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# Preparation of Photocatalytic Materials for Water Clarification via Organic Waste

İlker ERDEM*, M. Furkan BALTACIOĞLU, M. Furkan BİLGİ

Abdullah Gül University (AGU), Faculty of Engineering, 38100, Kayseri, Türkiye

**Abstract**: Photocatalytic oxidation is a preferable method for clarification of fresh water polluted by colourful pollutants, pesticide-like hard-to-treat organic pollutants, and microbiological metabolites. Titanium dioxide ($TiO_2$), having superior physicochemical properties, is one of the most common catalyst in heterogeneous photocatalysis. Free electron formed by the absorption of light by titanium dioxide triggers formation of free radicals and results in oxidation of polluting compounds. Titanium dioxide is photocatalytically more active under the relatively shorter (100 nm < λ < 400 nm) UV wavelength region. This forces the usage of UV lamps for supplying UV light, which is only present at low ratios in the sunlight (8%). Doping with various elements, preparing of its composites with different oxides, usage of dyes absorbing sunlight were investigated for enhancing the photocatalytic activity of titanium dioxide and using the sunlight as energy source and some enhancements were reported. Using titanium dioxide in nano-size was also reported to be enhancing its photocatalytic activity. In this work, while organic wastes rich in carbon were milled to increase their surface area, nano-sized titanium dioxide was synthesised via sol-gel method. Using these two materials C element and titanium dioxide in couple possible enhancement of the photocatalytic activity of the synthesised material was investigated. Walnut shells were used as organic waste.

**Keywords:** Photocatalysis; titania; sol-gel; organic waste.

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*Corresponding author. E-mail: ilker.erdem@agu.edu.tr

## INTRODUCTION

The amount and variety of the wastewaters is increasing with the increase in the number and quantity of chemically synthesised products. This results in the insufficiency of conventional applications for water treatment. Therefore, research on improving present conventional methods, introducing new and effective water treatment methods and usage of them integrated to conventional ones has been carried out. (1)

Photocatalytic oxidation is one of the methods preferred for clarification of fresh water contaminated by colourful pollutants, hard-to-clean pesticide-like persistent organic pollutants (POPs), and microbiological metabolites (1–4). Hydroxyl radicals occurring during photocatalytic oxidation are strong oxidising agents, which may react with plenty of organic and inorganic water-soluble pollutants at high reaction rates (1,3).

Titanium dioxide (titania, $TiO_2$) is a widely used catalyst in heterogeneous catalysis due to its superior physicochemical properties (4–6). The free electron formed by absorption of light energy by titanium dioxide triggering the formation of free radicals results in oxidation of pollutants in the environment (1). It has the potential to oxidise many of the organic pollutants to relatively non-hazardous pollutants; $CO_2$ and $H_2O$ (3). Titania may be present in different crystallographic phases. Most abundant ones of these phases are anatase, rutile and brookite (2,6). Results about highest photocatalytic activities for different reactions have been reported for pure anatase phase or pure rutile phase or mixture of anatase and rutile phase (as in the commercial titania; Degussa P-25) (1,5). Titanium dioxide mainly shows its photocatalytic activity at the presence of low wavelength ultraviolet (UV) light (100 nm < λ < 400 nm). This enforces the usage of special light sources for supplying UV which is only present in a small ratio in the daylight (8%). Research has been performed on doping of different elements in titania, preparation of its composites with different oxides and utilisation of daylight absorbing dye materials as additives for the use of daylight as light source and increasing the photocatalytic efficiency of titania and some enhancements have been reported (2,4,5). The photocatalytic property of titania was reported to be increased when titania is used in nano-size (6). In this work, organic residues were ground to increase their surface area and nano-sized titania was prepared via sol-gel method. The possible enhancement of photocatalytic activity of the composite material was investigated which was synthesised by combining carbon-rich organic residue and synthesised nano-titania. Clarification (decolourisation) experiments of a resistant dying material; methylene blue, of which resistance to exogenous factors is high (7), were performed for this purpose.

## MATERIALS AND METHODS

Sol (Ti-Sol) which was prepared via sol-gel method as described in previous work (8,9) was used as the titania source for synthesising the novel material in this work. Titanium(IV) isopropoxide (97%, Sigma-Aldrich), nitric acid (67%, Merck), isopropyl alcohol (99.8%>, Merck, Emsure) and deionised water were used in preparation of Ti-Sol. The particle size distribution of the sol was determined via a laser light scattering instrument (NanoZS, Malvern).

Shells of walnuts purchased from a local market were used as organic waste. Walnut shells were mechanically crushed first, following grinding via ball-milling (Retsch MM400) and finally sieved through 400-micron sieve. The grounded particles passed through the sieve were used for the experiments.

The Ti-sol and ground walnut shell were heat treated at appropriate temperature (400-500 °C) under modified atmosphere (with nitrogen gas introduction). The ground walnut shell was used with two aims. First, it would be a support for the photocatalyst (titania) and second the carbon-rich material was expected to increase the activity of photocatalyst.

Photocatalytic experiments were performed in the biosafety cabinet (Faster) equipped with both visible (vis) and ultraviolet (UV) light sources. Methylene blue (MB) (Sigma) solutions (500 ppm) were used as substrates for these reactions. Photocatalytic materials were added to one of the MB solution (2 g/L) and not added to the other solution (0 g/L), which was used as blank sample for that experiment. Commercial nano-sized titania (Aldrich-718467, 21 nm (TEM)) was used for comparing the photocatalytic activity of the novel material (C-$TiO_2$) prepared via ground walnut shell and nano-titania prepared via sol-gel method. The substrate (MB) solutions both photocatalytic material added and not were magnetically stirred under different light sources (UV or vis) and the change in absorbance values ($\lambda$ = 664 nm) in time were determined via a spectrophotometer (Shimadzu UV-1800). The absorbance readings were continued for samples kept at dark overnight (AN) in the following day. The intensities of the light sources used were determined as 1 and 4 $W/m^2$ for UV and visible (vis) light sources, respectively (Apogee Solar Radiation, MP-200).

## RESULTS AND DISCUSSION

The average particle size (Stoke's diameter) of the Ti-sol was determined as 23 nm via laser light scattering, which would assist formation of a fine microstructure after heat treatment. Most of the

particles in the sol were around 3 nm with some agglomerated impurities, which increased the average particle size.

The results for photocatalytic experiments performed via commercial nano-sized titania under visible light (vis) are shown in Figures 1 & 2. There is no considerable difference between the decolourisation (clarification) ratios for samples with and without photocatalyst addition.

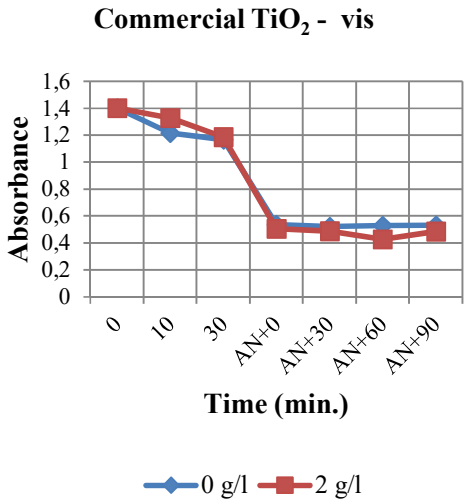


**Figure 1**: The change of absorbance in time for sample with and without commercial nano-sized titanium dioxide (Aldrich, 21 nm) exposed to visible light (vis).

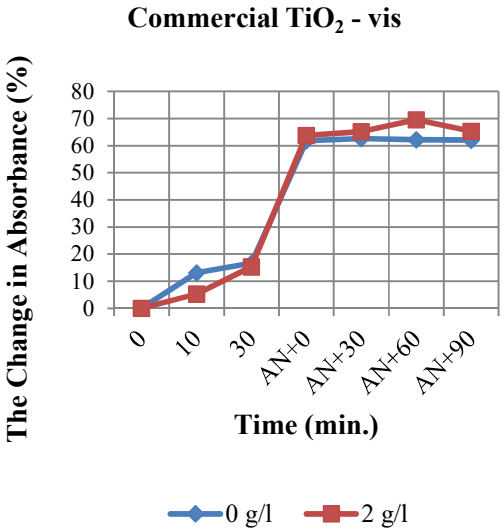


**Figure 2**: The change of absorbance (%) in time for sample with and without commercial nano-sized titanium dioxide (Aldrich, 21 nm) exposed to visible light (vis).

The results for photocatalytic experiments performed via commercial nano-sized titania under UV are shown in Figures 3 & 4. A decolourisation rate of 69% was observed for the sample with

commercial photocatalyst. It was only 33% for the sample without the commercial photocatalyst.

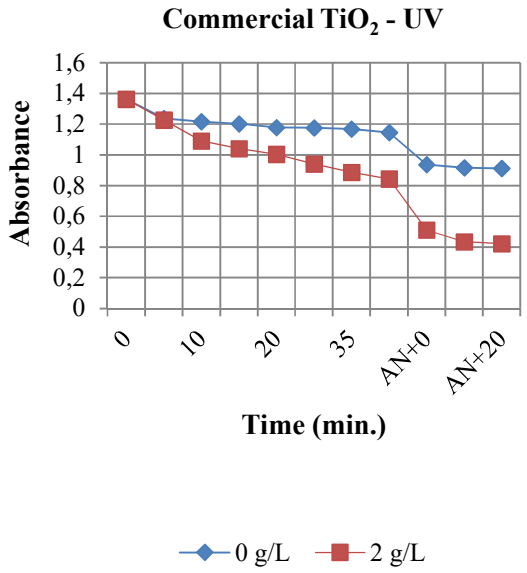


**Figure 3**: The change of absorbance in time for sample with and without commercial nano-sized titanium dioxide (Aldrich, 21 nm) exposed to ultraviolet light (UV).

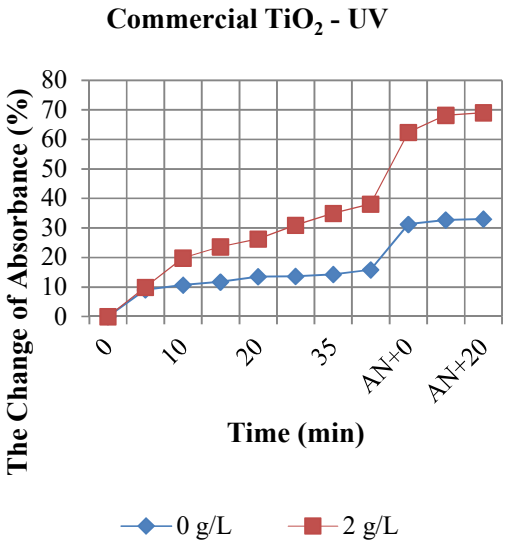


**Figure 4**: The change of absorbance (%) in time for sample with and without commercial nano-sized titanium dioxide (Aldrich, 21 nm) exposed to ultraviolet light (UV).

The results for photocatalytic experiments performed via synthesised material (C-$TiO_2$) under UV are shown in Figure 5 & 6. A decolourisation rate of 84% was observed for the sample with synthesised photocatalyst. It was 22% for the sample without it.

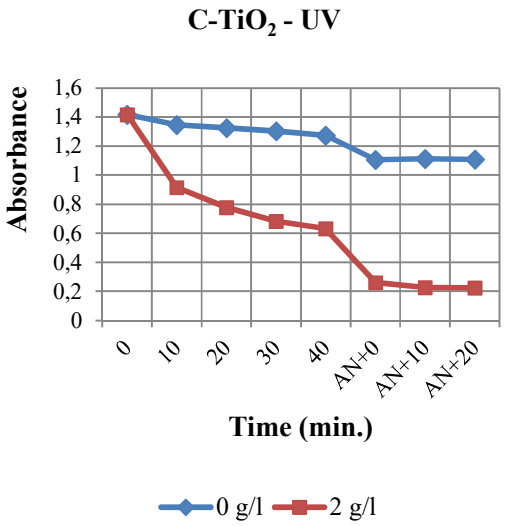


**Figure 5**: The change of absorbance in time for sample with and without synthesised material (C-$TiO_2$) exposed to ultraviolet light (UV).

The results for photocatalytic experiments performed via synthesised material (C-$TiO_2$) under visible light (vis) are shown in Figure 7 & 8. A decolourisation rate of 58% was observed for the sample with synthesised photocatalyst. The decolourisation was only 20% for the sample without it.

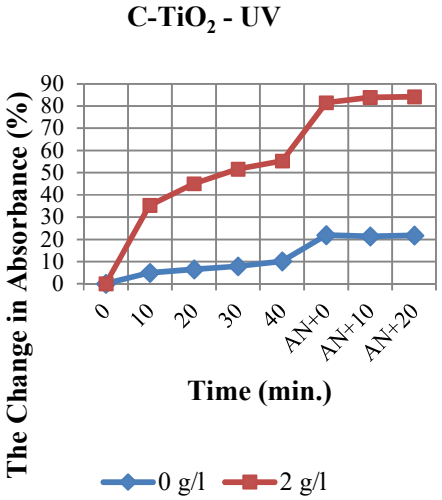


**Figure 6**: The change of absorbance (%) in time for sample with and without synthesised material (C-$TiO_2$) exposed to ultraviolet light (UV).

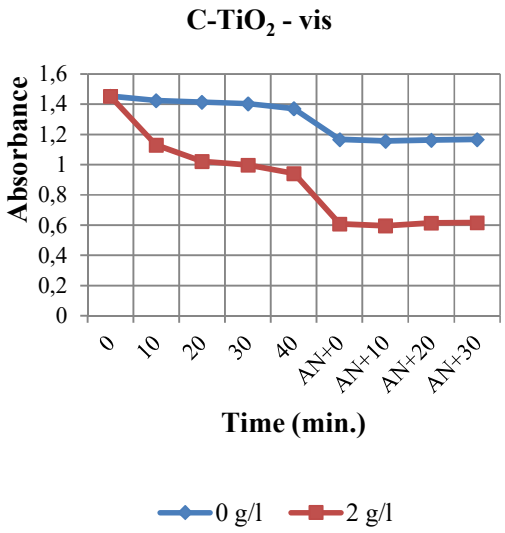


**Figure 7**: The change of absorbance in time for sample with and without synthesised material (C-$TiO_2$) exposed to visible light (vis).

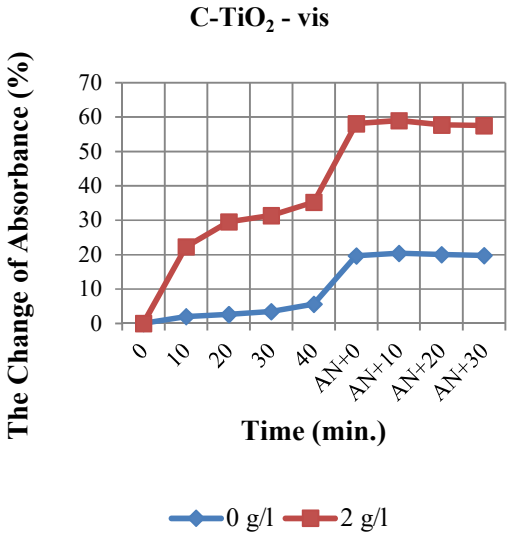


**Figure 8**: The change of absorbance (%) in time for sample with and without synthesised material (C-$TiO_2$) exposed to visible light (vis).

It was observed that the photocatalytic activities of materials were different from each other under different light sources (UV/Vis) and decolourisation occurs mainly under UV exposure. The synthesised material (C-$TiO_2$) was more efficient in decolourisation compared to the commercial nano-sized titania. The decolourisation rates for the samples with and without commercial titania were almost similar when exposed to visible light. There was an enhancement when UV was the light source, where the decolourisation for the sample with the commercial photocatalyst was 33% better than the sample without commercial photocatalyst. The decolourisation rates for the

synthesised material (C-$TiO_2$) were relatively higher at both experiments with different light sources (UV/vis). The decolourisation of the sample with synthesised material (C-$TiO_2$) exposed to visible light was 38% better than the sample without photocatalyst. The best enhancement for decolourisation rate was observed for the sample with synthesised photocatalytical material addition under UV exposure, which was 62% higher than the sample without photocatalyst addition. The initial rates of decolourisation observed for the synthesised material (C-$TiO_2$) also shows a relatively higher rate of decolourisation than the commercial photocatalyst.

The decrease in absorbance continued for the samples left in the dark overnight (AN). One of the most probable reasons of this incidence is considered to be adsorption of the dye on the surface of the photocatalyst. Therefore, more research activities should be performed for determining the ratios of two main possible decolourisation mechanisms on the process: photocatalysis and surface adsorption. The effect of parameters like the synthesis conditions and concentration of the synthesised photocatalytic material will be the subject of the following works.

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**Türkçe Öz ve Anahtar Kelimeler**

# Organik Atıklar Kullanılarak Su Temizleme için Fotokatalitik Malzemelerin Hazırlanması

İlker ERDEM, M. Furkan BALTACIOĞLU, M. Furkan BİLGİ

**Öz**: Fotokatalitik yükseltgeme, renkli kirliliklerle, pestisit benzeri ve muamelesi zor organik kirliliklerle ve mikrobiyolojik metabolitlerle kirlenmiş içme suyunun temizlenmesi için tercih edilen bir yöntemdir. Titanyum dioksit ($TiO_2$) üstün fizikokimyasal özellikleriyle heterojen fotokatalizde en yaygın kullanılan katalizördür. Titanyum dioksit tarafından ışığın soğurulması ile oluşan serbest elektron serbest radikallerin oluşmasını tetikler ve kirlilik verici bileşiklerin yükseltgenmesi ile sonuçlanır. Titanyum dioksit fotokatalitik olarak, nispeten kısa (100 nm < λ < 400 nm) UV dalgaboyuna sahip olan ışıkla daha aktiftir. Bu da UV ışığını sağlamak amacıyla UV lambalarının kullanılmasını zorunlu kılar, bu lambaların sağladığı ışık güneş ışığının küçük bir kısmını (%8) oluşturur. Çeşitli elementlerle aşılama, farklı oksitlerle kompozit hazırlama, güneş ışığını soğuran boyar maddeleri kullanma yöntemleri titanyum dioksidin fotokatalitik aktivitesinin artırılmasında incelenmiş ve güneş ışığı enerji kaynağı olarak kullanılmış ve varılan bazı ilerlemeler bildirilmiştir. Nano boyutta titanyum dioksidin kullanılması fotokatalitik aktivitesini artırmak için denenmiş ve bildirilmiştir. Bu çalışmada, yüzey alanını artırmak için karbonca zengin organik atıklar değirmende öğütülmüş ve sol-jel yöntemiyle nano boyutta titanyum dioksit sentez edilmiştir. Karbon elementi ve titanyum dioksit kullanılarak sentez edilmiş malzemenin fotokatalitik aktivitesindeki olası artış incelenmiştir. Ceviz kabukları organik atık olarak kullanılmıştır.

**Anahtar kelimeler:** Fotokataliz; titanya; sol-jel; organik atık madde.

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