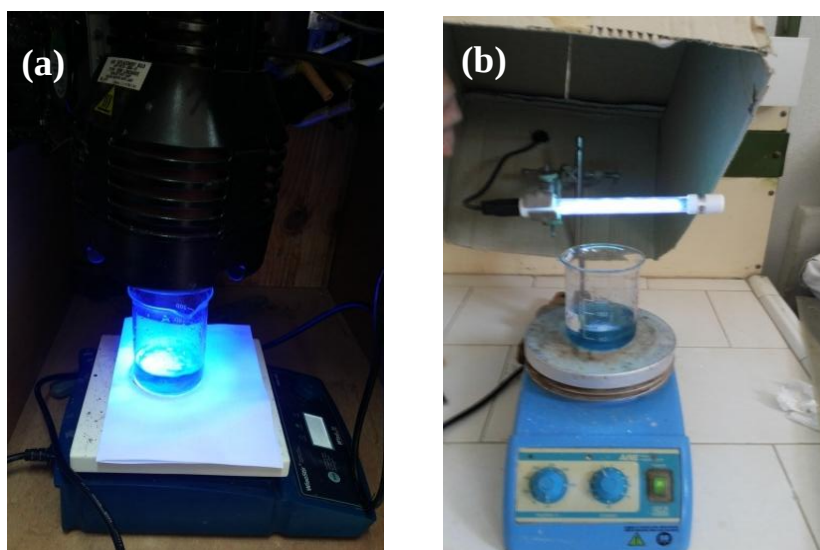


Figure 3.15: Different Intensity of UV Lamp(a) 100W. UV-lamp (b) 10 W. UV-lamp

Reaction system was setup by adding 0.005 g of nanosized photocatalyst MnTiO_3 into 50 ml dye solution (MB) prepared in appropriate concentrations using distilled water (1×10^{-5} M, pH=6.4). The dye solution is stirred in the dark for 15 min after the addition of the catalyst to establish an adsorption/desorption equilibrium. Samples of suspension are withdrawn at regular intervals and were immediately centrifuged at 4000 rpm for 10 min to completely removal of catalyst particle, and UV measurement was done.

3.3.2.2. The degradation of MB dye

The percent degradation of MB dye was calculated as follows[73]:

$$D(\%) = \frac{(A_0 - A_t)}{A_0} \times 100$$

Where D is the percent degradation, A_0 is the absorbance of initial MB; A_t is the absorbance of the solution after illumination at time t . The measurement was repeated at two times for each sample drawn from one batch of material, and each result was averaged.

3.3.2.3. The kinetic of adsorption

A kinetic analysis of a certain reaction can be conventally made by measuring physical properties that show linear dependence on concentration of one or all of the reagents present in a reaction mixture. The adsorption kinetics shows the evolution of the adsorption capacity through time and it is necessary to identify the types of adsorption mechanism in a given system.

To analyze degradation kinetics of the MB dye, Langmuire Hinshelwood (L-H) kinetics is commonly used [74]. This L-H model is described by the first-order kinetic equation as follows:

$$\ln \frac{C_t}{C_0} = -kt$$

When C_0 and C_t are concentration at the beginning and at a certain time, t is the irradiation time. $k(\text{min}^{-1})$ is the rate constant of the first-order kinetic.

Adsorption kinetics investigations were carried out by agitating 50 mL of MB ($1 \times 10^{-5} \text{M}$) dye solution of known initial concentration with 0.005 g of adsorbent prepared by SG-1 and SG-2 routes, at pH of 6.4 and at 240 min for different time intervals.

3.3.3. Application of MnTiO_3 powder nanostructures for treatment of real industrial textile wastewater sample using sun light

The active photocatalysts MnTiO_3 was applied for degradation of real wastewater treatment plant. The experiments are carried out in the sun light as a light source. Reaction system was setup by adding different loadings of nano-photocatalyst MnTiO_3 (prepared by SG-2) into 50 ml wastewater (pH=3). The wastewater solutions are stirred in the dark for 15 min after the addition of the catalyst to establish an adsorption/desorption equilibrium. The suspension was withdrawn at regular intervals and immediately centrifuged at 4000 rpm for 10 min to ensure complete removal of catalyst particle. Degradation of wastewater contaminants by active photocatalysts was followed by measuring the absorbance for 0, 1, 2 and 3 h intervals of illumination under sun light. This absorption data was used in the determination of degradation percent of the dye through comparison with the absorbance at a certain time as a percentage of the initial absorbance.

Improving of photooxidative efficiency of MnTiO_3 as example of inorganic semiconductors has become a significant importance for many research groups to meet the requirements of environmental protection. Many approaches have been pursued to promote the photo-oxidative activity of MnTiO_3 such as the choice of synthesis methods. Sol-gel process approach to ceramic materials synthesis, also in form of nanosized powders, is a well-known method which takes advantage of a direct preparation at low crystallization temperatures without any additional calcinations steps. The photocatalytic activity of MnTiO_3 nanoparticuls and its application in wastewater treatment have rarely been reported. So in this chapter, we present the results of photodegradation of a cationic dye, methylene blue, in the presence of MnTiO_3 nanocatalyst. The influence of many factors such as the initial concentration of dye, pH, amount of semiconductor, light intensity, etc. has been studied. Kinetic studies show that this reaction follows pseudo-first order kinetics. Also, we applied this technique in wastewater treatment.

4.1. Characterization of MnTiO_3 nano-particles prepared

4.1.1. X-Ray Diffraction (XRD)

The XRD is usually used for identification of the crystal phase as well as crystalline size of this phase. Figures 4.1 and 4.2 present the XRD patterns of the manganese (II) titanate, MnTiO_3 , nanoparticles synthesized by sol-gel:

- Method 1 (SG-1) , using Titanium dioxide powder P-25, 70% TiO_2 anatase and 30% TiO_2 rutile, as precursor, and calcinated at 900 °C for 6 hours.
- Method 2 (SG-2), using Titanium isopropoxide as precursor and fired at 900 °C for 6 hours.

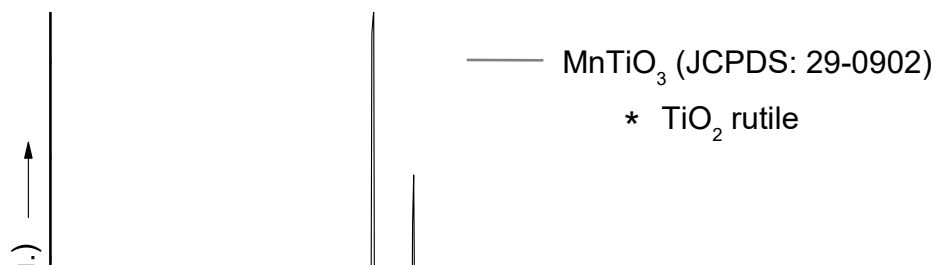


Figure 4.1: X-ray diffraction pattern for synthetic MnTiO_3 using Titanium dioxide powder P-25 precursor

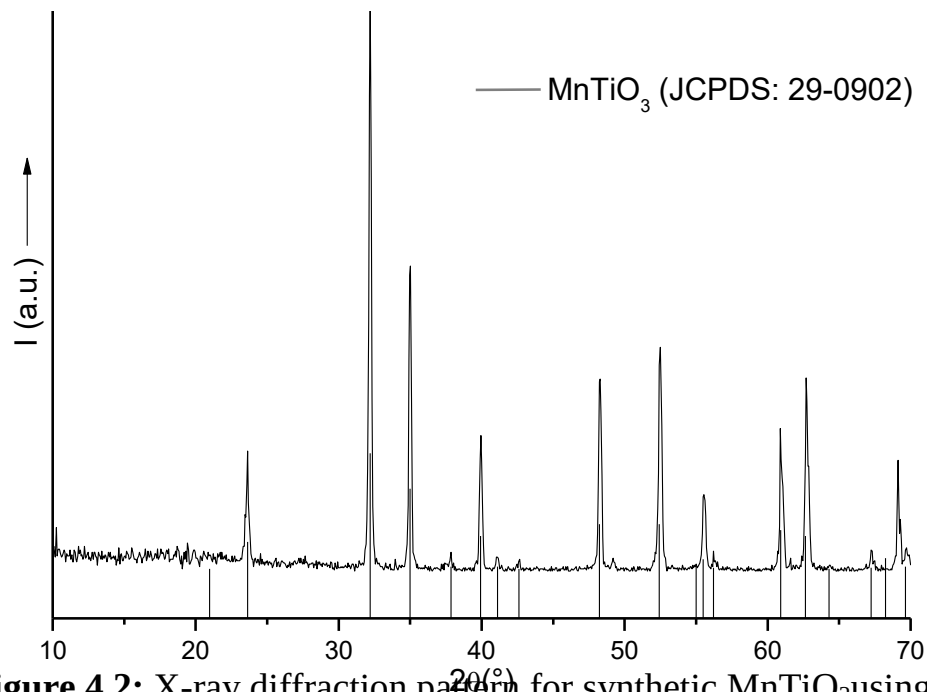


Figure 4.2: X-ray diffraction pattern for synthetic MnTiO_3 using Titanium isopropoxide precursor.

X-ray diffraction patterns in Figure 4.1 confirm that the crystallisation of rhombohedral MnTiO_3 phase along with traces of TiO_2 rutile phase ($2\theta = 27.59^\circ$,

33.12, 36.22 and 54.61°) (* marked peaks, JCPDS: 78-1508). Semi quant % of MnTiO₃ and TiO₂ are given in Table 4.1.

Table 4.1: Semi quant % of MnTiO₃ and TiO₂ for powder prepared by sol-gel, method 1 (SG-1)

Ref. Code	Compound Name	Chemical Formula	Semi Quant %
29-0902	Manganese(II) titanate	MnTiO ₃	77.6
78-1508	Titanium Oxide	TiO ₂	22.4

Figure 4.2 shows the XRD patterns of the product synthesized by using Titanium isopropoxide as precursor. All the reflection peaks can be indexed to rhombohedral pyrophanite phase MnTiO₃ when the precursor was calcined at 900 °C for 6 h. All the MnTiO₃ nano-particles exhibit rhombohedral phase (JCPDS 29-0902). No peaks corresponding to rutile phase are detected in the XRD pattern, which shows the high purity of the product.

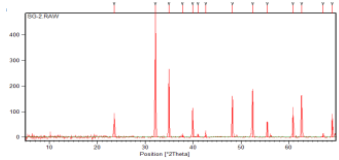
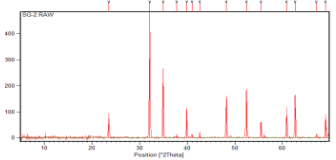
The crystallite sizes of the particles were estimated from XRD peak half widths using the Scherrer equation [72], after correction for instrumental broadening:

$$D = \frac{0.9 \lambda}{b \cos \theta}$$

Where D is the average crystallite diameter (nm), λ is the X-ray wavelength (nm), b is the full width at half maximum (FWHM) of the peak corrected for instrumental broadening (radian.) and θ is the Bragg's angle (degree). The calculated values average particle diameters for MnTiO₃ powders synthesized

by sol gel method SG-1 and SG-2 were approximately 29.16 and 35.46 nm respectively. Small crystallite growth by annealing at 900 °C is observed from measured particle sizes. The results are presented in Table 4.2.

Table 4.2: Peak position and particle size values for different synthetic MnTiO₃ by (a) sol-gel method 1 and (b) sol-gel method 2.

Sol-gel method 1 (SG-1)			Sol-gel method 2 (SG-2)		
					
Peak position [2θ °]	FWHM	D (nm)	Peak position [2θ °]	FWHM	D (nm)
5.497	0.864	9.205	23.530	0.236	34.355
18.874	0.216	37.283	32.142	0.236	35.001
23.621	0.288	28.180	34.943	0.177	47.027
27.515	0.288	28.399	37.751	0.708	11.850
32.185	0.288	28.709	39.884	0.236	35.779
33.014	0.288	28.770	41.069	0.354	23.950
35.013	0.288	28.924	42.599	0.177	48.146
36.125	0.288	29.014	48.235	0.236	36.850
39.918	0.288	29.347	52.449	0.236	37.492
48.276	0.216	40.303	55.502	0.295	30.409
52.496	0.216	41.007	60.895	0.236	39.014
54.503	0.288	31.028	62.642	0.295	31.502
55.429	0.576	15.579	67.180	0.236	40.375
60.956	0.288	32.006	69.089	0.216	44.651
62.797	0.288	32.316			
65.842	0.864	10.953			
69.133	0.216	44.663			
Average particle diameter		29.158	Average particle diameter		35.457

4.1. 2. TEM microscopy

Transmission electron microscopic (TEM) observation of typical samples indicates that the nanocrystalline nature of particles is almost spherical or slightly stretched. This is well shown in Figure 4.3. Rather dark crystalline spots can be observed beside less dark region. These dark spots and less dark spots can be attributed to the different orientation of MnTiO_3 nanocrystallites, because the brightness and darkness of an item in TEM image depend on its orientation.

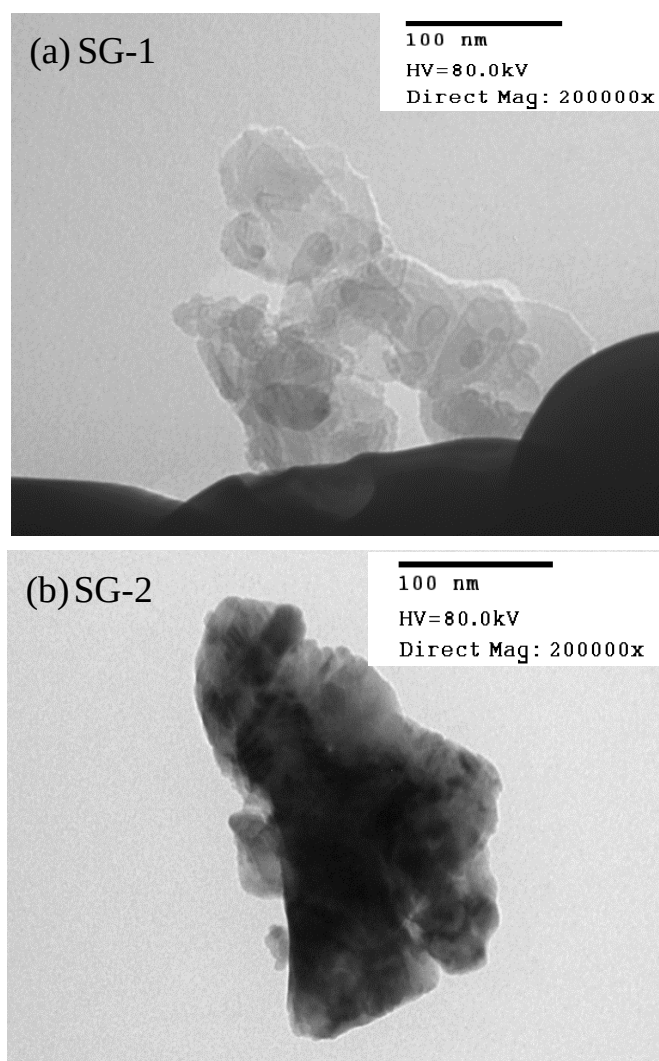


Figure 4.3: TEM pictures of MnTiO_3 nanopowders prepared by sol-gel method (a) SG-1 and (b) SG-2 calcined at 900 °C.

Thus, the fine powder with limited aggregation can be observed. It has a narrow size distribution ranging between 15–30 nm, but still has a certain extent of agglomeration. This observation is inconsistent with the XRD results.

4.1. 3. *TG –TD thermal analyses*

To investigate the domains of stability and decomposition of MnTiO_3 calcinated at 900 °C in more details, Thermogravimetric analysis of pyrophanite, prepared by sol–gel process (SG-1 and SG-2), was performed, over the temperature range 25-1200 °C, with a heating rate of 5 °C.min⁻¹, The thermograms in Figures 4. 4(a) and (b) show no thermal effects accompanied by mass losses.

A first analysis of thermal curves clearly shows almost the same behavior never the less of the chosen synthesis protocol.

Indeed, the endothermic peak observed for both synthesis sol-gel routes between 80 °C and 250 °C can be attributed to dehydration of water molecules. In the temperature range of 250 to 450 °C, no weight loss was exhibited, that proves the absence of hydroxyl groups and/or organic residues such as alkoxy groups in the powder of MnTiO_3 . It showed that no significant changes were observed both in DTA and TGA curves even up to 1200 °C. As we expected, the thermal stability of MnTiO_3 was improved effectively.

For the compound prepared by sol-gel method 1 ,were titanium dioxide powder P-25, 70% TiO_2 anatase, 30% TiO_2 rutile used as starting precursor, a slight endothermic effect is identified accompanied with low mass loss observed around 1000 °C, Figure 4.4(a). From the foregoing XRD characterization, the presence of titanium dioxide TiO_2 was observed in the calcined

powder SG-1 at 900 °C. According to these observations, we can hypothesize that the endothermic peak around 1000 °C corresponds to the decomposition or loss of TiO_2 phase.

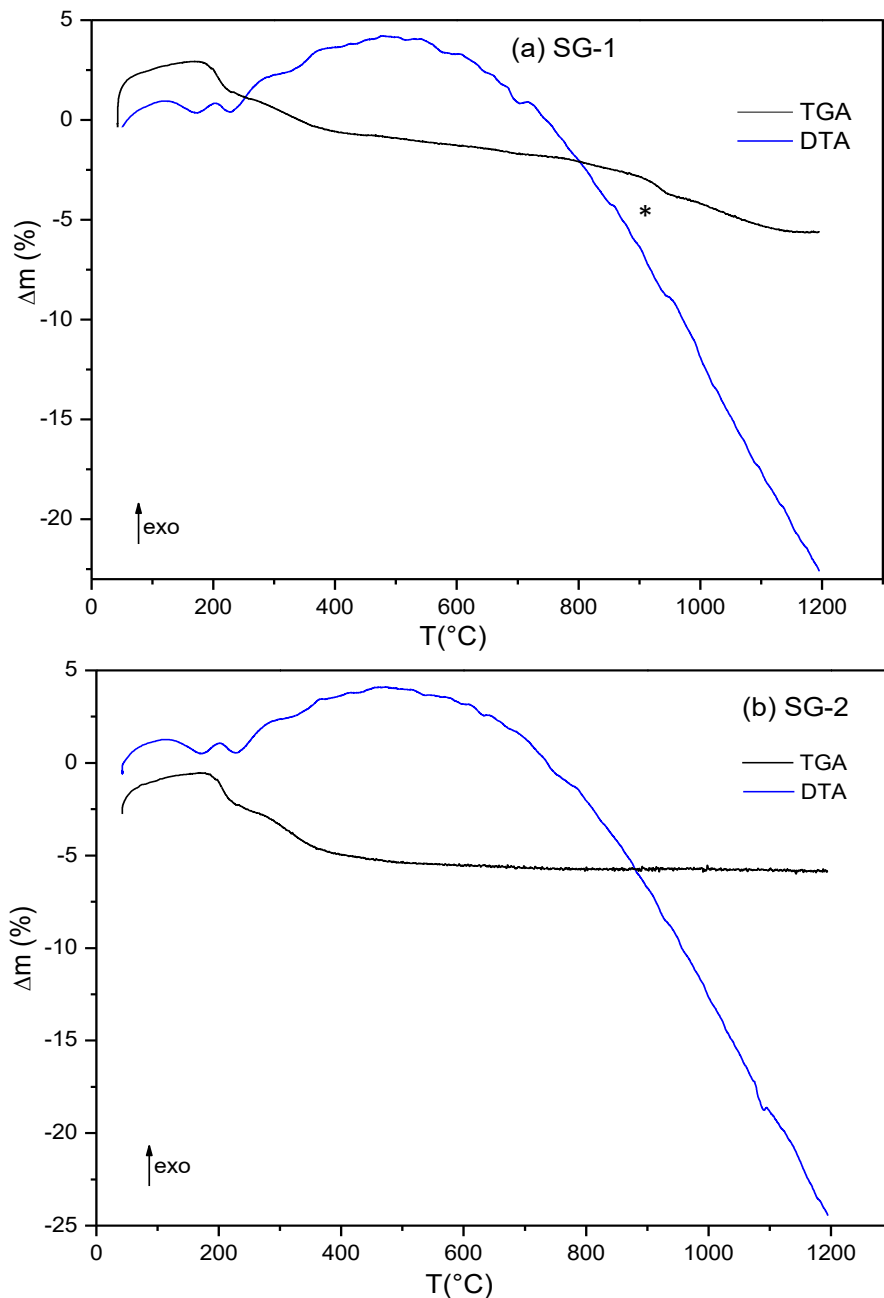
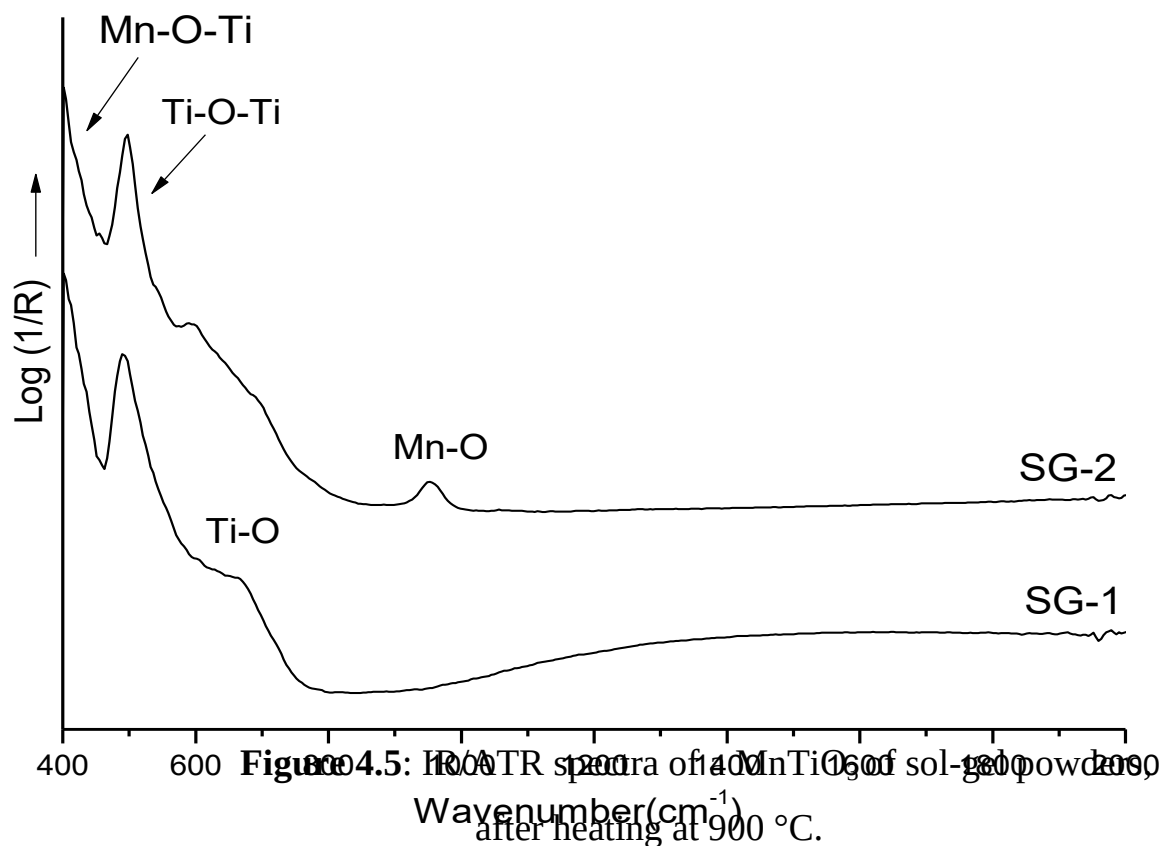


Figure 4.4: TG-DTA curves of the as-synthesized powder
(a) SG-1 and (b) SG-2 methods.

4.1.4. Infrared spectroscopy

FTIR spectroscopy provides important information about the chemical composition and structure of amorphous, poor or well crystallized materials, it is also helpful to identify the active centers on the oxide surface. Room temperature FTIR/ATR spectra recorded for MnTiO_3 samples prepared by both synthesis routes (SG-1 and SG-2) and measured in the range of $400\text{--}2000\text{ cm}^{-1}$ spectral region are shown in Figure 4.5. This region contains the bulk absorption bands attributed to Ti–O, Ti–O–Ti, Mn–O, Mn–O–Mn and Mn–O–Ti vibrations, as well as lattice vibration modes.



IR absorption spectra are characterized with main absorption bands in the IR/ATR spectra of MnTiO_3 centered at 407, 494, and 656 cm^{-1} . All these bands were

assigned to the Ti–O bond vibrations. The bands at 407 and 494 cm^{-1} , can be assigned to Mn–O–Ti, and O–Ti–O vibrational modes, respectively [75]. The band centered around 657 cm^{-1} observed in SG-1 sample can be also attributed to corresponding Ti–O modes of crystalline rutile TiO_2 .

Figure 4.5, shows the broad band between 800 and 1000 cm^{-1} , which was assigned to Mn–O bonds for SG-2 sample [76].

4.1.5. Raman spectroscopy

In recent years, Raman spectroscopy has become an increasingly valuable tool for the investigation of the supported catalysts [77-79]. Raman spectra of complex oxide systems are known to be strongly affected by defect structures within the material producing large shifting and broadening of some of the spectral peaks. Raman spectra were related to the oxygen stoichiometry of the material and not due to any internal stress or grain size effects. The spectra of MnTiO_3 prepared by both routes (SG-1 and SG-2) are comparatively shown in Figure 4.6.

In the Raman spectrum of pyrophanite MnTiO_3 , there are 10 Raman active modes ($5A_g + 5E_g$) [80]; among them the most prominent are the bands centered at 208, 238, 265, 339, 362, 469, 611, and 688 cm^{-1} [81]. The intensive Raman band at 688 cm^{-1} is regarded as the most typical feature for MnTiO_3 . This A_{1g} symmetric stretching mode arises from the highest frequency vibrational mode of octahedral MnO_6 moiety [80].

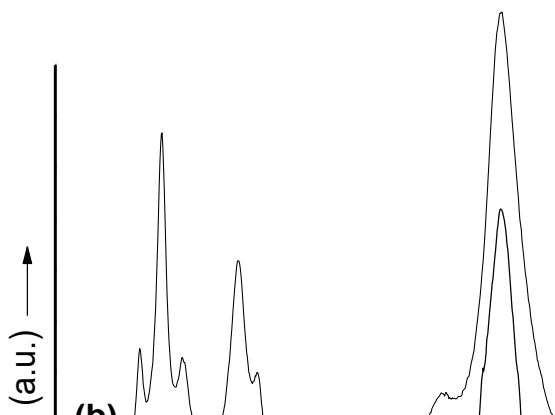


Figure 4.6: Room temperature Micro-Raman spectra of MnTiO_3 synthesized using sol-gel technique (a) SG-1 and (b) SG-2.

Raman spectra of MnTiO_3 sample, synthesized by sol-gel method (SG-1), Figure 4.6(a), shows asignatures of the impurity phase in the form of weak lattice mode of TiO_2 observed at 441 cm^{-1} . According to the data, this is attributed to E_g rutile mode [82].

4. 2. Photocatalytic activity of MnTiO_3 nanoparticles.

In photocatalytic degradation of methylene blue (MB) dye in aqueous phase, under the followings operating parameters, such as, contact time, light source, pH of the solution to be degraded, initial concentration and photo catalytic dose. These parameters will be considered in sequence as they influenced the photocatalytic processes of the degradation of MB dye in waster.

Moreover, this section includes results of kinetics studies of photochemical decomposition of methylene blue dye in the presence of MnTiO_3 nanoparticles as photocatalyst.

4.2.1. Absorption characteristic of methylene blue (MB) dye

Characteristic wavelength of maximum absorption λ_{max} for methylene blue, are determined from the absorption spectra shown in Figure 4.7.

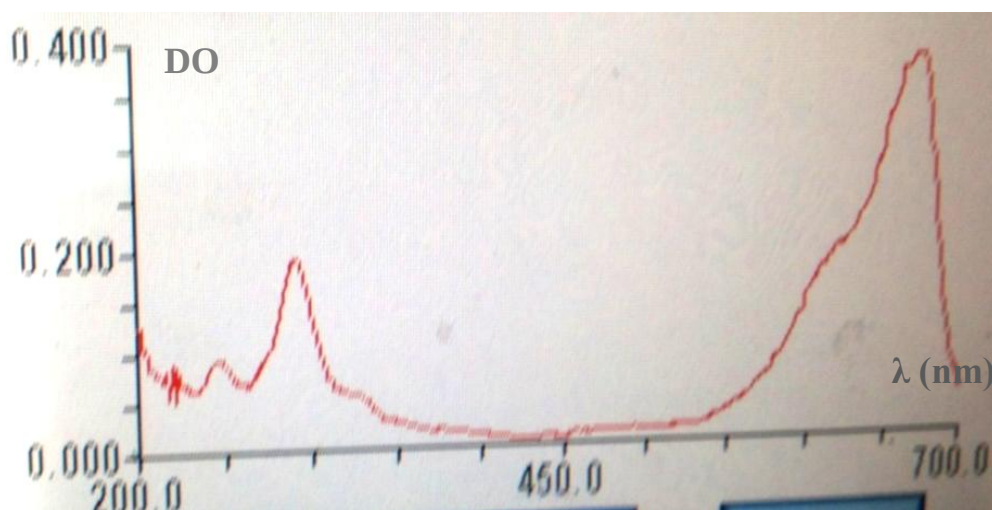


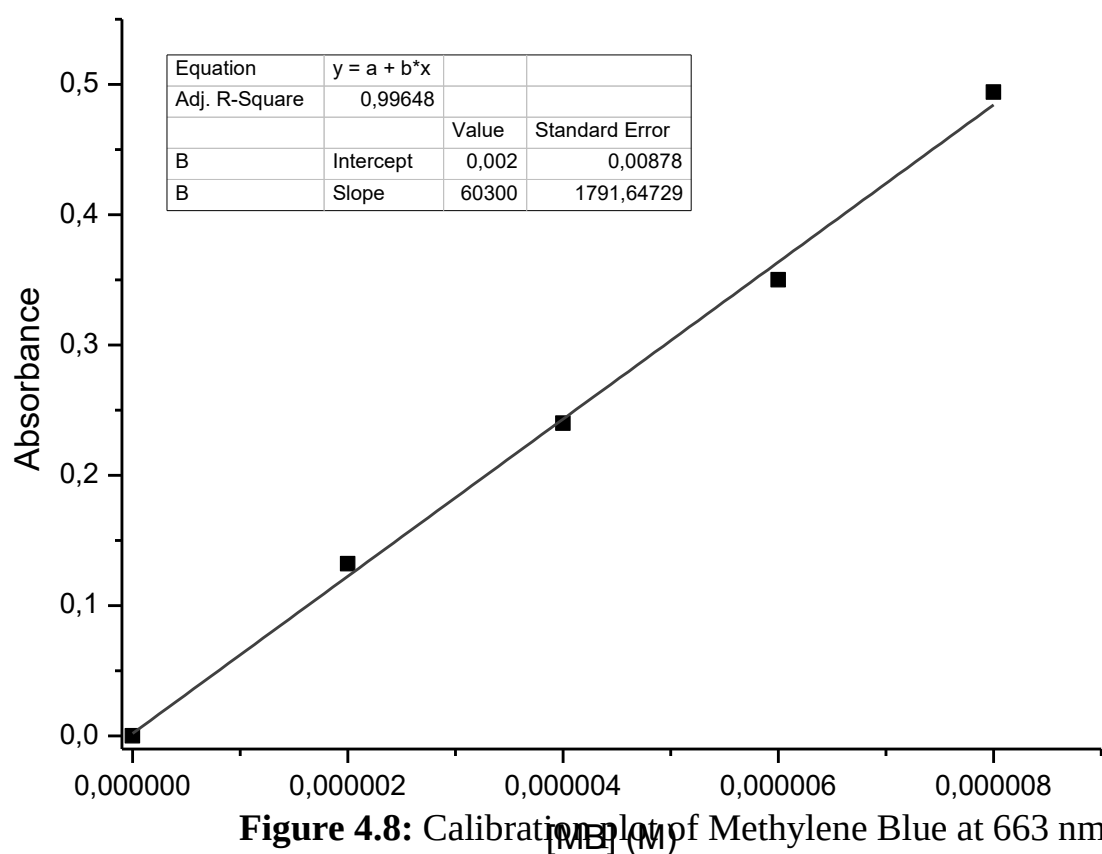
Figure 4.7: Absorption spectrum of the aqueous solution of 1×10^{-5} M Methylene Blue at pH 6.4.

The absorption spectrum of an aqueous solution of methylene blue (1.10^{-5} M) at pH = 6.4 shows three absorption bands, a main characteristic band with an absorption maximum at 663 nm, another band was located at 240 nm, and at lower wave length, a third was located at 300 nm.

The spectra reveal that, the value λ_{max} is 663 nm for methylene blue. This λ_{max} value was then used for all absorbance measurements throughout all the experiments.

In order to determine the concentration of methylene blue dye, a calibration curve was generated from the standard solution of methylene blue.

Calibration plot for methylene blue (Figure 4.8), illustrate that the absorbance value follow Lambert-Beer's law in the range of concentrations examined as evidenced by the fact that the calibration plot is linear. The calibration curve between absorbance and concentration of MB dye gave a high linear regression of 0.99 at 663 nm.



4.2.2. Photocatalytic of methylene blue using solar light source

To understand photodegradation phenomenon of methylene blue dye using semi-conductor MnTiO_3 nanoparticles as catalyst, we studied the influence of

several factors on the degradation process, including contact time, photocatalyst loading, initial concentration, pH and the nature of light source.

4.2.2.1. Effect of contact time

Adsorption of methylene blue on MnTiO_3 nanocatalyst surface, obviously, is a function of the contact time, which is corresponding to the time of adsorption, or the state of saturation of the absorbant surface by the absorbate (dye). In equilibrium this case, the experimental procedure is a 0.005 g of nanocatalyst was added to an Erlenmeyer flask containing 50 ml of dye aqueous solution. The catalyst and methylene blue mixture was kept in the dark for 30 minutes at room temperature, prior to illumination, to allow for adsorption of the methylene blue onto the surface of the catalyst, under continuous stirring with an electronic stirrer. The mixture was irradiated by sun light for different time intervals 0–240 min. The mixture was filtered, and the filtrate was measured by UV-Vis spectrophotometry. The same procedure was repeated using different weights of the catalyst (0.01 g). Absorbance values are recorded and the results are summarized in Table 4.3.

Effect of contact time on the removal of methylene blue from aqueous solution is presented in Figures 4.9(a) and (b) by MnTiO_3 , (SG-1 and SG-2) synthesized under different conditions. The results show that the catalysis of photodecomposition of methylene blue occurs. It was observed

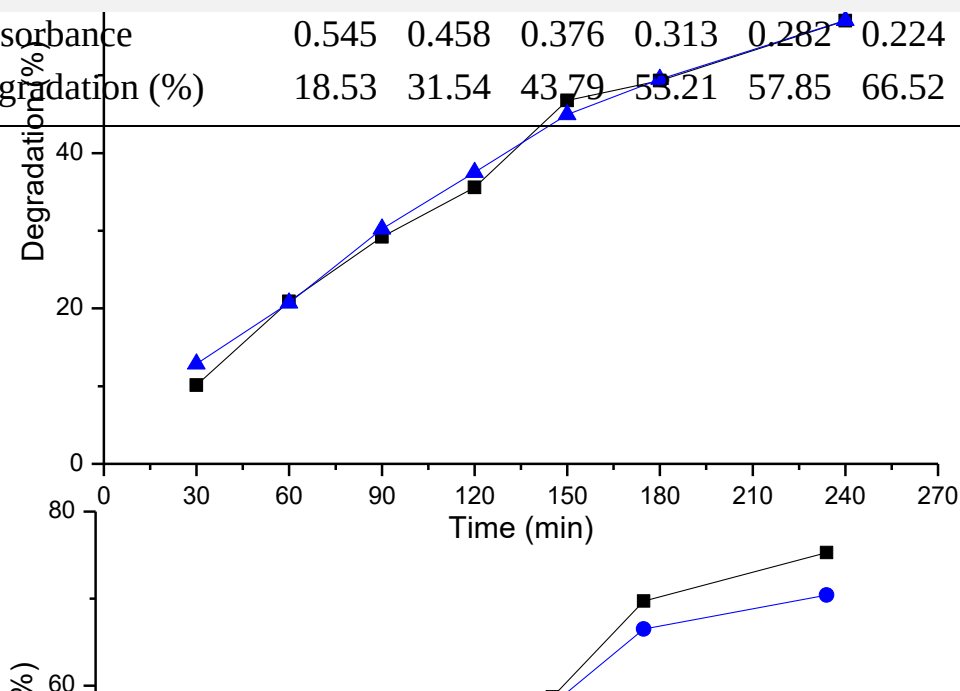
that the degradation percent decreased after 240 min to less than 75%.



Color change of 1×10^{-5} M Methylene Blue at pH =6.4 with two dose
of MnTiO_3 catalyst after 4 hours irradiation time

Table 4.3: Values of Absorbance and degradation % under solar light using two weights (a) 0.005g and (b) 0.01g of MnTiO_3 , prepared by SG-1 and SG-2 methods, as function of contact time.

N° of experiment	1	2	3	4	5	6	7
Time/min	30	60	90	120	150	180	240
(a) 0.005 g							
SG-1($\text{MnTiO}_3/\text{TiO}_2$)							
Absorbance	0.594	0.523	0.468	0.426	0.352	0.335	0.284
Degradation (%)	10.14	20.88	29.20	35.55	46.75	49.32	57.03
SG-2 (MnTiO_3)							
Absorbance	0.611	0.556	0.489	0.438	0.386	0.354	0.301
Degradation (%)	12.84	20.69	30.24	37.52	44.94	49.5	57.06
Time/min	30	60	90	120	150	180	240
(b) 0.01 g							
SG-1($\text{MnTiO}_3/\text{TiO}_2$)							
Absorbance (a)	0.608	0.497	0.405	0.345	0.311	0.228	0.186
Degradation (%)	19.26	33.99	46.21	54.18	58.7	69.72	75.3
SG-2 (MnTiO_3)							
Absorbance	0.545	0.458	0.376	0.313	0.282	0.224	0.198
Degradation (%)	18.53	31.54	43.79	53.21	57.85	66.52	70.4



(b)

Figure 4.9: Effect of contact time on % of removal of methylene blue dye with MnTiO₃ (a) dose 0.005g/50 mL and (b) dose 0.01g/50 mL at pH 6.4.

As shown in Figure 4.9(a), it is indicated that the efficiency of methylene blue decolorization using the individual MnTiO₃ catalyst is substantially identical as compared with the mixture MnTiO₃/TiO₂ catalyst.

However, for a more amount of photocatalyst, when the photocatalyst were mixed MnTiO₃/TiO₂, the degradation was not quite high (75%) as compared with the pure MnTiO₃ nanoparticle (70%) (Figure 4.9(b)). The possible reasons may be simultaneous photo excitation of the photocatalysts and quickly passing the electrons to the dye molecules thereby preventing the reunion of electrons & hole pair, this triggers the various reactions leading to the degradation of dye.

4.2.2.2. Effect of catalyst loading

In order to examine the effect of catalyst dose on the removal efficiency and degradation of MB dye, experiments were set up with different amounts of MnTiO_3 catalyst. While keeping initial dye concentration 1.10^{-5} M at pH= 6.4. The values of absorbance obtained and percentage of degradation calculated are collected in Table 4.4.

Table 4.4: Values of Absorbance and degradation % under solar light using different weight of nanosize catalyst, prepared by SG-1 and SG-2 methods.

(a)	$\text{MnTiO}_3/\text{TiO}_2$ (SG-1)				
Wt. of catalyst	0.005	0.01	0.02	0.03	0.04
A (t = 0 h)	0.621	0.65	0.705	0.73	0.719
A (t= 4 h)	0.149	0.162	0.186	0.214	0.224
D%	76.01	75.07	73.62	70.68	68.84
(b)	MnTiO_3 (SG-2)				
Wt. of catalyst	0.005	0.01	0.02	0.03	0.04
A (T = 0 h)	0.567	0.559	0.564	0.536	0.462
A (T = 4 h)	0.213	0.232	0.238	0.249	0.206
D%	62.43	58.49	57.8	53.54	55.41

The decolorization of dye was observed after 4 h of irradiation. As shown in Figure 4.10, the color of methylene blue changed from blue to bluish white.



Figure 4.10: Color change of Methylene Blue with different amounts of catalyst suspension following photocatalytic degradation after 4 hours irradiation time.

Figures 4.11(a) and (b) show the degradation of MB dye using MnTiO_3 nanoparticle synthesized by SG-1 and SG-2 respectively.

It has been observed that the rate of photo-degradation was higher using lower amount (0.005 g) of semiconductor, 76% of MB degradation for catalyst obtained by SG-1 (Figures 4.11(a)) and 62.43 % of MB degradation for catalyst prepared by SG-2 (Figures 4.11(b)). Whereas the presence of an amount of the TiO_2 in the powder of MnTiO_3 , prepared by SG-1 synthesis, increased the reaction of photodegradation of MB dye. The excellent photo-catalytic activity of TiO_2 had been reported by many researchers for the decomposition of organic pollutants [83, 84].

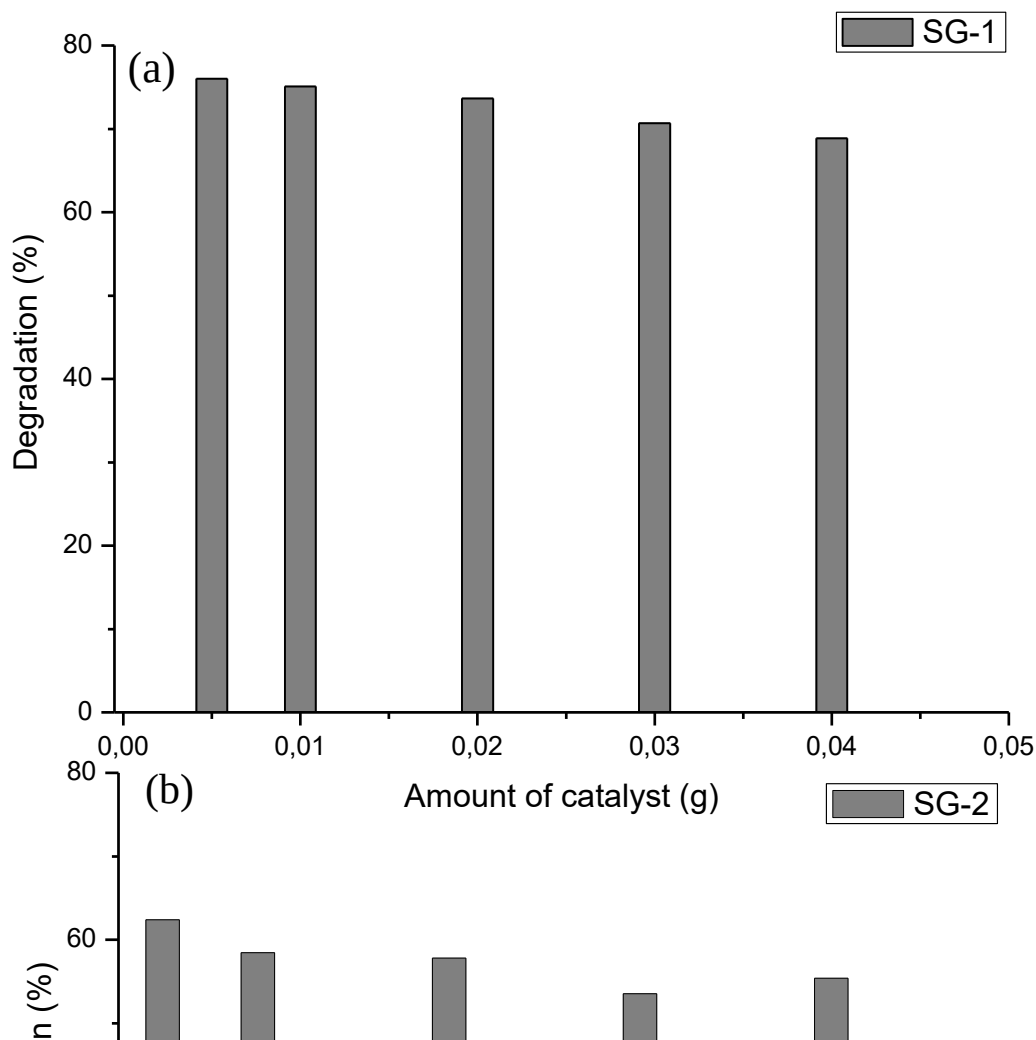


Figure 4.11: Effect of adsorbent dose (MnTiO_3) prepared by (a) SG-1 and (b) SG-2 method on the methylene blue removal.

Beyond 0.005 g of MnTiO_3 nanoparticle, the percentage degradation of MB dyes increases only slightly up to 0.04 g. This can be rationalised in terms of availability of active sites on MnTiO_3 surface and the light penetration of photoactivating light into the suspension. The availability of active sites increases with the suspension of catalyst loading, but the light penetration and, hence, the photoactivated volume of the suspension shrinks. The trade-off between these two effects is that at low solute concentration, when there are excess active sites, the balance between the opposing effect is evenly poised and change in suspension loading makes little difference on the percentage degradation. At high solute concentration availability of excess active sites outweighs the diminishing photoactivated volume and significantly greater percentage is achieved at increased MnTiO_3 loading [85].

Thus, the decreased percentage degradation at higher catalyst loading may be due to deactivation of activated molecules by collision with ground state molecules.

Hence, an optimum catalyst has to be added in order to avoid unnecessary excess catalyst and also to ensure total absorption of solar light photons [86] for efficient photomineralisation.

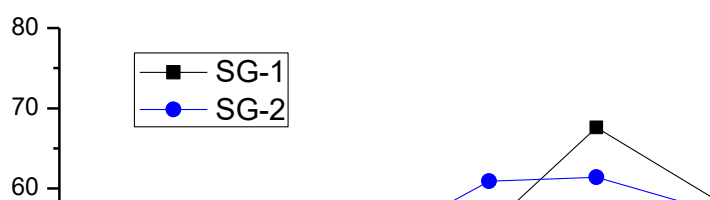
4.2.2.3. Effect of the initial concentration of methylene blue

The concentration of the organic pollutant is a very important parameter in wastewater treatment. For this reason the influence of this parameter on photocatalytic process is studied.

Effect of variation of dye concentration was studied by taking different concentrations of dye i.e. 2.10^{-6} M - $1.5.10^{-5}$ M, with 0.005 g of photocatalyst were added, under solar light irradiation (4 h). The results are tabulated in Table 4.5 and represented in Figure 4.12.

Table 4.5: Values of absorbance and percentage degradation using 0.005g of MnTiO_3 , prepared by SG-1 and SG-2 methods, as function of dye's concentration.

Dye's concentration	SG-1			SG-2		
	A_0	A_t	D%	A_0	A_t	D%
2.10^{-6}	0.294	0.160	35.7	0.245	0.168	31.4
4.10^{-6}	0.308	0.173	43.8	0.313	0.171	45.3
6.10^{-6}	0.361	0.179	50.4	0.382	0.177	53.6
8.10^{-6}	0.391	0.175	55.2	0.651	0.254	60.9
1.10^{-5}	0.559	0.182	67.6	0.589	0.227	61.4
$1.5.10^{-5}$	0.514	0.269	47.4	0.606	0.292	51.8



Figures 4.12: Effect of concentration of MB on percentage degradation with nanosize catalyst, prepared by SG-1 and SG-2 methods.

From the observed data, it can be seen that the percent of photocatalytic degradation increases with increasing initial concentration of the dye. The percent of degradation was found optimum at 1×10^{-5} M. It was decreased on further increasing the dye concentration.

When dye concentration increases, number of dye molecules absorbed on catalyst surface increases. Also, Increasing concentration of dye also caused the dye molecules to adsorb light and the photons never reached the photo-catalyst surface; finally, it causes reduced efficiency of dye removal [87, 88]. Thus, typical application of photo-catalytic degradation of MB was found better at low concentration, i.e. $[MB]_0 \leq 1 \times 10^{-5}$ M.

4.2.2.4. Effect of pH

An important parameter in the photocatalytic reactions taking place on the particulate surfaces is the pH of the solution, since it dictates the surface charge properties of the photocatalyst and size of aggregates it forms.

The pH of the dye solution was studied with the change in pH, the percentage of degradation of dye was also changed. The pH of methylene blue solution was adjusted by adding HCl or NaOH (1M). About 0.005g of photocatalyst was added to a 50 ml solution of MB (concentration = 1×10^{-5} M). The mixture was irradiation by solar light for a given time interval and the percentage of degradation was determined.

The effect of pH on photocatalytic degradation was investigated in the range 2 to 9 and the results are given in Figure 4.13 for photocatlyst prepared by SG-1 and SG-2 methods.

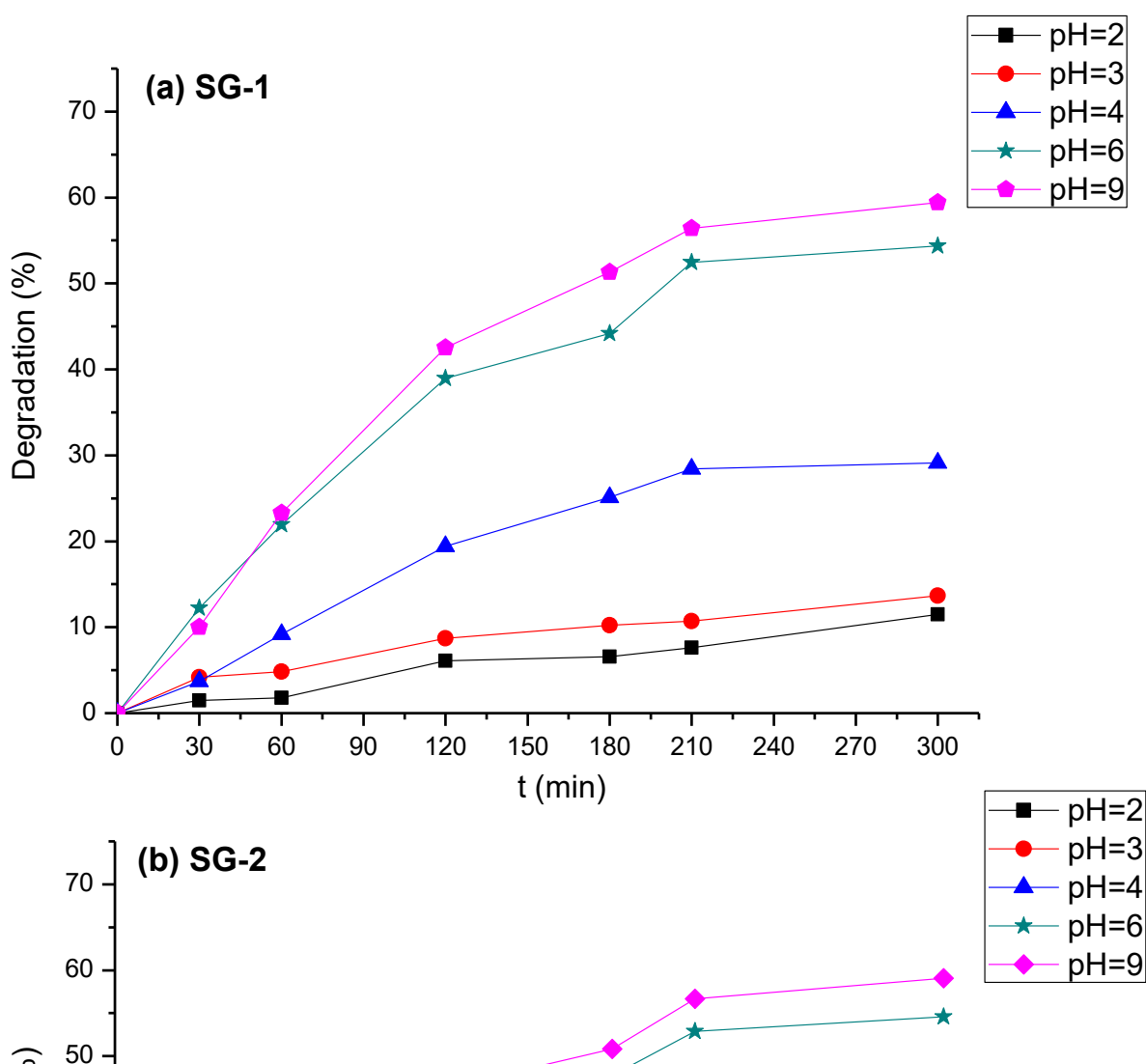


Figure 4.13: Influence of pH and time irradiation on the photocatlytic degradation.

$$[\text{MB}]_0 = 10^{-5} \text{ mol/L}, T = 19^\circ \text{C}, m_{\text{catalyst}} = 0.005 \text{g}.$$

The removal of dye by adsorption onto nanosized MnTiO_3 was found to be slow at the initial period of contact time, and then to become rapid with the increase of contact time. The percent of degradation of MB dye was found to increase with the increase in pH from 2 to 9. The percentage of removal increases from 15 % in $\text{pH} = 2$ to 60 % in $\text{pH} = 9$ of the solution, for the two nanosized photocatalytic materials prepared by SG-1 and SG-2 routes.

The effect of pH on the degradation of MB dye under 5 hours contact irradiation time as shown in Figure 4.14.

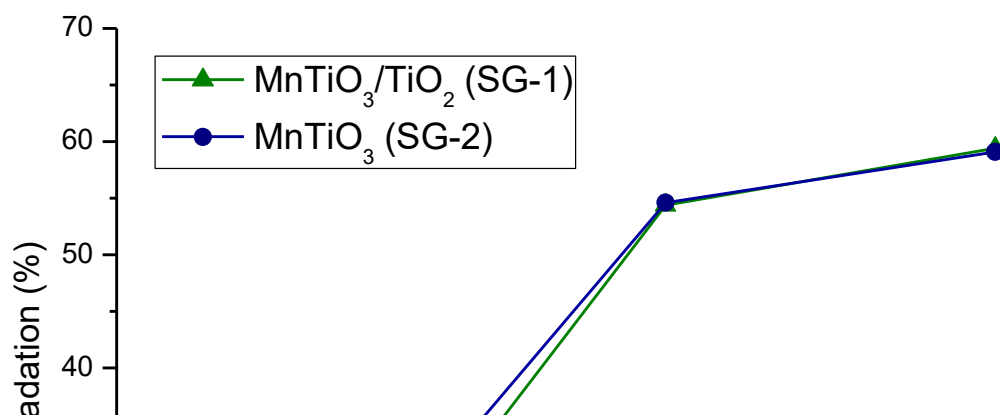


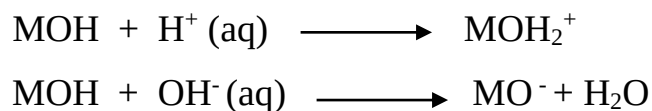
Figure 4.14: Effect of pH on the MB removal. Initial MB concentration 1×10^{-5} M, adsorbent dose 0.005 g/ 50 mL, contact time 5 h.

The results are shown in Figure 4.14, from the graph, it is observed that the adsorption of MB dye with pH on $\text{MnTiO}_3/\text{TiO}_2$ catalyst prepared by SG-1 and MnTiO_3 catalyst prepared by SG-2 method, is highly pH dependent

The percentage of MB adsorption on MnTiO_3 and $\text{MnTiO}_3/\text{TiO}_2$ increased with increasing pH and reached a value around 55% at pH = 6, whereas in the range 6 - 9, the adsorption amount was only slightly affected by pH.

The interpretation of pH effects on the photocatalytic process is very difficult task because of its multiple roles such as electrostatic interactions between the semiconductor surface, solvent molecules, substrate and charged radicals formed during the reaction process.

The ionization state of the surface of the photocatalyst can be protonated and deprotonated under acidic and alkaline conditions, respectively, as shown in following equations:



The point of zero charge (pzc) of the MnTiO_3 is reported at $\text{pH} \sim 7.8$ [89]. Thus, the MnTiO_3 surface will remain positively charged in acidic medium ($\text{pH} < 7.8$) and negatively charged in alkaline medium ($\text{pH} > 7.8$).

As pH of the system decreased, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favor the adsorption of positively charged dye cations due to electrostatic repulsion. In addition, lower adsorption of methylene blue at acidic pH might be due to the presence of excess H^+ ions competing with dye cations for the available adsorption sites [90, 91].

Some authors have reported that methylene blue adsorption usually increases as the pH is increased [92, 93].

4.2.3. Photocatalytic degradation of MB with UV-Lamp source

The light intensity determines the extent of light absorption by the semiconductor catalyst at a given wavelength. Intensity of light, the effect of light wavelength and irradiation time both have affect on the rate of photo degradation of pollutants [94-96]. In order to compare different UV irradiation intensities on the percent of decolorization of MB dye, two kinds of lamps, 10 W UV-C and 100 W UV-A produce a different wavelengths $\lambda = 254$ and 356 nm respectively, were used. Table 4.6 summarizes the values of absorbance and percentage of degradation of methylene blue (1×10^{-5} M) using 0.005 g MnTiO_3 catalyst.

Table 4.6: Values of absorbance and percentage degradation as function of UV light intensity.

SG-1						
Lamp UV (100 W)						
Time	0 h	1 h	2 h	3 h	4 h	5 h
Absorbance	0.345	0.295	0.310	0.307	0.296	0.296
D%	0	4.4	10.1	11.1	14.2	14.2
Lamp UV (10 W)						
Time	0 h	1 h	2 h	3 h	4 h	5 h
Absorbance	0.625	0.561	0.455	0.392	0.368	0.348
D%	0	10.2	28.8	37.2	41.1	44.3
SG-2						
Lamp UV (10 W)						
Time	0 h	1 h	2 h	3 h	4 h	5 h
Absorbance	0.687	0.566	0.518	0.503	0.478	0.458
D%	0	17.6	24.5	26.7	30.4	33.3

Figure 4.15 illustrates the effect of the variation of light intensity on the degradation of MB dye. From the observed data, it is evident that the degradation of Methylene Blue using solar light irradiation was more efficient than that with artificial UV light irradiation. The percent of degradation of methylene blue was significantly improved with UV-C radiation compared to UV-A radiation.

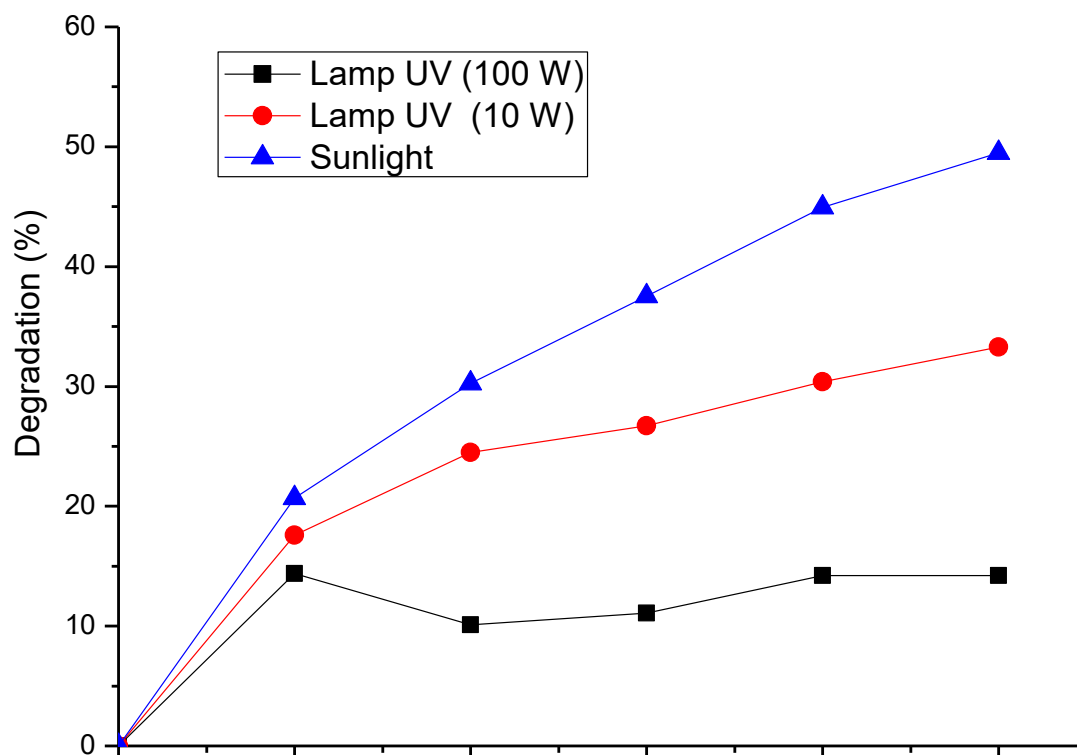


Figure 4.15: Effect of solar/UV light source on the degradation of MB dye.

4.3. Kinetic study of adsorption of MB by MnTiO₃ nanoparticle

Study of adsorption kinetics is important because the rate of adsorption (which is one of the criteria for efficiency of adsorbent) and also the mechanism of adsorption can be concluded from kinetic studies.

In order to analyze the adsorption kinetics of MB (1×10^{-5} M), the first order kinetic equation given by the Langmuir-Hinshelwood model at low initial concentrations [74] was tested.

Absorbances of the samples at 663 nm were measured, and the remaining concentrations of methylene blue after different reaction times were calculated. The total time period investigated was 240 min. The results are indicated in Table 4.7.

Table 4.7: The values of parameters of the Langmuir-Hinshelwood model.

SG-1				SG-2		
$C_0 = 12.5 \times 10^{-5}$ M				$C_0 = 11.5 \times 10^{-5}$ M		
Time	A	$C \times 10^{-5}$	$\ln(C_0/C)$	A	$C \times 10^{-5}$	$\ln(C_0/C)$
0	0.753	12.5	0	0.665	11.5	0
30	0.608	10.09	0.21	0.545	9.42	0.19
60	0.497	8.25	0.41	0.458	7.92	0.37
90	0.405	6.72	0.62	0.376	6.50	0.57
120	0.345	5.72	0.78	0.313	5.41	0.75

150	0.301	4.99	0.91	0.282	4.87	0.85
180	0.228	3.78	1.19	0.224	3.87	1.08
240	0.186	3.08	1.39	0.198	3.42	1.21

Figures 4.16(a) and (b) show the reaction kinetics of MB degradation in the presence of pure MnTiO_3 (obtained by SG-2 route) and $\text{MnTiO}_3\text{-TiO}_2$ (prepared by SG-1 synthesis). By plotting $\ln(C_0/C)$ vs t , a straight line was obtained. It can be found that the adsorption kinetic could be quite successfully fitted by a first-order kinetic reaction. From the graphs it is seen that the photocatalytic methylene blue dye degradation follow the first order-kinetics as the correlation constant for the fitted line to be $R^2 > 0.95$.

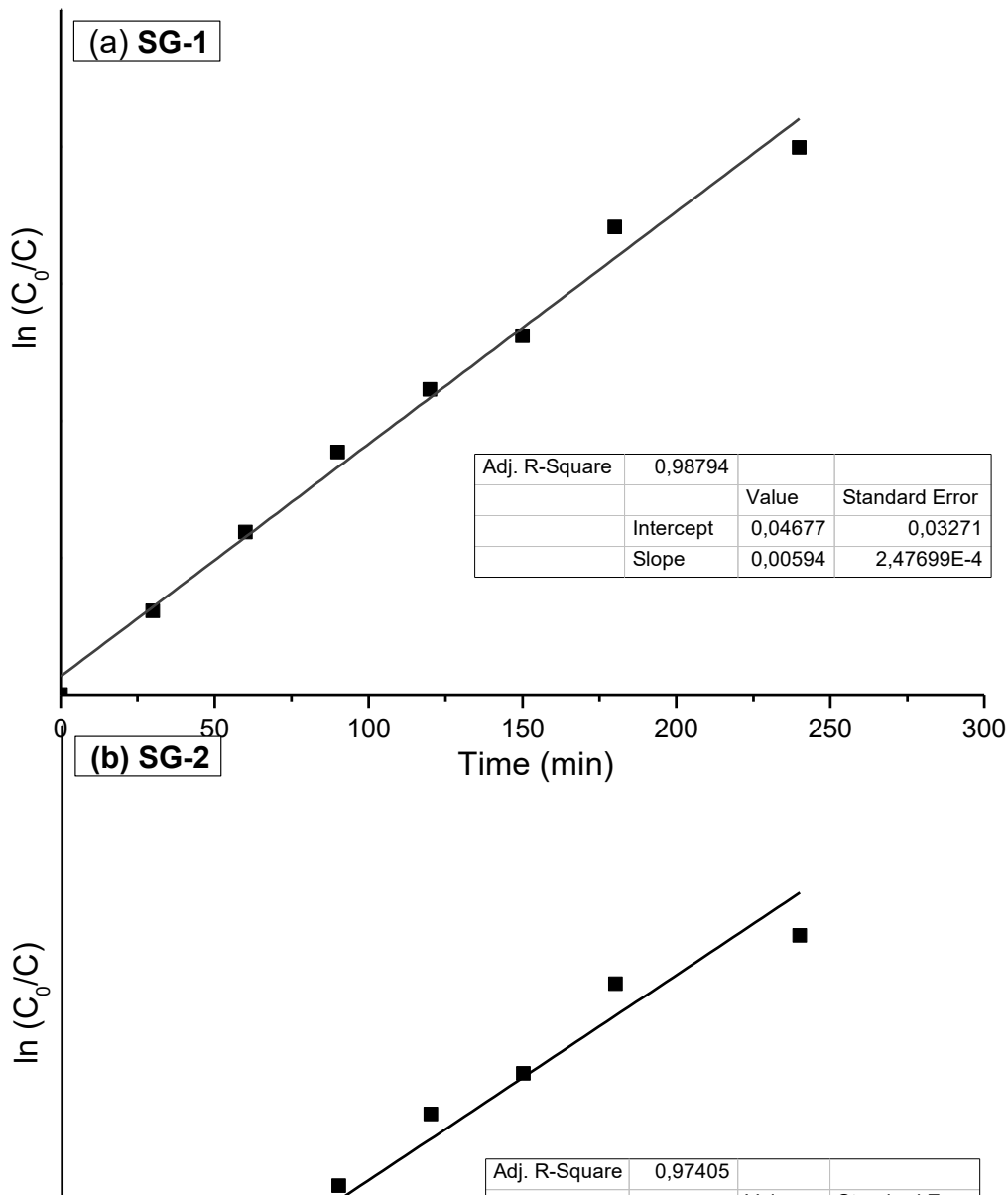


Figure 4.16: Kinetics of the solar photocatalytic decolorization of MB in solution with (a) MnTiO₃-TiO₂ (SG-1) and (b) MnTiO₃ (SG-2) as catalyst.

The values of the rate constant k and corresponding linear regression correlation coefficient R^2 were presented in Table 4.8. A good correlation to the first order reaction kinetics ($R^2 = 0.988$ for MnTiO₃-TiO₂ (SG-1) and $R^2 = 0.974$ for MnTiO₃) was found.

Table 4.8: Kinetics constants and their correlation coefficients

Adsorbents	k (min^{-1})	R^2
MnTiO ₃ /TiO ₂ (SG-1)	0.00594	0.98794
MnTiO ₃ (SG-2)	0.00525	0.97405

4.4. Photocalalytic degradation of real industrial textile wastewater by semiconducting MnTiO₃

Water pollution is a very serious problem faced throughout the world especially by chemical industries because of the toxic/hazardous. Sun light is abundantly available natural energy source; its energy can be conveniently exploited for the irradiation of semiconducting materials. Solar might seem an ideal energy source, as it is free and virtually limitless. In our study, we applied the active photocatalyst (MnTiO_3) for real industrial textile wastewater treatment using sun light as a renewable energy resource. Figure 4.17 and Table 4.9 show the photocatalytic behavior of MnTiO_3 prepared by sol-gel method 1 (SG-1) for the solar decolorization of real factory wastewater.

Table 4.9: Decolorization of the textile waste water at different irradiation time intervals in the presence different dose of MnTiO_3 nanophotocatalyst.

MnTiO_3	0.005 g		0.01 g		0.02 g		0.03 g	
Time	A	D (%)	A	D (%)	A	D (%)	A	D (%)
0 h	0.849		0.829		0.797		0.766	
1 h	0.397	53.2	0.358	56.8	0.350	56.0	0.362	52.7
2 h	0.328	61.3	0.346	58.2	0.267	66.4	0.252	67.1
3 h	0.274	67.7	0.281	66.1	0.222	72.1	0.223	70.8

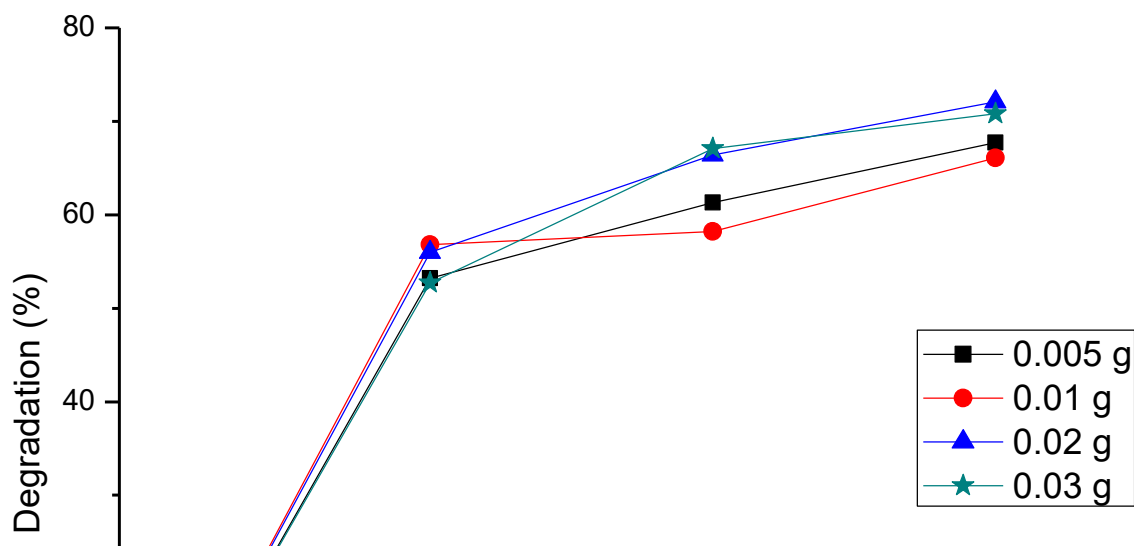


Figure 4.17: The photocatalytic properties of MnTiO_3 nanocrystals at different sun light irradiation time intervals on industrial wastewater sample.

Figure 4.17 shows the degradation of real wastewater sample in presence of MnTiO_3 , which indicated that the real factory wastewater undergo decolorization. The decolorization increased obviously with the increase of irradiation time. The decolorization reached to 72 % for 0.03 g of MnTiO_3 nanocrystals catalyst, after passing 3 h from irradiation. Therefore, MnTiO_3 prepared by sol-gel at 900 °C is a promising candidate under solar light.

This study shows that manganese titanate MnTiO_3 has been suggested to be efficient for the degradation of a cationic dye, the methylene blue (MB), in aqueous medium. The sol-gel chemistry route has successfully been used to prepare nanosized of pure MnTiO_3 or mixed $\text{MnTiO}_3/\text{TiO}_2$ respectively from Manganese (II) chloride and Titanium (IV) isopropoxide or Titanium (IV) oxide dissolved in water. This sol-gel technique appears as one of the most efficient method to obtain polycrystalline powder of pyrophanite with a narrow size distribution ranging between 15–30 nm.

Based on recent representative investigations, the role of various operating parameters on the photocatalytic degradation of methylene blue dye has been explored in this work. The experimental results are summarized as follows:

- ✓ The photo-degradation was higher using lower amount (0.005 g) of semiconductor, 76 % and 62.4 % of MB degradation for nanosized MnTiO₃/TiO₂ and MnTiO₃ catalysts respectively under 4 hours solar light irradiation.
- ✓ Under the conditions tested (MnTiO₃ = 0.005g/50mL, 4 h solar light irradiation), the percent of degradation was found optimum at 1×10^{-5} M initial concentration of the MB dye. It was decreased on further increasing the dye concentration.
- ✓ The pH has an important role in this photodegradation process. Under conditions tested ([MB]₀ = 1×10^{-5} M, MnTiO₃ = 0.005g/50mL, 4h sunlight irradiation), the percentage of MB adsorption on MnTiO₃ and MnTiO₃/TiO₂ increased with increasing pH and reached a value around 55% at pH = 6, whereas in the range 6 – 9, the adsorption amount was only slightly affected by pH (60 %).
- ✓ The degradation of methylene blue using sunlight irradiation was more efficient than that with artificial UV light irradiation. The percent of decolorization of MB dye was significantly improved with UV-C radiation compared to UV-A radiation.

The adsorption kinetics could be quite successfully fitted by a first order kinetic according to Langmuir-Hinshelwood model. The correlation constant for the fitted line was calculated to be $R^2 = 0.974$ and 0.988 for MnTiO₃ and MnTiO₃/TiO₂, respectively.

The rate constant for degradation of MB using pure MnTiO₃ and mixed MnTiO₃/TiO₂ was calculated to be 5.25×10^{-4} and $5.94 \times 10^{-4} \text{ min}^{-1}$ respectively.

The nanosized MnTiO₃ catalyst is applied successfully to photodegrade textile real wastewater containing reactive dyes.

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