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Treatment of recalcitrant organic pollutants in water by heterogeneous catalysis using a mixed material (TiO_2-diatomite of algeria)

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ABSTRACT

The aim of this work was to study the photocatalytic degradation of Methylene Blue and phenol by nano-particles coated on diatomite as a new nano-composite catalyst. Titanium dioxide (Degussa P25) was immobilized on diatomite powder at different compositions by a very simple and low cost technique. Diatomite powder (also called Kieselguhr) is an Algerian substance with a snow-white color and porosity greater than 72%. High porosity allowed the diatomite powder to float on the surface of water providing a means for the treatment process that enabled separation from water without any need for pumping as well as the exposure to solar radiation when supported beneath titanium dioxide (TiO_2) during photocatalysis. The morphology characterization of the prepared catalysts was carried out by X-ray diffraction analysis, scanning electron microscopy and infrared spectroscopy (IR). Photocatalytic activity was initially tested in a single reactor followed by pH, conductivity and absorbance analyses. Photocatalytic treatment of synthetically polluted water with Methylene Blue and phenol showed good performance for the two new nano-composites using immobilized TiO_2 on diatomite.

Keywords: Kieselguhr; Titanium dioxide (TiO_2); Photo-catalysis; Methylene blue; Phenol

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1. Introduction

Heterogeneous photocatalytic water treatment process has gained wide attention, and recently published works in the field of photocatalytic oxidation of toxic organic materials investigated the effect of various parameters on the photocatalytic degradation of various predominant organic contaminants in wastewater effluent. Worldwide studies on photocatalytic technology started in 1970 [1] and photocatalytic oxidation has been proposed for the first time in 1980 as an effective method for the treatment of toxic organic substances [2]. Extensive research has therefore focused on the enhancement of photocatalysis by modification of TiO_2. Furthermore, devoted researchers have spent considerable efforts to accomplish extensive research, and the technology of immobilization of photocatalysic TiO_2 nano-particles seemed the most successful photocatalysis reported on solids since then [3,4]. Various techniques have been developed for the immobilization of TiO_2 on a solid substrate including dip coating suspension [5,6], spray coating and sol–gel. Moreover, different types of substrates were tested such as glass beads [7], glass tubes [8], fiber glass [9], quartz [10], stainless steel [11], aluminum [12], activated carbon [13], silica [14] and glass plates [15] and modified diatomite [16,17]. It is worth noting that fresh water supply is currently under pressure due to rapid population growth and therefore reuse of wastewater effluent is rapidly growing and becoming a necessity for water utilities. Furthermore, considerable efforts have been devoted to developing a suitable purification method that can destroy biologically recalcitrant organic contaminants and extensive studies have been conducted on reagents and processing conditions such as inorganic bases and acid attacks [18], ammonium salts of carbonate [19], chloride [20] and heat treatment [21].

Methylene Blue and especially phenol are being continuously introduced into the aqueous environment although they are well known for their biological recalcitrance and acute toxicity. Understanding the impact of the various process parameters that govern their photocatalytic degradation efficiency is of paramount importance for the treatment of wastewater. Moreover, development of efficient photocatalytic water purification process for large scale applications is a recent research challenge. In this work, effort was made to provide a technique for using TiO_2 nano-particles more effectively and at minimum cost. Titanium dioxide (Degussa P25) was immobilized on diatomite powders as a new photocatalyst in the degradation of Methylene Blue and phenol and its photocatalytic activity was compared to steel and glass fibers coated with TiO_2. Diatomite was chosen as a substrate for TiO_2 due to numerous advantages such as high porosity, low density, rich natural composition, lack of toxicity and low cost [22]. The mineral material, also called Kieselguhr or diatomite, is composed of siliceous fossil diatom shells deposited for thousands of centuries and which have relatively insoluble and non-compressible structure [23]. They are also frequently used in industry as filters, clarifiers and reinforcing agents [24] or as chromatographic and catalytic supports [15]. However, this mineral material is originally not pure and contains various mineral impurities [25]. For this reason, it was necessary to modify this raw material before use.

2. Experimental procedures

Ideal for large scale applications, a simple and effective method was used for the immobilization of TiO_2 nano-particles. The same technique was applied with minor modifications to the TiO_2 coating formulation on diatomite powders and their use as photocatalysts. Details of the experimental procedure, equipment used and the preparation of catalysts are described in the following sections.

2.1. Samples preparation

Initially, 0.5 g of titanium dioxide powder (Degussa P25) was added to 18 mL of ethanol as a basic medium of the slurry in which the titanium powder can be properly dispersed. Once the titanium dioxide was added, the powder easily dispersed with ethanol in a shape of a cloud producing slush. Next, 1.5 mL of acid nitric pH 3.5 was added and the slush started to be more uniform and cloudiness began slowly to disappear. The prepared solutions were then used for the immobilization process of TiO_2 and quantities (1, 2.5 g) of diatomite powders previously washed with distilled water were added to the prepared suspension. Diatomite powder is highly porous and can naturally act as a good adsorbent, particularly on slush. It was therefore mixed with slush for thirty minutes [5,6]. Finally, slush was calcined at 450℃ for 30 min. This process allowed the titanium to adhere more strongly to the pores of the powder of diatomaceous earth. Once the coating process was complete, the diatomite powder was sufficiently cooled and again carefully washed with water for a few minutes to remove the titanium particles not properly attached to the pores of the diatomite powder. This process permitted to obtain the new materials used. Two prepared catalysts samples labeled M1 and M2 were used for the photodegradation of Methylene Blue and phenol (Table 1).

One of the actions in the heterogeneous photocatalytic treatment of wastewater is to drive the process by visible light. Herein, photocatalytic tests were analyzed using a single reactor with UV–vis light absorption. A schematic illustration of the reactor is shown in Fig. 1. The absorbance detector is set at 660 nm for Methylene Blue and 270 nm for phenol. Solution samples of 20 mL for Methylene Blue and 20 mL for phenol were taken every 15 min. For both Methylene Blue and phenol, the solutions were placed in the dark under a single UV light source radiation, using lamps emitting at 365 nm over TiO_2 in the simple reactor. The samples were filtered on a 0.45 μm membrane paper and the absorbance by a UV–vis spectrophotometer measured.

2.2. Structural characterization of TiO_2 and diatomite catalysts

To investigate the TiO_2 crystalline anatase and rutile forms, morphology of the prepared catalysts with diatomite was determined using the Scanning Electron Microscope SEM-Leo type 440i. In addition, X-ray diffraction (XRD) analyses of the different samples were conducted at the Laboratory of Materials (University of Oran), using Bruker DRX type D4 with a source of Cu Kα X-ray and infrared spectroscopy analysis was carried out by a "Perkin–Elmer" spectrum one device.

Table 1
TiO_2 and Kieselguhr quantities used in the preparation of samples

	Phenol (50 mg L^{-1})		Methylene Blue (10 mg L^{-1})	
	TiO_2 (g)	Kieselguhr (g)	TiO_2 (g)	Kieselguhr (g)
M1	0.5	1.0	0.5	1.5
M2	0.5	2.5	0.5	2.5

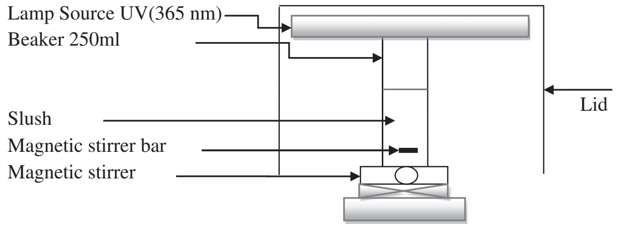


Fig. 1. Reactor Pilot of Laboratory LSTGP.

2.3. Photocatalytic procedure

To examine the photocatalytic degradation of Methylene Blue and phenol, organic pollutants solutions were subjected to a UV light radiation source using a same medium pressure lamp (Osram 125 W). The immobilized TiO_2 catalysts on the diatomite powder were poured into the solutions containing 10 mg L^{-1} of Methylene Blue and 50 mg L^{-1} of phenol, respectively. The solutions were then placed stirred under the UV radiation source located at 7 cm above the samples. Solutions of were filtered at 0.45 μm of milli-pores before analysis.

3. Results and discussion

Diatomite is a volcanic material with high porosity (>72%) [22]. The characterization of the diatomite used in this work is reported in Table 2. The micrographs shown in Fig. 2 identified the morphological observations using scanning electron microscopy (SEM). For instance, micrographs Fig. 2(a) and (b) show diatomite with a presence of impurities while Fig. 2(c) clearly shows good porosity of the treated diatomite. The morphology of TiO_2 is shown in photograph Fig. 2(d). X-ray fluorescence (XRF) analysis allowed the identification of the main chemical components of the diatomite. The components and the proportions are SiO_2 (67.32%), $CaCO_3$ (19.11%), Al_2O_3 (1.91%), FeO_3 (1.63%), MgO (1.32%), K_2O (0.75%), Na_2O (1.12%), TiO_2 (7%) and H_2O (5.63%).

The use of SEM techniques provided additional details from the structural point of view. Crystal coatings of Degussa P25 containing 20% rutile and 80% anatase underwent significant structural change. After diatomite calcination at 600℃, a color change was observed with respect to the natural product. The color changed from a snow-white to a yellowish white. This characteristic is due to the transformation of iron oxide to colorless iron silicate under temperature effect as previously suggested by Mellah [20]. Micrographs Fig. 2(a) and (b) are the illustrations of the untreated diatomite. Changes in the pore structure of the most porous membranes were released as illustrated in Micrograph Fig. 2(c). The significant decrease of pores was due to the absence of impurities. Fig. 3

Table 2
Algerian diatomite characterization results

pH	7.9
Pore diameter	200–2,000
Total porosity	72%

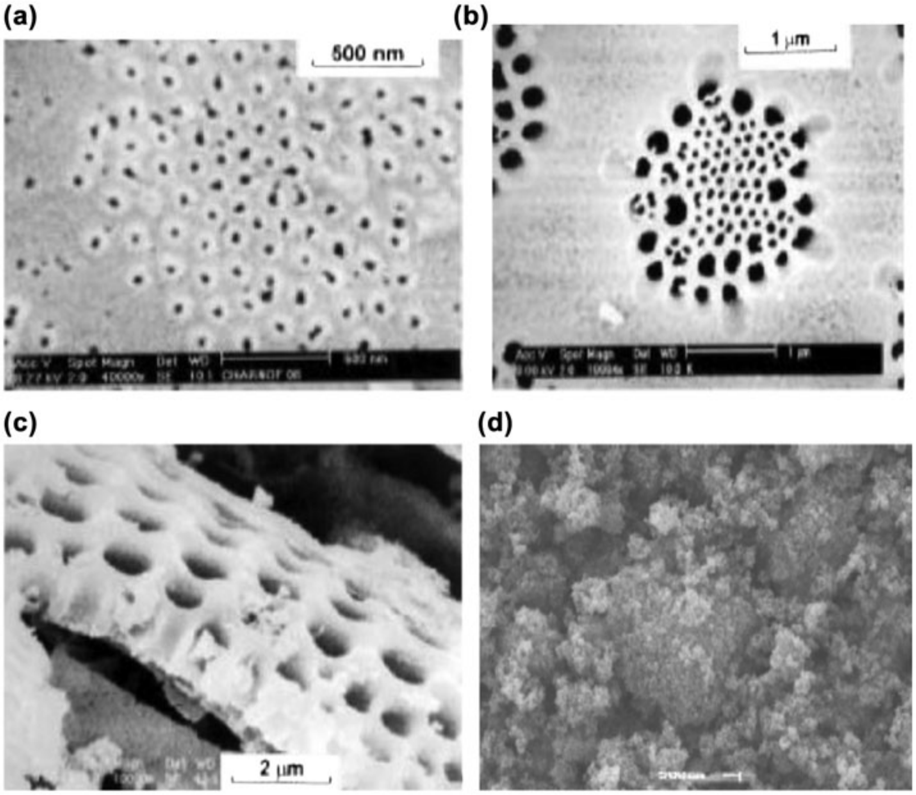


Fig. 2. SEM images before heat treatment: (a) diatomite with irregular pores, (b) diatomite with more irregular pores, (c) destroyed pores of diatomite, and (d) TiO_2.

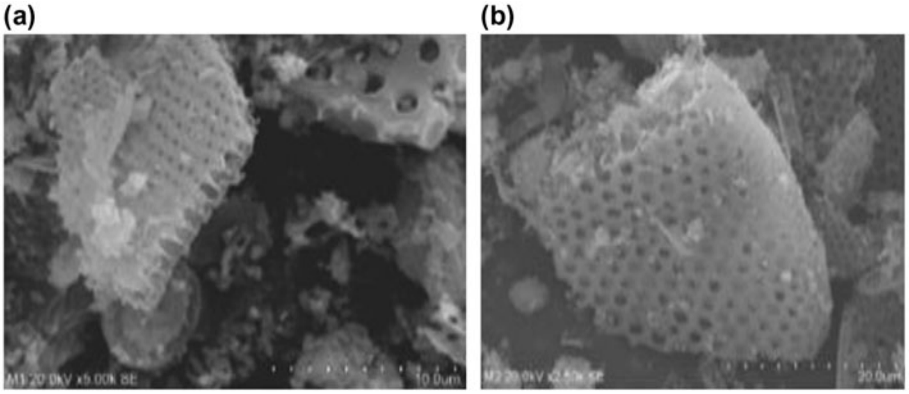


Fig. 3. SEM micrographs of TiO_2 after diatomite heat treatment: (a) M1 solution sample and (b) M2 solution sample.

shows the SEM photographs of the prepared catalysts surfaces calcined during 30 min at 450℃.

3.1. X-ray diffraction (XRD) analysis

XRD spectra are depicted in Fig. 4. XRD analysis showed that the used diatomite contained three crystalline phases. These were SiO_2 in a quartzite and amorphous forms, calcite and dolomite ($CaCO_3$). However, clay phases were absent in this material unlike many other diatomite substances originating from other sources [23].

As for the XRD spectrum obtained for the sample coated on diatomite, arc shaped disorders were

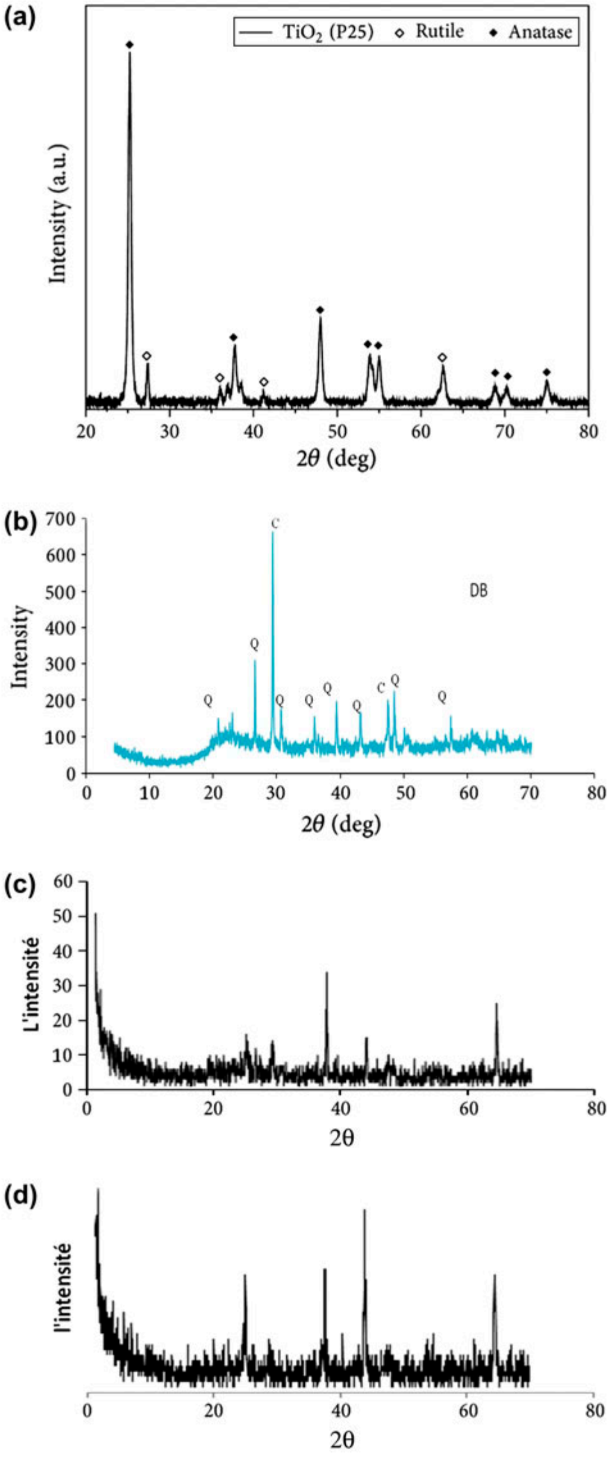


Fig. 4. XRD of: titanium dioxide P25 (a), crude (SIG) diatomite (b), M1, M2 catalysts (c) and (d).

observed in baseline. This can be attributed to the presence of amorphous phases in diatomite. intensive reflections related to TiO_2 phase represents an increase of about 25˚, 38˚, which corresponds to the anatase form and as it was observed in the catalysts M1, M2. The rutile phase is the source of the small sizes of nano-crystals TiO_2 corresponds to $2\theta = 26^\circ$, 42˚ observed in the spectra (c) and (d). Intense quartz-like reflections due to increase in peaks of $2\theta = 38^\circ$ were observed as well as for calcite and dolomite as they are related to the diatomite phase.

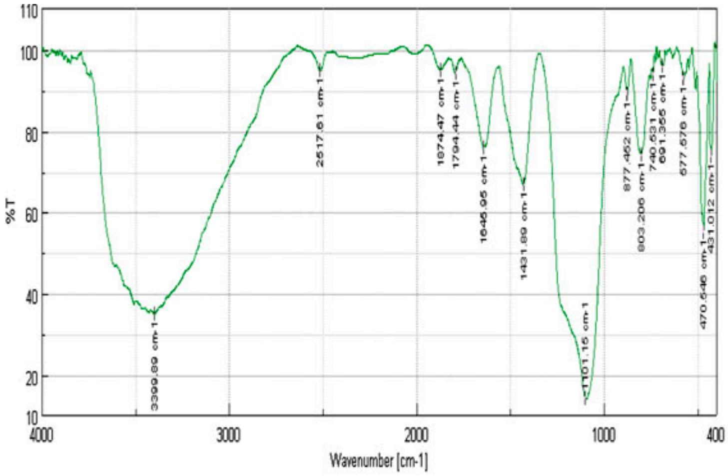
3.2. *Infrared spectroscopy (IR) monitoring*

Infrared spectroscopy (IR) was used to investigate the functions of diatomaceous earth and TiO_2 composites as well as the prepared catalysts M1, M2. Fig. 5 illustrates the Infrared spectroscopy spectra of Kieselguhr catalysts M1 and M2. The IR spectrum of diatomite is characterized by the presence of bands between 1,050 and 1,250 cm^{-1}. This was assigned to the asymmetric Si–O–Si vibration stretching of the meso-porous diatomite structure. A 3,422 cm^{-1} band was attributed to the functional groups –OH and the 476 cm^{-1} band was associated to SiO_2 vibration.

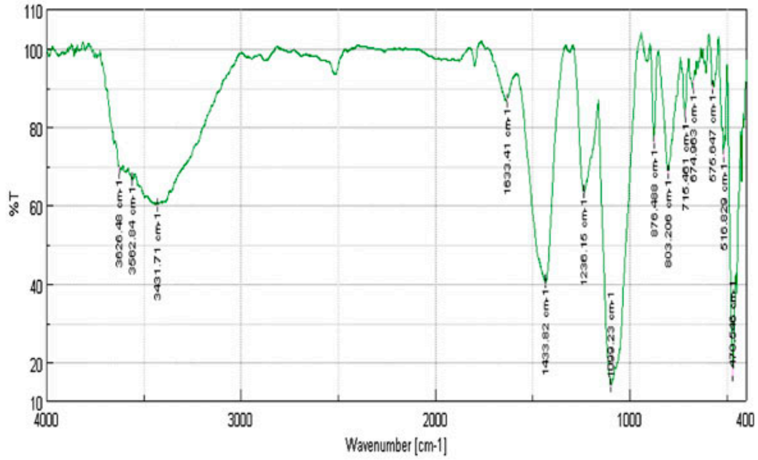
The spectra displays of some absorption peaks were characteristic of the nature of titanium and diatomite, namely (a) the two bands of vibrations related to the groups OH (650–3,000 cm^{-1}) corresponded to the CO_2 bands strain, respectively; (b) the mode of the vibration wave ranging between 1,000 and 1,300 cm^{-1} was assigned to the stretching vibrations of the O–Ti–O linkage and (c) the vibration mode ranging between 800 and 1,000 cm^{-1} indicated the Si–OH linkage related to the presence of silanol groups and also to the existence of Ti–O–Ti bond in the range of 450–550 cm^{-1}.

4. Photo-degradation experiments

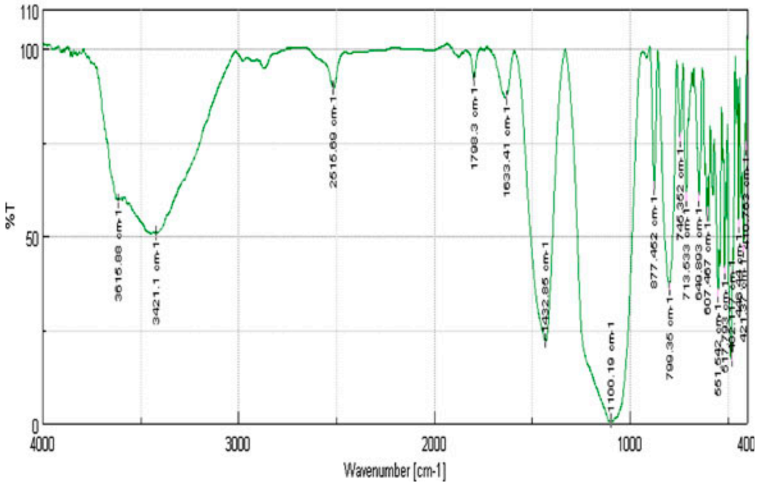
Prior to the evaluation of the photocatalytic activity of the catalysts M1 and M2, an experiment was designed to measure the degradation percentage or adsorption of Methylene Blue and phenol by the prepared catalysts M1 and M2 in the dark and at 365 nm. In these experiments and according to the protocol described above, we took 250 mL of Methylene Blue or phenol with a catalyst concentration of 50 and 10 mg L^{-1}, respectively. Figs. 6 and 7 show the results of the photocatalytic reaction and the effectiveness of the prepared catalysts. The corresponding values and comparison of the experimental results with those of past experiments are reported in Tables 3 and 4, respectively.



Natural diatomite



M1



M2

Fig. 5. Infrared spectroscopy of Kieselguhr catalysts M1 and M2.

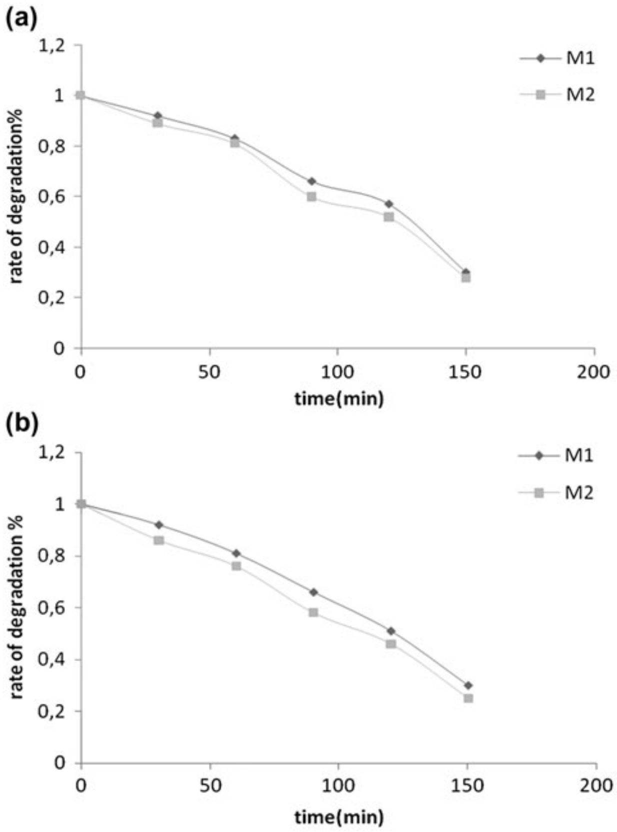


Fig. 6. Evolution of photo-degradation rate in catalysts: (a) Methylene Blue catalyst and (b) phenol catalyst.

Table 3
Values of photocatalytic reaction and effectiveness of the prepared catalysts

Pollutants	Materials	K_{app} ($\times 10^{-1}$)	Degradation rate (%)
Phenol	M1	2.9	65
	M2	3.2	72
Methylene Blue	M1	2.0	77
	M2	2.5	79

The apparent rate of catalyst M2 was 2.5×10^{-1} for Methylene Blue and 3.2×10^{-1} for phenol as compared to about 2.0×10^{-1} for Methylene Blue and 2.9×10^{-1} for phenol with catalyst M1. Although both catalysts showed more or less a good photocatalytic activity, catalyst M1 showed smaller degradation rate than M2. The degradation rate of catalyst M2 reached 79% for Methylene Blue and 72% for phenol.

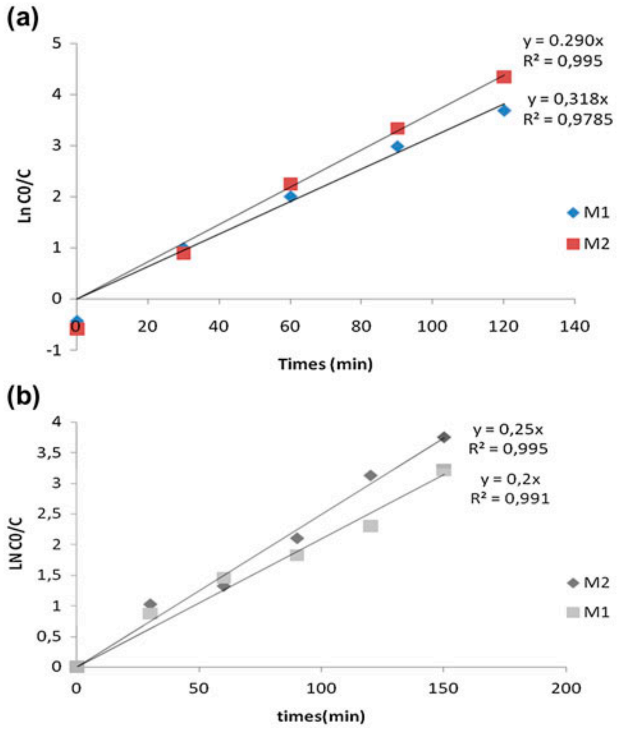


Fig. 7. Evolution of photo-degradation order and determination of apparent rate constant: (a) Methylene blue and (b) phenol.

Table 4
Comparison of present and past experimental results of both catalysts

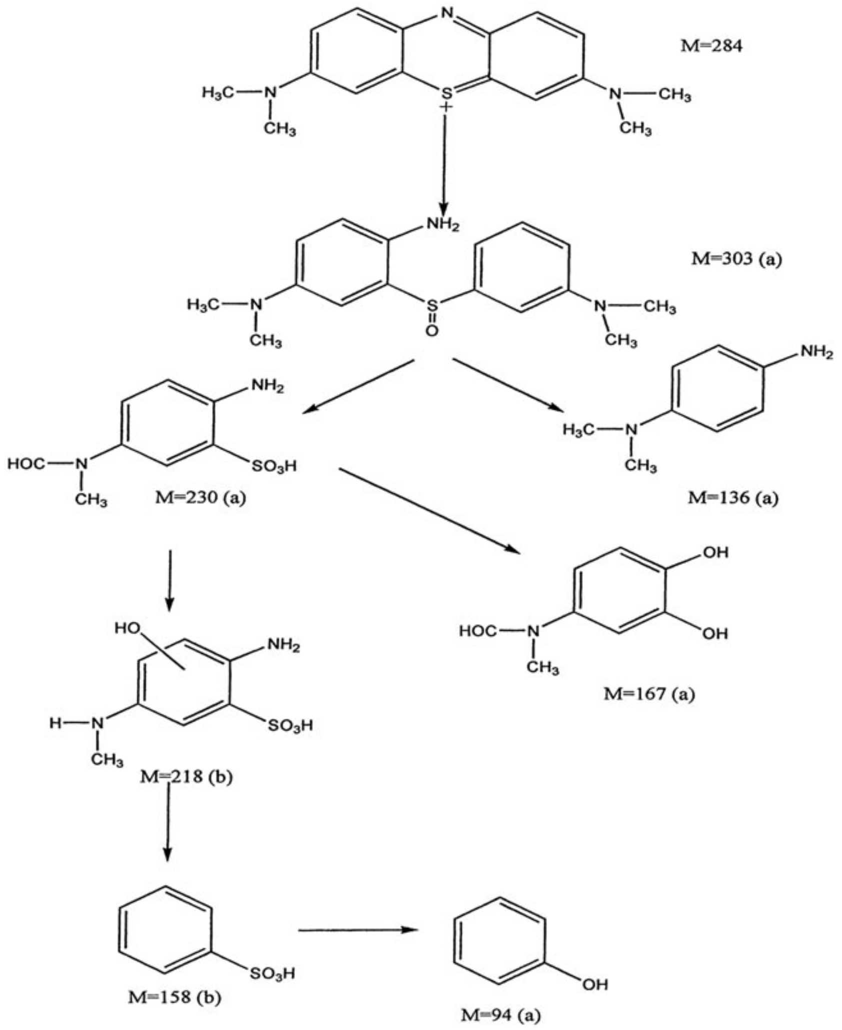
Support	Degradation rates (%)	Refs.
TiO_2 P25	98.4	[23]
TiO_2 P25	73.7	[5]
TiO_2-glass	92,2	[23]
TiO_2-steel fiber	73,2	[23]
M2	72	Phenol, current study
M1	79	Methylene Blue, current study
M2	65	Phenol, current study
M1	77	Methylene Blue current study

5. Mechanism of degradation of Methylene Blue

The following Methylene Blue degradation mechanism has been proposed by Houas et al. [26] Fig. 8.

6. Mechanism of degradation of phenol

Likewise, we propose the following mechanism by Sobczynski et al. [27] (Fig. 9).



(a) detected by GC/MS (extraction of ions)
(b) detected by LC / MS

Fig. 8. Mechanism of degradation of Methlyne Blue.

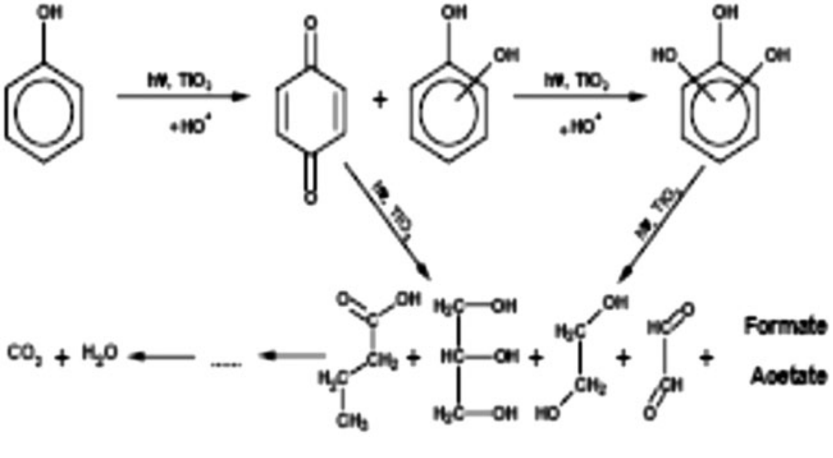


Fig. 9. Mechanism of degradation of phenol.

7. Conclusion

This work focused on the performance of two catalysts prepared using diatomite and TiO_2 as nanoparticles by photocatalytic oxidation of Methylene Blue and phenol. Based on the obtained results, the following conclusions could be drawn:

(1) Heterogeneous photocatalytic oxidation employing diatomite and TiO_2 proved to be a good process and demonstrated a promising solution for the degradation of Methylene Blue and phenol, thus producing more biologically degradable and less toxic substances.
(2) Selection of two catalysts for large scale treatment processes can be considered as easier and less expensive. Washed and calcined diatomite can be taken into account in operating conditions.
(3) The prepared catalysts showed good photocatalytic activity with respect to the degradation of the two pollutants with a preference for M2.
(4) Results of immobilized catalyst M2 seemed better than M1 due to the large amount of diatomaceous earth which is greater than the amount used in the catalysts M1.
(5) Diatomite alone has a weak catalytic activity [24] because of its porosity and low specific surface. Previous studies showed that the diatomite was a good adsorbent [15,25].
(6) Photo-degradation kinetics analysis obeyed a pseudo first order model.

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