

An-Najah National University

Faculty of Graduate Studies

PHOTOCATALYTIC DEGRADATION OF ORGANIC CONTAMINANTS BY CLAY- SUPPORTED NITROGEN-DOPED TIO₂ NANOPARTICLES

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Dedication

To my dear family, who supported and encouraged me all the time. To them, I send all my appreciation and respect.

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Praise to Allah who guided my steps in all my work till the very end.

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Declaration

I, the undersigned, declare that I submitted the thesis entitled:

PHOTOCATALYTIC DEGRADATION OF ORGANIC CONTAMINANTS BY CLAY- SUPPORTED NITROGEN-DOPED TIO₂ NANOPARTICLES

I declare that the work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

Student's Name:	
Signature:	
Date:	

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PHOTOCATALYTIC DEGRADATION OF ORGANIC CONTAMINANTS BY CLAY- SUPPORTED NITROGEN-DOPED TIO₂ NANOPARTICLES

By Mohammed J. M. Kharouf Supervisor Prof. Hikmat Hilal Dr. Ahed Zyoud

ABSTRACT

Responding to the strong demands on new optimum photocatalyst, to decompose organic pollutants from the contaminated waste water. Titania is very effective as a photocatalyst. To achieve maximum absorption of sun light, doping was used to lowering the band gap energy. supporting on the clay successfully enhance the catalytic properties in addition to minimizing the effort of catalyst recovery.

The photocatalytic activity of variety of catalysts has been studied utilizing with varying synthesis circumstances (annealing temperature, cover gas, etc.) and compositions (rutile, anatase) supported and unsupported on the clay surface. Two doping methods were made for comparison.

The X-ray diffraction methods and scanning electron microscope and another elemental analysis were used to identify the catalyst states. There are no inter-layer intercalation titanium dioxide inside the clay, according to solid state studies. Another thing to note is that when the annealing temperature rises, the anatase begins to change to rutile form.

Solid catalysts were used in order to photo-depredate the phenazopyridine contaminated water. Rutile and anatase titanium dioxide (naked and clay supported) types were invested as photocatalysts.

Nitrogen doping using urea as a source of nitrogen effectively lowers the band gap energy, which inhibits the photocatalytic activity. On rutile, doping increases the catalytic properties and has no observed effect on band gap energy.

The TiO_2 (Rutile)/Clay supported catalyst outperforms the other catalysts and was successful in phenazopyridine photodegradation under simulated solar light. In addition, the ideal conditions were stated (pH, Temperature, quantities effect).

Studying catalyst recovery where made for $TiO_2(Rutile)/Clay$ after four times, the efficiency of the recovered solid catalyst has not any noticeable loss. The full degradation was confirmed using TOC and HPLC which can be achieved under simulated sun light after 3 hours under the reaction conditions.

As a result, supporting titania on the clay surface enhances the catalytic properties, recovery of the catalyst by simple decantation. And the doping affect differently according to the catalyst type and doping method.

Keywords: Photocatalytic, Titanium dioxide, Doping, XRD, SEM.

Chapter One

Introduction

1.1 Overview

Huge demand, by the increasing human population living requirements, causes rapid increase in factories and industries. The directive and nondirective environmental pollution at all levels (soil, water, air, plants...) then increased.

The main water resources for Palestinians in the West Bank are the West Bank aquifer. Which located under the West Bank lands and receives most of its rain, according to the Israeli occupation policies, it become shared. In addition, very small quantity allowed for the Palestinian community to use. This makes Palestine one of the countries that suffer water scarcity. Water pollution is another threat, which in turn, needs water treatment. Treatment of waste water to keep the aquifer water contain less than the WHO limits of the pollutants [1, 2].

Physical, biological and finally chemical treatment of the wastewater (sewage, agricultural and industrial) has become a priority. Pretreated wastewater contains many chemicals classified as inorganic (Pb, $NO_3^-,...$) and organic pollutants(Phenols, Nitrobenzene,...) [3-5].

The researchers have investigated organic pollutant degradation methods such adsorption, coagulation, filtration, ion exchange, ozonation, sedimentation, electrolysis, chlorination, and chemical deposition. The high cost and the low efficiency in addition to appearance of the undesired bi-products in the treated water are the main limitations for these methods [6, 7]

Steam distillation and electrochemical elimination require high energy consumption and mostly used in complete removal. Chemical oxidation, which requires addition of large quantities of chemicals, is not effective from economic and environmental points of view [8].

Adsorption is an effective method commonly used in water purification, but it has a disadvantage. The adsorbed contaminant needs its own treatment or re-desorption to recover the adsorbent material itself and to permanently remove the pollutant.

Therefore, contaminant molecules must be completely mineralized. Catalytic photodegredation is another stage for future water purification [9]. Nowadays, Advanced Oxidation Processes (AOPs) are widely investigated in water purification. Titanium dioxide nanoparticle (TiO₂) are an example of known photo-catalysts widely studied in contaminated-water purification [10, 11].

1.2 The Catalyst

1.2.1 The Heterogeneous Catalyst

The catalyst is "a substance that increases the rate of a chemical reaction without undergoing any permanent chemical change by itself". In other words, chemical reactions occur faster with catalyst presence. The catalyst provides an alternative reaction pathway with a smaller activation energy than the non-catalyzed mechanism, as shown in Figure a.1 in appendix A. In catalyst-containing mechanisms, the catalyst usually activate reactants to form intermediates, but after the end, the catalyst is recreated again through a catalytic cycle with no change [12].

A substance which offer a mechanism with a higher activation energy does not decrease the rate, because the reaction mechanism has an alternative to go by the non-catalyzed route. The substance which lowers the reaction rate is called reaction inhibitor, not a catalyst [13].

The catalysts can be classified as homogeneous and heterogeneous catalysts. A homogeneous catalyst has molecules that exist in the same phase (usually gaseous or liquid) as the reactant molecules. But the heterogeneous catalyst is one not in the same phase with the reactant molecules. Generally, the heterogeneous catalyst provides its surface to adsorb the gas or liquid molecules. Enzymes and other biocatalysts are often considered as a third category [14].

1.2.2 Transition Metal Oxide Surface

Transition metal oxides are one of the most common heterogeneous catalysts. Their reactivity located in the insufficient array of its surface coordination bonds [15].

The metal oxide crystal structure is either a hexagonal-close packed (hcp) or a facecentered-cubic (fcc). The crystals involve close-packed arrays of oxygen anions, with metal cations occupying interstitial sites. Both structures have octahedral and tetrahedral interstices. The majority of transition metal dioxides (MO₂) have the *rutile structure*, where filling half of the octahedral sites of the hcp oxygen anion array are occupied by cations as shown in Figure a.2 in appendix A [16].

Crystal cleavages along the planes create surfaces. Along a given plane, the cleavage will make surface ions different from the bulk structure. The surface ions have incomplete coordination numbers and are highly energetic. Minimum Gibbs energy indicates thermodynamically stable form, which the surface array should change (See Figure a.3 in appendix A) [16].

Surface polarity is defined as the stability of the surface structures of metal oxides. It describes the coordinative unsaturation and defects. We know little about the surface Gibbs energy of metal oxides, so comparison of stabilities for different surface structures are needed. By better understanding of polarity of the surface and the degree of coordinative unsaturation in addition to study defect sites which have a large effect on the surface stability, The complete control of catalyst activity can be accomplished [17].

Near the surface of the particles and the crystal defects, or in general, on the granule boundaries, the coordination bonds are less than the bulk. The bulk forms six coordinative bonds in rutile TiO_2 as an example, each Ti ion bounded with six oxygen ions which in turn are attached to Ti cations.

This array of the bonds is very stable. But near the edges, the coordination bonds will be minimized depending on the *cleavage plane* [18].

Because of low coordinative bond saturation and high Gibbs energy as the relative surface area increases, the valance band becomes higher in energy level and the conduction band lower. This phenomenon was the key that opened the door of Photocatalysis and Nano-science in general [19].

The other index that influences the catalytic activity is the acid and base character. This is directly related to the size and charge of the metal ions and the strength of M-O bond. The number of oxygen anion electrons that filled the metal d-orbital indicates the M-O strength (according to molecular orbital theory) [16, 17].

The surface relaxations control the surface coordination. Sites of high unsaturation can also occur from oxygen or metal ion vacancies. Structural defects affect the acidity or basicity [20].

1.2.3 Particle Size Effect on the Catalytic Activity

The relative surface area has a huge impact on the catalytic activity. So, it is considered as a main key character that can control the qualitative properties of the catalyst.

The Gibbs free energy of the surface array of atoms is high due to the coordinative unsaturation. This makes the surface chemically active in order to reach lower energy. Therefore, in smaller particle size, the relative surface area increases. Consequently, defect density increases [21].

This effect is easily observed when the particle size of transition metal oxide is in the Nano-scale. For example, the color of the same transition metal oxide changes with change in particle size in Nano-scale [22].

1.2.4 Semiconductor Photocatalysis

In conductors, the conduction band and valance band have negligible energy between them from each other, which allow exited electron to jump from VB to CB easily with low energy required. This energy required for electron-hole separation in this situation is called Band Gap Energy (E_{bg}) and it is less than 0.5 eV for the conductors. In fact, most of the conductors have continuous band of electronic status. Means that the thermal change will be enough to make flow of electrons to the conduction band [17, 19, 23].

In contrast to metals, the conduction band of insulator is separated widely from its valance band and have a large energy band gap ($\geq 4 \text{ eV}$). They need much higher energy to excite the electrons form VB to CB to form electron-hole separation.

Between this and that, the semiconductor has band gap energy moderate, vary between 0.5 eV and 4.0 eV. To simplify these numbers, the 1.0 eV energy is achieved by photon with wavelength equal 1240 nm. This can be justified according to the *Einstein-Plank equation*:[24]

E=hc/λ

Where;

- \mathbf{E} = the photon energy,
- **h** = Planck's constant,
- \mathbf{c} = the speed of light and
- λ = the wave length.

In the middle of the band gap and at zero Kelvin temperature, a hypothetical line express the total distribution of electrons between highest occupied molecular orbital (HOMO) in VB and lowest unoccupied molecular orbitals (LUMO) in CB is called Fermi level (See Figure a.4 in appendix A) [25].

The holes can move through the whole semiconductors crystal, as an electron but positively charged species. In dark, the electron-hole conjunction exist in the valance band in the semiconductors. When proper wavelength photon ($\geq E_{bg}$) excites the electron, it jumps up to the exited state in the conduction band leaving a hole behind in the valance band (See Figure a.5 in appendix A) [26].

These photo-generated electrons and holes may recombine either in bulk or on surface of the semiconductor within a very short time. Heat and emissions are the forms of energy that result from this recombination. Travelling to the surface is the key to undergo oxidation-reduction reactions on the surface of the catalyst. Investing on this property, the Photocatalysis is the most effective method for water treatment. Through series of oxidation-reduction reactions by creating OH[•] radicals that reacts with the organic pollutants repeatedly to moralize them to safe inorganic compounds [27]. The reaction mechanism for TiO₂/photodegredation catalysis is shown in Figure a.6 in appendix A.

1.3 TiO₂ Nanoparticles

Among all the commonly used photocatalysts, the most efficient photo-catalyst is titanium dioxide, which is cheap, stable, with acceptable band gap and harmless. The first discovery was in 1791 from Ilmenite (*as iron-titanium oxide ore, with general formula FeTiO, and a weak magnetic metallic or black colored solid*). The first observation of the Photocatalytic activity of titania was in 1929, while it was used only as white coloring pigment before that. Anatase, rutile and brookite are the most common phases of titania. The most stable form is rutile which can be prepared by heating other forms [29, 30].

Titania (TiO₂) is enormously used as a catalyst in organic pollutant photodegradation, self-cleaning surfaces, water splitting, antibacterial effects, photovoltaics and photosynthesis [31-39]. The researchers used it widely in the environmental disposal of organic contaminants as CO_2 and other inorganic harmless minerals. This, and other properties such as the suspensibility of TiO₂ nanoparticles in the wastewater, make it proper for water decontamination processes [33, 40-44].

The Nano-sized particles in general have special interest. Nano-sized particles have size range from 1- 100 nm, The properties of the materials sharply change with size. Nanoparticles of the materials have new different kinetic energies in conduction band than bulk materials [45, 46].

As a result, as the size of the semiconductor particle is smaller than the critical diameter, the spatial confinement of the charge carriers within a potential well, causes them to behave quantum mechanically like a "particle in a box,". As a result, the bands in the VB and CB split into discrete electronic states (quantized levels), and the nanoparticle begins to behave more like a large atom.

Nano-sized semiconductor particles that exhibit size-dependent optical and electronic properties known as quantized particles (Q-particles) or quantum dots [46-51].

Many researchers studied and showed the extraordinary difference of properties of nano-crystalline materials from bulk. Catalytically, they have higher surface active sites than bulk sites.

Therefore, nano-materials have more advantages than bulk materials. They completely decompose most of organic compounds. TiO_2 nano-photocatalysts resist corrosion in the presence of water and other active chemicals such hydroxyl radicals. They are thermally and chemically stable, easily available and have no toxicity [52-55].

Different shapes of nanotitania have been produced lately as nanoparticles (NP), nanotubes, nanowires, inverse opals, nano ribbons and nano-sheet arrays [56-62]. Different precursors were used for these NPs such as titanium tetra-iso-propoxide (TTIP), tetrabutyl titanate (TBOT) and titanium tetrachloride (TiCl₄). Different methods were used to synthesize them such as sol-gel, hydrothermal, precipitation, etc [61, 63-65].

1.3.1 TiO₂ Nanoparticles in Photocatalysis

The light absorption efficiency of NPs is high, due to their high relative surface areas, which gives a large light-surface interaction to achieve high photo-induced carrier density.

The two common crystalline structures of TiO_2 are anatase and rutile phases. The anatase has higher photocatalytic activity than the rutile [66]. That can be explained by the non-ordinary thermodynamic stability of its NPs. The TiO_2 should not be highly crystalline with large particle size and should be mesoporous. Therefore, TiO_2 NPs with high percentage anatase phase, large specific surface area and small crystalline boundary dimensions are favorable to achieve high photocatalytic activity [67-71].

The photodegredation ability of TiO_2 NPs qualifies them to photocatalyse various organic pollutant degradations in wastewater. The E_{bg} fits with near UV-light present in the tail of solar light, which can be invested as a photocatalyst to oxidize hydrocarbons, alcohols, carbon monoxide, ammonia, SO₂ and bacteria. It is also useful in photocatalytic cancer therapy [72-74].

1.3.2 TiO₂ Doped with Nitrogen

Many articles reported that "because of increasing the redox ability, the smaller crystalline size of doped nano-TiO₂ would result in wider band gap, which requires higher energy of excitation (E_{EX})". In addition, the quantum size also affects the photocatalytic activity [75].

The high band gap (3.0 eV for rutile and 3.2 eV for anatase), and suitable potentials of the conduction and valence band edges, in addition to the higher mobility of the charge carriers within the valence and the conduction bands, make the TiO_2 conversion efficiency low under the solar light. Rutile absorbs the photon with wavelength 405 nm while anatase needs 385 nm. Here further modification is required [76]. One of these solutions is doping with various types of atoms and compounds. It enhance the photocatalytic activity.

Metal ions or non-metal atoms (such as nitrogen) are doped into the crystalline structure of TiO_2 NPs. This sometimes increases the stability, and sometimes minimizes it.

Explained by the increased the internal energy in catalyst structure and surface Gibbs free energy, the increasing of the stability against self-destruction process is directly related to the stability of the bulk and surface, which leads to increase in band gap energy. In order to optimize this parameter, the research shows the best and most efficient photocatalyst that offers higher stability with lower band gap [77-79].

The dopant could prohibit the electron-hole recombination of the generated exciton that in turn accelerates the hydroxyl radical formation. Consequently, this increases the reaction rate. It creates a charge space carrier region on the surface, and could offer active sites for the pollutant on the surface of the catalyst, if the charge is different for the dopant and the doped material which maximize the photodegredation efficiency.

Doping TiO₂ with nitrogen gives a stable catalyst and lowers the band gap to be less than 3.0 eV for rutile and less than 3.2 eV for anatase.[80] The scientists studied different parameters required to increase the photoactivity of the doped NPs such as the temperature of calcination, the concentration of starting materials, the dopant percentage and doping depth in the nanoparticles [80].

1.3.3 Supported TiO₂

Separation of photocatalyst for further reuse is necessary. Some methods are used, but all are costly or inefficient. Supporting the nano catalyst onto solids with large surface areas is a good method. Some studied glass spheres as a support. The separation of the TiO_2 NPs supported on the glass spheres was used. In addition, according to the glass variety from UV- transparent to oblique, it is expected to have different reaction rates from faster to slower compared to the free NPs. However, the glass is not expected to offer enough active sites for the reactants and the catalyst in the same way. Clay supported NPs can be better as shown down in this thesis [80-82].

1.4 The Adsorption

Adsorption can be defined as a process in which material (adsorbate) travels from a gas or liquid phases and forms a superficial monomolecular layer on a solid or liquid condensed phase (substrate) [83].

The adsorption study is very important in photocatalytic study. When there is surface for the reaction to occur, that will minimize the required activation energy of the reaction. And the question here is how could this happen?

The proper direction of the collisions in the reaction container is essential to direct the reaction. This needs minimum kinetic energy equals to activation energy. This energy can be minimized catalytically by offering a reaction surface that bind the reactants together near each other and offers a reaction with less energy and higher rates depending on the number of active sites [83].

1.5 The Clay Support

The clay can be defined as a class of aluminosilicate materials. It is composed of many layers of tetrahedral and octahedral unit sheets [84].

As shown in Figure a.7 in appendix A, the clay has many types of atoms with different percentages. Mainly, silicon is the basic one. The silicon atoms are in the centers of tetrahedrons at equivalent distances from four oxygen atoms in the silica tetrahedral unit layer. As a result of arrangement of tetrahedrons, a hexagonal network appears infinitely

in two directions to form silica tetrahedral sheet. Octahedral unit sheets involve closely packed oxygens and hydroxyls [85-87].

1.5.1 The Clay Modeling and Types

There are different types of sheets according to the type of cations in octahedral sheets.

Clays are stacked in polymeric tetrahedral and octahedral layers. Three main features enable us to determine the type of layer in the clay array, number and arrangement of these sheets in addition to the type of cations between them such as $(Mg^{+2}, Fe^{+2}, Na^{+}$ and $K^{+})$ [88].

Clays may be expandable and non-expandable depending on bonding between layers. Examples of clays are:

- 1. **Montmorillonite**: It is part of clay groups that has two tetrahedral and one octahedral sheets per layer. (2:1 clay mineral) Figure a.8 in appendix A.
- 2. **Kaolinite:** a non-expandable clay with one octahedral sheet and one tetrahedral sheet per layer. (1:1 clay mineral) Figure a.9 in appendix A. There are many other classifications, but these two are the most common ones.

1.5.2 Catalytic Applications of Clay

In the clay, free positively-charged cations exist to equalize the net negative framework charge variation. This may enable the surface to initiate, absorb and facilitate reactions. For these reasons, polar materials, such as water adsorb strongly into the clay surface. They may catalyze reactions by activating different trapped molecules, like in zeolites. Cavities and layers may also speed up reactions by bringing reactants in close distances inside cavities. So the clay can be used as a heterogeneous catalysts and/or as supports for other catalysts. Clays are commonly used in health-care products, therapeutic products and waste management [89].

1.6 Phenazopyridine

Phenazopyridine is a heterocyclic azo-compound used in medication. Phenazopyridine hydrochloride, used as an analgesic drug, is an example of stable medically active substances that resist conventional degradation methods [90, 91]. In this work phenazopyridine hydrochloride was chosen as a model analgesic pharmaceutical that may contaminate environment. Analgesic market is in the order of billions of dollars [92, 93]. It has been chosen in this study due to its ease of detection and the stability of its forms as HCl. Its azo group comes out with oxidation to the NOx pollutions in small amount (see Figure a.10 in appendix A).

1.7 Scope of This Thesis

The main purpose of this work is to study the photocatalytic activity of the nitrogen doped TiO_2 which is supported into a cheap, natural, and available clay to reclaim water from organic pollutants. In this work, the organic contaminants will be removed from phenazopyridine-containing waste water in two steps: adsorption onto the clay surface and then catalytic degradation under simulated sunlight (which resembles direct solar light) using an available, safe, low cost semiconductor material TiO_2 . TiO_2 nanoparticles are supported on solid natural clay to facilitate the reactions, and for easy reuse. The evaluation of the process will be verified in terms of catalytic efficiency, cost, environmental impact, economic values and the proper optimized conditions. Recovery and reuse of the supported catalyst will also be investigated.

Technical objectives include:

- 1. Prepare annealed granules of clay (75-300 μm)
- 2. Preparation of new nano-sized composite material (rutile and anatase TiO₂/Clay), nitrogen doped and non-doped, and characterize using XRD and different methods.
- 3. Using the prepared catalyst powder in photodegradation of organic compound (phenazopyridine) with simulated solar light.
- 4. Using naked TiO₂ in photodegradation of phenazopyridine with simulated solar light.

- 5. Studying effects of temperature, pH, time of contact, phenazopyridine and the catalyst concentration on photocatalyst activity and photodegradation process efficiency.
- 6. Studying recovery and reuse of the photocatalyst for multiple times in photodegradation process

This work is expected to reduce the concentration of pollutants in water, especially phenazopyridine, using a simple and inexpensive method without using any dangerous or expensive materials.

1.8 Novelty of This Work

During recent years photocatalysis processes have been widely investigated for the purification of water from many toxic organic pollutants. It is a new promising environmental protection technology. Naked TiO2 and ZnO have been used as photocatalysts for degradation of widespread pharmaceutical wastes [94]. Other studies used three different types of clay structures as supporting material for nano-TiO₂ catalyst [95, 96]. Earlier studies did not use nitrogen doped TiO₂ onto the natural clay as supported photocatalysts. In this work, nitrogen doped and non-doped TiO₂ nano particles, supported onto natural clay, are used for the degradation of phenazopyridine under simulated sunlight. To our knowledge, nitrogen doped and non-doped TiO_2 (as anatase and rutile) were not supported on natural clay for photocatalysis purposes. The newly prepared composite TiO₂/Clay is used for photocatalytic degradation of phenazopyridine, by solar simulated light, for the first time. On one hand, nano-TiO₂ supported onto clay is expected to provide high efficiency due to clay distinctive physical properties, such as large specific area, layered structure and high adsorption. On the other hand, supporting the catalyst will facilitate catalyst recovery and reuse for additional degradations [97-99].

Chapter Two

Materials and Methods

2.1 Materials

Commercial Titanium dioxide with serial number of (*anatase: A21J10 and rutile: 13208DS*), Triton X-100 (*non-ionic surfactant*), Isopropanol (*99.8wt%*), Titanium (IV) isopropoxide (*TTIP*, *97%*) were purchased from *Sigma Aldrich*, and NaOH, HNO₃ from *Frutarom Co*. The phenazopyridine samples were donated from *Birzeit Pharmaceutical Co.*, Ramallah, Palestine. The natural clay was collected in a paste form Jaba, Jenin, Palestine (32.326250, 35.217202°). All were used in preparing the naked and supported nitrogen-doped composite TiO₂/Clay nanoparticles.

2.2 Equipment

75-300 µm diameter sieved clay fine powders using meshes were prepared with help of the Civil Engineering Department. The photodegradation experiments were made using 250 ml flasks and with heat controller on the magnetic stirrer under the sun light simulators. Adjustment of the intensity of light on the water sample under study was made using A Lux-meter (Lux-102 light meter).

HPLC grade (sigma Aldrich) 1525 High performance liquid chromatograph, equipped with water 2998 photodiode array UV-Visible detector and auto sampler injector and detection wavelength of 280 nm, was used to study the remaining phenazopyridine and organic contaminants concentrations. The eluent solution was (25% water, 75% acetonitrile) with flow rate 1 ml/min. The injection volume was 20 μ l.

In order to simulate the solar light in the photodegredation experiments, HLX64657 EVC 24V250W halogen lamp was used.

A Jenway 3510 pH meter was used to adjust the reaction mixture pH as desired. A Perkin-Elmer LS50 Luminescence Spectrophotometer was used for photoluminescence measurements of each catalyst. Crystal structures of all solids were measured on X-Ray diffractometer (XRD) with Cuka ($\lambda_{1.5418}$ Å) as source, at Al-Ain University, UAE. A mercury thermometer was used to measure temperature.

2.3 Catalyst preparation

2.3.1 Clay preparation

The clay paste was plated in order to maximize the area exposed to air in addition to the high temperatures, and then heated into the furnace at 950° C for 24 h. The clay stone was then milled to fine powders and sieved. The 75-300 μ m meshes were taken. It was washed with diluted HCl and then with water. As a result, the clay was ready for supporting step.

2.3.2 Doping the TiO₂ Nanoparticles with Nitrogen

This research has studied two different doping:

2.3.2.1 Method I

After mixing 30 ml distilled water, 4.0 g urea in 250 ml round bottomed flask for an hour, 10.0 g of anatase were added to the solution and mixed for 15 min in dark (The water sonicator bath was used to release the accumulated granules). The same was done for rutile TiO_2 . Then the doping took place over the night in the dark. In the morning (14 hours later), the two round bottomed flasks were dried into vacuumed rotary evaporator (VRE). Then calcination via furnace for 1 h at 500 °C (or different temperatures) were done to achieve the purpose (under nitrogen cover once, and air the second time with slow and fast cooling). The dry powders were taken and milled softly and become ready to the next step of supporting and /or using directly.

2.3.2.2 Method II

This method was based on literature[80]. By doping the TiO₂ during sol-gel synthesis method. 10 drops Triton X-100 has been used as a binder, added to 100 ml of isopropyl alcohol, then adjusted with conc. HNO₃ to pH ~ 2 . Into a zero temperature cooled mixture, 10 ml of titanium (IV) isopropoxide was added drop wise for 4 hr as a titanium source. Then the solid was washed with water and dried using rotary evaporator at 70 °C for 60 min.

2.3.3 Supporting TiO₂ Nanoparticles onto Clay Powder

TiO₂/clay composite paste was prepared simply by adding 20 g of the clay (75-300 μ m) in 5 g of doped and non-doped TiO₂ (anatase or rutile), and then mixed well.

The resultant pastes were dried for an hour at 100 °C in the oven. The calcination has been done under different conditions, for an hour at different temperature. the calcination was undergo airflow fast and slow cooling methods cover used. The resulting powder washed with diluted HCl and then with distilled water and dried in the open air.

Table 2.1

Different	preparation	methods f	for the	catalysts.
				~

Cat. No.	Catalyst Type	Doped (yes /No)	Supporting (yes /No)	Calcination Temperature (°C)	Quenching Time	The Cover- Gas
1	Clay	No	No	950	Slow	Air
2	Anatase	No	No	-	-	-
3	Rutile	No	No	-	-	-
4	Anatase	No	Clay	400	Fast	Air
5	Anatase	No	Clay	400	Slow	Air
6	Rutile	No	Clay	400	Fast	Air
7	Rutile	No	Clay	400	Slow	Air
8	Anatase	No	Clay	500	Fast	Under N ₂
9	Rutile	No	Clay	500	Fast	Under N ₂
10	Anatase	No	Clay	500	Fast	Air
11	Rutile	No	Clay	500	Fast	Air
12	Anatase	No	Clay	750	Fast	Air
13	Anatase	No	Clay	750	Slow	Air
14	Rutile	No	Clay	750	Fast	Air
15	Rutile	No	Clay	750	Slow	Air
16	Anatase	No	Clay	950	Fast	Air
17	Anatase	No	Clay	950	Slow	Air
18	Rutile	No	Clay	950	Fast	Air
19	Rutile	No	Clay	950	Slow	Air
20	Anatase	Yes	No	500	Slow	Air
21	Rutile	Yes	No	500	Slow	Air

Cooling time was 3 min and 60 min for fast and slow cooling, respectively.

2.4 Photocatalytic experiments

2.4.1 Phenazopyridine Photodegredation

All the experiments were typically made in 250 ml beaker with stirring for an hour at fixed temperature using 50 ml of 20 ppm phenazopyridine with 0.4 g of the catalyst. Figure a.11 in appendix A describes the reaction setup used in photodegradation experiments.

To measure the change in organic contaminants concentrations with time, During the photocatalytic degradation reaction, UV-Visible spectrophotometry, TOC, and HPLC analysis were used.

The photocatalytic reaction was conducted under solar simulated light. The measured light intensity was 100,000 Lux (0.0146 w/cm^2) .

The photocatalytic reaction was studied under different conditions. Effects of Phenazopyridine concentration, type of Catalyst, incident radiation intensity, quantity of the catalyst, temperature and pH value were all studied.

2.4.2 Effect of Phenazopyridine Concentration on the Photocatalytic Activity of the Catalyst

10 ppm, 20 ppm, 30 ppm and 40 ppm solutions of phenazopyridine were prepared from a stock solution (1000 ppm phenazopyridine in 1000 ml volumetric flask) and then a certain amounts were taken and diluted into 100 ml volumetric flask

Table 2.2 shows phenazopyridine solutions prepared. The table shows corresponding amounts of 1000-ppm solution used to prepare 100 ml of each concentration.

Table 2.2

The Phenazopyridine Concentration (ppm)	Volume needed from 1000 ppm Phenazopyridine solution	Volume of distilled water added (ml)				
(mi)						
10	1.0	99.0				
20	2.0	98.0				
30	3.0	97.0				
40	4.0	96.0				

Different concentration of phenazopyridine preparation.

These solutions were prepared to study the effect of Phenazopyridine concentration on the photocatalytic study for 60 min, at room temperature (25 ± 1 °C).

2.4.3 Effect of pH

Initially, the pH of the 20 ppm phenazopyridine solution was measured to be 5.5. The pH value was controlled by adding drops of diluted sodium hydroxide (NaOH) solution and hydrochloric acid (HCl).

2.4.4 Temperature Effect on Photodegredation Process

Into a beaker, 50 ml of 20 ppm phenazopyridine were placed in a beaker. The beaker was placed in water bath after adjusting the temperatures to be 15, 25, 30, 35 and 45 °C, the temperature effect on the photocatalytic process was studied by adding 0.4 g catalyst under irradiation. The water bath-temperature was kept constant (± 1 °C) during each experiment.

2.4.5 Composition TiO2 (Rutile)/Clay

The clay weight in the whole catalyst weight was measured using SEM. Each 0.40 g TiO2(Rutile)/Clay contained 0.10 g rutile and 0.30 g clay. This was considered in catalyst loading calculations.

2.5 Control Experiments

The phenazopyridine (50 ml, 20 ppm) has been placed with no catalyst under the reaction conditions and simulated-light for 60 min. To study the UV-Visible spectra change on all experiments.

The clay adsorbed a traces of phenazopyridine, and can photo-catalyze another traces, and may phenazopyridine is light sensitive material. All are reasons effect on the results during the reaction. Hence, the control experiments necessary to ignore all this effects in the photodegredation process.

The phenazopyridine (50 ml, 20 ppm) with 0.3 g naked clay in the reaction conditions without TiO_2 .

2.6 Calibration Curve

Using the UV-Visible spectrophotometric analysis (200-800 nm), a calibration curve was made to measure the exact concentration of the phenazopyridine before and after the reactions. 1 ppm, 2, 4, 6, 10, 15, 20 ppm of phenazopyridine solutions were prepared, the UV-Visible spectra were recorded and plotted. The peaks at 430 and 350 nm were used in calibration curve and phenazopyridine concentration measurements.

2.7 Point of Zero Charge and Surface Charge Determination

Determining the pH at which the net catalyst surface charge will be zero was described earlier in Noh and Schwarz [100]. (0.01 M) NaCl solution was boiled to remove the dissolved CO₂, then it was kept to cool to 25 °C under nitrogen. After that, 50.0 ml solutions were added into each glass bottle. Then the pH was adjusted in each bottle. All the bottles were purged with nitrogen stream for 5 minutes. Then pH values were measured again and listed as initial pH.

Then 0.1 g of the catalyst was added into each bottle, with shaking suspension was for 24 hour at thermo-stated water bath shaker at $(25 \pm 2 \text{ °C})$. Then left for 2 hour to settle, then the final pH values were measured.

This process was repeated for each of the following catalyst: (Rutile TiO₂, Clay, Rutile TiO₂/Clay)

2.8 Clay Elemental Analysis and TGA Determination

The elemental analysis of clay components was done using inductively coupled plasma/mass spectrometry. In polypropylene bottle, 1 g of clay was added into concentrated Solution of HCl (~12 M) and HF (~22 M) with ratio 7:1 respectively.

Then the mixture was transferred to water bath with temperature ~ 60 °C for 2 h. Milky solution appeared. The polypropylene bottle was closed well and then cooled under the tap water in order to be ready for addition of 10 ml of saturated boric acid solution. After adding it, the bottle has been heated at ~ 70 °C until the solution becomes clear. After cooling, the mixture was diluted into 200 ml volumetric flask. The samples were then analyzed by inductively coupled plasma/mass spectrometry equipment.

TGA analysis was used to test dried and pre-annealed samples. The sample was heated up to 900 $^{\circ}$ under atmospheric air with ramp rate 20 $^{\circ}$ C.

Chapter Three

Results and Discussions

3.1 Solid Material Characterization

Table 2.1 shows all catalysts characterized using different methods. The specific surface area was 15, 350 and 335 m²/g for rutile TiO₂, clay and TiO2(Rutile)/Clay, respectively. By blocking the pores of clay, the rutile TiO₂ lower the clay surface area. In addition, the average mass percent of the rutile TiO₂ into the composite system was 26%. TiO₂(Anatase)/Clay was not catalytically effective, and therefore was not fully studied like TiO2(Rutile)/Clay.

3.1.1 XRD Results

X-ray diffraction patterns for natural clay, and XRD pattern for un-doped TiO_2 -rutile and anatase- were shown in Figures a.12, a.13, a.14 (appendix A) respectively.

Figure 3.1 shows all XRD patterns for anatase catalysts, including naked, claysupported, nitrogen doped and un-doped cooled slowly and quickly annealed at different temperatures. Comparison with Figure a.12 (appendix A) shows that the clay contains montmorillonite, little kaolinite and quartz. Comparison between Figures 3.1 and a.14 (appendix A), indicates the presence of anatase as a major phase in both anatase and TiO₂(Anatase)/Clay. For rutile, XRD patterns are shown in Figure 3.2.

Results of Figures 3.1, 3.2 and 3.3 are summarized in Table 3.1.
Figure 3.1

X-ray diffraction patterns of anatase based catalysts with different annealing conditions.



Figure 3.2





Based on the Scherer equation (1), calculations using 101, 004, 200 reflections for anatase, the average particle size is 50 nm while average particle size for $TiO_2(Anatase)/Clay$ which treated at 400 °C with slow cooling is 49 nm, whereas in fast cooling is 51 nm.

Table 3.1

The average particle size of the studied catalysts (A: Anatase, R: Rutile, N: Nitrogen doped).

Cat. No.	TiO ₂ Type	Doped	Supporting	Calcination Temperature (°C)	Quenching Time	The Cover- Gas	Average P. Size (nm)
1	А	-	-	-	-	-	50
2	R	-	-	-	-	-	50
3	А	-	Clay	400	Fast	Air	51
4	А	-	Clay	400	Slow	Air	49
5	R	-	Clay	400	Fast	Air	51
6	R	-	Clay	400	Slow	Air	48
7	А	-	Clay	500	Fast	Under N ₂	51
8	R	-	Clay	500	Fast	Under N ₂	61
9	А	-	Clay	500	Slow	Air	49
10	R	-	Clay	500	Slow	Air	62
11	А	-	Clay	750	Fast	Air	51
12	А	-	Clay	750	Slow	Air	48
13	R	-	Clay	750	Fast	Air	57
14	R	-	Clay	750	Slow	Air	59
15	А	-	Clay	950	Fast	Air	52
16	А	-	Clay	950	Slow	Air	54
17	R	-	Clay	950	Fast	Air	60
18	R	-	Clay	950	Slow	Air	67.5
19	А	Ν	-	500	Slow	Air	44
20	R	Ν	-	500	Slow	Air	55

(1)

Scherer Equation:

 $L = (K\lambda)/(FWHM)x(\cos\theta)$

Where,

L is particle size,

 θ is peak position (2 θ /2) in radian.

 λ is the wavelength of the X-ray used for the diffraction.

FWHM is width at half height (in radians).

K is a constant, called shape factor. If the crystallites considered as spherical, the value of K can be used as 0.94

From the Table 3.1 above we can demonstrate the effect of annealing temperatures and conditions onto the particle size and crystalline structure for different TiO_2 catalysts, summarized on Figure 3.3.

Figure 3.3 shows that in anatase form, the particle size is almost the same in fast cooling likewise in the slow cooling, it is stable till 750 °C, then the average particle size increases to reach 54 nm at 950 °C. This can be explained by the small portion conversion of anatase (less stable than rutile) into the rutile. This can be demonstrated by looking at the Figure A.15, at the signal for (110) face exist in the rutile form and not in the anatase, (At $2\theta = 27.4$). So, annealing anatase at high temperatures (950 °C) partly converts it into rutile form. The rutile particle size is larger than the anatase in general.

In the rutile form, the average particle size fluctuated around 60 nm when the annealing temperatures were above 500 °C in the fast cooling conditions. In general, slow cooling in rutile form causes larger particle size as the annealing temperature increases. exclude 400 °C, the average particle size was 51 nm. The slow cooling shows similar particle size (48 nm). This is observed at low annealing temperature where the cooling rate does not affect size.

Cooling time is an important parameter that affect the catalytic activity. Slow cooling gives the catalyst more time to form itself, which gives granules with larger particle size and more bond-sufficiency, that causes higher relative stability and smaller band gap energy. As a result, the fast cooling gives better results in photodegredation. This can be explained by the bond-deficiency that caused by the slow cooling as slow cooling does not give the catalyst time to reform itself.

Figure 3.3



Annealing temperature effect on the particle size of supported Rutile and Anatase TiO_2 .

Another thing to be noticed, in general, the particle size before supporting was 50 nm but after supporting, it was larger. This can be explained by the stacking of the titania particles on the clay surface, which gives a surface for granule to growth using the advantage of annealing temperature.

3.1.2 Scanning Electron Microscope Results

The scanning electron microscope tells about the solid surface. That facilitates the explanation of the granule size calculation and give us an a idea how the surface looks like. Figure a.16 in appendix A shows the SEM images for different catalyst types. The scales are at the same photos.

The size differs with the synthesis conditions. When size increased, the relative surface area decreases. This yields more bond deficiency of atoms in particle, notably at the surface. When particles combine together by chemical bonds, the size and stability increase. This affects the band gap energy from one side, and on the electron-hole couple recombination time and place from another side. In that case, it will affect the photocatalytic activity of the catalysts.

Table 3.2 shows the agglomerated granule sizes for anatase and rutile at different annealing temperatures and cooling rates. We can see the differences between the anatase and rutile. In general, at mild annealing temperature, the anatase crystallites stack together to minimize the bond deficiency. In rutile, the agglomerate size is somewhat smaller than in anatase. While when the temperatures increases above 750 °C, the rutile agglomerates are larger than anatase.

Table 3.2

Agglomerate (granule) size change with different annealing temperatures, according to SEM images.

Annealing Temperature	Granule size of Anatase (µm)	Granule size of <i>Rutile</i> (µm)
400 °C- Fast cooling	1.4	1.1
400 °C- Slow cooling	1.3	1.2
500 °C- Fast cooling- under N_2 cover gas	0.6	1.0
500 °C- Slow cooling	1.4	1.3
750 °C- Fast cooling	0.9	0.8
750 °C- Slow cooling	1.5	2.5

However, as the temperature increases, the agglomerate size increases due to more inter-crystallite sintering. The fast cooling agglomerate size gives general idea about the inter-particle bond strength.

For fast cooled anatase, the agglomerate size at 400 °C is 1.4 μ m which gets smaller at higher temperature up to 750 °C (0.9 μ m). As the annealing temperature increases, and due to the low bond energy in anatase phase, the broken bonds increase, which in fast cooling do not have enough time to reform new bonds during cooling.

However, rutile shows higher bond energy. This means smaller relative change in agglomerate size with temperature, from $(1.1 \ \mu\text{m})$ at 400 °C to $(0.8 \ \mu\text{m})$ at 750 °C.

Slow cooling gives the catalyst enough time to reform itself and increases the bonds to form larger agglomerate size. For anatase, the agglomerate size is (1.3 μ m) at 400 °C, and gets larger with higher temperature up to 750 °C (1.5 μ m). The same for rutile shows the same effect.

At 400 °C, the agglomerate size is not effected by the cooling rate, this temperature, which is still not enough to break large numbers of the agglomerate bonds and reform new ones. On the other hand, the difference between agglomerate size in slow cooling and fast cooling is obviously observed.

Cover gas during the calcination step affects the solid. We know that the catalyst have polarized Ti-oxygen bonds. These bond increases the charge polarization and also the energy on the catalyst surface. When the inert gas is nitrogen, it is exchanged with the granule boundary bounded oxygen atoms [101]. As long as the oxygen is more electrophile than the nitrogen, the catalyst granule becomes more stable. This can be demonstrated by the small agglomerate size for rutile and anatase. Moreover, the stacking of the under nitrogen heated catalyst onto the clay surface is less than under oxygen heated form. This indicates the dropping in the photocatalytic activity for under nitrogen annealed TiO_2 as shown later in the results.

3.1.3 Photoluminescence Spectra

In order to find the maximum wave length for each catalyst which indicates the place of activity in the light spectra, we used Fluorometer. The effects of doping and supporting on the band gap for the anatase form are shown in Figure A.17 in appendix A.

From Figure A.17, we can notice the doping effect on the anatase spectrum in both naked and supported forms. The maximum anatase absorption is at 378 nm, where after the doping it becomes at 395 nm. The band gap of the anatase become smaller after doping from 3.20 eV to 3.12 eV [76]. However, this change is very small and we expect it to have a small effect on the photocatalytic activity.

Effect of nitrogen doping on anatase band gap can be explained in nitrogen doping from N_2 gas, was studied. A deep study of the nature of the nitrogen doped anatase and the doping position inside the crystal structure demonstrate that under typical experimental conditions, nitrogen prefers to replace at a Ti-site and bond to two or three neighboring oxygen ions, this results in the formation of nitrite or nitrate ions, with one Ti-vacancy and under-coordinated oxygen ions.

In doping from nitrite or nitrate ions, the nitrogen donate electrons via sigma bond. Inside the crystal, the oxygen forms a frame work with bond order two. Similarly with the nitrogen, it forms sigma bonds with order one with each centered atom. (Hence, Nitrogen bond with oxygen considered as electron rich). This explains the lowering in the band gap energy in the nitrogen doped anatase TiO_2 . We can see this tails in the anatase spectra in Figure A.17 (appendix A).

Photoluminescence spectra were measured for rutile catalysis. From Figure A.18 in appendix A, we can notice the absorption peak between 350-425 nm for the rutile supported on the clay. For all the catalysts, the clay has no shifting in the spectrum except for the supported rutile.

The intensity of the peaks that refer to un-supported catalysts is higher than supported ones. This has two explanations; the first is due to high stability of electron-hole separation when the titania is supported, thus the intensity of the photoluminescence of e-h recombination is less. Secondly, the thin layer film was prepared with the same quantity of the solids, which means less titania for the clay-containing systems. As long as the intensity is quantity-dependent parameter, so it is less for the clay supported forms.

Figure 3.5 shows Photoluminescence spectra for all rutile and anatase doped by methods I and II.

Figure 3.4

Photo-luminescence spectra for different doped film catalysts: 1) nitrogen doped rutile, 2) nitrogen doped rutile supported on natural clay, 3) nitrogen doped anatase, 4) nitrogen doped anatase supported on natural clay and 5) method II doped TiO_2 and 6) method II doped TiO_2 supported on natural clay.



From Figure 3.5, the nitrogen doped anatase catalyst shows high photoluminescence intensity in the spectrum. on the other hand, during the photodegredation experiments, the catalytic activity is not good compared with the other catalysts as described latter. In the same side, the nitrogen doped rutile supported on natural clay shows weak photoluminescence spectra and good catalytic activity. Here we can conclude that the catalyst which has a small photoluminescence intensity, has more activity than the one with high photoluminescence intensity. This refers to electron-hole recombination intensity. More photoluminescence intensity leads to more e-h recombination process, means less effective e-h separation. As a result, less photodegredation activity.

Qualitatively, the e-h presence sign in the catalyst is the e-h recombination photoluminescence, because there is no e-h separation that lasts forever. So the presence of a sign on photoluminescence spectrum, means presence of e-h separation, and the blind spectrum means no e-h separation. The e-h separation stability means less catalytic-activity, and immediate recombination means not observable catalytic effect. So it's a controversial issue.

3.1.4 Clay Elemental Analysis (ICP)

The elemental analysis of the clay in order to determine the composition was done using Inductively coupled plasma/mass spectrometry. Table 3.3 describes the concentration of the clay content. Aluminum, Arsenic, Barium and Iron are the main components of the clay according to the given results from (ICP). Another notice, the presence of good concentration of Zink in the clay system, allows us to consider the clay as a catalyst itself.

Table 3.3

Composition of the clay given by Inductively coupled plasma/mass spectrometry.

Analyte	Mass	Conc. Mean	Conc. RSD	Sample Unit
Al	27	24694.3	2.8	Ppb
As	75	1160.8	2	Ppb
Ba	138	1228.4	1.4	Ppb
Cd	111	2.9	3.4	Ppb
Cr	52	473.1	1.7	Ppb
Co	59	145.8	23.2	Ppb
Cu	63	593.2	3.1	Ppb
Fe	57	17376.8	3.2	Ppb
Pb	208	11.2	5.2	Ppb
V	51	330.3	5	Ppb
Zn	66	1272.6	6	Ppb

3.2 Thermal Gravimetric Analysis

Figure A.19 (appendix A) shows a total mass loss of 10% for the pre-annealed TiO2 (Rutile)/Clay sample based on measured TGA profiles for the temperature range 25–900 °C. Evaporation of adsorbed humidity accounts for the 2% mass loss below 100 °C. Coordinated water removal is responsible for the 2.5 percent mass loss in the temperature range of 100–200 °C. At temperatures exceeding 200 °C, partial decomposition accounts for 5.5 percent of the mass loss. This is consistence with earlier literature [102].

3.3 Point of Zero Charge and Surface Charge Results

The pH in which the surface charge of the catalyst changes from negative to positive is pH_{pzc} . For annealed TiO₂ (Rutile)/Clay pH_{pzc} is found from plots $\Delta(pH)$ vs. (pH). Figure A.20 (appendix A) revealed that the unsupported Rutile TiO₂ exhibited positive surface charge at pH less than 6. Otherwise, it shows negative charge. And the clay negatively is charged at pH above 12.2. The supported TiO₂(Rutile)/Clay surface charge changed at pH ~12 (pH_{pzc}).

Here we focus our study on the rutile supported on the clay due to its special superiority in the photodegredation. This was to achieve the second purpose of this study which can be summarized as finding the optimum conditions for the best catalyst.

3.4 Photocatalytic Degradation of Phenazopyridine

The photocatalytic degradation study of phenazopyridine in water was carried out using different catalysis under various conditions and reaction parameters in order to find the optimum conditions for the process.

3.4.1 Calibration Curve

The calibration curve to determine the exact concentration of phenazopyridine in water during the process, using UV-Visible spectra, is shown in Figure A.21 in appendix A.

3.4.2 Doping and Supporting Effect

From Figure 3.6, the photocatalytic activity of rutile form slightly increased when its doped with nitrogen. While the supported rutile and doped rutile shows extra activity, and the supported rutile has superiority on the photodegredation of the contaminant as the solid characterization study expected.

Figure 3.5

Effect of doping and supporting on the activity of photocatalysts for TiO2 rutile phase catalyst. Experiments were carried out for 60 min at 25 ± 1 °C by adding fresh phenazopyridine (50.0 mL, 20 ppm) to the catalyst. The nominal fresh catalyst weight was 0.4 g (containing 0.1 g TiO2).



On the other hand, Figure A.22 (appendix A) with nitrogen. The nitrogen doped and supported anatase show higher activity than the naked ones. The best anatase activity is achieved by supporting the non-doped anatase.

The clay-supported rutile showed highest catalytic efficiency. Therefore, all study was made in presence TiO_2 (Rutile)/Clay unless otherwise stated.

3.4.3 Effect of pH on Phenazopyridine Photodegredation

The pH study for the catalytic reactions is important to give the complete image for the surface charge and the pH in which the catalyst attract or repels the pollutant. This information can benefit us in finding the proper reaction conditions for any pollutant added to the photoreaction container. Figure A.23 (appendix A) shows photodegredation results for all anatase based catalysts at different pH values. From the figure, commercial anatase shows high activity at pH 7.1. The doped anatase has almost no activity when the pH is high (\approx 10) where its photodegredation activity than the supported doped anatase shows lower activity than the supported

un-doped anatase in acidic medium. In neutral medium, the un-doped shows higher activity than the clay-supported doped anatase. Figure A.24 (appendix A) summarizes all results for supported rutile catalyst only.

The pH was measured and adjusted before adding the catalyst. Due to the basicity of the clay, the pH is immediately after adding the clay goes around 10. Another thing to be mentioned, the pH of 20 ppm phenazopyridine is 4.5. This was because of the form of the phenazopyridine HCl.

Therefore, the surface charge of the catalyst is opposite to the charge of the phenazopyridine at pH below 12, and the reaction is more active at pH is between 3.5 and 12. Here we can notice the slight effect of the solution pH within the active pH area. The higher degradation percentage is given at pH = 3.5-10.1. Otherwise, as the pH value has a slight effect on the photocatalytic activity.

3.4.4 Effect of Annealing Temperature

From the Figure A.24 (appendix A), we can see that the best annealing temperature was at 500 °C under the air flow. At 950 °C, the activity of the rutile are less than 10%. This confirms that smaller accumulate with larger specific surface area will gives higher catalytic activity. Annealing at high temperature gives larger particles with smaller specific surface areas, as observed from SEM results.

The photodegredation percentage with anatase form, annealed at 500 °C under nitrogen cover, is above 50%. This means that the catalyst is not deteriorated, and becomes more active. In some cases, annealing under nitrogen causes surface doping. This doping may show no effect on the band gap, but the effect appeared on delaying or targeting the e-h recombination. Overall, this will increase the catalyst efficiency [103].

3.4.5 Contaminant Concentration Effect

General speaking, if we increase the concentration of the reactants, under the same conditions, more degradation occurs. This phenomena is applicable here with some limitations.

From 10 to 20 ppm Phenazopyridine, as the phenazopyridine concentration increases, the photoreaction increases as shown in Figure A. 26 in appendix A. By the increasing

in the concentration of the reactants, the active proper collisions increase. We should not look at % degraded contaminant which decreases with higher concentration. From the Figure, the absolute amount of degraded contaminant increases with concentration. Notice that the increase in phenazopyridine concentration effectively increases the proper collisions and increases the number of reacted molecules. The dark degradation (by clay) also increases by increasing the phenazopyridine concentration.

3.4.6 Catalyst Concentration Effect:

The catalyst amount effect is shown in the Figure 3.6.

Figure 3.6

Catalyst amount effect of TiO2(Rutile)/Clay on the phenazopyridine photodegredation process, x-axis express the percentage of the lost amount of phenazopyridine, while y-axis is for TiO2(Rutile)/Clay amounts. Experiments were carried out for 60 min at 25 ± 1 °C by adding fresh phenazopyridine (50.0 mL, 20 ppm) to the catalyst. The nominal fresh catalyst weights were (0.1, 0.15, 0.2, 0.25, 0.3, 0.35 and 0.4) g (containing 0.1 g TiO2 per 0.4 g).



Figure 3.7 shows that increasing the catalyst amount increases the amount of degraded phenazopyridine. That is related to presence of more catalysts, which means using the maximum incident amount of light to degrade the phenazopyridine. This rule stays the judge until the revers effect of turbidity.

The catalytic efficiency can be expressed by different methods such as turnover number, turn over frequency, quantum yield. Where Turnover number (TON) describes the number of molecules of pollutant destroyed by one active site during the reaction time. Turnover frequency is TON/time of reaction, with unit (min ⁻¹). The quantum yield describes the number of pollutant molecules degraded by one photons per catalyst active site. From literature, for crystallite of ~50 nm, there is one active site per 10 TiO₂ units [104], and this ratio has been used in the calculations here. Table 3.5 summarizes catalyst efficiency in various terms.

Table 3.5

Photodegradation percent, Turnover number (TON), turnover frequency (TOF) and the quantum yield (QY).

	Phenazopyridine degradation %	Turnover Number (TON)	Turnover Frequency (TOF) (min ⁻¹) X10 ⁻³	Quantum yield (Q.Y.) (Molecule/Photone) X 10 ⁻⁷
R.com.	47%	0.18	2.95	0.86
N-R doped	30%	0.11	1.88	0.55
TiO2(Rutile)/ Clay N-	82%	0.31	5.14	1.51
TiO2(Rutile)/ Clay	68%	0.26	4.26	1.25
A.com.	29%	0.11	1.82	0.53
N-A doped	20%	0.08	1.25	0.37
A/Clay	40%	0.15	2.51	0.73
N-A/Clay	37%	0.14	2.32	0.68

Table 3.5 shows the superiority of rutile either doped or un-doped when supported on the clay. However, the doped rutile has lower efficiency compared with the supported un-doped ones. In the same way, doped unsupported anatase shows lower photodegredation efficiency. When supported, doping enhances the catalytic properties.

3.4.7 Effect of Temperature on Phenazopyridine Photodegredation

As Langmuir equation, as the temperature of the system increasing, the adsorption rate on the catalyst surface will increase. And as a result, the photoreaction rate should increase in our experiment.

Figure 3.7

The temperature effect on the photocatalytic activity of the rutile supported onto clay. Experiments were carried out for 60 min at (15, 20, 25, 30, 35, 40, 45) \pm 1 °C by adding fresh phenazopyridine (50.0 mL, 20 ppm) to the catalyst. The nominal fresh catalyst weights were 0.4 g (containing 0.1 g TiO₂).



For Figure 3.7, the speak is applicable until the reaction temperature reaches 35 °C. Increasing the temperature causes higher reaction rate if temperature is lower than 35 °C. Above 35 °C, as the temperature increased, the reaction rate becomes less and less.

The main essential element in the photodegredation processes is the presence of oxygen as we showed in the introduction. It is necessary to know that as the kinetic energy of the gaseous solute increases, its molecules have a greater tendency to escape the solvent molecules' attraction and return to the gas phase. As a result, as the temperature rises, the solubility of a gas drops.

Here we can explain the drop of photocatalytic efficiency at temperatures is >35 °C. it is due to the decreasing of the dissolved oxygen concentration in the reaction container as a result of increasing the temperature.

Generally speaking, as the temperature increases, the photocatalytic reaction rate increases until it reaches a point of balance, where the Langmuir's rate increases on one

hand, and the oxygen deficiency increases on the other hand. Above that point, the temperature increase will effect reversely.

3.5 Catalyst Recovery and Reuse

Figure 3.8

Photocatalytic efficacy retention for pre-annealed TiO2(Rutile)/Clay after recovery and reuse. Experiments were carried out at 25± 1 °C by adding fresh phenazopyridine (50.0 mL, 20 ppm) to the catalyst. The nominal fresh catalyst weight was 0.4 g (containing 0.1 g TiO2).



Because of their small size, naked TiO_2 nanoparticles are difficult to isolate from photodegradation reaction mixtures. Simple decantation was utilized to separate the $TiO_2(Rutile)/Clay$ composite catalyst. It was then employed in additional fresh photocatalytic tests. The recovered catalyst (< 0.20 g owing to handling loss) was combined with new phenazopyridine solution in each reuse experiment.

Experiments on recovery and reuse were carried out three times of reuse. Figure 3.8 depicts the results. After the 3rd reuse, there is no significant loss in relative catalyst efficiency. The lowering in phenazopyridine loss percent shown in the Figure is due to the loss of supported catalyst during handling.

The results demonstrate the added advantage of utilizing $TiO_2(Rutile)/Clay$ in photocatalysis for phenazopyridine degradation, as the catalyst may be recovered and reused many times in future applications.

3.6 Complete Mineralization of Phenazopyridine

Figure 3.9

Photodegredation of Phenazopyridine using TiO2(Rutile)/Clay with time. Experiments were carried out at 25 ± 1 °C by adding fresh phenazopyridine (50.0 mL, 20 ppm) to the catalyst. The nominal fresh catalyst weight was 0.4 g/ (containing 0.1 g TiO₂).



Photodegradation mineralized all of the reacted phenazopyridine molecules completely, as shown in Figure 3.9. Several methods were used to confirm this. The electronic absorption spectra (Figure 3.10) revealed a continued decrease in the absorption band in the 400–500 nm region, which is attributed to phenazopyridine, during the photodegradation reaction. Table 3.5 shows the results of total organic carbon (TOC) and HPLC measurements for the reaction dispersion. Confirming total organic carbon mineralization, TOC values measured during the reaction agreed with HPLC analysis values for the remaining unreacted Phenazopyridine contaminant.

Table 3.5

Confirmation of complete mineralization of phenazopyridine, by total organic carbon (TOC) values and HPLC peak areas, using TiO2(Rutile)/Clay. The reaction was conducted using phenazopyridine (50.0 mL, 20 ppm) and TiO2(Rutile)/Clay (0.4 g) at 25 ± 1 °C.

TOC anal	lysis		HPLC analy	/sis
Time	TOC	%L 088	HPLC	% Loss
(min)	(ppm)	70L035	(µV sec)	70 L035
0	20	0	1088826	0
40	10.2	50	535916	50.78
60	3.8	81	195486	82.05
80	1.78	91	94284	91.34
100	1.0	95	43822	95.97
120	0.81	96	38736	96.44
140	0.21	99	2599	99.76
230	0.062	99.7	724	99.93

Table 3.5 obviously shows small difference between HPLC and TOC results. HPLC fites to measure the phenazopyridine Electronic absorption peak, while all the other reaction-intermediats do not apears on the HPLC results while it has no absorption on the studed wavelength. On the outher hand, TOC measures all the organic-origions carbon (phenasopyridine and reaction-intermediats).

Figure 3.10

Electronic absorption spectra confirm full mineralization of phenazopyridine. Different spectra for aliquots of photodegradation reaction mixture measured over time are plotted. Experiments were carried out at 25 ± 1 °C by adding fresh phenazopyridine (50.0 mL, 20 ppm) to the catalyst. The nominal fresh catalyst weight was 0.4 g/ (containing 0.1 g TiO₂).



Figure 3.10 shows the UV-Visible spectra of the phenazopyridine during the reaction. The band concentrated at wavelengths around 430 nm continues to disappear with time. The drop in phenazopyridine concentration with time is observed.

Around wavelength 350 nm, a peak increases with drop in the Phenazopyridine presence, which can be due to appearing NO_2^- or NO_3^- ions, as described earlier [105]. Polarography test shows that for the solution after the reaction ended, no observable NO_3^- within the detection limits.

From the UV-visible spectral results shown in Figure A.27 (appendix A), the NO₂⁻ shows maximum absorption at λ =347 nm, with height 0.45 a.u. This means that the band at 350 nm in Figure 3.10 is either partly or completely due to NO₂⁻. Therefore, more analysis is needed to check that.

Figure A.29 (appendix A) shows HPLC results. The Figure indicates that the NO₂⁻ band in Figure 3.11 is only partly due to NO₂⁻ It also shows only 2.4 ppm for NO₂⁻ ion which is within the WHO, SDWA and BIS limits (10 ppm) for the allowed quantity in the drinking water. Based on HPLC, the band in Figure 3.10 is possibly due to Cl⁻ ions in addition to NO₂⁻ ions. This is because phenazopyridine contains Cl⁻, which may convert to other forms during the oxidation-reduction reactions. Other possible resulting species are ClO₂⁻, which has a maximum absorption at ~350 nm, as shown in Figure A.28 (appendix A).

Chapter Four

Conclusions and Future Research Interests

4.1 Conclusion

Photodegredation of phenazopyridine has been investigated using different catalysts that differ in the synthesis conditions (annealing temperature, cover gas, ..) or in the composition(Rutile, Anatase) supported and unsupported on to the clay surface. With studying two doping methods and making comparison.

Solid state studies showed that there are no inter-layer interactions between the clay and the titanium all along the way. And the anatase start to converted to rutile when the annealing temperature increased. While the effect of granule size is discussed in addition to the surface area.

The TiO2(Rutile)/Clay supported catalyst shows superiority over the other catalysts and was successfully used in phenazopyridine photodegredation under solar light simulation. Furthermore, the optimum conditions were listed (pH, Temperature, quantities effect).

Unlikely, the nitrogen doping for rutile using method I and method II shows lower activity in photodegredation under simulated solar light, especially when supported onto the clay surface. The opposite happens for the anatase, where doping enhance the anatase efficiency. Phosphorescence and XRD study show that the presence of nitrogen affects the band gap and photodegredation studies proved this enhancement. Annealing under nitrogen cover shows acceptable results for the anatase form, while deactivation on the rutile form.

4.2 Furthermore needed studies:

- 1. More crystallographic study is necessary to know effect of doping in crystal structure.
- Studying the photodegredation of the remaining catalysts in addition to TiO2(Rutile)/Clay.
- 3. Study the photocatalytic activity on the natural contaminated water.

4. Study the effect of visible light only, using a cut-off filter, on photodegredation activity for all catalysts.

Abbreviation	Meaning
Phenazopyridine	Phenazopyridine
AOPs	Advanced oxidation processes
CB	Conduction band
eV	Electron volt
Eg	Energy band gap
λ_{EX}	Excitation wavelength
НОМО	Highest Occupied Molecular Orbital
HPLC	High Performance Liquid Chromatography
h^+	Holes
OH•	Hydroxyl radical
М	Molarity
ppm	Part per million
t _R	Retention time
rpm	Round per minute
SEM	Scanning Electron Microscopy
UV-Vis	Ultraviolet-Visible
VB	Valence band
XRD	X-Ray Diffraction

List of Abbreviations

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Appendices

Appendix A

Figures of Study

Figure A.1

The activation energy with and without using catalyst [106]



Figure A.2

*The Rutile structure of TiO*₂ [16].


ball-stick model of two traces of TiO_2 (110). small black balls represent Ti atoms and large white balls represent oxygen atom[18].



Figure A.4

Schematic diagram for hypothetical Fermi level for a semiconductor [107].



Mechanism of electron-hole pair formation, recombination and transport in a semiconductor photocatalyst [108].





Photodegredation mechanism of a pollutant P using TiO_2 nanoparticles.



The structure of clay mineral [89, 98, 109]



Structure of 2:1 clay mineral (montmorillonite) showing two tetrahedral sheets [88]



Structure of 1:1 clay mineral (kaolinite) showing one tetrahedral sheet and one octahedral sheet [88].



Figure A.10

Phenazopyridine Hydrochloride



Reaction setup used in photodegradation experiments.



Figure A.12

X-ray diffraction patterns of for the natural clay sample containing different types crystal structures.



X-ray diffraction patterns of TiO₂ rutile (JCPDS card no. 21-1276).



X-ray diffraction patterns of TiO_2 anatase phase (JCPDS card no. 21-1272).



X-ray diffraction patterns of: A) Rutile. B) Anatase. C) The clay. D) the anatase form when annealed at 950 °C.



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The Scanning Electron Microscope images for all catalyst systems annealed at various temperatures.

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Annealing Temp.	Anatase	Rutile
400° C Fast cooling	SEI. 20KV VID1/2mmSS40 Sample: 2,2700 5µm - Feb.24,2020	TSEL 20kV WD10mmISS40 Somes X1.700 Aure Somes X1.700 Aure
400° C Slow cooling	Served a state of the served as a state of	SEI 20KV WD10mmSS40 k2,700 5µm Sample 0 Feb 24, 2020
500°C Under N ₂ cover	SEI 20kV WD11mm SS40 x2.700 5µm 0 Feb 27, 2020	SEI 20KV WD11mm SS40 Sample 0 Feb 27, 2020



Photo-luminescence spectra for a) commercial anatase, b) nitrogen doped anatase, c) nitrogen doped anatase supported on natural clay and d) anatase supported without doping.



Figure A.18

Photo-luminescence spectra for a) commercial rutile, b) nitrogen doped rutile, c) nitrogen doped rutile supported on natural clay and d) rutile supported without doping.



Thermal gravimetric analysis of TiO₂(Rutile)/Clay.



Plots of $\Delta(pH)$ vs. (pH). Measured for pre-annealed Rutile TiO₂, clay and TiO₂(Rutile)/Clay. Intercepts show pH values of pH_{pzc} for the solids.





The absorption calibration curve for the Phenazopyridine vs. different concentrations in (ppm).

Effect of doping and supporting on the activity of photocatalysts for anatase form. Experiments were carried out for 60 min at 25 ± 1 °C by adding fresh phenazopyridine (50.0 mL, 20 ppm) to the catalyst. The nominal fresh catalyst weight was 0.4 g (containing 0.1 g TiO2).



The pH effect on the photocatalytic activity of different types of anatase catalysts on Phenazopyridine. Experiments were carried out for 60 min at 25 ± 1 °C by adding fresh phenazopyridine (50.0 mL, 20 ppm) to the catalyst. The nominal fresh catalyst weight was 0.4 g (containing 0.1 g TiO2).



Figure A.24

shows the pH effect on the catalyst activity of clay-supported rutile on Phenazopyridine. Experiments were carried out for 60 min at 25 ± 1 °C by adding fresh phenazopyridine (50.0 mL, 20 ppm) to the catalyst. The nominal fresh catalyst weight was 0.4 g (containing 0.1 g TiO₂).



Effect of annealing temperature on the activity of photocatalysts for a) rutile and b) anatase. Experiments were carried out for 60 min at 25 ± 1 °C by adding fresh phenazopyridine (50.0 mL, 20 ppm) to the catalyst. The nominal fresh catalyst weight was 0.4 g (containing 0.1 g TiO2).



Contaminant concentration effect on the photodegredation activity of TiO2(Rutile)/Clay, dark and photodegredation. Experiments were carried out for 60 min at 25 ± 1 °C by adding fresh phenazopyridine (50.0 mL, 10, 20, 30, 40 ppm) to the catalyst. The nominal fresh catalyst weight was 0.4 g (containing 0.1 g TiO2).



UV-visible absorption spectrum measured for fresh 1 ppm NaNO₂ solution.





UV-visible spectra of some chlorine species in aqueous solution.

a) HPLC of the 20 ppm phenazopyridine before photodegredation at $\lambda = 347$ nm. b) HPLC of 1 ppm NaNO2 at $\lambda = 347$ nm. c) HPLC of the 20 ppm phenazopyridine after photodegredation at $\lambda = 347$ nm.









جامعة النجاح الوطنية كلية الدراسات العليا

التحلل الضوئي للملوثات العضوية المتميهة باستخدام جزيئات أكسيد التيتانيوم النانوية المطعمة بالنيتروجين المثبت على الفخار

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قدمت هذه الرسالة استكمالا لمتطلبات الحصول على درجه الماجستير في الكيمياء ، من كلية الدراسات العليا ، في جامعة النجاح الوطنية ، نابلس – فلسطين .

التحلل الضوئي للملوثات العضوية المتميهة باستخدام جزيئات أكسيد التيتانيوم النانوية المطعمة بالنيتروجين المثبت على الفخار

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الملخص

تعتبر عملية التحطيم الضوئي والإمتزاز من أكثر الطرق الحديثة فعالية في تنقية المياه من الملوثات الحيوية والكيميائية. تعتمد عملية التحطيم الضوئي على وجود حفاز (أكسيد التيتانيوم النانوي) الذي بدوره يقوم بامتصاص أشعة الشمس وتحويلها الى طاقة كيميائية لتحطيم الملوثات العضوية (الفينازوبيردين). قام الباحثون بتطوير العديد من التقنيات من أجل الحصول على فعالية جيدة للحفاز تكون مجدية إقتصادياً وعملياً.

في هذا البحث تمت المحاولة لتطعيم حبيبات أوكسيد التيتانيوم بالنيتروجين لتقليل فجوة الطاقة الضوئية اللازمة لتحطيم المركبات العضوية، من أجل استثمار اكبر كمية ممكنة من ضوء الشمس في تحطيم الملوثات العضوية. كذلك تم تثبيت الحفاز على سطح الفخار (الصلصال) لتحسين الإمتزاز على سطح الصلصال تمهيداً للتفاعلات القادمة، وتسهيل عملية استخلاص الحفاز بعد نهاية التفاعل والتخلص من الملوثات العضوية.

ولقد تمت دراسة خواص الحفاز باستخدام المسح المجهري الإلكتروني (SEM) وتمثيل الأشعة السينية (XRD)، بينما تمت دراسة مكونات الصلصال باستخدام تقنية (XRD) plasma/mass spectrometry وتم دراسة النتائج بتقنية تحليل تركيز الكربون الكلي ومطيافية الامتصاص الضوئي في تحليل التراكيز العضوية اضافة الى تقنية الكروماتوغرافيا السائلة عالية الكفاءة (HPLC).

في هذا البحث تم دراسة التحطيم الضوئي لمركب الفينازوبيردين باستخدام أكسيد التيتانيوم النانوي منفرداً مرة ومثبتا على الصلصال مرة أُخرى، كما تم استخدام حبيبات أكسيد التيتانيوم النانوي المطعم والغير مطعم تحت ضوء مضاه لأشعة الشمس. وقد حصل التحطيم الضوئي بواسطة جميع الحفازات المستخدمة في ظروف مختلفة (درجة حرارة الشوي، تأثير تركيز الملوث، تركيز الموث، تركيز الموث، تركيز المافرث، تركيز المافرث، الحفاز، الحفاز، المدة الزمنية، درجة الحرارة، ودرجة الحموضة). وأظهرت النتائج تأثير التطعيم على إزاحة أعلى إمتصاصية من الضوء باتجاه موجات الضوء الأحمر. أما التثبيت على الفخار فقد رفع كفاءة أعلى إمتصاصية من الضوء باتجاه موجات الضوء الأحمر. أما التثبيت على الفخار فقد رفع كفاءة الحفازات بنسب متفاوتة. كما واظهرت النتائج كفاءة عالية لأوكسيد التيتانيوم (Rutile) المثبت على الفخار دون تطعيم، حيث كانت نسبة التحطيم تقارب ال 85% في 60 دقيقة على درجة حرارة 25 درجة مئوية، وبلغت نسبة التحطيم عند استخدام الحفاز المطعم بالنيتروجين والمدعم على الفحار قرارة 25 درجة مئوية، وبلغت نسبة التحطيم عند استخدام الحفاز ملعم بالنيتروجين والمدعم بالصاصيل الموثي، كانت نسبة التحليم تقارب ال 85% في 60 دقيقة على درجة حرارة 25 درجة مئوية، وبلغت نسبة التحطيم عند استخدام الحفاز المطعم بالنيتروجين والمدعم حرارة 25 درجة مئوية، وبلغت نسبة التحليم عند استخدام الحفاز المطعم بالنيتروجين والمدعم حرارة 55 درجة مئوية، وبلغت نسبة التحليم عند استخدام الحفاز المطعم بالنيتروجين والمدعم حرارة 55 درجة مئوية، وبلغت نسبة التحليم عند استخدام الحفاز المطعم بالنيتروجين والمدعم برارة 55 درجة مئوية، وبلغت نسبة التحليم عند استخدام الحفاز المطعم بالنيتروجين والمدعم حرارة 50% من الفرد الحون بنامية الحرارة، التركيز والوقت. بينما كانت 40% عند المغاز الحفاز الحفرة والوليت. بينما كانت 40% عند المزوين والمدعم برانون والماضات.

تم أيضا دراسة كفاءة الحفاز المثبت بعد استخدامه في عملية التحطيم وقد لوحظ أن الحفاز لم يظهر أي نقصان ملحوظ في كفاءته حتى بعد استخدامه عدة مرات في المعالجة.

افضل النتائج كانت لأوكسيد التيتانيوم (Rutile) المثبت على الفخار دون تطعيم. وتكمن اهميته في كونه رخيص ومتاح بالإضافة الى كونه غير سام. تثبيت أوكسيد التيتانيوم (Rutile) على الفخار سهل عملية استرجاعه لأن حجم الحفاز كبير نسبيا. تكمن اهمية الحفاز العملية في سهولة استرجاعه وامكانية العمل بكفاءة عالية تحت اشعة الشمس دون الحاجة لأطوال موجية فوق بنفسجية.

الكلمات المفتاحية: التحطم الضوئي، اكسيد التيتانيوم، مُطَعم بالنيتروجين، الماسح المجهري الإلكتروني (SEM) وتمثيل الأشعة السينية (XRD).

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