# NANOMATERIALS BASED ON $TiO_2$ FOR EFFLUENT POLLUTANT PHOTODEGRADATION

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One of the most recent nanomaterials that has attracted great attention due to its unique properties is titanium dioxide. $TiO_2$ powders possess interesting optical, dielectrical and catalytical properties, which results in industrial applications such as pigments, fillers, catalyst supports and photocatalysts. Photocatalysis over titanium dioxide has been heavily investigated as a promising means of treating a wide variety of emerging pollutants and recent research effort has been devoted to improving the photocatalytic efficiency of $TiO_2$ through a variety of materials engineering approaches, such as enhancing the visible-light activity of $TiO_2$ through doping. Tannery wastewater represents a serious environmental and technological problem, owing to the large amounts of poorly biodegradable organic chemicals used. The use of photocatalytic $TiO_2$ nanoparticles to decontaminate industrial tannery wastewater has not been yet investigated. That is why, this paper aims to investigate the synthesis and characterization of $TiO_2$ and N doped $TiO_2$ nanoparticles used for the photodegradation of effluent pollutants from the leather industry. The new nanoparticles were synthesized through chemical routes and were characterized by dynamic light scattering and diffuse reflectance spectra measurements. Their photocatalytic activity was tested against an organic pollutant model, Orange II (OII).

Keywords: nanomaterials, $TiO_2$, photodegradation

## INTRODUCTION

Recently, water shortages are becoming an increasing problem due to scientific advances following rapid industrial growth, environmental pollution, depleted water resources, global warming causing abnormal climate changes and uncontrolled groundwater evolution (Fujishima *et al*., 2009).

The rapid development of manufacturing technology after the industrial revolution has significantly improved the standards of living, but it is becoming a threatening factor for human health and the environment. Pollutants are changing both quantitatively and qualitatively and the number of chemicals currently in circulation is 38,000, with more than 300 new materials being synthesized every year due to the diversification of industrial structures and high-tech industry (Schneider *et al*., 2014).

In line with national development, growth and policy, industrial wastewater is becoming more contaminated and difficult to process.

Organic compounds, toxic pesticides and manure emission from each industry are polluting drinking water and rivers, which is becoming a worldwide contamination with increased severity.

The wide area of water pollution, diversification and non-biodegradable compounds has become a problem that cannot be solved by the natural cleansing cycle (Malato *et al*., 2009; Chong *et al*., 2010).

Moreover, in the case of water treatment technology, which includes non-biodegradable organic compounds, it is very difficult to completely remove pollutants with existing treatment technology.

Tannery waste water represents a serious environmental and technological problem, owing to the large amounts of poorly biodegradable organic chemicals used. Nowadays, most tanneries have a wastewater treatment process that usually consists of three stages:

flow homogenisation, dosing coagulants and flocculants; primary decanting to remove suspended solids as well as most of the Chemical Oxygen Demand (COD); biological treatment with subsequent secondary decanting to remove most of the pollutant content (COD and Biological Oxygen Demand ($BOD_5$)). However, a tertiary treatment is often still required to refine the COD and remove the colour and/or some organic recalcitrant compounds. As a result, other methods are being increasingly explored as alternatives to classical physico-chemical and biological processes.

The search for the development of new and inexpensive methods for the treatment of industrial wastewater is always on progress.

Different methods of separation, degradation and elimination have been used on different polluting chemical agents which are generally present in wastewater coming out from the industrial sector. The treatment of such pollutants can be achieved using an advanced oxidation process (AOP), like the heterogeneous photocatalysis due to its efficiency and low cost, as well as to the fact that it allows the complete degradation of organic pollutants to $CO_2$ and inorganic acids.

Recently, the application of $TiO_2$ photocatalysts has mainly been focused on the decomposing toxic and hazardous organic pollutants in contaminated air and water, which is of great importance for the environmental protection (Shon *et al*., 2013; Sharma and Sharma, 2012; Cloete *et al*., 2012).

However, the use of photocatalytic $TiO_2$ coatings to decontaminate industrial tannery wastewater has not been investigated yet.

Titanium dioxide ($TiO_2$) is the most widely used semiconductor photocatalyst due to its stability, non-toxicity and relatively low cost (Savage and Diallo, 2013).

However, color removal from wastewater is the most complex and difficult task.

Dyes are usually the first contaminant to be recognized in industrial wastewater due to their high visibility even in minute concentrations (<1 ppm). These colored wastewaters are a considerable source of eutrophication as well as non-aesthetic pollution that can produce dangerous byproducts by further oxidation, hydrolysis, or other chemical reactions taking place in the wastewater phase. Beyond the toxic effects of dyes in wastewater streams, the presence of dyes can cause reduced light penetration resulting in reduced photosynthetic activity thus making oxygen unavailable for biodegradation of microorganisms in the water.

Textile industry, leather tanning industry, paper industry, food industry, hair colorings, photoelectrochemical cells and light-harvesting arrays also contribute to the presence of dyes in wastewater. Majority of dyes used in various industries are toxic and carcinogenic thus posing a serious hazard to humans as well as to marine ecosystem. Therefore, the impact of dyes released into the environment has been extensively studied in the last few years (Herrmann, 2011).

Among major dye categories, azo dyes are the largest group of colorants and over 50% of all the dyes used in industries are azoic dyes.

Apart from their physically unpleasant nature and toxicity, the ever increasing massive production rate of dyes due to increasing industrialization has led to the necessity of an effective treatment. Therefore, in order to treat such obvious and challenging effluents, a wide range of technologies have been tested to reduce their potential magnified impacts on the environment (Ohno *et al*., 2012).

Traditional physical techniques such as activated carbon, adsorption, reverse osmosis, ultrafiltration can be used for dye removal. However, these processes simply transfer the pollutants from one medium to another causing secondary pollution. This generally requires further treatment of solid-wastes and regeneration of the adsorbent, which adds more cost to the process. Chemical processes such as chlorination, ozonation, adsorption on organic or inorganic matrices, precipitation, chemical oxidation processes, advanced oxidation processes and photodegradation through photocatalysis are also commonly being used for synthetic dye removal.

However, toxic unstable metabolites as a result of most of these processes impart adverse effects on animal and human health.

Biological processes involving microbiological or enzymatic decomposition and biodegradation have also been used for dye removal from wastewaters. However, it has been found that these conventional biological treatment processes are ineffective for synthetic dyes having recalcitrant nature.

In recent years, a broad range of synthetic dyes have been extensively studied to develop a more promising technology based on AOP that has the ability to oxidize contaminants quickly and non-selectively. AOP rely on in situ production of highly reactive hydroxyl radicals ($OH^{\cdot}$) which can virtually oxidize any compound present in the water matrix, often at a diffusion controlled reaction speed. These radicals are produced with the help of one or more primary oxidants (e.g. ozone, hydrogen peroxide, oxygen) and/or energy sources (e.g. ultraviolet light) or catalysts (e.g. titanium dioxide).

Heterogeneous photocatalysis has proved to be as an efficient tool for degrading both atmospheric and aquatic organic contaminants. It uses the sunlight in the presence of a semiconductor photocatalyst to accelerate the remediation of environmental contaminants and destruction of highly toxic molecules. The type of the radiation used depends on the type of catalyst i.e. pure $TiO_2$ works under UV light (370–415 nm).

In order to assess the degree of dye photodegradation achieved during the treatment, general formation of $CO_2$ and inorganic ions is determined. However, it is impossible to measure the exact concentration of these ions in case of real wastewaters. In such cases the determination of total organic carbon (TOC) or the measurement of the chemical oxygen demand (COD) or the biological oxygen demand (BOD) is used to monitor extent of dye mineralization.

Among various types of photocatalysts, $TiO_2$ assisted photocatalytic oxidation has received much attention in the last few years due to its non-toxicity, strong oxidizing power and long-term photostability (Akpan and Hameed, 2010). $TiO_2$ is a white powder semiconductor having a wide band gap of 3.0–3.2 eV. In general, there are three types of titanium dioxide i.e. anatase, rutile and brookite. Most of the studies have been carried out with anatase phase due to its high photocatalytic efficiency and adsorption affinity for the organic compounds as compared to the rutile phase.

There are various research studies on photocatalytic degradation of dyes using $TiO_2$ in several modified forms for performance enhancement under visible light. These include adsorption and surface complexation on $TiO_2$, non-metal doping, lanthanide ion doping, transition metal doping, noble metal doping and multi-atom doping. The main purpose of doping is to decrease the band gap of pure $TiO_2$ (3.2 eV for anatase phase) to bring the absorption band from UV to visible region.

There are various reports available on non-metal doping of $TiO_2$, especially with boron, carbon, sulfur, nitrogen and fluorine.

The main objective of non-metal doping is to bring the absorption band of $TiO_2$ to visible region.

The nitrogen-doped $TiO_2$ photocatalysts have been tested for the decomposition of aqueous solutions of organic compounds and dyes under UV and visible light illumination (Sun *et al.*, 2014).

Parida and Naik (2012) reported the degradation of methylene blue and methyl orange using N-doped $TiO_2$ showing 67% and 59% of degradation after 4 hours irradiation under visible light source.

Selvaraj *et al*. (2013) measured the photocatalytic degradation of the reactive triazine dyes including reactive yellow 84, reactive red 120 and reactive blue 160 on N-doped $TiO_2$ anatase and P25 in the presence of natural sunlight. It was reported that reactive yellow 84 indicated a faster degradation on N-doped $TiO_2$ in sunlight than the commercial Aeroxide P25.

## EXPERIMENTAL

In this study, simple ($TiO_2$NPs) and N doped $TiO_2$ nanoparticles (N-$TiO_2$NPs) were synthesized via chemical routes. In order to prepare simple $TiO_2$ nanoparticles, titanium butoxide $Ti(OC_4H_9)_4$ (97% Sigma Aldrich) was used as starting material. N doped $TiO_2$ nanoparticles were obtained through the calcination of a mixture formed from $TiO_2$ nanoparticles and urea. The obtained nanoparticles are presented in Figure 1.

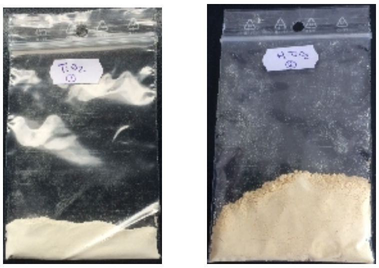

Figure 1. $TiO_2$NPs (left) and N-$TiO_2$NPs (right)

## RESULTS AND DISCUSSION

The new obtained nanoparticles were characterized by dynamic light scattering technique using Zetasizer Nano ZS, Malvern. The results are presented below.

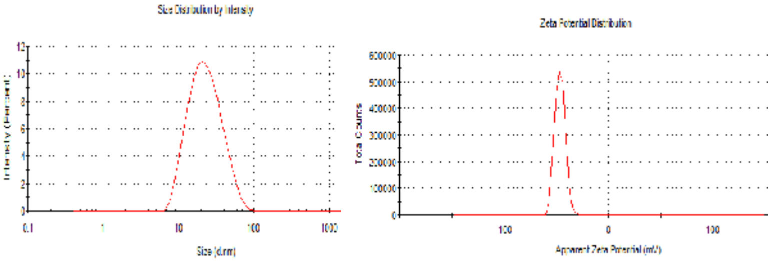


Figure 2. Size distribution (left) and Zeta potential (right) for $TiO_2$NPs

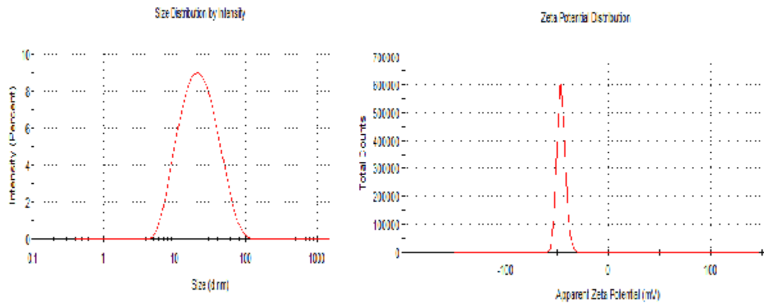

Figure 3. Size distribution (left) and Zeta potential (right) for N-$TiO_2$NPs

$TiO_2$ nanoparticles have sizes of about 25 nm, the N-doped around 30 nm and Zeta potential is -45 mV for the simple and -47 mV for the doped ones, suggesting high stability of samples.

In order to have more information about the reactions of the photocatalyst materials with photon energies, UV-Vis diffuse reflectance spectra were recorded.

In Figure 4 are presented diffuse reflectance spectra of N-$TiO_2$NPs comparative with undoped $TiO_2$.

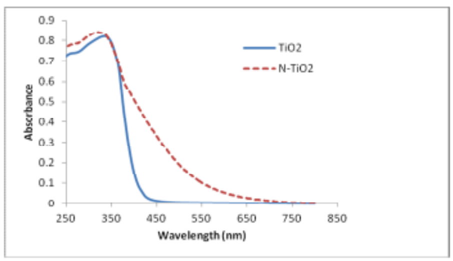


Figure 4. UV-Vis diffuse reflectance spectra for simple and N doped $TiO_2$ nanopowders

Figure 4 shows a significant absorption shift in the visible domain for N-$TiO_2$ powder.

To evidence photocatalytic degradation for a 20 ppm OII solution, in the presence of 0.1 g/L $TiO_2$ and N doped $TiO_2$ nanoparticles, absorbance spectra under visible light irradiation (150 W halogen lamp) were recorded (Table 1).

Table 1. UV-Vis absorbance of OII solutions with $TiO_2$ based nanoparticles after 1 hour of irradiation

| Nanoparticles | Absorbance |
|---|---|
| $TiO_2$ | 0.28 |
| N-$TiO_2$ | 0.05 |

Knowing that the initial value for the absorbance of OII was around 1, one can observe that the best value was obtained for N doped $TiO_2$ nanoparticles.

N-$TiO_2$NPs exhibited a significant increase in OII discoloring efficiency as compared with $TiO_2$ ones.

## CONCLUSIONS

New doped nanoparticles with improved photocatalytic properties for effluent pollutant photodegradation were developed. $TiO_2$ dispersions characterized by dynamic light scattering technique indicate that these are very stable and well dispersed. The shifted photocatalytic activity in visible domain, depending on the type of doping element, was evidenced by diffuse reflectance spectra.

Owing to its many advantages mainly involving most stable and active naturally occurring photocatalyst, $TiO_2$ is, so far, seen as the best catalytic material for degradation of various contaminants and sustainable environmental remediation technology.

Photodegradation of industrial dyes using improved $TiO_2$ has presented a somewhat promising and effective treatment technology.

The results demonstrate the potential use of new synthesized photocatalytic $TiO_2$ nanoparticles in tannery waste water treatment.

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