PREPARATION OF DOPED TiO₂ PHOTOCATALYSTS AND THEIR DECOLORIZATION EFFICIENCIES UNDER SOLAR LIGHT

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Abstract

Photocatalysis has gained a great interest for the degradation of organic pollutants in aqueous media. This effective advanced oxidation technique is basically based on the oxidation of the target molecule by hydroxyl radicals. The most widely preferred and powerful photocatalyst is titanium dioxide (TiO₂), but it has limited use under solar light because of its band gap energy. This is a major drawback for various possible applications. In order to overcome this disadvantage, doping the photocatalyst with metals and non-metals to narrow the band gap can be applied. In this work, we have prepared visible light active photocatalysts by using wet-impregnation method. Decolorization of two different classes of dyes, Rhodamine B and Congo Red, was carried out under simulated solar light with doped TiO₂. The photocatalytic performances of non-metal doped (C, N, Se), metal doped (Cu, Fe) and codoped (N/S) TiO₂ photocatalysts were investigated by UV-vis studies and removal percentage calculations.

Keywords

1. Introduction

The removal of organic pollutants in water and air, which cause environmental pollution, is an increasingly relevant subject in today’s world. The subject has gained great importance and new environmentally friendly methods for removing these pollutants are being developed every day.

One class of pollutants is synthetic organic dyes which are widely used in different industries (Méndez-Martínez et al., 2012). Depending on their chemical constitutions, dyes can be classified as azo dyes that contain one or more azo bonds (-N=N-) and non-azo dyes. The release of azo dyes into the water streams can cause severe environmental problems. Furthermore, studies have shown that the toxicity and carcinogenic character of azo dyes can be threatening for human health (Turkten et al., 2017). Rhodamine dyes which are also known as fluorone dyes are used extensively for biotechnology applications because they show fluorescence and can be detected easily. Rhodamine dyes are also suspected to be carcinogenic and further studies are required for their removal from aqueous media.

In this work, we have prepared visible light active photocatalysts by wet-impregnation method and carried out the decolorization of two different classes of dyes, Rhodamine B and Congo Red, under solar light. Evonik P25 powder, which is a mixture of anatase and rutile phases (79% anatase, 21% rutile) was chosen as the photocatalyst for doping. P25 TiO₂ which is the standard photocatalyst has high activity with a well-established structure and photocatalytic data. The photocatalytic performances of non-metal doped (C, N), metal doped (Cu, Fe, Se) and codoped (N/S) TiO₂ photocatalysts were investigated and compared by following UV-Vis data of the decolorization process and commenting on removal percentages.

2. Literature Survey

Advanced oxidation processes (AOP) stand out as alternative methods for the destruction of synthetic organic species resistant to conventional removal methods. The idea of AOP is based on the highly reactive hydroxyl radicals (Kudo et al., 2003, Gaya et al., 2008). Heterogeneous photocatalysis method which is one of the AOP, is a technique that enables the decomposition of organic pollutants in water and air into small molecules such as CO₂, H₂O, HCl in the presence of low energy UV-A light and a semiconductor. With the photocatalytic oxidation of the process, organic pollutants in the gas or liquid phase are partially or completely converted into harmless substances (Herrmann et al., 1993, Bahnemann et al., 1994, Mills et al., 1997, Pichat, 1997, Guillard et al., 1999, Bahnemann, 2004).

Since the first time the photocatalytic activity of TiO₂ was discovered (Fujishima et al., 1972), there has been an ongoing interest on its possible applications as a photocatalyst. The photocatalytic removal of organic pollutants is an economical method since it operates at ambient conditions, does not require energy input or additional chemicals other than atmospheric oxygen (Pelaez et al., 2012). There is a variety of reasons that TiO₂ is the most widely preferred and the most efficient photocatalyst. The advantages of TiO₂ include high stability, non-solubility in water, low-cost, chemical inertness and non-toxic as well as being a highly oxidative semiconductor (Suib, 2013).

The basis of the accepted mechanism of TiO₂ photocatalysis can be explained by the formation of electron-hole (e⁻/ h⁺) pairs as a result of excitation by UV light and the obtained e⁻/ h⁺ pairs lead to oxidation and reduction reactions on the TiO₂ surface. The electrons are trapped in the distorted regions (Ti³⁺) on the particle surface and move away from the medium by reacting with molecular oxygen to form the superoxide anion radical and more hydroxyl radicals. The resulting holes react with the adsorbed water molecules or OH⁻ ions on the surface to form hydroxyl radicals. Hydroxyl radicals are thought to be the main reactive particles involved in the formation of photocatalytic reactions (Xu et al., 2007). The mechanism of photocatalytic degradation is given below;

\[
\text{TiO}_2 + \text{hv} \rightarrow e^- + h^+ \\
h^+ + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+ \\
h^+ + \text{OH} \rightarrow \cdot\text{OH} \\
e^- + \text{O}_2 \rightarrow \cdot\text{O}_2^- \\
e^- + \cdot\text{O}_2^- + \text{H}^+ \rightarrow \text{H}_2\text{O}_2 \\
\text{O}_2^- + \cdot\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{H}_2\text{O} \\
2\text{O}_2^- + 2\cdot\text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
e^- + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{OH}^- \\
e^- + \text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \cdot\text{OH} + \text{H}_2\text{O} 
\]
However, the major drawback of titanium dioxide as a semiconductor-based photocatalyst is that it has a wide band gap energy of 3.2 eV and is able to absorb only 5% of sunlight. In order to overcome this disadvantage, numerous methods have been proposed and developed such as coupling with metal oxides (Ibadon et al., 2008, Liao et al., 2008), depositing on magnetic ferrite activated carbon (Wang et al., 2010), synthesizing composite materials (Wang et al., 2007, Woon et al., 2009, Yu et al., 2017) and surface modification (Kaya et al., 2017). One of these methods is doping the TiO$_2$ with metals or non-metals for an enhanced activity (Diebold, 2003, Gurkan et al., 2012, Birben et al., 2015).

Recently, doping with metal and non-metals has been carried out in order to increase the efficiency of TiO$_2$ photocatalysts under visible light. For this purpose, doping of TiO$_2$ with metal elements (Ag, Pt, Cr, V, Se, Fe, etc.) and non-metal elements (B, C, S, F, N, etc.) is conducted for increasing the visible photocatalytic activity. Metal ion doping enhances the photocatalytic activity by reducing the recombination of electron–hole pairs and narrowing the charge distribution distance. Transition metal ions are the most commonly used dopants for reducing the band gap and increasing the activity of TiO$_2$. Metal ions are usually replaced by Ti$^{4+}$ ions in the crystal network and make TiO$_2$ visible light active by adding electrons to the valence band or by placing additional electronic levels in the band space. In addition, metal ions slow the association rate of the charge carriers on the surface and play a role in increasing the photocatalytic activity of TiO$_2$. Dopant ions act as traps for electrons and holes. Numerous studies have been conducted on the effect of metal ions and while some researchers suggest that metal ions increase the activity of TiO$_2$, others have reported that metal ions have negative effects on the photocatalytic activity of TiO$_2$ (Karakitsou et al., 1993, Kang, 2003, Zhou et al., 2005, Wellia et al., 2011).

Metal-doped photocatalysts have low thermal resistance and metal ions also may act as new coupling centers for charge carriers, which has led researchers to search for new dopant ions. Recent studies show that non-metals such as N, C, S, B and P are suitable doping ions (Ohno et al., 2004). Among them, nitrogen doping is the most widely preferred one of these studies (Asahi et al., 2001, Jagadale et al., 2008, Yalçın et al., 2010). This is due to the fact that the radius of nitrogen is very close to that of oxygen, is stable and has low ionization energy. Some researchers suggest that NO$_x$, NH$_x$ and N$^2$ groups on the TiO$_2$ surface produce visible light activity, while others suggest that the energy of the valence band increases with the nitrogen contribution and thus the band gap is narrowed (Sakthivel et al., 2004, Sato et al., 2005). Subsequent studies with anion dopants have shown that carbon doping also shifts the absorption of TiO$_2$ into the visible region (Sakthivel et al., 2003). The results obtained with carbon doping were interpreted differently from nitrogen. Carbon acts as both a cation by replacing with Ti$^{4+}$ in the crystal network and an anion by replacing with oxygen. However, the impurity levels in the non-metal doped TiO$_2$ act as charge recombination centers and reduce photocatalytic activity at high dopant concentrations.

Another doping approach is codoping the TiO$_2$ with two different ions (Sun et al., 2006, Yu et al., 2006, Gurkan et al., 2017). Codoping of TiO$_2$ has increased the photocatalytic activity as compared to single doping due to synergistic effects of two different non-metals (Li et al., 2005). Codoping with a metal and a non-metal is also found to increase the degradation of p-nitrophenol under both UV-A light and visible light (Gurkan et al., 2017).

3. Materials and Methods

In this work, we have prepared non-metal doped (C, N), metal doped (Cu, Fe, Se) and codoped (N/S) TiO$_2$ photocatalysts using the well-established wet impregnation method. Evonik P25 TiO$_2$ was used as the photocatalyst. TiO$_2$ was doped 0.50% wt using CH$_2$N$_2$O (urea), C$_6$H$_5$O$_6$ (glucose), Fe(NO$_3$)$_3$·9H$_2$O (iron (III) nitrate nonahydrate), Cu(NO$_3$)$_2$·3H$_2$O (copper (II) nitrate trihydrate), SeCl$_4$ (selenium tetrachloride) and CH$_3$N$_2$O and NH$_2$CSNH$_2$ (urea and thiourea, respectively) as N, C, Fe, Cu, Se and S/N sources, respectively. All doping sources were purchased from Merck. Congo Red and Rhodamine B was purchased from Sigma Aldrich. All chemicals were used as received without further purification. Deionized water was used for the preparation of the solutions.

3.1. Preparation of the Doped Photocatalysts

The impregnation method can be briefly described as follows: 10 g TiO$_2$ Evonik P25 was mixed with 15 mL of aqueous solutions of dopant and stirred for 1 h at room temperature. Dopant concentration was decided as 0.50% wt. for all photocatalysts as it was determined in our previous work (Birben et al., 2015, Birben Nazmiye et al., 2016, Birben et al., 2017, Gurkan et al., 2017, Turkten et al., 2019). The prepared photocatalysts were washed several times with di. water and then dried at 378 K for 24 h to eliminate water completely. Dried photocatalysts were then calcinated at a predetermined temperature for several hours. Afterwards, the obtained samples were ground and sieved for a more homogeneous size distribution. Calcination temperatures and times were previously determined and are given in Table 1.
Table 1.Calcination Times and Temperatures for the Preparation of Doped Photocatalysts.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Calcination Temperature and Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-doped</td>
<td>500°C, 3 h</td>
</tr>
<tr>
<td>C-doped</td>
<td>500°C, 3 h</td>
</tr>
<tr>
<td>Fe-doped</td>
<td>500°C, 5 h</td>
</tr>
<tr>
<td>Cu-doped</td>
<td>500°C, 5 h</td>
</tr>
<tr>
<td>Se-doped</td>
<td>350°C, 3 h</td>
</tr>
<tr>
<td>N/S -codoped</td>
<td>350°C, 3 h</td>
</tr>
</tbody>
</table>

The preparation steps of Fe-doped TiO$_2$ is given in Figure 1 as an example to the wet impregnation method.

![Figure 1. Wet Impregnation Steps for the Preparation of Fe-doped TiO$_2$ (DI.water: Deionized water)]

In addition to previous characterization results, Fourier Transform Infrared (FTIR) spectra of the prepared catalysts were taken using a Perkin Elmer Spectrum Two with Universal ATR accessory with diamond/ Zn-Se crystal. Spectra were obtained from 8 scans with a resolution of 2 cm$^{-1}$ in the range of 4000 - 500 cm$^{-1}$.

### 3.2. Decolorization of the Chosen Dyes

Azo-dye Congo Red (CR) and fluorone dye Rhodamine B (RB) were chosen as model dyes for the determination of the decolorization efficiencies of the newly prepared photocatalysts under solar irradiation. The chemical structures of the dyes are given in Figure 2.

![Figure 2. Congo Red, MW= 670 g/mole, $\lambda_{max}$= 498 nm (left) and Rhodamine B, MW= 479 g/mole, $\lambda_{max}$= 552 nm (right)]

Photocatalytic decolorization of the dyes were performed in an ATLAS Suntest CPS+ simulator as solar photocatalytic reactor, equipped with an air cooled Xenon lamp (250 W m$^{-2}$ and wavelength range of 300-800 nm) as the light source. 50 mL of 20 mg L$^{-1}$ dye solution was put in a 150 mL cylindrical Pyrex reaction vessel and subjected to solar photocatalytic oxidation process in the presence of 0.25 mg mL$^{-1}$ photocatalyst. An ultrasonic water bath was used for the preparation of a homogenous suspension. Continuous stirring was applied during the experiments. After the experiments, samples were filtered through 0.45 $\mu$m Millipore filters in order to remove TiO$_2$ specimens from the solution prior to analyses via UV-Vis spectrometer. $\lambda_{max}$ values were 498 nm for CR and 552 nm for RB.

### 4. Results and Discussion

#### 4.1. Characterization of the Prepared Photocatalysts

In order to effectively characterize the doped photocatalysts, a variety of methods were used. BET surface area of doped TiO$_2$ samples were found to change in the range of 45-55 m$^2$g$^{-1}$ and band gap energies were in the range of 2.55-2.90. The decrease in the band gap energies compared to 3.2 eV band gap energy of bare TiO$_2$ confirmed that the doping procedure shifted the band gap towards visible region (Gurkan et al., 2013, Birben et al., 2015, Birben Nazmiye et al., 2016, Birben et al., 2017, Gurkan et al., 2017, Turkten et al., 2019).

The FTIR spectra of doped TiO$_2$ photocatalysts are given in Figure 3. The main characteristic bands that are observed in similar wavenumbers include the broad band at 3300 cm$^{-1}$, which corresponds to the stretching
vibration of the hydroxyl group O-H of the TiO$_2$, the band at 1630 cm$^{-1}$ which is caused by the bending vibration of adsorbed water Ti-OH, and the bands between 800-600 cm$^{-1}$ corresponding to Ti-O-Ti bending (Yalçın et al., 2010). Any peaks corresponding to dopant phases were not detected. This was attributed to the low doping percentage. All spectra of doped samples were found to exhibit almost identical peak characteristics and intensity trend.

Figure 3. FTIR Spectra of the Prepared Photocatalysts

4.2. Photocatalytic Efficiencies

Photocatalyst performances were evaluated from the removal percentage values of CR and RB. Removal percentages were determined from Equation (1), where $C_0$ is the initial concentration of the dye and $C$ is the dye concentration at time $t$.

$$\text{Removal} \ % = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

Prior to solar irradiation, removal of dyes by adsorption onto the photocatalyst surface were investigated. In the following data, 0 min represents the adsorption values of dyes onto the photocatalysts without applying any solar light.

When the removal % values given in Figure 4 are taken into account, it can be said that adsorption of CR on the photocatalyst surface (without the application of solar light) is significantly higher than RB. This behavior can be explained by the higher affinity of two negative oxygen moieties (SO$_3^-$) on CR towards Ti atoms on the catalyst surface, making it prone to forming complexes. This causes approximately 12 – 20% of CR to be removed by adsorption depending on the catalyst. However, in the case of RB, it can be said that since only less than 1% dye is adsorbed on catalyst surface, RB removal can directly be attributed to photocatalytic decolorization rather than adsorption.

Photocatalytic decolorization results of the dye solutions after treatment with solar light for 60 minutes are given in Figure 5.
Figure 5 shows that overall, CR removal was more efficient than RB removal reaching as high as 85% for all investigated photocatalysts. This finding could implicate a better removal efficiency for azo dyes compared to fluorone dyes under solar light using doped photocatalysts.

When the photocatalysts were compared with respect to each dopant, both CR and RB had higher removal % for non-metal doped photocatalysts, namely C doped and N doped. For both dyes, co-doping was found to increase the removal efficiencies compared to metal doped photocatalysts. Overall, best decolorization performances were obtained with C-doped and N-doped photocatalysts for both CR and RB. This finding is in agreement with literature where carbon doped TiO\(_2\) was found to have superior photocatalytic activity than unmodified TiO\(_2\) for the solar light degradation of some phenol derivatives and azo dye remazol red (Sakthivel et al., 2003). Nitrogen doped visible light active photocatalysts were also investigated and found to be visible light active for the degradation of varying model pollutants such as phenols, dyes, and volatile organic compounds (Pelaez et al., 2012).

While C and N-doped photocatalysts have similar removal efficiencies between 83-85%, Se which is also a non-metal causes a somewhat lower removal percentage of 77%. This can be explained by the fact that Se is also considered as a metalloid with properties that are similar to sulfur, arsenic and tellurium. It was argued by Gurkan et al. that Se doping produces additional electronic states and contributes to a higher visible light activity (Gurkan et al., 2013).

Although codoping with N and S provides a higher decolorization of the studied dyes compared to metal doped photocatalysts, the visible light activity of NS-doped catalyst was lower than non-metal doped ones. It was previously shown that while codoping is believed to be superior to single non-metal doping, codoping at two anionic sites could distort the crystal structure and promote the recombination rate of the charge carriers (Sun et al., 2013).

Metal doped photocatalysts were less efficient in terms of dye decolorization with 49-54% for CR and 13-33% for RB using Fe-doped and Cu-doped photocatalysts, respectively. It is known that incorporating transition metals into the TiO\(_2\) crystal lattice could cause the formation of new energy levels between valence and conductance bands decreasing the band gap energy. Nonetheless, there are also explanations as to why photocatalytic activity or the visible light activity is not enhanced with metal ion doping as expected. This low visible light activity despite the decrease in band gap energy could be explained by the low incorporation of the metals into the TiO\(_2\) lattice and the blocking of the surface by excess metal ions (Kang, 2005). Other possible drawbacks include photocorrosion and the promotion of charge recombination at metal sites (Pelaez et al., 2012).

Detailed decolorization values for both dyes at 0 min and 60 min are presented in Figure 6 for comparison. It can be said by removal % values of 0 min and 60 min, RB is only removed from the aqueous solution by photocatalysis with the prepared doped catalysts under solar light. CR on the other hand, clearly adsorbs onto the catalyst surface as high as 20%, indicated by the 0 min results. In order to clarify the means of removal from the solution and decolorization; 0 min, 60 min removal % results and the difference between them is given in Table 2.
In Table 2, differences between 0 and 60 min results yield the normalized value of removal which solely originates from heterogeneous photocatalytic degradation of the dyes. These results indicate that C-doped TiO$_2$ and N-doped TiO$_2$ show the highest visible light activity for CR and RB, respectively. The lowest visible light active photocatalyst was determined to be Fe-doped catalyst for the removal of both dyes, with removal values of 39.4 % and 13.3 % for CR and RB.

5. Conclusion

In this work we have shown that Evonik P25 TiO$_2$ can successfully be doped with metals and non-metals using wet impregnation method. We have conducted a comparative investigation on the decolorization performance of the doped photocatalysts and shown that the newly prepared catalysts can indeed perform decolorization of the chosen dyes under simulated solar light. When adsorption onto the doped TiO$_2$ surfaces were taken into account, CR was found to be more prone to adsorbing to the surface of TiO$_2$ than RB. This was attributed to the affinity of negative moieties on CR towards Ti atoms. Both CR and RB had higher removal % for non-metal doped photocatalysts. For both dyes, co-doping increased the removal efficiencies compared to metal doped photocatalysts. Overall, best decolorization performances were obtained with C-doped and N-doped photocatalysts for CR and RB, respectively. Future work includes evaluating the photocatalysis kinetics in order to shed light on the reaction mechanism.

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Conflict of Interest

No conflict of interest was declared by the authors.

References


