Adsorption and photocatalytic degradation of malachite green by vanadium doped zinc oxide nanoparticles

L. Khezami, Kamal K. Taha, Imed Ghiloufi and Lassaad El Mir

ABSTRACT

Herein the degradation of malachite green (MG) dye from aqueous medium by vanadium doped zinc oxide (ZnO:V3%) nanopowder was investigated. The specific surface area and pore volume of the nanopowder was characterized by nitrogen adsorption method. Batch experimental procedures were conducted to investigate the adsorption and photocatalytic degradation of MG dye. Adsorption kinetics investigations were performed by varying the amount of the catalyst and the initial dye concentrations. Adsorption and photocatalytic degradation data were modeled using the Lagergren pseudo-first-order and second-order kinetic equation. The results showed that the ZnO:V3% nanopowder was particularly effective for the removal of MG and data were found to comply with Lagergreen pseudo-first-order kinetic model.

Key words | adsorption, kinetics, malachite green, nanostructures, photocatalytic degradation

INTRODUCTION

Several industries use dyes to color their final products. When discharged in wastewater, these dyes may affect the human’s health even at low concentration. Among these dyes is malachite green (MG) (color index: C.I. basic green 4), a triarylmethane basic dye, generated from many industrial processes such as paper, cotton, wool, acrylic, leather tanning industry as a dye as well as a biocide in aquaculture industry. Moreover, this dye has other beneficial uses such as antiseptic external applications on the wounds and ulcers. It is also used as a therapeutic agent to treat bacterial, fungal and parasitic infections in fish and fish eggs. Although MG has a large use in versatile fields, it is hazardous to health when consumed orally, i.e. it causes carcinogenesis, mutagenesis, teratogenesis and respiratory toxicity (Berberidou et al. 2011). Accordingly, it is necessary to remove MG from wastewater before its discharge. Various techniques are adopted for the removal of dyes from wastewater including adsorption by different porous materials such as activated carbons (Malik 2004), alumina, silica, metal hydroxides (Grini 2006) and photocatalytic degradation using visible and ultraviolet (UV) light in the presence of catalysts (Arabi & Sohrabi 2014). The most commonly used catalysts are nanosized metal oxides. The nanosized oxides such as titanium dioxide (TiO2) and zinc oxide (ZnO) are increasingly being used as photocatalysts for mineralization of toxic organic and inorganic compounds. However, these semiconductors are known to be poor absorbers of photons in the solar light due to their wide band gap (3.2 eV) (Xiao et al. 2011; Xu et al. 2008). Lachheb et al. (2002) studied the degradation of dyes by TiO2 under UV irradiation where they indicated that hydroxide (OH) radical is the initiator of the photodegradation process leading to the evolution of carbon dioxide (CO2) from the aromatic ring and ammonium (NH4+) from nitrogen-containing functional groups. The mechanism for the degradation of organic compounds using nanomaterial (Kansal et al. 2007) involves the formation of electrons and holes in the conduction and valence bands that facilitate the formation of active radicals that degrade the organic substrates.

One strategy that has been adopted for improving photocatalytic activity is to dope semiconductors with different elements such as transition metals that can increase the...
concentration of charge carriers due to the generation of donor or acceptor states in the bandgap (Zheng et al. 2011). In the literature, a number of studies have revealed that vanadium doped ZnO improve optical and structural properties of ZnO (Anandan et al. 2007; Xiao et al. 2007; Rehman et al. 2009). Slama et al. (2011) observed a red shift in zinc oxide bandgap after doping with vanadium that enabled it to function in the visible light. Vanfard & Abedi (2010) reported the oxidation of MG using vanadium in acidic medium at 625 nm. Since ZnO is a suitable alternative to TiO2 as it has a similar bandgap and is a dilute semiconductor (Xiao et al. 2011; Xu et al. 2012) and doping it with vanadium will enhance its photocatalytic activity. Therefore, vanadium doped ZnO will be investigated in this paper. Their findings had motivated the study of the adsorption and photodegradation of MG under dark, visible and UV irradiation. Adsorption kinetics investigations were performed by varying the amount of the catalyst and the initial dye concentrations.

EXPERIMENT

Materials

For activity tests, MG dye was purchased from Fluka and was used as received without any further purification. The vanadium doped ZnO catalyst was already prepared (Slama et al. 2011) via a modified sol-gel method proposed by El Mir et al. (2008). The structure and morphology of the prepared nanopowders were previously investigated using x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) (Slama et al. 2011). On the other hand, the photoluminescence (PL) experiment was carried out to determine its optical luminescence properties (Slama et al. 2011).

Surface characterization

The characterization of pores was essentially made from the data of sorption-desorption of N2 at 77 K, obtained by using an apparatus ASAP 2020 (Micromeritics). The dye sample was introduced in the ASAP 2020 after being out-gassed for 12 hours. The mean surface area was classically evaluated from the Brunauer–Emmett–Teller (BET) equation while the volume of micro-pores and the surface area of mesopores were calculated from the t-plot method of Lippens & De Boer (1965).

Photo-reactor and experimental procedure

The photocatalytic activities of prepared nanopowders, i.e. ZnO and ZnO:V3% catalysts, were scrutinized by the degradation of MG dye under UV and visible light irradiations. All photocatalysis experiments were carried out in a photoreactor equipped with a Pyrex cell with a circulating water jacket. The irradiation sources were a Philips HPK 125 W lamp (365 nm) and an Osram Lumilux daylight lamp (58 lm/W) for UV and visible irradiations, respectively. The photoreactors used were an immersed and an external lamp photoreactors, respectively, for UV and visible photodegradation.

The MG initial solution concentration ranged between 0 and 500 mg.L−1, while that of the catalyst was 100 to 500 mg.L−1. The change in the dye concentration was monitored by ultraviolet-visible (UV–Vis) dual beam personal computer (PC) scanning spectrophotometer (Labomed, Inc., UVS-2800) at λmax = 618 nm (Lachheb et al. 2002). Only the mean values are reported in this paper. The maximum deviation observed was less than 5%.

RESULTS AND DISCUSSION

Adsorption of nitrogen

As shown in Figure 1, the adsorption-desorption isotherm of N2 at 77 K for ZnO:V3% and ZnO are clearly of type II, according to the International Union of Pure and Applied Chemistry (IUPAC) classification of sorption isotherms (Rouquerol et al. 1999), formerly designated as Brunauer’s classification. The isotherm is a type H4 hysteresis loop, characteristic of aggregated particles with nonporous or macroporous adsorbents and unrestricted monolayer-multilayer adsorption (Rouquerol et al. 1999).

Figure 1 | Adsorption-desorption isotherms of N2 at 77 K of vanadium doped zinc oxide and zinc oxide.
By examining the results of ZnO:V3% and ZnO, it is clear that the doping process has decreased the specific surface area and pore volume of the ZnO (Table 1). Accordingly, the average pore size and volume have decreased for ZnO:V3% (143 Å, 4.96 × 10² cm³·g⁻¹) compared with ZnO (465 Å, 7.14 × 10² cm³·g⁻¹).

### MG adsorption study

The adsorption tests were carried out in dark batch mode by adding different masses of vanadium doped zinc oxide to 500 ml of a MG solution at known concentration and pH in a 1,000 ml beaker. The beaker containing the suspension is well wrapped in aluminum foil in order to be completely isolated from light to avoid the photolysis phenomena. After variable time of contact, 2 ml of suspension were taken out from the beaker by a syringe and separated using a centrifuge (Hettich Zentrifugen, EBA 20) at 6,000 rpm for 10 min. Their concentrations in non-adsorbed free pollutant were measured by absorption spectrometry.

### Effect of initial concentration of MG

The effect of the initial concentration of MG was investigated in the range 25–700 mg.L⁻¹ with constant amount of ZnO:V3% (0.2 g.L⁻¹) and a fixed pH value equal to 7. When the amount of ZnO:V3% in the suspension was equal to 0.2 g.L⁻¹, 99% of the initial MG with a concentration ranged between 25 and 400 mg.L⁻¹ is adsorbed. On the other hand, at an initial concentration of about 500 mg.L⁻¹, the amount of MG removed drops to 90%. The decrease in degradation as the dye concentration was increased had been reported (Chen et al. 2010), where it was explained as the equilibrium adsorption of dye on the catalyst surface active sites increases, the competitive adsorption of OH⁻ on the same sites decreases, leading to a lower formation rate of OH radical, which is the principal oxidant necessary for a high degradation efficiency. The photodegradation of MG at neutral pH (7.0) was found to be the highest using ZnO nano particles (Bansal et al. 2009). Tadjarodil et al. (2014) used CdO nanoparticles to degrade MG at pH = 6 and argued that at low and high pH excess charges will be present, resulting in an electrostatic repulsion and reduction in organic molecules adsorption on the active sites that will instead be occupied by the produced cationic and anionic species.

### Adsorption kinetic study

In the present study, the adsorption kinetic was tested in order to predict the photocatalytic degradation data of MG dye as function of time using a Lagergren pseudo-first order. According to Namasivayam & Kadirvelu (1999) and Gupta et al. (2001) the pseudo-first-order model can be expressed as follows:

\[ q_t = q_e (1 - \exp(-k_{ads}t)) \]  

where \( q_e \) and \( q_t \) (both in mg.g⁻¹) are the solute amounts adsorbed per unit mass of adsorbent at equilibrium and at time \( t \) (min), respectively, and \( k_{ads} \) (min⁻¹) is the adsorption rate constant. The values of \( k_{ads} \) and \( q_e \) are determined by the simulation of the model by Origin 7 software (see Figure 2).

The validity of the kinetic model is tested by the magnitude of the regression coefficient \( r^2 \), given in Table 2. It is important to note that all of these coefficients are greater than 99%. Therefore, the Lagergren pseudo-first-order model is suitable for modeling the adsorption of MG by ZnO:V3% as has been reported earlier (Hameeda & El-Khaiary 2008). The degradation kinetics of MG was found to obey the pseudo-first-order with degradation rate constants between 0.0062 and 0.4012 h⁻¹ (Yong et al. 2015).

### Table 1 | Pores structure of ZnO:V3% and ZnO

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>Pore diameter (Å)</th>
<th>Pore volume (cm³·g⁻¹) \times 10²</th>
<th>Surface BET (m²·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>465</td>
<td>7.13</td>
<td>8.3</td>
</tr>
<tr>
<td>ZnO:V3%</td>
<td>143</td>
<td>4.96</td>
<td>8.1</td>
</tr>
</tbody>
</table>

### Figure 2 | Adsorption kinetics of MG by ZnO:V with different masses of catalyst.
Effect of the amount of ZnO:V3%

The effect of the concentration of ZnO:V3% on the kinetic of MG removal is investigated by testing three values of the mass: 100, 300 and 500 mg/L at a temperature of 25 ± 1 °C and fixed initial concentration of MG equal to 300 mg.L⁻¹ for all the experiments. The evolution of the adsorption data of MG as a function of time are illustrated by Figure 3. It appears that for all the dye concentrations a rapid initial rise of the adsorption capacities qt is achieved and an the equilibrium is almost reached within 160 min. As indicated in Figure 4 and Table 2, the adsorption rate was slightly enhanced by the addition of catalyst and equilibrium is reached faster with a 500 mg mass of catalyst but, curiously, the amount of adsorption is better pronounced for 300 mg of ZnO:V3%, indicating that it seems to be an optimum of adsorption capacity. This discrepancy may be attributed to the dye aggregation. The decrease of degradation rate with the high catalyst load reported in this work agrees with the findings of Chen et al. (2007), who attributed the phenomenon to the aggregation of nanoparticles at such high concentration resulting in less surface active sites number. Moreover, there is a scattering of the irradiation light due to a high nanoparticles load, causing a reduction in the photonic flux within the irradiated suspension (Saquib & Muneer 2003).

Adsorption dynamic study

Since it was found that the equilibrium time is about 160 min, this time was chosen for the dynamic study of the MG adsorption (fixed concentration = 300 mg.L⁻¹) on different amounts of ZnO:V3%. Experimental data were simulated with both Langmuir and Freundlich models recommended for the dye adsorption. The linear form of Langmuir (1918) and Freundlich (1906) equations are expressed as follows:

\[ \frac{C_e}{q_e} = \frac{1}{Q_0} C_e + \frac{1}{Q_0 b} \]  \text{linear form of Langmuir equation (2)}

\[ \ln q_e = \frac{1}{n} \ln C_e + \ln k \]  \text{linear form of Freundlich equation (3)}

where \( q_e \) is the amount of metal ions adsorbed per unit mass of adsorbent (mg.g⁻¹); \( C_e \) is the equilibrium concentration of solute in the bulk solution (mg.L⁻¹); \( Q_0 \) the solid phase concentration corresponding to the complete monolayer coverage of adsorption sites (Huang & Smith 1981); \( b \) is the constant related to the free energy of adsorption. The constants \( k \) and \( n \) of the Freundlich model can be related to the strength of the adsorptive bond and the bond distribution (Gupta et al. 2000). The adsorption was found to follow the Langmuir adsorption model (Figure 3(a), \( R^2 = 0.99 \)) and the maximum adsorption capacity of MG Langmuir constants, \( q_L \) and \( K_L \), were found to be equal to 443.44 mg/g and 26.69 \( 10^{-3} \) L/mg, respectively. When the Freundlich model was simulated (Figure 3(b)), the 1/n value was found to be 0.88, indicating a normal Freundlich isotherm (\( R^2 = 0.99 \)), as

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Pseudo-first-order adsorption constants and MG equilibrium adsorption amount for different masses of catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO:V3% mass (mg.L⁻¹)</td>
<td>( k_{ads} \times 10^3 ) (min⁻¹)</td>
</tr>
<tr>
<td>100</td>
<td>15.05</td>
</tr>
<tr>
<td>200</td>
<td>22.25</td>
</tr>
<tr>
<td>300</td>
<td>21.23</td>
</tr>
<tr>
<td>500</td>
<td>24.28</td>
</tr>
</tbody>
</table>

Figure 3 | (a) Langmuir isotherm and (b) Freundlich isotherm for the MG adsorption by ZnO:V3% catalyst.
well as less heterogeneity of the surface (Arabi & Sohrabi 2014).

Photocatalytic degradation study

MG photocatalytic degradation under UV irradiation

Figure 4 shows the simulation of kinetic experimental data of the degradation of MG (300 mg L\(^{-1}\)) with different concentrations of ZnO:V\(_{3\%}\) catalyst.

The values of the pseudo-first-order \(k_{\text{deg}}\) obtained by the simulation with the correlation coefficients are listed in Table 3. It can be shown that the experimental data are well fitted by the first order model for at least the first 2 hours.

MG photocatalytic degradation under visible irradiation

The kinetic results of photocatalytic degradation under visible irradiation is presented in Figure 5. The experimental results are well simulated by a pseudo-first-order, and the obtained apparent rate constants are listed in Table 3. As can be observed, photolysis has no effect on the degradation of MG but the presence of the photocatalyst, even with the lowest dose, reduces extremely the concentration of MG. Slama et al. (2011) attributed the improved efficiency of vanadium doped ZnO nanoparticles to the oxygen vacancies resulting from the incorporation of vanadium. The PL spectra of the vanadium doped zinc oxide nanopowder was found to consist of an emission band in the visible range. That was attributed to deep level in the ZnO band gap which can be excited by visible light (Slama et al. 2011). For ZnO to absorb visible spectrum of solar radiation, band gap energy of ZnO photocatalysts must have to be decreased or divided into different sub-band gaps, either by doping with transition metal ions or nitrogen or sulphur atoms (Ueda et al. 2001). From the TEM, SEM and TEM analysis results, Slama et al. (2011) reported dispersed particles of 15–30 nm size. Such a nanoparticles size has the maximum adsorption and degradation capacity as reported by Shen et al. (2008), who indicated a higher efficiency of 32 nm compared to 64 nm nanoparticles. Also, the optimum effective size for TiO\(_2\) photoactivity has been reported to be in the range of 25–40 nm (Almquist & Biswas 2002).

Effect of the ZnO:V\(_{3\%}\) amount on the UV and visible degradations

The effects of UV and visible photodegradation on the apparent kinetic constant (\(k_{\text{app}}\)), have been studied with respect to the amount of catalyst. As shown by Figure 6, visible light photodegradation of MG results in significantly higher values of \(k_{\text{app}}\) with optimum catalyst mass ranged between 200 and 300 mg. Whereas for UV photodegradation, lower

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**Table 3** Apparent kinetic constants of MG degradation under UV and visible irradiation

<table>
<thead>
<tr>
<th>Catalyst (mg L(^{-1}))</th>
<th>UV (k_{\text{app}}) (\times 10^2) (min(^{-1}))</th>
<th>(r^2) (%)</th>
<th>Visible (k_{\text{app}}) (\times 10^2) (min(^{-1}))</th>
<th>(r^2) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.09</td>
<td>90.11</td>
<td>1.1</td>
<td>91.32</td>
</tr>
<tr>
<td>100</td>
<td>5.65</td>
<td>94.25</td>
<td>10.97</td>
<td>99.62</td>
</tr>
<tr>
<td>200</td>
<td>5.74</td>
<td>97.13</td>
<td>12.65</td>
<td>99.72</td>
</tr>
<tr>
<td>300</td>
<td>6.64</td>
<td>98.35</td>
<td>12.85</td>
<td>99.52</td>
</tr>
<tr>
<td>500</td>
<td>8.08</td>
<td>98.75</td>
<td>11.49</td>
<td>99.36</td>
</tr>
</tbody>
</table>
apparent kinetic constants are obtained, even though values of catalyst mass beyond 200–300 mg has no additional effect at this treatment. In any case, a mass of 300 mg is sufficient to attain convenient results. Soni & Kumar (2014) degraded MG in UV light irradiation using TiO2 and found that a catalyst loading of 20.0 mg brought about an absolute discoloration. The degradation of MG by nanosized CeFeO2 was reported to decline beyond 0.05 g/50 ml of dye solution (Ameta et al. 2014).

Degradation of MG

Degradation of MG can take place through different mechanisms such as the dissociation of carbon methane bond, N-demethylation (aromatic ring opening) (Modirshahla & Behnajady 2006) and conjugated structure destruction (Li et al. 2002). In biological systems, the reduction of MG to its leuco form was achieved using intestinal bacteria (Henderson et al. 1997) bacillus (Lal & Srivastava 2011). The toxicity of the dye and its leuco form was tested by mouse cell cytotoxicity and antimicrobial tests. The results of the first test revealed higher toxicity of the products, while the antimicrobial tests gave opposite results (Chen et al. 2010).

Ameta et al. (2014) proposed that the MG molecule is excited to the singlet state after absorbing a radiation and the excited state molecules undergo intersystem crossing to the triplet state. Meanwhile, the catalyst utilizes the same radiation to excite and electron from the valence to the conduction band. This electron is then abstracted by an oxygen atom to form a superoxide anion radical (O2·⁻) that reduces the dye to its leuco form and, ultimately, to its final products. Liua et al. (2010) suggested sensitization assisted photocatalytic degradation of adsorbed MG, where the molecules absorb visible light and get excited. They indicated the formation of a cationic dye radical. The electron ejected by the catalyst produces hydrogen peroxide (H2O2) that ultimately generates OH⁺ to react with the dye and give off the final products. In a recent study, Saikia et al. (2015) reported the mineralization of MG and the CO2 evolution as a result of its degradation under solar light. Yong et al. (2015) employed gas chromatography-mass spectrometry (GC–MS) to identify the MG degradation products, where the detection indicated that most products were carboxylic acid, alcohol, and amine. Such species are not likely to cause severe hazards to the environment.

In this work, the pH for the degradation of the dye was set at 7.0. The choice of this pH value was due to the fact that organic dyes and pollutants’ main degradation reaction is governed by the hydroxyl radical attack, which can be advantageous by the high hydroxyl radicals’ concentration at around neutral pH values of the solution (Kim & Lee 2010).

The photocatalytic degradation of organic pollutants in solutions is initiated by photoexcitation of the semiconductor, followed by the formation of an electron–hole pair on the surface of catalyst.

\[ \text{ZnO:V} \text{V}_3\% + h\nu \rightarrow \text{ZnO:V}_3\%(e^- + h^+ \text{V}_3\%) \]  

The doping of the ZnO prevents the recombination of electron–hole pair (Khani & Sohrabi 2012). The oxygen present may react with the electron to produce the superoxide anion

\[ e^- + O_2 \rightarrow \cdot O_2^- \]  

As the medium is neutral, the superoxide anion will not react to form hydroperoxyl (HO2·). Still, reaction (2) is important to consume the electrons and retard the recombination process.

On the other hand, the hole reacts with the water molecule or OH⁻ present in the medium to generate OH radicals

\[ h^+ + H_2O \rightarrow H^+ + \cdot OH \]  

\[ h^+ + OH^- \rightarrow OH^+ \]  

The powerful oxidant HO', that reacts with organic compounds a high rate constant of \(10^{7}–10^{10} \text{M}^{-1} \text{s}^{-1}\)
(Buxton et al. 1988), can degrade the MG to the mineralization products (Yong et al. 2015).

CONCLUSIONS

In this investigation, the adsorption and photocatalytic activities of the 3% vanadium doped ZnO were studied using the MG under visible and UV irradiation. The adsorption experimental data were modeled using the pseudo-first-order and the pseudo-second-order kinetics models. In the dark tests, the adsorption rate was slightly enhanced by the addition of a catalyst but, interestingly, the amount of adsorption was better pronounced for 300 mg of ZnO:V3%, which was considered as an optimum of adsorption capacity. The results of the visible and UV irradiation showed that the nanopowder was particularly improved for the photodegradation of MG and data were found to comply with pseudo-first-order kinetic model. Moreover, visible light photodegradation of MG results in significantly higher values of kapp with optimum catalyst mass of between 200 and 300 mg. The vanadium doped zinc oxide seems to be an effective material for the photocatalytic degradation of MG and the use of visible light and UV irradiation improves the time of its removal from wastewater.

RECOMMENDATION

The dye removal was enhanced by pre-treatment, such as supporting the nanoparticles onto bentonite (Weng et al. 2014), activated carbon (Muthirulan et al. 2015) or zeolites (Benkli et al. 2005). Due to their cage-like structure and ion exchange capacity, zeolites can be employed in dye removal pre-treatment. Moreover, zeolites are available in considerable amounts in the study. Therefore, we suggest a fixed bed reactor to be incorporated in the system to improve the removal of the dye.

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