Preparation and Photocatalytic Properties of Silver Doped Titanium Dioxide Nanoparticles and Using Artificial Neural Network for Modeling of Photocatalytic Activity

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Abstract: This paper presents a study on the preparation method for Ag-TiO2 nano particles. Photodeposition of silver on TiO2 nanoparticles was carried out by adding a desired volume of aqueous AgNO3. Ag-deposited TiO2 catalyst was characterised by XRD, TEM, SEM. The Ag-TiO2 catalyst was evaluated for their photocatalytic activity towards the degradation of Malachite green (MG) under UV irradiation. An artificial neural networks (ANN) model was developed to predict the performance of degradation efficiency by Ag-TiO2/UV process based on experimental data obtained in a laboratory batch reactor. A comparison between the predicted results of the designed ANN model and experimental data was also conducted. The model can describe the color removal percent under different conditions.

Key words: nanoparticle, Ag-TiO2, Malachite green, Neural network modeling.

INTRODUCTION

Synthetic dyes are the major industrial pollutants and water contaminants (Modirshahla et al., 2007; Behnajady et al., 2007; Brown et al., 1981; Vaidya et al., 1982). One of the most active areas in environmental research is the development of highly efficient methods for the elimination of hazardous pollutants from air, soil and water (Castro et al., 2008). There is a need to develop effective methods for the removal of organic pollutants, either by transformation to less harmful compounds or by complete mineralization (Khataee, 2009). There has been intense study of TiO2 as a photocatalyst because of its high chemical stability, no toxicity, low cost and excellent degradation for organic pollutants (Wang et al., 2008). The development of UV/TiO2 process to achieve complete mineralization of organic pollutants has been widely tested for a large variety of industrial dyes (Behnajady et al., 2007).

Heterogeneous photocatalysis via combination of TiO2 and UV light is considered one of the promising AOPs or destruction of water-soluble organic pollutants found in water and wastewater. When a light with \( \lambda < 390 \text{ nm} \) is illuminated on TiO2, it excites an electron out of its energy level and consequently leaves a hole in the valence band. Indeed, electrons are promoted from the valence band to the conduction band of TiO2 to give electron–hole pairs (Equation (1)) (Khataee et al., 2009; Daneshvar et al., 2003; Daneshvar et al., 2006).

\[
\text{TiO}_2 + h\nu (\lambda < 390\text{nm}) \rightarrow e^- + h^+
\] (1)

The valence band (\( h^+ \)) potential is positive enough to generate hydroxyl radicals at the surface of the TiO2 and the conduction band (\( e^- \)) potential is negative enough to reduce molecular oxygen. The hydroxyl radical is a powerful oxidizing agent and attacks organic pollutants (P) present at or near the surface of the TiO2. It causes, ultimately, complete decomposition of toxic and bioreistant compounds into harmless species such as CO2 and H2O (Khataee et al., 2009).

The deposition of metals on the surface of TiO2 would produce traps to capture the photo-induced electrons or holes, leading to the reduction of electron-hole recombination and thus improving the photocatalytic efficiency (Wang et al., 2008).

Silver is particularly suitable for industrial applications due to its low cost and easy preparation. The effect of Ag dopants on the lattice or surface of TiO2 have been examined. TiO2 loaded with silver enables the catalyst to perform more effectively and shortens the illumination period (Lee et al., 2005).

Most studies of noble metal-modified TiO2 photocatalysts have focused on the details of the photo induced electron transfer from the conduction band of UV-irradiated TiO2 to noble metals for improving the photocatalytic activity of TiO2 under UV irradiation (Sung-suh et al., 2004). But only a few studies have been reported the ANN modeling for dyes removal percent (Daneshvar et al., 2006; Khataee and mirzajani, 2010).
In the present work, Ag nanoparticles on TiO$_2$ powders were prepared by a simple sol-gel route. The photocatalytic efficiency of these particles was evaluated in the removal of Malachite green (MG) as a refractory.

The effect of operational key factors such as initial dye concentration, UV light intensity, irradiation time and dosage of Ag-TiO$_2$ nanoparticles were studied. The best aspect of the present study is the application of ANN for predicting the performance of MG removal by prepared nano Ag-TiO$_2$ in the presence of UV light that it has not been reported so far.

**MATERIALS AND METHODS**

**Materials:**

Tetraisopropylorthotitanate Ti(O$i$_{4}$C$_{3}$)$_{3}$, methanol (MeOH), MG and silver nitrate (AgNO$_{3}$) were obtained from Merck (Germany) and used without any further purifications. Deionized water was used throughout the work. The structure and other characteristics of MG are reported in Table 1.

<table>
<thead>
<tr>
<th>Table 1: Characteristics of MG.</th>
<th>Malachite Green (MG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical structure</td>
<td><img src="image" alt="Chemical structure" /></td>
</tr>
<tr>
<td>Molecular mass</td>
<td>972.02 g mol$^{-1}$</td>
</tr>
<tr>
<td>Maximum of absorption spectrum</td>
<td>619 nm</td>
</tr>
<tr>
<td>Chemical class</td>
<td>Thriphenyl methane</td>
</tr>
<tr>
<td>C.I.number</td>
<td>42000</td>
</tr>
</tbody>
</table>

**Ultrasonic Bath (T 460/H):**

The ultrasonic bath Elma (GmbH) was used with the operating frequency of 35 kHz and a rated output power of 170 W. The bath has the dimensions of 240 mm×137 mm×100 mm. The total internal body is made from stainless steel.

**Method:**

In order to get nanostructured TiO$_2$, 12 ml Ti(O$i$_{4}$C$_{3}$)$_{3}$ solution was dissolved in 1.35 ml MeOH and the mixture was sonicated for 3 min and agitated at 70°C for 210 min under magnetic stirrer. Water was added dropwise into the hot solution (70°C) during this period of time (Ghanbary et al., 2011).

Photodeposition of silver on TiO$_2$ nanoparticles was carried out by adding a desired volume of aqueous AgNO$_3$ (10$^{-3}$ M) so as to attain 1 wt. % of Ag onto the TiO$_2$ nanosol followed by irradiation with visible light source (200 W halogen lamp) for 120 min. Finally, the product was centrifuged, washed with distilled hot water and organic solvents to remove the adsorbed impurities, and calcined at different temperatures for 3 h.

**Photocatalytic Experiments:**

All experiments were carried out in a batch photoreactor. The radiation source was a low pressure mercury UV lamp (30 W, UV-C, $\lambda_{max} = 254$ nm, manufactured by Philips, Holland), which was placed above a batch photoreactor of 0.5 L volume. The incident UV light intensity was measured by a Lux-UV-IR meter (Leybold Co.). In each experiment, a known amount of Ag-TiO$_2$ was added to 500 ml of the solution and a magnetic stirrer was used in order to achieve a homogeneous mixture.

**1.5 Analytical Method:**

In the presence of Ag-TiO$_2$ as photocatalyst, MG was used as pollutant. Sample solutions were sonicated before irradiation for 5 min. At known irradiation time intervals, the samples (5 ml) were taken out and then analyzed by UV-Vis spectrophotometer (Ultrspec 2000, Biotech Pharmacia, England) at 619 nm. A linear correlation was established between the MG concentration and the absorbance, in the range 0–60 mg/L with a correlation coefficient, $R^2=0.995$. The equation used to calculate the photocatalytic removal efficiency (R) in the experiments was:

$$R(\%) = \left(\frac{C_0 - C}{C_0}\right) \times 100$$

(2)

where $C_0$ is the initial concentration of the MG (mg/L) and $C$ is the concentration of the MG (mg/L) at time $t$.

The crystal structure of the powders was checked by powder X-ray diffraction (XRD) using Siemens X-ray diffraction D5000 with Cu Ka radiation. An accelerating voltage of 40 kV and emission current of 30 mA were
used. The average crystalline size of the samples was calculated according to the Debye–Scherrer formula (Patterson, 1939; Bartram and Kaelble, 1967; Rodríguez and Fernández-García, 2007):

\[ D = \frac{0.89\lambda}{\beta \cos \theta} \]  

(3)

Where \( D \) is the average crystallite size (Å), \( \lambda \) is the wavelength of the X-ray radiation (Cu Kα = 1.54178 Å), \( \beta \) is the full width at half maximum intensity of the peak and \( \theta \) is the diffraction angle. If a sample contains anatase and rutile forms, the mass fraction of rutile (\( \chi \)) can be calculated from the following equation (Yassine et al., 2007).

\[ \chi = \frac{IA}{IA + IR} \]  

(4)

where \( I_A \) and \( I_R \) represent the integrated intensity of the anatase (101) and rutile (110) peaks, respectively.

Scanning electron microscopy (SEM) of samples was carried out on a Philips XL 30 microscope. The morphology and grain size of Ag-TiO₂ nanopowders were investigated by transmission electron microscopy (TEM) on a Philips CM operating at 200 kV.

**ANN Software:**

All ANN calculations were carried out using Matlab 7.8 (2009R) mathematical software with ANN toolbox. A three-layer network with a sigmoidal transfer function with back-propagation algorithm was designed in this study.

**RESULTS AND DISCUSSION**

**Preliminary Results:**

A thermal treatment is necessary to improve the crystallinity of amorphous compounds. Several syntheses conditions have been assayed. When Ag-TiO₂ powders are calcinated at higher temperature, crystal structure transformations may occur. The amorphous-anatase and anatase-rutile transitions depend strongly on the calcination conditions.

The prepared Ag-TiO₂ nanopowders have been characterized by XRD, SEM and TEM. (Figs 1, 2, 3).

![Fig. 1: X-ray diffraction patterns of Ag-TiO₂ nanopowders calcinated at 350-700°C. (A 350, B 450, C 550, D 700).](image)
Fig. 2: SEM images of Ag-TiO₂ nanopowders calcinated at 350-700°C. (A 350, B 450, C 550, D 700).

Fig. 3: TEM images of Ag-TiO₂ nanopowders calcinated at 350 and 700°C. (A 350, B 700).

The results for structural and morphological properties of the prepared samples have been presented in Table 2.

Table 2: Crystallization conditions, species of phase and Crystallite size.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallization Temperature</th>
<th>Species of phase</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Anatase Percent</td>
<td>Rutile Percent</td>
</tr>
<tr>
<td>A</td>
<td>350°C</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>450°C</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>550°C</td>
<td>85.78</td>
<td>14.22</td>
</tr>
<tr>
<td>D</td>
<td>700°C</td>
<td>-</td>
<td>10</td>
</tr>
</tbody>
</table>

Interesting correlations can be established between the morphology and the hydrothermal conditions of preparation. All the prepared samples present heterogeneity in shapes and sizes of nanoparticles. We can ascribe this observation to different crystal growth rates.

In order to test and ensure the phase stability of the prepared samples some calcination experiments were performed under different temperatures, ranging from 350 to 700°C. If the physical properties of the samples be compared it could be seen (Table 2), that the anatase phase remains pure and stable until 450°C, some rutile conversion starting at 550°C and the change of anatase to rutile phase was completed at 700°C where the grain sizes of samples are different. This is due to the fact that at low temperatures, the crystallization is slow, and it performs at low rate and a more homogeneous way (Castro et al., 2008).
Photocatalytic Studies:

In order to examine the photocatalytic activity of the prepared samples, the photocatalytic removal of MG in presence of nonopowders was studied. The results have been given in Fig. 4. It was found that the photocatalytic performance of various Ag-TiO₂ samples decreased in the following order 350 > 450 > 550 > 700. The results can be explained in terms of the preparation steps involved in the synthesis of these samples. Photocatalytic activity of Ag-TiO₂ is strongly dependent on its phase structure, crystallite size and pore structure (Baomei et al., 2005). It is well known that anatase type Ag-TiO₂ has higher photocatalytic activity than rutile type Ag-TiO₂ and in anatase phase the samples with small grain size have higher photocatalytic activity than the others, which also is consistent with the experimental results (Zolt´an et al., 2008; Maocheng et al., 2005). Additionally, it has been reported that calcination also reduces the number of hydroxyl ions on the surface of the catalyst, leading to an overall reduction in the photoactivity of catalysts (Baomei et al., 2005; Ghanbary et al., 2011).

![Fig. 4: Removal Percent of MG in the presence of Ag-TiO₂ nanophotocatalysts (A, B, C, D, E).](image)

Neural Network Modeling:

ANNs are direct inspiration from the biology of human brain, where billions of neurons are interconnected to process a variety of complex information. Accordingly, a computational neural network consists of simple processing units called neurons (Gontarski et al., 2000; Slokar et al., 1999). In general, a neural net (multilayered perceptron), as shown in Fig. 5, has interconnected structure in parallel form consisting of: (1) input layer of neuron (independent variables), (2) a number of hidden layers, (3) and output layer (dependent variables). The number of input and output neurons is fixed by the nature of the problem. The hidden layers act like feature detectors there can be more than one hidden layer. Universal approximation theory, however, suggests that a network with a single hidden layer with a sufficiently large number of neurons can interpret any input–output structure (Daneshvar et al., 2006).

The topology of an ANN is determined by the number of layers in the ANN, the number of nodes in each layer and the nature of the transfer functions. Correct identification of the set of independent input variables and the output variables is the first task in building ANN model for a process. Optimization of ANN topology is probably the next important step in the development of a model. We used threelayered feed forward back propagation neural network (4:8:1) for modeling of UV/Ag-TiO₂ process (Fig. 5). In the present work, the input variables to the feed forward neural network were as follows: initial nano Ag-TiO₂ dosage (mg/L), removal time (min), UV light intensity (W/m²), initial concentration of MG (mg/L). MG removal percent (R (%)) was chosen as the experimental response or output variable.

![Fig. 5: Structure Of the used ANN in the present study.](image)
In this work, we tested different numbers of neurons, from 2 to 12, in the hidden layer. Each topology was repeated three times to avoid random correlation due to the random initialization of the weights. Fig. 6 illustrates the relation between the network error and the number of neurons in the hidden layer. The mean square error (MSE) was used as the error function. MSE measures the performance of the network according to the following equation:

$$MSE = \frac{1}{N} \sum_{i=1}^{N} (t_i - a_i)^2$$

(5)

where $N$ is the number of data points, $t_i$ the network prediction, $a_i$ the experimental response, and $i$ is an index of data. We can see that the performance of the network stabilized after inclusion of an adequate number of hidden units just about eight. The network with too few neurons in the hidden layer cannot converge effectively.

![Fig. 6: Effect of the number of neurons in the hidden layer on the performance of the neural network.](image)

In this work, for three-layer network the sigmoid (logsig) and linear (Purelin) transfer functions were used as transfer functions in hidden and output layers, respectively. The train gradient descent with momentum and adaptive learning rate (traingdx), as a transfer function and the training-and-test method were used to evaluate the ANN. Traingdx is a network training function that updates weight and bias values according to gradient descent and an adaptive learning rate. The range of variables studied is summarized in Table 3. Totally 128 experimental sets were used to feed the ANN structure. The data sets were divided into training, validation and test subsets, each of which contains 64, 32 and 32 samples, respectively. The validation and test sets, for the evaluation of the validation and modeling power of the networks, were randomly selected from the experimental data.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Range of variables studied.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable Range</td>
<td><strong>Input Layer</strong></td>
</tr>
<tr>
<td><strong>g/L</strong> Nano Ag-TiO$_2$ initial dosage 0.01-0.05</td>
<td></td>
</tr>
<tr>
<td>Time (min) 0-60</td>
<td></td>
</tr>
<tr>
<td>UV light intensity (W/m$^2$) 8.6-45.3</td>
<td></td>
</tr>
<tr>
<td>MG initial concentration (mg/L) 5-40</td>
<td></td>
</tr>
<tr>
<td><strong>Output Layer</strong></td>
<td></td>
</tr>
<tr>
<td>Removal percent of MG 0-100</td>
<td></td>
</tr>
</tbody>
</table>

For best result all samples from the training, validation and test sets were scaled to a new value with `premnx` function in Matlab. In order to calculate training, validation and test error, all of the predicted responses by `postmnx` function in Matlab (outputs) were returned to their original scale and compared them with experimental responses.

Training initial weights were randomly selected and training was terminated when the error gradient was less than $10^{-3}$. A weakness of the neural network is that it can be easily overfitted, causing the error rate on validation data to be much larger than the error rate on the training data. It is therefore important not to overtrain data. Overfitting is more likely to occur at later epochs than earlier ones. A good method for choosing the number of training epoch is to use the validation data set periodically to compute the error rate for it while the network is being trained. The validation error decreases in the early epochs of backpropagation but after a while, it begins to increase. The point of minimum validation error is a good indicator of the best number of epochs for training and the weight at that stage are likely to provide the best error rate in new data (Khataee and Mirzajani, 2010; Khataee et al., 2010). Our results indicated that the minimum error of the validation set could be achieved in the epochs just about 500 (Fig. 7).
Fig. 7: The progress of the mean square (MSE) with the number of iterations.

Fig. 8 shows a comparison between calculated and experimental values of the output variable for test sets by using neural network model. Plot in this figure has correlation coefficient of 0.991 for test set. These results confirmed that neural network model reproduces the removal in this system, within experimental ranges adopted in the fitting model.

![Image](image_url)

**Fig. 8:** Comparison of the experimental results with values calculated via neural network modeling for test set.

The neural net weight matrix can be used to assess the relative importance of the various input variables on the output variables. It was proposed an equation based on the partitioning of connection weights (Aleboyeh et al., 2008):

\[
I_j = \frac{\sum_{m=1}^{m=N_N} \left( \left| W_{jm}^{ih} \right| \left| \sum_{k=1}^{k=N_h} W_{km}^{ih} \right| \times \left| W_{mN}^{ho} \right| \right)}{\sum_{k=1}^{k=N_N} \sum_{m=1}^{m=N_N} \left( \left| W_{km}^{ih} \right| \left| \sum_{k=1}^{k=N_h} W_{km}^{ih} \right| \times \left| W_{mN}^{ho} \right| \right)}
\]

(6)

where \( I_j \) is the relative importance of the \( j \)th input variable on the output variable, \( N_i \) and \( N_h \) are the numbers of input and hidden neurons, respectively, \( W \)s are connection weights, the superscripts ‘i’, ‘h’ and ‘o’ refer to input, hidden and output layers, respectively, and subscripts ‘k’, ‘m’ and ‘n’ refer to input, hidden and output neurons, respectively.

The relative importance of input variables on the value of MG removal efficiency (%) was calculated by Eq. (6) and shown in Table 4. As can be seen, all of the variables have strong effects on the MG removal efficiency. But the effect of time is more than others. Therefore, none of the variables studied in this work could have been neglected in the present analysis.
Table 4: Relative importance of input variables on the value of MG removal efficiency.

<table>
<thead>
<tr>
<th>Input Variable</th>
<th>Importance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano Ag-TiO₂ (g/L)</td>
<td>20.9</td>
</tr>
<tr>
<td>Time (min)</td>
<td>38.1</td>
</tr>
<tr>
<td>UV light intensity (W/m²)</td>
<td>17.9</td>
</tr>
<tr>
<td>MG initial concentration (mg/L)</td>
<td>23.1</td>
</tr>
</tbody>
</table>

**Effect Of Nano Ag-TiO₂ Dosage:**
The photocatalytic removal of MG in aqueous solution with various nano TiO₂ dosage (prepared at 350°C) was studied. The experimental and ANN calculated values of removal percent were shown in Fig. 9. Apparently, in this work, the photodegradation efficiency of MG increased when the concentration of Ag-TiO₂ increased from 0.01 to 0.05 g/L. The comparison between ANN and experimental data in Fig. 9 shows that the results are in good agreement.

**Effect Of UV Light Intensity:**
The variation between experimental and ANN calculated values of MG removal efficiency during the reaction period under different UV light intensity have been presented in Fig. 10. The figure clearly shows that the removal rate increases by increasing UV irradiation intensity. The increase of radiation intensity from 8.6 to 45.3 W/m², increases the removal from 29.13 to 94.26%. This increase is due to the enhanced production of hydroxyl radicals.

**Effect Of MG Initial Concentration:**
It is important from an application point of view to study the dependence of removal efficiency on the initial concentration of the MG. Therefore, the effect of MG concentration on the removal efficiency was investigated at different MG initial concentrations. The experimental and ANN predicted values of MG removal percent was plotted versus initial MG concentration (Fig. 11).

When the MG concentration increases, the amount of MG molecules adsorbed on the surface of the catalyst increases. This affects the photocatalytic activity of AG-TiO₂ and reduce the photocatalytic efficiency. The increase in the MG concentration also decreases the path of photons into the MG solution. At high concentration, the MG molecules may absorb a significant amount of light and this may also reduce the photocatalytic efficiency (Chakrabarti and Dutta, 2004).
Effect Of Irradiation Time:

Reaction time influences the treatment efficiency of the UV/Ag-TiO₂ process. Fig. 12 shows the relationship between the removal efficiency and the photocatalytic reaction time. According to the results showed in Fig. 12 the optimum reaction time was 60 min for MG removal from solution. It shows good agreement between predictions from ANN model and experimental results. From this plot it can be seen that obtained results from the proposed ANN model are in good agreement with the experimental data.

Conclusion:

Ag-TiO₂ prepared by sol–gel route was optimized using MG during photocatalytic test. The results presented the anatase-type Ag-TiO₂ has higher photocatalytic activity than rutile type Ag-TiO₂ and in anatase phase the samples with small grain size have higher photocatalytic activity than the other's. A simulation based on the ANN model can estimate the behavior of the process under different conditions. One of the characteristics of modeling based on artificial neural networks is that it does not require the mathematical description of the phenomena involved in the process, and might be useful in simulating and up-scaling complex photochemical systems. The removal performance of MG was successfully predicted by applying a three-layered neural network with 8 neurons in the hidden layer, and using back-propagation algorithm. The results indicated that the minimum error of the validation set could be achieved in the epochs just about 500.

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