Characterization of ZnO and TiO₂ Nanopowders and their Application for Photocatalytic Water Treatment

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Zinc oxide ZnO nanoparticles synthesized by sol-gel method and commercial titanium dioxide TiO₂ were studied in the present work. The structural properties of the ZnO and TiO₂ nanoparticles were determined by Fourier transform infrared (FTIR), X-ray diffraction (XRD) and Raman spectra techniques (RS). The average crystallite sizes were calculated by using the powder X-ray and were found to be 48 nm and 20 nm and the specific surface areas were about 1047 m² g⁻¹ and 381 m² g⁻¹ for ZnO and TiO₂, respectively. The FTIR and Raman spectroscopy results have shown high purity of the ZnO and TiO₂ samples and they are consistent with the one obtained from XRD. The ZnO and TiO₂ nanoparticles were used as catalysts for the elimination of an azo dye, Mordant Violet 5 (MV5), in aqueous solution, by an advanced oxidation process which is heterogeneous photocatalysis. Synthesized ZnO was more efficient than commercial TiO₂ to degrade MV5 under UV irradiation. The adsorption of MV5 on TiO₂ and ZnO was found favorable by the Langmuir approach. The MV5 adsorption constant on TiO₂ was higher than that obtained in the case of ZnO. The photocatalytic reaction of MV5 in presence of each catalyst was investigated at different concentration of the dye and at different conditions of pH. The solar radiation of MV5 in the presence of each catalyst was also tested.

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1. Introduction

Nanostructured semiconductors are of great interest because of their improved properties and promising technological applications, such as photochemical solar cells, photocatalysts, photosensors, electroluminescent displays, and biolabels.

Nanoscale zinc oxide (ZnO) and titanium dioxide (TiO₂) are absorbers of ultraviolet (UV) light and are considered as the more efficient semiconductors that promote photocatalysis [1–4]. This is because of their attractive properties, such as their low cost, non-toxic nature, and high catalytic efficiency [5, 6]. Both catalysts have been extensively studied for the removal of organic compounds from contaminated air and water by using the photocatalysis process [6–8]. However, very few studies have directly compared the photocatalytic activity of ZnO to TiO₂ to degrade dyes under UV light.

ZnO and TiO₂ nanoparticles have nearly the same band gap and similar electronic properties [9, 10] and therefore, their photocatalytic capacity is expected to be similar. However, in the case of ZnO, photocorrosion frequently occurs with the illumination of UV light, leading to a decrease of photocatalytic activity in aqueous solutions [8]. However, in many works, ZnO has been reported to have higher photocatalytic efficiency for the degradation of some organic compounds in comparison to TiO₂ [11, 12]. ZnO (band gap of 3.37 eV) can absorb over a larger fraction of UV radiation, and

the corresponding threshold of ZnO is 425 nm [13]. In the case of TiO₂, there is many crystalline forms, anatase (band gap of 3.2 eV (385 nm)) and rutile (band gap of 3.0 eV (410 nm)) are the most common forms. The photocatalytic activity of ZnO and TiO₂ depends on their phase structure, crystallite size, specific surface areas and pore structure. In fact, TiO₂ has longer known history for its photocatalysis properties and ZnO came in light much later and is relatively new in the field. Nowadays both are easily available at almost the same cost. One reason for the less attraction of ZnO could be the comparatively large solubility in acidic medium. However, by taking into account his high photocatalytic activity, this reason would not be enough to prevent its use in water purification application.

Colored waste waters pose an environmental problem because they contain dyes that can be toxic, non-biodegradable, and resistant to destruction by physicochemical treatment methods [14]. Mordant Violet 5 (MV5) was chosen as a model pollutant in this study, it is a dye that belongs to azo class. Azo dyes are considered as the largest class of dyes that are used in industry [15]. The presence of azo dyes in textile effluents is an issue of major concern because of their potential impact on the environment and human health [15, 16]. In fact, several toxic and potentially carcinogenic compounds such as aromatic amines can be formed during azo dye degradation [17].

The heterogeneous photocatalysis process in presence of nanopowders as catalysts allows the destruction of organic pollutants, such as dyes, while leading to complete mineralization [14]. The photocatalytic process depends mainly on the characteristics of the molecule to

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be degraded, the light source and the structural proprieties of semiconductor, playing the role of the photocatalyst. Its main advantages are: low cost, ease of initiation and cessation of reaction, the possibility of using solar energy as a source of irradiation, the variety of degradable pollutants, and the high efficiency of mineralization of pollutants.

In the present study, nanoparticles of Zinc oxide were synthesized by the sol-gel method. The structural properties of the obtained ZnO and commercial TiO₂ nanoparticles were determined by Fourier transform infrared (FTIR), X-ray diffraction (XRD), and Raman spectra techniques (RS).

The application of the synthesized ZnO nanopowder and the commercial TiO₂ in the heterogeneous photocatalysis treatment of waters containing an azo dye: Mordant Violet 5 (MV5), used strongly in the textile industries, was investigated. Both nanopowders have not been tested and compared before as Mordant Violet 5 catalysts.

The study of the efficiency of the photocatalytic process in presence of each of the two catalysts has been carried at different concentration of the dye and at different conditions of solution pH. The solar radiation of MV5 in the presence of each catalyst was also tested.

2. Materials And Methods

2.1. Reagents and chemicals

The substrate chosen as a model pollutant is a dye that belongs to azo class: Mordant Violet 5 (MV5) (C₁₆H₁₁N₂NaO₅S). The chemical structure of MV5 is presented in Fig 1. The natural pH of the aqueous MV5 solution is 5.9. The pH of the solutions was adjusted using H₂SO₄ from Merck and NaOH from Carlo Erba. Water used to prepare experimental solutions was purified by Milli-Q system (Millipore).

2.2. Reactor and procedure

The photocatalysis experiments were carried out with 50 mL of solution with a desired dye concentration (10 mg/L) and catalyst loading (1 g/L) at natural pH. The suspension was placed in a glass reactor equipped with a jacket allowing the water circulation in order to control the temperature (20 °C) and at a stirring speed of 500 rpm. The adsorption step is carried out in the dark until the equilibrium state of concentration is reached in the reactor. Once the adsorption equilibrium is reached, the photocatalytic process can be started. In photocatalysis, the procedure is simple and comprises the following steps: (i) Start of the irradiation (UV), (ii) Samples of 3 mL of suspension are taken at different reaction times using a syringe followed by filtration on a Millipore filter prior to analysis.

The irradiations were carried out using a Philips HPW125 (UV-A, $\lambda_{\max}$ = 365 nm) low-pressure mercury UV lamps, surrounded by a cylindrical mirror. The light

Fig. 1. Molecular structure of Mordant Violet 5 (MV5).

intensity of the radiation (2.5 mW cm⁻²) was measured using a UV radiometer (VLX-3W). The Pyrex reactor, equipped with a water cooling jacket, is placed in the system axis.

The decolorization of Mordant Violet 5 (MV5) in the solution was determined using a UV-Visible spectrophotometer (Helios α -Unicam spectronic) by measuring absorbance at 500 nm.

2.3. Catalysts

The semiconductors used in our study, are the most commonly known in photocatalysis, namely: ZnO and TiO₂. The Titanium dioxide used in this study is a commercial catalyst. The nanoparticles of Zinc oxide are synthesized by the sol-gel (citrate route) method, in this method the Zinc acetate (ZnC₄H₆O₄) is used as the starting material and the Citric acid C₆H₈O₇·H₂O is used as a complexing agent.

2.4. Structural characterization

Fourier transform infrared spectra (FTIR) have been studied to ascertain the purity and nature of the ZnO and TiO₂ particles. The FTIR spectrum was obtained on KBr pellets at ambient temperature using an 8201PC SHIMADZU FTIR spectrometer. The structural properties of the metals were determined by X-ray diffraction using a BRUKER ADVANCE D8 diffractometer with Cu (λ = 1.5406 Å) radiation. A SENTERRA Raman spectrometer was used for characterization of crystal structures of ZnO and TiO₂ with a light source of Ar laser (532 nm). Raman spectroscopy is an effective supplement of XRD for structural characterization.

2.4.1. FTIR Spectroscopy

FTIR spectra of ZnO and TiO₂ particles are shown in Fig. 2. Generally all the metals and their oxides give the FTIR peaks at lower wave number than 1000 cm⁻¹ arising from inter-atomic vibrations. Hence, the distinct bands observed on the two FTIR spectrum frequencies below 1000 cm⁻¹ are characteristic of ZnO and TiO₂, and are due to the vibration of the Zn-O and Ti-O bonds, respectively [18].

Fig. 2. FTIR of ZnO and TiO₂ catalysts.

The low peaks observed at 3487 cm⁻¹ and at 1512 cm⁻¹ for ZnO, and 3390 cm⁻¹ and 1635 cm⁻¹ for TiO₂ corresponds to the stretching vibrations of the -OH group and the deformation of the H-O-H bond, which are associated with small amounts of water adsorbed on the zinc oxide and titanium oxide surfaces. The peaks corresponding to 2112 cm⁻¹ and 2463 cm⁻¹ for ZnO and TiO₂, respectively, are related with CO₂ molecules that exist on the surface of catalysts. These data are similar to the results observed by others [18, 19] for ZnO and [20] for TiO₂. Anyhow, the FTIR results have shown high purity of the obtained ZnO and the commercial TiO₂ particles.

2.4.2. X-ray diffraction (XRD) studies

Figure 3 shows X-ray diffraction patterns of ZnO and TiO₂ powders in the wide range of 2θ of 5 to 100°. The peaks appeared at 2θ range of 31°, 34°, 36°, 47°, 56°, 63° and 25°, 38°, 48°, 53°, 55°, 60° for ZnO and TiO₂, respectively. These values correspond to pure ZnO structure (JCPDS card No. 00-036-1451) and pure anatase TiO₂ structure (JCPDS Card No. 21-1272). Diffraction pattern corresponding to impurities are found to be absent for both catalysts indicating that it have pure hexagonal structures.

To evaluate the mean crystallite size of the catalysts, the Debye-Scherrer formula was used:

$$D = K \frac{\lambda}{\beta \cos \theta} \quad (1)$$

Fig. 3. X-ray diffraction patterns of ZnO and TiO₂ catalysts. Fig. 4. Raman spectra of ZnO and TiO₂ catalysts.

where D (nm) is the mean crystallite size, K is a constant which is taken as 0.90, λ is the wavelength of the X-ray radiation, β is the reflection full-width at half maximum (FWHM), and θ is the diffraction angle. From the XRD data, the average crystallite sizes were found to be 48 nm and 20 nm, and the specific surface areas were obtained using the Guassian method and were about 1047 m²/g and 381 m²/g for ZnO and TiO₂, respectively.

2.4.3. Raman spectrometer

Figure 4 shows the Raman spectra of ZnO and TiO₂ nanoparticles in the range 45–800 cm⁻¹. The ZnO Raman spectrum presents peaks at 98, 332, 378, 438, 591, and 689 cm⁻¹. The peak at 438 cm⁻¹ was E_{2H} corresponding to the presence of crystalline wurtzite phase in ZnO. The peak at 98 cm⁻¹ that is associated with vibration of the zinc sublattice E_{2L} is one of the most intense modes. The other weaker peak present at 332 cm⁻¹ is due to the difference in frequency between E_{2H} and E_{2L} . This can be attributed to a multiple-phonon scattering phenomenon [21]. The peaks at 378 and 583 cm⁻¹ are due to A_{1T} and E_{1L} modes, respectively. These results provided information regarding the good crystallinity of the ZnO structure, they are consistent with the one obtained from XRD and are in good agreement with other works [22, 23].

The analysis of TiO₂ Raman spectrum revealed pure anatase phase with high crystallinity, corresponding to five Raman active modes. The principal peak locating around 143 cm⁻¹ (E_g) was in good accordance with the XRD patterns. The other peaks centered around 199 cm⁻¹ (E_g), 398 cm⁻¹ (B_{1g}), 516 cm⁻¹ ($A_{1g} + B_{1g}$) and 642 cm⁻¹ (E_g) are modes of anatase TiO₂.

3. Result and discussion

3.1. Adsorption of MV5 on photocatalysts surfaces

The primary factor of photocatalytic degradation is the adsorption of dye onto the catalyst surface. Dark adsorption was performed to evaluate the adsorption of MV5 onto ZnO and TiO₂ surfaces. The amount of dye adsorbed onto the catalysts (mg/g) was calculated using the following relationship:

$$Q_{ads} = \frac{V}{m} (C_o - C_t), \quad (2)$$

where Q_{ads} (mg/g) is the adsorbed quantity at time t , C_o (mg/L) is the initial dye concentration, C_t (mg/L) is the dye concentration at the moment t of the process of adsorption, V (L) is the volume of the solution, and m (g) is the weight of adsorbent.

The interaction behavior between the solutes and adsorbent can be best described by isotherm models. The dye solutions were magnetically stirred in the dark for 90 min with samples collected regularly. For both catalysts, the adsorption equilibrium was rapidly attained (in 15 min). This behavior looks like the Langmuir isotherm, the linear transformation of Langmuir equation is used to fit the experimental data:

$$\frac{1}{Q_e} = \frac{1}{Q_{max}} \left(1 + \frac{1}{K_L C_e} \right), \quad (3)$$

where Q_e (mg/g) is the amount of the dye adsorbed on the catalyst when equilibrium is achieved, Q_{max} (mg/g) is the theoretical maximum amount of dye adsorbed onto the catalyst surface, C_e is the dye concentration at adsorption equilibrium and K_L (L/mg) is the Langmuir adsorption constant.

The linear transforms are given in Fig. 5. The ordinate at the origin is equal to the reciprocal of Q_{max} , whereas K_L can be calculated from the slope $(Q_{max} K_L)^{-1}$.

The Langmuir isotherms of MV5 in presence of each of the two catalysts were found to be linear over the whole concentration range studied and the correlation coefficients R^2 were extremely high, indicating that the Langmuir isotherm represent well the experimental adsorption data of MV5 on ZnO and TiO₂. This model assumes unique adsorption sites, the adsorption is monolayer with a uniform distribution of sites and no interaction between the adsorption sites. It appears that the adsorption coverage is small for both catalysts and TiO₂ ($Q_{max} = 25.4$ mg/g and $K_L = 0.04$ L/mg) exhibits the higher adsorbed quantity than ZnO ($Q_{max} = 12.4$ mg/g and $K_L = 0.02$ L/mg).

Fig. 5. Langmuir adsorption isotherm of MV5 on ZnO and TiO₂: $Q_e = f(C_e)$ In the inset: transformation of Langmuir isotherm: $1/Q_e = f(1/C_e)$: ([catalyst] = 1 g L⁻¹ and pH = 5.7 ± 0.2 and $T = 20^\circ\text{C}$).

The inset of Fig. 5 ($Q_e = f(C_e)$) shows an isotherm of L-shape for both catalysts according to the classification of Giles et al. [24]. This type means that there is no strong competition between the solvent and the adsorbate to occupy the adsorbent surface sites [25, 26].

The dimensionless separation factor R_L indicates the shape of the Langmuir isotherm. It can be either favorable when $0 < R_L < 1$, unfavorable when ($R_L > 1$), linear for $R_L = 1$, or irreversible when $R_L = 0$ [27].

$$R_L = \frac{1}{1 + K_L C_o}, \quad (4)$$

where K_L is the Langmuir constant and C_o is the highest initial concentration. It was observed that the R_L values obtained with ZnO and TiO₂ are equal to 0.89 and 0.83, respectively, showing that the adsorption of MV5 on both catalysts was favorable at the experimental conditions that have been studied.

3.2. Kinetic of photocatalytic degradation

Figure 6 shows the kinetic of the photocatalytic degradation of two aqueous solution of MV5 (10 mg/L) at natural pH (pH = 5.9), where one contains a suspension of ZnO particles and the other contains a suspension of TiO₂ under UV irradiation at 365 nm, the masse of catalysts was taken at 1.0 g/L. The evolution of C_t/C_o as a function of irradiation time show that the time required for almost total elimination of this solution is about 30 min for ZnO and 60 min for TiO₂. The results indicate that the heterogeneous photocatalysis in presence of ZnO or TiO₂ as photocatalysts is a suitable method for a rapid degradation of organic pollutants such as dyes in aqueous solution.

To describe the kinetics of degradation of MV5, we are inspired by results reported in the literature. In most cases, the kinetics of the photodegradation of many dyes are described as those of apparent first order, with a rate that obeys the equation [28, 29]:

$$r = -\frac{dC_t}{dt} = k_{app} \times C_t, \quad (5)$$

Fig. 6. Kinetic of MV5 degradation by photocatalysis process in the presence of each of ZnO and TiO₂ as catalyst and UV light. In the inset: Representation of $\ln([MV5]_0/[MV5]_t)$ versus irradiation time. ($[MV5] = 10 \text{ mg L}^{-1}$, $[\text{catalyst}] = 1.0 \text{ g L}^{-1}$, $\text{pH} = 5.9$ and $T = 20^\circ\text{C}$).

where r (mg/L/min) is the photocatalytic degradation rate, k_{app} (min^{-1}) is the apparent degradation constant, C_t (mg/L) is the solution concentration of the dye at any reaction time and t (min) is the reaction time. The integration of this equation (with the limitation: $C = C_0$ when $t = 0$) leads to the following equation:

$$\ln\left(\frac{C_0}{C_t}\right) = k_{app} \times t. \quad (6)$$

A plot of $\ln(C_0/C_t)$ versus t will yield a slope of k_{app} (inset in Fig. 6). The linear curves obtained and the correlation coefficient close to unity indicate that the photocatalytic degradation of the dye studied follows indeed a pseudo-first order kinetics for both catalysts. It was found that the correlation coefficients were larger than 0.99. The apparent rate constant of MV5 degradation by photocatalytic degradation process was about 0.131 min^{-1} and 0.048 min^{-1} for ZnO and TiO₂, respectively.

The results obtained show that the degradation of MV5 strongly depends on the type of catalyst. This is due to physico-chemical properties that differ from one catalyst to another. The apparent degradation constants of MV5 in presence of ZnO (0.131 min^{-1}) was about 2.7 times higher than that obtained in presence of TiO₂ (0.048 min^{-1}).

The ZnO appears than as the most powerful photocatalyst. Various factors can explain the greater reactivity of ZnO in comparison with TiO₂ for the MV5 degradation. It can be explained by its larger surface area ($1047 \text{ m}^2/\text{g}$). More specific surface area means more possible area of contact between the dye molecules and the catalyst surface and hence it supplies more active sites and higher number of adsorbed substrates [13]. However, the surface area is not the only factor that affects the photocatalysts performance. In our earlier works, a comparative study has been performed on different commercial catalysts of TiO₂ having different surface areas for the

photodegradation of synthetic dyes [7, 30], the results have shown that TiO₂ particles size and surface area are not the only factors influencing their photocatalytic activity, but it is rather surface properties such as surface acidity and the crystalline phase. Vorontsov et al. [31] have also concluded, in their study on the photocatalytic activity of several synthesized samples of TiO₂, that TiO₂ surface area and particle size are only secondary factors influencing photocatalytic activity, while other surface properties such as acidity, surface structure, and also extent of surface hydroxylation should play a major role in obtaining high performance of the photocatalytic process. In the case of ZnO, ZnO nanostructures of different morphologies were fabricated by Morales et al. [32], and compared for dyes photocatalytic degradation. The results have shown that the photocatalytic activity of ZnO nanostructures depends not only on their sizes, basically due to enhanced specific surface area of smaller structures, but also on the shape of the nanostructures that has also seen to affect their photocatalytic performance strongly.

Comparative studies on ZnO and TiO₂ photocatalysts have been performed by some other researchers, where synthetic ZnO has shown a higher activity compared to TiO₂ regardless of which one has the larger surface area [33–36]. Hence, the activity of ZnO compared to TiO₂ in our study can not only be accounted by its higher surface area, but differences in the intrinsic characteristics of ZnO and TiO₂ might have a key role. The quantum efficiency is a factor that could explain the differences in photocatalysts activities. ZnO has a higher quantum efficiency than TiO₂ [37]. The results of the photocatalytic activities give indirect evidence that ZnO may have ability to absorb a larger fraction of photon energy more efficiently than TiO₂ [38].

3.3. Factor influencing MV5 photodegradation

3.3.1. Influence of dye concentration

The rate of photocatalytic degradation of MV5 solutions is shown in Fig. 7, where the curve was obtained with solute concentrations of 10 to 40 mg/L, at $\text{pH}=5.9$ and 1.0 g/L concentration of each of ZnO and TiO₂.

For both catalysts, the MV5 decolorization rate constant decreases with increasing dye concentration. The rate constant of MV5 degradation at 10 mg/L concentration was observed to be about 6.5 and 4 times higher than the rate constant at 40 mg/L of dye concentration for ZnO and TiO₂, respectively. Several explanations of this behavior can be envisaged. First, it is possible that the photogeneration of h^+ holes and/or $\bullet\text{OH}$ radicals on the catalyst surface is reduced due to the covering of the active sites by the dye. This result is due to the fact that a high concentration of dye gives rise to a screen effect that prevents radiation from penetrating the aqueous suspension and reaching the entire semiconductor [39]. As a result, a significant quantity of light will be absorbed by the dye molecules rather than the photocatalyst, reducing its activity [39]. Another

Fig. 7. Effect of the MV5 initial concentration on the degradation rate in the presence of each of ZnO and TiO₂. ([catalyst] = 1.0 g L⁻¹, pH = 5.9 and T = 20 °C).

Fig. 8. Effect of solution pH on the degradation rate of MV5 in the presence of each of ZnO and TiO₂. ([MV5] = 10 mg L⁻¹, [catalyst] = 1.0 g L⁻¹ and T = 20 °C).

reason that can explain this result is that the increase of the initial dye concentration increases the number of MV5 molecules presents in the solution while the number of •OH radicals produced remained constant. This fact reduces the degradation reaction of the dye.

3.3.2. Influence of pH

The parameter pH effects on the surface properties of solids and the state of the pollutant. This state has to be degraded depending on its pK_a — a factor that characterizes the water to be treated. In fact, the dispersion of the particles and the surface charge of the catalyst are influenced by the pH of the mixture [40]. Figure 8 illustrates the variation of MV5 degradation rate constant as a function of pH of solution in presence of each of ZnO and TiO₂ nanopowders.

The results obtained show that the pH influences the rate constant of MV5 degradation. For both catalysts, a higher efficiency of the photocatalytic process to degrade MV5 is obtained at free pH (pH = 5.9). It has also been noted that, for both catalysts, the dye degradation is faster in alkaline medium than in acidic medium.

Since the zero point charge (pH_{zpc}) of ZnO is (9.0 ± 0.3) [41], the catalyst surface is positively charged at pH < 9, whereas it is negatively charged at pH > 9. In the case of TiO₂, its zero point charge pH_{zpc} is about 6.5. Hence, the catalyst surface is positively charged at pH < 6.5 and it is negatively charged at pH > 6.5.

On the other hand, the MV5 has a pK_a of 6.25 [42]. Thus, one can expect the MV5 in molecular form to be at pH < pK_a - 1 = 5.25, while in the anionic form at pH > pK_a + 1 = 7.25.

For both catalysts, in alkaline pH media, the repulsion between the molecules of the MV5 dye in its anionic form and the negatively charged surface of the catalyst leads to a decrease in the rate of degradation compared to natural pH. However, with both catalysts, the efficiency of photodegradation in basic medium was higher than that obtained in acidic medium. This can be attributed to the production of hydroxyl radicals favored by the increase in the concentration of OH⁻ ions which react with positive holes according to the following equation [43]:

In the case of ZnO, the important decrease in the rate of degradation at acidic pH, especially at pH < 3, is attributed to the photodecomposition of ZnO in acidic solutions [44].

3.3.3. Solar photocatalysis of MV5

In order to be closer to natural conditions, two solutions of MV5 with a concentration of 10 mg/L, at free pH = 5.9, and for a fixed concentration of catalyst of 1 g/L (ZnO or TiO₂), were exposed to sunlight. The solar irradiations were carried out in Constantine (north Algeria) in a solar station during a sunny day. The suspension was placed in a cylindrical Pyrex reactor (40 cm long and 2.5 cm in diameter) placed vertically. The MV5 photocatalytic degradation kinetic is shown in Fig. 9.

Figure 9 shows that almost complete decolorization was obtained with an MV5 removal efficiency of 94% and 96% after 15 and 30 min of treatment for ZnO and TiO₂, respectively. This confirms the effectiveness of sunlight in the photodegradation of the MV5 dye.

The comparison of the degradation rate of MV5 between the two systems in solar and artificial light (inset in Fig. 9) shows that the MV5 rate constant is relatively twice higher when solar light is used as source of irradiation with a ratio of 1.8 and 2.1 for ZnO and TiO₂, respectively. This result was expected since the photon flux received by the solutions is more intense in sunlight compared to that of artificial light (365 nm). The rate of degradation increases in presence of solar irradiation because the more the photons fall on the photocatalyst, the more the •OH radicals are produced. The photocatalytic activity increases when photogeneration of electrons and holes increases. All photons with energy larger than the photocatalyst band gap can be absorbed and used for photo-electron and hole generation. The use

Fig. 9. Kinetic of MV5 degradation by photocatalysis process under solar light in the presence of each of ZnO and TiO₂ as catalyst. In the inset: Comparison of MV5 degradation under UV and solar light. ([MV5] = 10 mg L⁻¹, [catalyst] = 1.0 g L⁻¹, pH = 5.9 and T = 20 °C).

of sunlight implies that a larger part of the spectrum is usable for photo-electron (e^-) and hole (h^+) generation compared to a monochromatic light source, since sunlight is a continuous spectrum. Hence, the photocatalytic activity will be improved.

Another consideration is that if the incident photon energy is much larger than the catalyst band gap (sunlight case), then the excess energy ($h\nu - E_g$) will probably released as heat and lead to increasing the material temperature. Such heat might play a role in determining the photocatalytic activity. In several works an increased photocatalytic degradation efficiency of organic molecules was observed as the temperature was raised [45]. When the temperature is increased, it causes the bubbles formation in the solution which results in generating free radicals. Additionally, the increase in temperature helps the degradation reaction to overcome electron-hole recombination. Besides that, the increasing temperature may enhance the oxidation rate of organic molecules at the interface [46].

Solar light is therefore a source of wastewater treatment that has a beneficial effect for countries with high levels of sunshine like Algeria.

4. Conclusion

Zinc oxide synthesized by the sol-gel method and commercial TiO₂ were investigated in the present study. From the characterization study, the average crystallite sizes were calculated by using the powder X-ray (XRD) and were found to be 48 nm and 20 nm and the specific surface areas were obtained using the Gaussian method and were about 104 m²/g and 381 m²/g for ZnO and TiO₂, respectively. The FTIR and Raman spectroscopy results have shown high purity of the ZnO and TiO₂ samples and they are consistent with the one obtained from XRD.

The efficiency of ZnO and TiO₂ nanopowders as photocatalysts was investigated for the degradation of MV5 dye under monochromatic radiation at 365 nm. The adsorption in the dark of MV5 on both catalysts was found favorable by the Langmuir approach and TiO₂ exhibits the higher adsorbed quantity compared to ZnO.

The photocatalysis kinetic study showed that ZnO and TiO₂ are effective photocatalysts and MV5 at 10 mg/L was totally eliminated from the aqueous solution in only 30 min and 60 min of treatment and the apparent degradation constants in presence of ZnO was about 2.7 times higher than that obtained in presence of TiO₂. The synthesized ZnO appears than as the most powerful photocatalyst, the higher activity of ZnO in comparison of TiO₂ can not be only accounted by its larger surface area (1047 m²/g), but also may be due to its greater quantum efficiency.

The increase in the dye initial concentration results in a decrease in the yield of the photodegradation reaction as well as the degradation rate constant.

For both catalysts, the study of the pH effect showed that a better degradation of MV5 is obtained at free pH. However, the degradation is faster in basic medium compared to the acidic medium. The effect is attributed, on one hand, to the production of hydroxyl radicals favored by the increase in the concentration of OH⁻ ions in basic medium, which react with the positive holes. On the other hand, the effect is attributed to the repulsion between the molecules of the MV5 dye in its anionic form and the negatively charged surface. In the case of ZnO, the important decrease in the rate of degradation at acid pH, especially at pH < 3, is attributed to the photo-decomposition of ZnO in acidic solutions.

The photocatalytic process in the presence of solar radiation is 1.8 times more effective for the MV5 degradation than in the presence of artificial UV radiation, with almost complete decolorization after 15 and 30 min for ZnO and TiO₂, respectively. Hence, despite its low stability in acidic medium, ZnO appears to be a suitable alternative to TiO₂ for water treatment either in UV or solar irradiation.

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