SYNTHESIS OF CHITOSAN AND TITANIUM DIOXIDE BASED PLASMONIC CATALYSTS FOR THE CATALYTIC REDUCTION OF PHENOLIC COMPOUNDS

FENOLİK BİLEŞİKLERİN KATALİTİK OLARAK İNDİRGENMESİNDE KULLANILMAK ÜZERE KİTOSAN VE TİTANYUM DİOKSİT DESTEKLİ PLAZMONİK KATALİZÖR SENTEZİ

GÖKÇE ERDEM
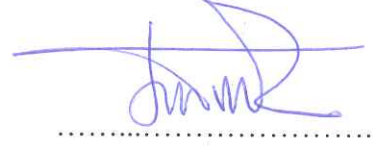
PROF.DR. HÜLYA YAVUZ ERSAN

Supervisor

Submitted to Graduate School of Science and Engineering of
Hacettepe University as a Partial Fulfillment to the Requirements for the
Award of the Degree of Master of Science in Chemical Engineering

2017

This work named "**Synthesis of Chitosan and Titanium Dioxide Based Plasmonic Catalysts for The Catalytic Reduction of Phenolic Compounds**" by **GÖKÇE ERDEM** has been approved as a thesis for the Degree of **MASTER OF SCIENCE IN CHEMICAL ENGINEERING** by the below mentioned Examining Committee Members.
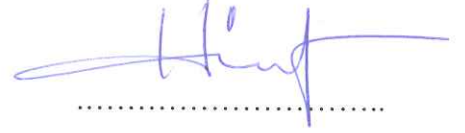
Prof. Dr. S. Ali TUNCEL
Head

Prof. Dr. Hülya YAVUZ ERSAN
Supervisor

Doç. Dr. İsmail Cengiz KOÇUM
Member

This thesis has been approved as a thesis for the Degree of **MASTER OF SCIENCE IN CHEMICAL ENGINEERING** by Board of Directors of the Institute for Graduate School of Science and Engineering.

Prof. Dr. Menemşe GÜMÜŞDERELİOĞLU
Director of the Institute of Graduate School
of Science and Engineering

'Science is the most reliable guide in life.'

Mustafa Kemal ATATÜRK

To my beloved parents, my brother and my uncle whose supportive hands I have felt on my shoulders all through my life…

ETHICS

In this thesis study, prepared in accordance with the spelling rules of Institute of Graduate Studies in Science of Hacettepe University,

I declare that

- all the information and documents have been obtained in the base of the academic rules
- all audio-visual and written information and results have been presented according to the rules of scientific ethics
- in case of using other Works, related studies have been cited in accordance with the scientific standards
- all cited studies have been fully referenced
- I did not do any distortion in the data set
- and any part of this thesis has not been presented as another thesis study at this or any other university.

18/01/2017

GÖKÇE ERDEM

ABSTRACT

SYNTHESIS OF CHITOSAN AND TITANIUM DIOXIDE BASED PLASMONIC CATALYSTS FOR THE DEGRADATION OF PHENOLIC COMPOUNDS

Gökçe ERDEM

Master of Science, Department of Chemical Engineering
Supervisor: Prof. Dr. Hülya YAVUZ ERSAN
January 2017, 72 pages

The purpose of this thesis is the fabrication and performance evaluation of new catalysts which enable the elimination of toxic pollutants such as 4-Nitrophenol (4-NP) by means of heterogeneous catalytic reduction in an aqueous environment. Production of two different catalysts was achieved by the immobilization of the plasmonic gold nanoparticles (AuNP) into the chitosan and titanium dioxide support materials, respectively. The plasmonic catalytic activities of fabricated catalysts were evaluated within the reduction of 4-Nitrophenol in the presence of sodium borohydride ($NaBH_4$) as a reducing agent. The effects of type of support material and size of nanoparticle as performance enhancing parameter, loading amount of nanoparticle, catalyst amount and initial 4-Nitrophenol concentration as operational parameters are evaluated in batch fashion.

In line with this purpose, firstly the support materials were synthesized. Chitosan microgel beads were obtained by the chemical modification of chitosan solution. The monodisperse chitosan microgel beads, 3 mm in size with the specific surface area of 1.3 m^2/g, were synthesized by crosslinking reaction in which glutaraldehyde served as a cross-linker. Titanium dioxide (TiO_2) spheres as second support material, were obtained by one-step sol-gel method. TiO_2 spheres in the size range of 0.7-1.2 μm with the specific surface area 277.4 m^2/g were synthesized along with the hydrolysis of titania precursor, titanium

isopropoxide in a continuous medium including methanol and acetonitrile. TiO_2 spheres were derivatized with Aminopropyltriethoxysilane (APTES), that enables TiO_2 to adsorb gold atoms through the amine groups on its surface. In the next stage, the support materials were added into the solutions of gold nanoparticles that have been synthesized with Turkevich (12 nm) and Martin (3 nm) Methods, respectively. The bare, Turkevich AuNP decorated and Martin AuNP decorated support materials were characterized by energy-dispersive x-ray spectroscopy, scanning electron microscopy, transmission electron microscopy, x-ray diffaraction spectrophotometry and surface area analysis via nitrogen adsorption- desorption method.

The gold nanoparticle decorated chitosan microgel beads and TiO_2 spheres were used in the reduction of 4-Nitrophenol, individually. The decoration with Martin AuNPs with lower size resulted in a significant enhancement in the plasmonic catalytic reduction rate owing to the electron transfer characteristics of AuNPs with lower size. The complete reduction of 4-Nitrophenol having initial concentration of 7.5 ppm was achieved within 12 minutes in the presence of 10 mg Martin AuNP decorated chitosan microgel beads as catalyst (%2.5 (%w/w) AuNP loading). On the other hand, the complete reduction of 4-Nitrophenol having initial concentration of 7.5 ppm was achieved within 60 seconds in the presence of 12.5 mg Martin AuNP decorated TiO_2 spheres as catalyst (%2 (%w/w) AuNP loading). The recovery and reusability studies, conducted under the same experimental conditions, indicated that the catalysts are reusable for reduction of 4-Nitrophenol.

In the plasmonic catalytic reduction of 4-Nitrophenol via Au/chitosan and Au/TiO_2 catalysts, higher catalytic activities were obtained when compared to the other treatment methods, introduced in literature, involving catalysts supported with similar forms of different materials or different forms of similar materials. In this thesis, for the first time, Au/chitosan catalyst in the microgel bead form and Au/TiO_2 catalyst in sphere form having novel structures and sizes were synthesized via simple, cost-effective, energy and time saving and environmentally friendly methods. Moreover, this study introduces biodegradable, porous, low-cost, mechanically stable catalysts that are able to form strong interaction with metal nanoparticles to the catalytic applications in favor of high catalytic activities.

ÖZET

FENOLİK BİLEŞİKLERİN DEGRADASYONUNDA KULLANILMAK ÜZERE KİTOSAN VE TİTANYUM DİOKSİT DESTEKLİ PLAZMONİK KATALİZÖR SENTEZİ

Gökçe ERDEM

Yüksek Lisans, Kimya Mühendisliği Bölümü

Tez Danışmanı: Prof. Dr. Hülya YAVUZ ERSAN

Ocak 2017, 72 sayfa

Bu tez kapsamında, atık sularda sıklıkla rastlanan toksik fenolik bileşiklerden 4-Nitrofenolün sulu ortamda katalitik indirgenme yoluyla giderimi için uygun 2 yeni heterojen plazmonik katalizör sisteminin geliştirilmesi ve bu sistemlerin katalitik performansının belirlenmesi amaçlanmıştır. Heterojen katalizörlerin üretiminin, plazmonik altın nanopartiküllerin (AuNP), son yıllarda önem kazanmış ve gelecek vaadeden kitosan ve titanyum dioksit destek maddelerine immobilizasyonu ile gerçekleştirilmesi hedeflenmiştir. Katalizörlerin katalitik aktiviteleri 4-Nitrofenolün indirgeme ajanı olan $NaBH_4$ varlığında indirgenmesi sırasında değerlendirilmiştir. Bu deneylerde, destek madde-metal nanopartikül etkileşiminin, AuNP boyutunun, AuNP yükleme miktarının, katalizör miktarının ve başlangıç 4-Nitrofenol başlangıç konsantrasyonun katalitik aktiviteye etkisi kesikli sistemde belirlenmiştir.

Bu amaç doğrultusunda ilk olarak katalizör destek maddeleri üretilmiştir. Mikrojel formundaki kitosan tanecikler, kitosan çözeltisinin kimyasal modifikasyonuyla meydana gelmiştir. Glutaraldehitin çapraz bağlayıcı olarak kullanıldığı çapraz bağlama işleminin sonucunda 3 mm çapında, eş boyutlu, 1.3 m^2/g yüzey alanına sahip kitosan tanecikler elde edilmiştir. Diğer bir katalizör destek maddesi olan TiO_2 küreler ise tek aşamalı sol-jel yöntemiyle üretilmiştir. Küreler, titanyum isopropoksit prekürsörünün, methanol ve

asetonitrilden oluşan çözücü ortamında hidrolizi ile elde edilmiştir. İşlem sonucunda, 0.7-1.2 μm boyut aralığında, 277.4 m^2/g yüzey alanına sahip küreler sentezlenmiştir. Küreler, yapısına altın nanopartiküllerin bağlanabilmesi için Aminopropiltrietoksisilan (APTES) ile muamele edilmiş ve yapısına fonksiyonel amin grubu eklenmiştir. Katalizör destek maddeleri, Turkevich ve Martin metotlarıyla sentezlenen, sırasıyla 12 ve 3 nm boyutlarına sahip altın nanopartiküllerinin çözeltilerine ayrı ayrı eklenmiş ve bu nanopartiküllerle dekore edilmişlerdir. Altın nanopartiküllerle dekore edilmiş ve edilmemiş kitosan mikrojel tanecikler ve TiO_2 küreler taramalı elektron mikroskobu, geçirimli elektron mikroskobu, X-ışını kırınım spektrofotometresi, EDX ve azot adsorpsiyon-desorpsiyon yöntemiyle yüzey alanı analizi ile karakterize edilmişlerdir.

Heterojen katalizörler 4-Nitrofenolün katalitik indirgenmesi işleminde kullanılmışlardır. Küçük altın nanopartiküllerin elektron transfer karakteristiklerinden dolayı, Martin AuNP ile dekore edilmiş kitosan mikrojel taneciklerin ve TiO_2 kürelerin Turkevich AuNP ler ile dekore edilenlerle kıyaslandığında plazmonik katalitik aktivitede önemli bir gelişime yol açtığı gözlenmiştir. 2.5 % (w/w %) Martin AuNp yükleme miktarına sahip 10 mg Au/Kitosan katalizörün, 7.5 ppm başlangıç konsantrasyonuna sahip 4-Nitrofenolü 12 dakika sonunda tamamen indirgediği gözlenmiştir. %2 Martin AuNp yükleme miktarına sahip 12.5 mg Au/TiO_2 katalizörün ise 7.5 ppm başlangıç konsantrasyonuna sahip 4-Nitrofenolü 60 saniye sonunda tamamen indirgediği gözlenmiştir. Katalizörlerin geri kazanımının ve aynı reaksiyon şartlarında tekrar kullanılmasının mümkün olduğu gözlenmiştir.

Literatürde önerilen benzer maddelerin farklı formlarını veya farklı maddelerin benzer formlarını içeren heterojen katalizörlerin kullanıldığı giderilme yöntemleriyle karşılaştırıldığında, 4-Nitrofenol bertarafının, üretilen Au/Kitosan ve Au/TiO_2 katalizörlerin varlığında yürütülen katalitik indirgeme yöntemiyle daha hızlı ve daha yüksek verimle gerçekleştiği belirlenmiştir. Bu çalışmayla, ilk kez, basit üretim yöntemleriyle ve kısa zamanda, enerji tasarruflu, biyouyumlu, yüksek katalitik aktiviteye sahip mikrojel tanecik formunda Au/kitosan ve özgün boyut ve yapıya sahip küre formunda Au/TiO_2 üretilmiştir. Mekanik dayanımı yüksek, yüksek metal etkileşim kapasitesine sahip destek maddelerine yeni bir kullanım alanı kazandırılmıştır.

Anahtar Kelimeler: Atıksu Arıtımı, 4-Nitrofenol, Plazmonik Katalizleme, Altın Nanopartikül, Kitosan Mikrojel Tanecikler, Titanyum Küreler

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

SYMBOLS AND ABBREVIATIONS

Symbols

C_v	Coefficient of variation
pKA	Logaritmic acid dissociation constant

Abbrevations

AOP(s)	Advanced Oxidation Process(es)
4-AP/PAP	4-Aminophenol/ para-Aminophenol
APTES	Aminopropyltriethoxysilane
Au	Gold
AuNP(s)	Gold Nanoparticle(s)
BET	Brauner-Emmett-Teller
CTAB	Hexadecyltrimethylammonium bromide
DD	Degree of deacetlyation
DDI	Distilled deionized water
DP	Degree of polymerization
EPA	Environmental Protection Agency
EU	European Union
GA	Glutaraldehyde
$HAuCl_4$	Auric chloride
HCl	Hydrochloric acid
IsOH	Isopropanol
$NaBH_4$	Sodiumborohydride
NaOH	Sodium hydroxide
4-NP/PNP	4-Nitrophenol/ para-Nitrophenol
SEM	Scanning Electron Microscope
SSA	Specific Surface Area
TEA	Triethylamine
TEM	Transmission Electron Microscope
TIP	Titanium isopropoxide

TiO$_2$	Titanium dioxide
UV	Ultraviolet-visible
WHO	World Health Organization

1. INTRODUCTION

4-Nitrophenol, used in the production of pesticides, insecticides, dyestuff, pharmaceuticals, explosives, plasticizers, is one of the most abundant hazardous organic pollutants in industrial wastewaters. 4-NP is placed among the prior toxic pollutants for being toxic and for threatening living-beings even at low concentrations. It is persistent and non-degradable in nature due to the high electron affinity of $-NO_3$ group in its structure [1]. Therefore, the traditional wastewater treatment methods remain incapable in the elimination of 4-NP. In recent years, advanced oxidation processes and catalytic reduction processes have come to the fore for providing rapid, controlled and efficient conversion, preventing the formation of toxic intermediates. Plasmon-enhanced catalytic reduction process is based on the reduction of 4-Nitrophenol to 4-Aminophenol (4-AP) by an excess amount of sodium borohydride ($NaBH_4$) and plasmonic metal nanoparticles that serve as reducing agent and heterogeneous catalyst, respectively. BH_4^- and 4-NP molecules are transferred to the heterogeneous catalyst through diffusion, followed by the adsorption and reaction of ions on the surface of AuNPs [2]. The reduction product, 4-AP is a byproduct in the production of paracetamol. 4-NP that involves $-NH_2$ group in its structure, is 500-fold less toxic than its corresponding nitroaromatic, 4-NP [3].

Gold nanoparticles (AuNPs), amongst all other metal catalysts such as Ag, Cu, Ni, Pd, Pt, become prominent for being chemically inert and stable, exhibiting size-dependent unique properties, being highly active under temperate conditions, at ambient temperature as well. But still, naked AuNPs usually suffer from serious agglomeration, leading to the rapid decay of catalytic activity and the poor durability of the catalyst. Hence, in order to stabilize AuNPs, to improve catalytic performance, to reduce production costs and to make them easily recoverable and reusable, gold may be alloyed with other metals to give it special properties [4]. The size of catalytically active particles and the choice of appropriate stabilizer are two main challenges in the fabrication of supported catalysts in concern with its metal affinity and surface area.

TiO_2 is one of the favourable candidates as a support for metal nanoparticles in heterogeous catalysis based upon its strong interaction with metal support, chemical and thermal stability, mechanical resistance and non-toxic, non-corrosive nature amongst all other metal oxide support materials [5]. In heterogeneous catalysis, the metal-oxide based catalysts are usually produced in the form of extremely small particles in the nanometer

range. The reason of this is to obtain higher surface areas in order to interact with higher amount of metal nanoparticles. However, the particles in nanometer scale are not stable enough and tend to agglomerate.

Chitosan, a polycationic polysaccharide, is favoured due to the high adsorption capacity, high biodegradability and biocompatibility. Chitosan does not need additional chemicals to be derivatized owing to the naturally occurred functional amine and carboxyl groups in its structure. These functional groups enable chitosan to interact with active catalysts [6] and to be synthesized in several physical forms such as resins, membranes, microspheres, fibers and hydrogels by chemical modifications. The choice of specific physical form is related mainly with on the system requirement to be used for specific applications. Bead form of chitosan has been proved to be a promising adsorbent due to to the high chelating ability with metals. Microgel bead form of chitosan functions as a matrix and prevents the dispersion of nano-sized gold particles. The mechanically stable beads may prevent the dispersion of catalyst nanoparticles since they serve as a porous scaffold. The applications of microgel bead form of chitosan as a support material in the catalytic processes, especially in the elimination of 4-nitrophenol in terms of the plasmon-enhanced catalytic reduction are lacking.

The supported catalysts are fabricated by simple mixing of polymer beads and metal-oxide spheres with nanoparticles, individually. The gold nanoparticle decorated chitosan microgel beads and TiO_2 spheres are used in the reduction of 4-Nitrophenol. In the light of above given information, the scope of our study is determined as the treatment of 4-Nitrophenol containing wastewaters by a promising, cost-effective and advanced method that does not lead up to the production of by-products in the presence of novel biopolymer based and non-toxic metal-oxide based catalyst systems.

2. LITERATURE REVIEW

2.1. Wastewater and Common Pollutants

Water is an essential element in the maintenance of all forms of life. It is the one and only substance that supplies energy without being exposed to a structural change. Water has a great impact on the reproduction, growth and development of living organisms, establishment of relationship between nature and society, formation of natural conditions and ecological balance, generation of nutritional sources and various raw materials by technological developments, economic relations between nation [7]. Water exists in all regions of the earth. Seas and oceans are the most voluminous source by covering the 97 percent of worldwide water resources. However, salt water should be exposed to desalination process to some extent depending on the purpose of usage. Groundwater formed from spring water and surface water formed from lakes, rivers, streams, reservoirs are the renewable freshwater resources of our planet that only cover the 3 percent of worldwide water resources [8]. After the years of negligence of necessity for water storage, treatment and distribution systems, human nation has to take up the challenge of preserving the quality and quantity of these resources.

The world's population is estimated to reach up to 9.7 billion in 2050. This growth is the addition of the world population growth over this period to the net moves from the current rural population [9]. As the populations throughout the world multiply at an alarming rate, contributes to urbanization, soil erosion by irrigation and deforestation and the increasing amount of facilities in order to produce the basic necessities of individuals, the existing surface and ground water and land resources remain incapable of satisfying the water demand. On the top of this situation, inadequate collection and treatment, direct or indirect disposal of municipal effluents from these facilities without considering waste water quality criteria, result in the destruction of structure of the limited freshwater resources, thus ecosystems. Another source of pollution is the atmospheric deposition of runoff that moves over and through the ground. The snow water, rain water, cloud and fog droplets may contain organic compounds as a result of condensation of direct emissions. Besides, the runoff picks up and drags away human-made and natural pollutants as it moves, eventually entering to rivers, coastal and ground waters, wetlands and lakes [1].

Municipal wastewater is the water that is anthropogenically affected in quality and originated from industrial, agricultural, domestic facilities and urban runoff. It causes

physical, biological, chemical pollution when disposed to the water bodies. Domestic effluents are the combination of wastewaters from washing machines, laundries, food residues, flush toilettes that can possibly cause the formation of pathogenic microorganisms. The most important pollutants in agricultural runoff are wastes that appear after industrial processing of agricultural products. They involve sediment, inorganic salts and minerals, plant nutrients, forest and crop residues, animal wastes, pesticides and insecticides, fertilizers that cause eutrophication, i.e. vanishing of water life which needs oxygen for survival. There is a pressure over water bodies based on the negative influence of wastewater discharges generated by manufacturing industry. Waste volumes vary depending on the quality and quantity of product produced. Although small quantities of water are consumed in industrial processing, large volumes are usually returned as waste. These wastes may include heavy metals, persistent and/or toxic organic matters, chemicals, oxygen consuming biological contaminants, radioactive materials, high or low concentrations of coloured matters, odorants [10]. Urban wastewater poses a particularly serious threat when combined with untreated industrial wastes. Across the world, the total amount of sewage, agricultural and industrial wastewaters discharged into the waterways reaches to 2 million tonnes every year. Treated urban sewage is largely limited to high income countries, while in developing countries about 90% of sewage is discharged without any treatment [9].

All surface waters should be in adequate quality to support aquatic life. The main objective of wastewater treatment is to minimize the level of toxic contaminants discharged into the water bodies to an insignificant level in which their negative impact to surroundings is excluded and to provide reuse of effluents without endangering health and environment. Industries that generate a large volume of high strength wastewater cause an overloading on the municipal treatment plants. In order to overcome this issue, urban wastewaters and industrial wastewaters should be exposed to a pre-treatment separately for the reduction of the amounts to discharge limits imposed by directives [11].

Industrial contamination tends to be more concentrated, more toxic and harder to treat than other pollutants. The degradation and rate of movement of these contaminants through the environment and hydrological cycle takes a long time for their persistant nature. The effluents discharged from manufacturing plants as a result of large scale industrial processes and enter water bodies, are the major sources of organic, synthetic organic and inorganic pollution. Numerous organic chemicals, several inorganic ions,

mostly the heavy metals are classified as toxic water pollutants. If a substance is environmentally hazardous and exists in polluted water, then it is qualified as a prior toxin [8]. Toxicity is related to either acute or chronic effects of a substance on organisms by bioaccumulation. Persistence and treatability are also important factors.

The majority of the pollutants that are mentioned in The List of Toxic Pollutants by US EPA [12] can be categorized into 10 groups: *Halogenated aliphatics* are used in refrigerants, pesticides and solvents. *Monocyclic aromatics* are used in production of chemicals, fungicides and herbicides, explosives and dyes. These compounds damage the liver and kidneys for them being central nervous system depressants. *Ethers* are solvents for polymer plastics. *Nitrosamines* are strong carcinogens and are used in manufacturing of organic chemicals and rubber. *Phatalate esters* are used in the production of polyvinylchloride and thermoplastics. *Polycyclic aromatic hydrocarbons* are included in pesticides, herbicides and petroleum products. Applications of these products are restricted by the EPA. *Polychlorinated biphenyls* had been used in paints, insecticides, electric capacitors, transformers, plastics and insecticides until they were banned from production in 1979. The toxicity levels of *heavy metals* vary and some are subjected to biomagnification. *Phenolics* are industrial compounds used basically in production of pigments, pesticides and fungicides, synthetic polymers [8].

Phenolics are compounds consisting of one or more aromatic rings with one or more hydroxyl groups. Phenolics are the manufactured forms of weakly acidic, water-soluble chemical compounds. The derivatives are formed by the attachment of chloro-, nitro-, methyl and alkyl groups to aromatic ring of phenol. A substantial amount of phenolics is found in the effluents of pulp and paper manufacturing plants, coke and resin manufacturing, oil refineries, dyestuffs, textile, steel, petrochemicals, explosives, rubber, pesticides, pharmaceutical industries, while some are synthesized during natural processes within the species. Reduced blood pressure, liver and kidney damages, cardiac toxicity and cardiac depression are the reported impacts in humans that are seriously exposed to phenol by the oral route. Even low concentrations of phenolics are persistent in nature and lethal for humans. Due to these negative health effects of phenolics, World Health Organization (WHO) has set a limit in microgram levels in order to regulate the concentration of phenol in surface water resources [13]. Therefore, it is vital to eliminate these pollutants from industrial effluents before the discharge to water bodies.
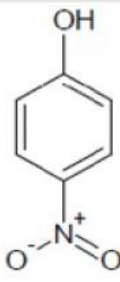
2.2. Nitrophenolic Compounds

Nitrophenolic compounds form one of the most common and significant group of organic industrial chemicals. The main reaction used in order to synthesize nitroaromatic compounds is nitration. This reaction occurs between sulfuric acids and nitric acids and results in the generation of nitronium ions. As a consequence, simplest forms of nitrophenols are produced by the conversion of phenol. These compounds are composed of at least one nitro group on the aromatic ring. As the amount of functional groups attached to a benzene ring increases, stability and persistence of nitrophenols increase as well. The nitrophenols mainly perform as starting compounds in the synthesis of insecticides, herbicides and fungicides. Nitrophenols can also form naturally in atmospheric and aqueous environments. The emissions resulting from incomplete combustion of fossil fuels, atmospheric nitrogen dioxide serve as reactants for nitration. The hydroxyl radicals formed by solar radiation of dissolved nitrates and nitrites in water may catalyse the nitration and halogenation reactions of anthropogenic or naturally occurring organic compounds [14].

2.2.1. Properties and Sources of 4-Nitrophenol

Mononitrophenols exist in three isomeric forms. Amongst them p-nitrophenol (PNP) also called as 4-Nitrophenol (4-NP) forms by the attachment of a nitro group to a hydroxyl group on the aromatic ring from opposite (para) position. 4-NP, a crystalline solid, has a slight odor when dissolved in water. 4-Nitrophenol solution appears to be in pale yellow color, while its phenolic salts appear to be in bright yellow color. It takes place in the manufacturing of paracetamol as an intermediate, in the manufacturing of a highly toxic insecticide, parathion and in the chemical analysis as a pH indicator. It also serves as leather tanning agent, fungicide and pesticide. However, the same properties that make 4-NP preferable in these applications also make them the member of The List of Priority Pollutants by the EPA [12] since 1976 due to its noxious influence. They are persistent against biotic decomposition and conventional chemical treatment methods. They have have cumulative effect and acute toxicity, because of the histopathological changes and mutagenesis toward humans and other living organisms [15, 16].

Table 2.1. Physical and chemical properties of 4-Nitrophenol

Chemical Name	4-Nitrophenol p-nitrophenol 4-Hydroxynitrobenzene
Chemical Formula	$C_6H_5NO_3$
Chemical Structure	
CAS Number	100-02-7
Molecular Weight	139.11 g/mol
Color	Light yellow
Physical State	Crystalline solid

Melting Point	113-114 oC
Boiling Point	297 oC
Density	1.27 g/cc at 20 oC
Odor	Slight odor
Odor Treshold	Water : 2.5 mg/L Air : 2.3 mg/m3
Solubility	Distilled water : 16,000 mg/L at 25 oC Sea water : 10,795 mg/L at 20 oC Organic Solvents : Soluble in toluene, ethanol, chloroform, ethyl ether, alkali hydroxides
Vapor Pressure	0.0003 at 30 oC
Autoignition Temperature	283 oC

In Turkey, the release and quality standards of phenolic compounds are specified within the total phenolic compound disposals and their absolute values are not accessible to the public. Akbal *et al*. investigated the surface water quality by collecting samples from 10 rivers that fed Mid-Black Sea coast of Turkey. 0.18 mgL^{-1} of total phenol was detected as an average concentration [17]. Loos *et al.* carried out a study in order to analyse 35 selected polar organic contaminants in 122 water samples from rivers of 27 European countries. The results indicated that the 4-Nitrophenol was one of the most prevalent compounds found in the rivers with a frequency of detection of 97%, a maximum concentration of 3471 ngL^{-1} [18]. Wennrich *et al.* investigated 11 nitrophenols in samples that were taken from groundwater in the vicinity of former ammunitions plant in Germany. 4-NP was found to be the second most abundant nitrophenol with a concentration of 88 μgL^{-1} [19]. The limit value for 4-NP in surface water, near industrial and urban areas, was limited to 100 ngL^{-1} in Environmental Quality Standards Directive by European Commission in 2006 [20]. These studies draw attention to the necessity for the large scale evaluation on the environmental risks and for the advanced treatment methods especially for the agricultural and industrial effluents.
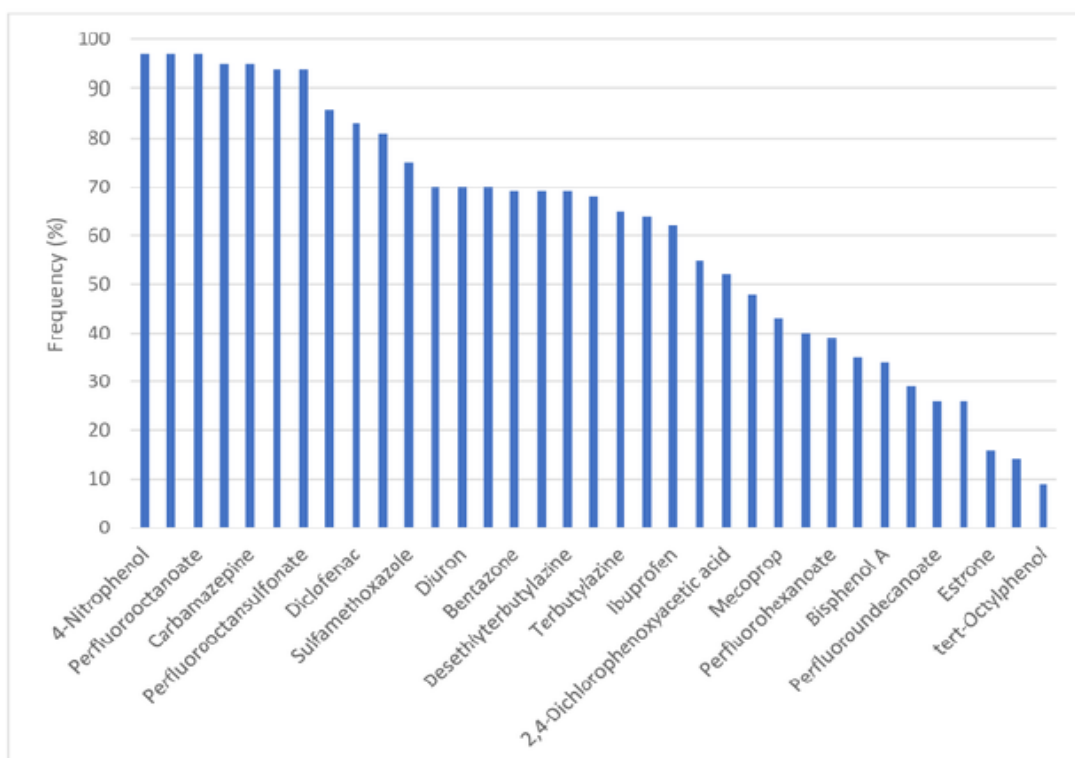
Figure 2.1. Frequency of appearance of the contaminants in the samples of European Rivers [18]

2.2.2. Toxicological Profile of 4-Nitrophenol

4-Nitrophenol is the most examined component above all mononitrophenols in terms of their frequencies of appearance in soil and water resources, releases to air and health effects. Living organisms may be exposed to toxic chemicals by inhalation, oral and dermal ways. Although 4-NP was not found to be carcinogenic, mutagenic or teratogenic, it threatens the aquatic and terrestrial life as a result of its extensive use as agricultural chemicals. Although there is no decisive information about effects of 4-NP on humans, it causes injuries in blood cells, damage in the central nervous systems of rats. EPA stated that 4-NP is a clastogen for mammalian cells, not mutagenic in these cells [21]. Genotoxic assessment by Eichenbaum *et al.* revealed that 4-NP concentration of 750 μgL^{-1} causes chromosome aberrations in Chinese hamster ovary cells [22]. Chronic administration of 4-NP to mammals caused pathological changes. The limiting dose was established as 0.0025 mgL^{-1} for the collapse of conditioned reflex activity. The acute values for 4-Nitrophenol exposure is given as 4200 μgL^{-1} for fishes. The concentration should not exceed 550 μgL^{-1}/ day for the protection of freshwater aquatic life. The known effects of 4-Nitrophenol that were demonstrated through experiments on animals are methemoglobinemia, difficulty in breathing and progressive depression. 4-Nitrophenol may be found in human urine as a consequence of the breakdown of a pesticide, parathion, which is used frequently used in some agricultural products. People who obtain and consume water near irrigated areas or industrial sites may also be subjected to higher levels than limiting levels of 4-Nitrophenol owing to the intensive use of pesticides [23].

2.2.3. Treatment Methods of 4-Nitrophenol

The choice of a treatment process is evaluated by considering the quality of the wastewater effluents, size-time-efficiency of application, consumption of energy and chemicals. The recent advances introduced in literature for 4-NP removal involve separation processes and catalytic conversion processes. In the case of conversion, there are several convenient treatment methods, mainly as oxidation and hydrogenation reactions resulted in complete degradation or reduction of contaminants to several non-hazardous intermediates.

The most frequently studied separation processes of 4-NP from wastewater are adsorption [24] and micro-extraction. *Adsorption process* is commonly used in the purification of diluted wastewaters based on its favourable properties such as cost-

effectiveness, removal efficiencies in higher concentration ranges and ease of operation [25]. The adsorbents that have been introduced for the separation of 4-NP are activated carbons, fly ash, alginate, graphene oxide, activated natural zeolites, silicates, resins of the amberlite family (e.g. XAD-4), ion exchangers, cross-linked polymeric adsorbents. Adsorption via activated carbon has drawn considerable attention amongst others for having higher adsorption capacities for 4-NP [26]. Since the regeneration of activated carbon based adsorbents poses a problem, several regeneration techniques were improved such as hot water regeneration. However, they were found to be time and energy consuming, thus expensive [27]. Therefore, following the adsorption process, the fate of saturated adsorbent bed is to be removed by burning in furnaces.

Solvent extraction process is based on the principle of the separation of 4-NP from effluents by dissolving it in another solvent due to its relative solubility in two different immiscible liquids. Several hydrocarbons and oxygenated compounds such as benzene, toluene, acetate esters, cyclohexane, ethylbenzene serve as an extracting agent in the process. The major drawbacks of the process are the requirement of large volumes of poisonous disperse solvents [28], incomplete treatment of pollutant and thus necessity for secondary treatment [27]. Moreover, only the effluents having lower flow rates can be processed in extraction columns and exposed to many stages in order to enhance the efficiency. Despite these two conventional separation approaches can offer high removal efficiencies by transferring compounds from a diluted to a concentrated stream, they could not provide an influential degradation of the compounds and cause secondary pollution [29].

Catalytic wet air oxidation process (CWAO) provides reduction or complete oxidation of organic contaminants to innoxious inorganic compounds such as dissolved ions, CO_2, H_2O, typically under oxygen partial pressure in a range of 5-25 bar and at temperature in a range of 80-300°C and in the absence or presence of a homogenous [30] or heterogeneous catalyst [31]. Most of the catalysts, introduced for the removal of phenolics by this method, are solid materials including noble metals as Ru, Rh, Pt, which have relatively better catalytic activity, or cations of transition metals as Fe, Cu, Mn, Co, which are relatively less expensive [32]. Levec *et al.* drew attention to the importance of incorporation of catalytically active metals into a lattice of a support material such as TiO_2, CeO_2 and ZrO_2 in order to reduce leaching and corrosion effect, to achieve stability under reaction conditions and provide reusability without a loss in activity [33]. The number of

studies concerning 4-NP degradation by CWAO increased within a decade. Amongst them Stüber *et al.* achieved better degradation efficiency, 75% over Fe/activated carbon catalyst by increasing oxygen pressure to 9 bar and temperature to 140°C [34]. However, the air oxidation technologies provided rapid oxidation, they were found to be expensive because of the necessity of high temperature, pressure and significant amount of power in order to pressurize the oxidizer [35].

Advance oxidation processes (AOP) are described as the processes in which the OH$^-$ radicals are generated in adequate amounts through the oxidation of the complex chemicals in the presence of hydrogen peroxide (H_2O_2), ozone and/or UV light and ultrasound. *Heterogeneous Fenton oxidation* is an AOP in which the ferrous salts (Fe^{2+}) generate strong oxidizing agents for 4-NP together with hydrogen peroxide is qualified. This method is attractive for employing cheap and non-toxic active catalysts, for decomposing chemicals rapidly and for eliminating mass transfer limitation [16]. However, the requirement of acidic conditions for higher efficiencies constitutes acidic sludge that causes disposal problems. Zhang *et al.* reported that removal rate of 4-NP increases with the increasing H_2O_2 dosage [36]. Unfortunately, hydrogen peroxide qualified as corrosive and harmful in Dangerous Substances Directive (67/548/EEC) by EU. *Photocatalysis* method is based on the ability of a semiconductor in creating electron-hole pairs under the UV irradiation and in generating hydroxyl radicals that are able to undergo secondary reactions [27]. As an inexpensive and non-toxic photocatalyst, TiO_2 is resistant to photo-corrosion and has high oxidative power. In order to enhance the efficiencies obtained for photocatalytic degradation of 4-NP, certain surface modification methods such as noble metal deposition, ion doping and surface sensitization by organic ligands, coupling agents and surfactants have been applied to TiO_2 [37]. Unfortunately photocatalysis of 4-NP faced economic inefficiencies arose from the usage of expensive unit process and continuous UV irradiation [38].

Electrochemical oxidation of pollutants is a promising method due to the treatment of industrial effluents without secondary pollution generation and additional chemicals requirement. It uses clean electron and operates at mild operational conditions [38]. The degradation efficiencies and performances are directly related to the electrode material. High operating cost can be reduced with suitable anode material selection [27]. Pt, SnO_2, TiO_2, IrO_2, PbO_2, diamond electrodes and dimensionally stable anodes are commonly employed electrode materials in electrochemical oxidation of 4-NP. 4-NP is conversed into

organic acids by high oxygen over potential boron-doped diamond (BDD) anodes. The studies that compared the activities of BDD and other electrodes indicated that the total organic carbon minimization, 4-NP removal efficiency and chemical oxygen demand were higher via BDD [39]. However, the industrial applications of BDD are limited owing to its high energy consumption, cost and limited technology for the fabrication of BDD in industrial size.

Oxidative biological degradation studies include mineralization and biotransformation of 4-Nitrophenol by pure or mixed cultures of microorganisms under aerobic and anaerobic conditions [40, 41]. In the process of mineralization, isolated bacterial strains use 4-NP as their only carbon and energy source by transforming them into inorganic compounds, CO_2, methane and water. These methods may be preferred for having low investment and operation costs. Although 4-NP can be decomposed by many biological treatment processes, all of these methods are suffering from the sensitivity of microorganisms to pH and temperature. Salehi *et al.* reduced the long degradation periods to 150 minutes by using mixed cultures in a slurry bubble column [41]. However, the most of the cultures have capability of degrading 4-NP only at low concentrations because the high concentrations of 4-NP is toxic and growth rate inhibiting to most of the microorganisms [27]. Although Ramteke *et al.* and Shen *et al.* prevented these limitations by offering novel combined approaches in which aerobic biological degradation performed as a secondary treatment method for the removal of easily digestible intermediates, these methods still remain impractical for large-scale applications [16, 42].

2.3. Plasmon-Enhanced Heterogeneous Catalysis of 4-Nitrophenol

Due to the strong electron affinity of nitro group, nitrophenols are difficult to oxidize. Nevertheless, the recalcitrant nitrophenols can be reduced to amino-nitrophenols by plasmon-enhanced catalytic hydrogenation reaction. This is a simple, efficient, time and energy saving, industrially applicable reaction that proceeds under mild conditions, prevents the generation of additional pollutants.

Sodium borohydride ($NaBH_4$) is one of the most efficient reducing agents for the reduction of some esters, ketones, acid halogenides. However, the reagent has lower ability to reduce nitro compounds due to the kinetic barrier arose from the potential difference between the donor and the acceptor molecules. By considering the redox potentials of 4-Nitrophenol and $NaBH_4$, reduction reaction is thermodynamically feasible but kinetically restricted [43]. Therefore, in 1969, a common way for the conversion of 4-NP was firstly

reported by Suzuki *et al.* that introduces novel $NaBH_4$ ‾ transition metal salt system [44]. It was indicated that the addition of transition metal to the solution enhances the reducing ability of $NaBH_4$ by allowing the electron transfer from reducing agent to target molecule.

In 2002, Pal *et al*. and Esumi *et al.* firstly employed the reduction reaction in the evaluation of the catalytic activity of nano-sized metal particles. Since the potential of nano-sized metal particles lays between the potentials of BH_4^- ions and the nitroaromatics and serves as an electron relay, 4-Nitrophenol can be effectively reduced into 4-Aminophenol. They also drew attention to the importance of size properties of metal catalysts and choice of reducing agent for the kinetics of reaction. In the course of these studies it is proved that the reaction did not proceed by other mild reducing agents such as hydrazine, molecular hydrogen and ascorbate anion even in the presence of nano-sized (reduced) metal particles as it proceeds in the case of $NaBH_4$ assisted reaction [45, 46]. The free or immobilized nano-sized metal particles are used extensively in catalytical applications.

The bulk properties of metals change and they become very active in chemical reactions when they attain nanosize domain [47]. The common transition metals that are used in the reduction of 4-NP to the 4-AP are Ag, Pt, Pd, Ni, Rh, Au in the forms of nanostructures [48-53]. The nano-sized transition metal particles are placed on the line between homogenous and heterogeneous catalysis, since they have ability to activate as both with regard to the high ratio of surface atoms to total atoms in them. The nano-metallic catalysis takes place either in solution or on the surface of nanoparticle by atoms or ions that leach out from the nanoparticle surface. If the reaction is heterogeneous type, $NaBH_4$ adsorption on the surface of a nanoparticle always produces H_2 gas that causes a blue-shift in the surface plasmon band (SPB) of nanoparticles. On the other hand, if the reaction is homogenous type, the ions leach out of from the nanoparticle surface that causes the aggregation of nanoparticles and a red-shift in the SPB of nanoparticles.

El Sayed *et al.* verified that the metal catalyzed conversion mechanism of 4-Nitrophenol in the presence of excess amount of sodium borohydride proceeded according to heterogeneous type mechanism [54]. Thus, Ballauff *et al.* explains the reaction kinetics with a mechanism which is suggested by Langmuir in 1921 and further developed with Hinshelwood in 1926. This mechanism involves the adsorption of reactants onto the surface of nanoparticle. The adsorbed ions further react on the NP surface and 4-Aminophenol molecules are desorbed from the surface. $NaBH_4$ decomposes by hydrolysis

and the active hydrogen is formed by the addition of catalyst in the 4-Nitrophenol solution. The active hydrogen is then transferred to the metal surface and reacts with the surface in order to give Au-H bonds and then to give 4-AP by the reaction with adsorbed 4-NP [2]. The optimum operational conditions are determined by the evaluation of parameters that influence the reduction rate and improve the catalytic activity. The common parameters are catalyst dosage, initial substrate concentration, metal nanoparticle loading and size.
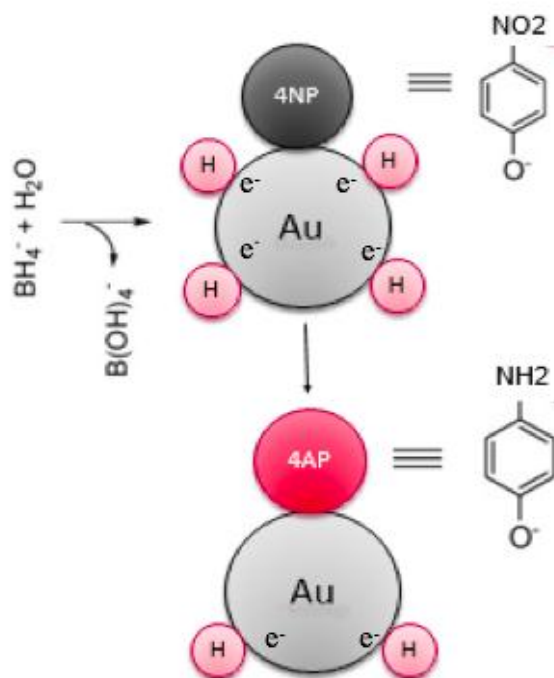
Figure 2.2. The reduction mechanism of 4-NP to 4-AP in the presence of nano-sized AuNps as plasmonic catalyst and $NaBH_4$ as a reductant [2]

In the advancing years this catalytic reaction has become a benchmark method by many researchers in the investigation of the catalytic performances of metal particles based on its ease of operation and easy measurement of both 4-NP and 4-AP by UV-vis spectroscopy. In this study, the plasmon-enhanced heterogeneous catalysis method is preferred for the treatment of 4-NP for providing conversion without producing toxic by-products and for being cost-effective and energy-saving, time saving and environmentally friendly. Besides, 4-AP, produced within the catalytic conversion of 4-NP takes place in many applications for being a photographic developer, an anticorrosion lubricant, a drying agent, a precursor for the production of analgesic drugs. It is a significant intermediate in the production of paracetamol. On average, aromatic amines are 500-fold less toxic than their corresponding nitroaromatic [55].

2.3.1. Properties and Synthesis of AuNPs as Plasmonic Catalyst

Metal nanoparticles attract attention in various fundamental areas such as electronics, catalysis, biomedicine, photonics and sensors due to their extremely smaller sizes and higher surface to volume ratio with respect to their bulk counterparts. Haruta *et al.* discovered the catalytic properties of AuNPs in low-temperature CO oxidation and this study has led to the extensive use of metal nanoparticles in catalytic reactions [56]. Since Pal et al. has firstly reported the catalytic conversion of 4-NP by Ag nanoparticles, various nano-sized noble metals have been obtained by chemical and biological synthesis. Among all metal nanoparticles, gold nanoparticles have received particular attention as a catalyst in oxidation, hydrogenation, reduction and water-gas shift reactions due to the physical, chemical and supramolecular properties. The reduction of nitroaromatics is one of the most crucial one amongst the transition metal-catalyzed redox reactions [57].

The surface plasmon resonance serves as an essential tool for monitoring the morphological property of AuNPs. Gold nanoparticles become prominent for being chemically inert, stable and exhibit size-dependent unique properties that are very different from those of bulk gold based upon the large surface-to-volume ratio, quantum confinement effect, and more negative Fermi potential. The size of AuNPs governs the properties of the nanoparticles and the applications for which they are used. In the catalytic applications, it is taken advantages of some unique properties of AuNPs such as being highly active under temperate conditions including ambient temperature, compared to other catalysts.

The catalytic activity of gold is just observed at nanometric scale. AuNPs between 1 and 10 nm in diameter present size-dependent electronic and optical properties which make them superior to their bulk counterparts. Despite the unique properties of AuNPs, a meticulous control over the size and reproducibility in same sizes is required and it has proved to be a difficulty. The size control is a necessity in order to overcome nanoparticle aggregation caused by flocculation at room temperature [58].

Two decades before, Brust and Schiffin introduced organic ligand molecules as monolayer protection coatings on nanoparticle surface in order to solve aggregation problem by creating physical barrier between the gold core and solvent [59]. Although that was an exact solution to size stability, the synthesis method remained incapable in generating monodisperse nanoparticles. Therefore, the synthesis of them with maximum control over the composition and structure and with a narrow size distribution is appeared

as an important challenge for the preparation of nanoparticles. Ghosh *et al.* observed that the rate constant increases as the size of AuNPs decreases for being proportional to the total surface area of AuNPs [60].

The techniques for generating different AuNPs in size and shape can be categorized as "bottom up" methods or "top down" methods owing to the principles. The top down processes require elimination of matter from bulk material in order to obtain nanostructure. The bottom up method, includes chemical, sonochemical, photochemical, electrochemical, templating and thermal reduction techniques, involves assembly of atoms into desired nanostructures. The bottom up techniques are the commonly used ones that are based on the principle of generation of gold nanoparticles having desired shape and size by reduction of chloroauric salt ($HAuCl_4$), in the presence of a reducing agent. The addition of reductant causes the reduction of Au^{3+} ions to Au^{+} ions in an aqueous medium, followed by a chemical reaction in which 3 Au^{+} ions causes the generation of Au^{3+} and 2 Au^{0} atoms that serve as center of nucleation. The size of synthesized gold nanoparticles could be controlled by varying concentration of reducing agent.

Since the applications of nano-sized noble metal in different structures depend on their shape, composition and size, two convenient methods, namely Turkevich and Martin Methods are chosen to synthesize spherical AuNPs in this thesis. The influence of AuNP sizes on catalytic activity is evaluated, individually, after the deposition on novel support materials. Turkevich and Martin Methods have ease of operation and involve cheap, non-toxic reducing agents.

2.3.1.1. Turkevich Method

Turkevich method, also known as citrate reduction method, was introduced by J. Turkevich *et al.* in 1951 and was improved by G. Frens in 1970. This method is based on the principle of reduction of gold salt, $HAuCl_4$, by citrate ions. Trisodium citrate has become one of the mostly preferred reducing agents in the synthesis of monodispersed and nano-sized gold particles suspended in water. It is preferable since it is cheap, non-hazardous and allows size-controlled synthesis of gold NPs by varying its concentration. It serves as both reducing and capping agent. One can synthesize spherical AuNPs of 10-20 nm in diameter by applying this method. The size of nanoparticles could be adjusted by increasing or decreasing the amount of citrate ions added into the reaction medium. In order to obtain larger particles, lower amount of sodium citrate should be added but it results in the disturbance in monodispersity and shape of particles. The decrease in the

quantity of sodium citrate causes the reduction in the quantity of citrate ions available for stabilizing the obtained particles and this results in the aggregation of smaller particles into bigger ones [58, 61].
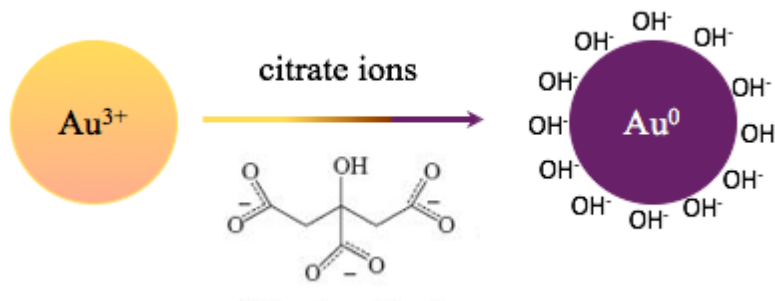
Figure 2.3. Citrate reduction of gold ions

2.3.1.2. Martin Method

Martin *et al.* introduced a new synthesis method in 2010 for the production of AuNPs by reducing the total synthesis time from 24 hours in the Brust method, to less than 10 minutes. They discovered a "sweet zone" for aqueous gold NPs starting from scratch and revealed a procedure for size-controlled synthesis of "naked", in other words "stabilizer-free" gold nanoparticles between 3.2 and 5.2 nm in diameter. Diluted HCl solution was used in the preparation of $HAuCl_4$ while NaOH solution was used in the preparation of $NaBH_4$ solution. This method enables a reproducible diameter tuning with a control over the reduction stoichiometry by adjusting the ratio of BH_4^+/OH^- ions (reducing agent) to $AuCl_4^-/H^+$ ions. The generated aqueous gold colloids are stable on account of their high charge from the excess ions in solution. The particles can be coated by various hydrophilic functionalities, or mixed with hydrophobic molecules for applications in non-polar solvents. Despite all the reaction by-products remain in the water-phase, there is not a necessity for post-synthesis cleaning or size-filtering. This method enables a rapid, size-controlled synthesis of monodisperse nanoparticles having larger surface area without aggregation and makes them more useful for the biological and chemical applications as drug delivery, bio-sensing, molecular recognition and water-treatment [58, 62]
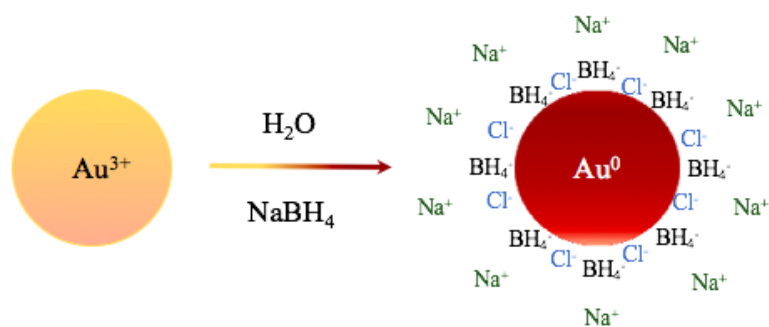
Figure 2.4. Sodium borohydride reduction of gold ions

2.3.2. Properties and Synthesis of a Support Material

The most of the metal catalysts, participate in the catalytic reduction reaction, and highly rely on noble metals that are in the form of nano-sized particles. The reason of using nano-sized catalysts is to obtain higher surface areas as the catalytic reactions proceeds on the particle surface. Unfortunately, naked NPs are not stable and they tend to agglomerate by virtue of having high tendency to minimize their high surface energy and strong interactions, leading to a rapid decrease in catalytic activity and poor durability of the catalyst [63]. In order to overcome, various support materials or carrier systems with high surface areas can be used to keep the active metal catalyst stabilized and dispersed in the reaction medium [64].

The catalytic activity is affected not only by the size distrubution, interparticle distance and shape of deposited nanoparticles, but is also significantly affected by the surface structure and nature of support material, as well, in terms of stabilization ability, AuNP affinity, and large surface area [65]. This is particularly important because it allows for more effective and economic usage of the precious metal catalysts, facilitates catalyst removal, recovery and recycling and provides a greater resistance to poisoning, compared to bulk-metal systems. Moreover, the difficulties in recycling pose a threat to the nature because of the toxicity of metal nanoparticles and limit their widespread applications of metal nanoparticles.

Holden *et al.* observed that Ag–Au bimetallic NPs aggregate in the absence of triblock copolymer surfactant as a protection, but the surfactant stabilized nanoparticles remain colloidally stable at room temperature for long time [66]. Li *et al*. also found colloidal metal nanoparticles to focculate within a catalytic reduction of 4-NP without stabilization by silica spheres, that can lead to a gradual loss of their catalytic activity and selectivity [67].

The organic and synthetic polymers, metal oxides, peptides and proteins, carbon nanotubes, MOFs, natural extracts and dendrimers are the common support materials introduced in previous studies for the reduction of 4-NP. Amongst them, metal oxides such as TiO_2, SiO_2, CeO_2, AlO_3, Fe_3O_4 and polymer beads exhibit great potential for applications in heterogeneous catalysis [57].
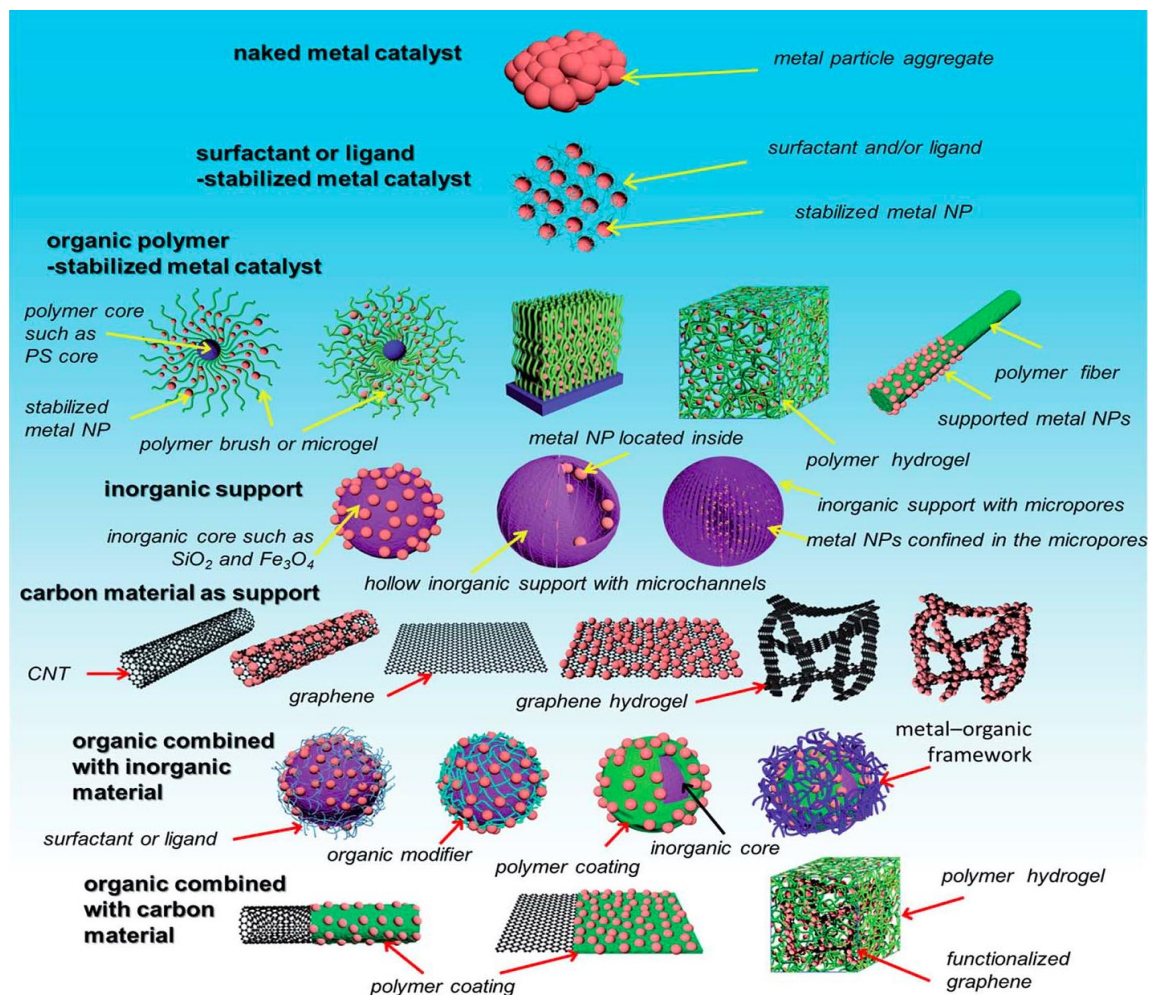
Figure 2.5. Common stabilizing systems used in the metal catalyzed 4-NP reduction [63]

Au-TiO_2 catalyst is the mostly studied metal-oxide based catalyst system for having strong interaction between metal and support, being chemically stable, thus showing high catalytic performance in 4-NP reduction [68, 69]. The usage of various forms of chitosan biopolymer as promising support materials for heterogeneous catalysis is on the rise as well, based on the functional hydroxyl and amino groups in its structure. The unique properties of chitosan enhance its convenience for chelation of metal complexes through covalent attachment. As Liu *et al.* reported, the catalytic behavior is influenced by the surface functional groups of polymeric support material [70].

Chitosan and TiO$_2$ supported gold catalysts are mostly synthesized by a deposition-precipitation or in-situ methods. Although these methods offer high dispersity without aggregation of AuNPs or one-pot synthesis of a catalyst, it is not easy to control the size and shape. Therefore, stabilization method of metal NPs, nature of the protecting material can be considered as a challenge as well, for the catalytic performance of nanoparticles [58]. Since they are able to form stong interaction with metals, chitosan and TiO$_2$ are chosen as support materials for our study to enhance the catalytic activities of metal NPs previously introduced in literature. Herein, we prefer simpler loading method for the production of AuNP decorated chitosan beads and metal oxide spheres as catalysts.
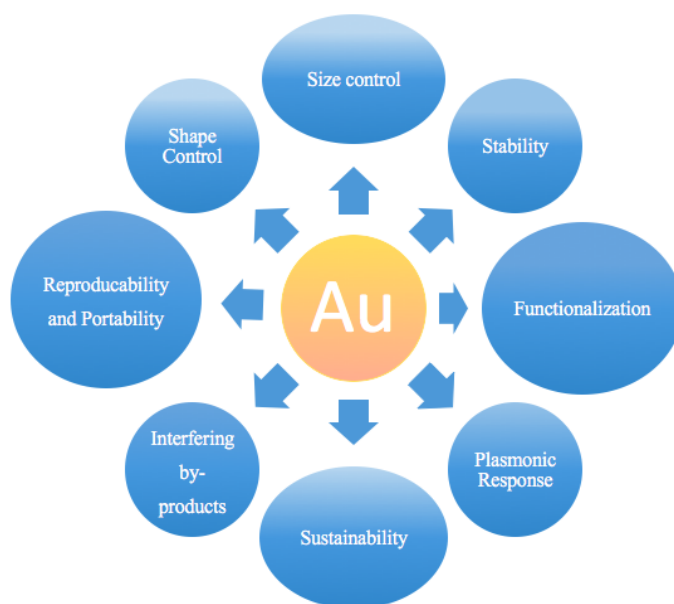
Figure 2.6. Main issues concerning the supported plasmonic catalysts

2.3.2.1. Chitosan as a Support Material

Chitosan is a straight-chain polysaccharide derived by deacetylation of chitin. It is the second most abundant natural biopolymer originated from exoskeletons of crustaceans and also from cell walls of fungi and insect. Degree of deacetylation of chitosan ranges between 40% and 98% while the molecular weight ranges from 50 to 2000 kDa. The molecular weight of chitosan is based upon two important parameters, degree of deacetylation (DD) and the degree of polymerization (DP), which control its acid–base properties and solubility. Chitosan has primary and secondary free hydroxyl groups in C6 and C3 positions, respectively and one primary amine group in C2 position per repeat unit which allow many possibilities for physical and chemical modifications in order to customize its property [6].

The functional amine groups of chitosan, having a pKa value that lies between 6.2 and 6.7, are completely protonated to $-NH^{+3}$ in aqueous acids including acetic acid and formic acid. The chemical reactivity with negatively charged substances, polarity, the degree of electrostatic repulsion and solubility of chitosan depend on the amplitude of cationic sites formed by the protonation of amine groups in the polymeric chain. Besides, at alkali solutions, chitosan is negatively charged due to the dissociation of carboxyl groups or the adsorption of hydroxyl from the solution and can be used to remove positively charged substances [71].

The physical and chemical modifications preserve the original biochemical and physicochemical properties of chitosan while bringing new or improved properties to it. Chitosan can be modified by alkylation, quaternization, oligomerization, acylation, thiolation, hydroxyalkylation, graft copolymerization, carboxyalkylation, sulfation, phosphorylation and can be formed in many physical forms such as membranes, resins, microspheres, fibers, hydrogels. The choice of spherical form and the preparation method depends mainly upon factors such as application requirement, thermal and chemical stability and reproducibility of the final product. The forms of chitosan take place in biomedical applications as wound healing, tissue engineering for being regenerative, biocompatible, non-toxic, biodegradable and anti-microbial [72]. Chitosan also comes to the fore in water treatment, textile industry, paper industry, food processing, agriculture, cosmetics and pharmaceutical industry because of its low-cost and desirable property of hydrophilicity.

The previous studies revealed that the flakes, fibers, gels and gel beads of chitosan are promising polymeric substances for the elimination of metals and organic contaminants from industrial wastewaters and natural waters due to the high adsorption capacity rises from polycationic nature [72]. They serve as either an adsorbent or a support material in water treatment processes due to their metal anchoring functional groups. Crini *et al.* reported that chitosan based adsorbents, synthesized in hydrogel bead form, have the highest adsorption capacity for the treatment of textile dyes [73]. Mansur *et al.* produced chitosan microspheres and used as polymeric resin in the packed column treatment of oily wastewater via adsorption. The microspheres found to be highly efficient in oil removal, with rates above 90% [74].

Zhang *et al.* demonstrated that the crosslinked chitosan beads are efficient chelating agent and heavy metal trapper due to the regeneration ability without losing the original

activity and stability in the metal up-take [75]. These studies proved that higher adsorption capacity, metal affinity, recoverability, reusability, mechanical strength and low-cost of chitosan hydrogel beads could exhibit great potential for the fabrication of heterogeneous catalyst as a support material to promote the efficiency of chemical reactions. Zhao *et al.* introduced a double functional TiO_2/chitosan beads that are used in the photocatalytic degradation of a textile dye and adsorbtion of metal ions concurrently. The photocatalyst reused more than ten cycles and did not lose its degradation and adsorption ability by proving the efficiency of chitosan gel beads either as support material and adsorbent [76].

In recent years, the researchers began to fabricate beads supported metal catalysts and employed them in the reduction of nitroaromatics, especially in the reduction of 4-Nitrophenol, due to its high toxicity. Haruta *et al.* developed a catalyst by the direct deposition of AuNPs on the surface of commercially available polymethyl methacrylate (PMMA) beads and employed it in the conversion of 4-NP to 4-AP with $NaBH_4$. Bead form of PMMA showed the highest catalytic activity amongst other forms of PMMA supported AuNPs, as previously introduced [77]. In spite of the advanced properties, bead form of chitosan could not find place in the plasmon-enhanced catalytic 4-Nitrophenol reduction yet. In large number of studies, chitosan flakes serve as matrix in the reduction of Au salt and in the stabilization of obtained AuNPs [78, 79].

Guibal *et al.* prepared a chitosan-supported palladium catalyst by treating chitosan powder directly with the cross-linker and then mixing it with a palladium salt solution in the presence of a reductant [80]. Wu *et al.* prepared Au/chitosan flakes as a catalyst by the in-situ formation of AuNPs in chitosan hydrogel via photoreduction of gold salt. The as-prepared AuNPs showed a good catalytic activity in the reduction of an nitroaromatic pollutant benefited from the excellent encapsulation ability of chitosan [79]. The size of metal nanoparticles can be kept smaller, surface roughness of a catalyst can be increased and reduction reaction can be promoted by these methods but controlling the size still remains as a difficulty. Besides, the recovery and reusability of the flakes remain as a challenge. Moreover, the catalysts are prepared by complex and pH-dependent methods. In this study, AuNPs are generated in a liquid phase with controllable sizes, and then deposited onto the surfaces of solid supports as microgel beads in order to overcome these challenges without making pH adjustment.

Hydrogels are 3D structured polymer networks which could absorb large amounts. In the preparation of soft, wet chitosan gels, chitosan dissolves in dilute organic acid

solutions to form viscous solutions followed by precipitation to form water-insoluble complexes. Hydrogels appeared as matrix, film, or micron-sized bead forms that depend on the technique of polymerization involved in the preparation process [81]. The chitosan gel preparation can be materialized by different methods such as solvent evaporation method, cross-linking method and neutralization etc.

In the production of spherical gel beads of different size, small-molecule cross-linking method is mainly used in which the chitosan solution added dropwise into the solution of cross-linker. In each process, chitosan is either chemically cross-linked or physically associated to form hydrogel [82]. Covalently crosslinked chitosan hydrogel beads are formed by irreversible covalent links. Stable hydrogels can be formed by the addition of crosslinkers or the direct interaction of polymeric chains. This type of cross-linking is applied for the amine, hydroxyl, carboxylic acid based functionality containing polymers and can not be reversed by light, acid, base or heat [81]. The surface area, thermal properties, size and mechanical strength of resultant beads are substantially related with the cross-linking agent. Glutaraldehyde is the widely used cross-linking agent owing to its hydrophilic nature, powerful and quick fixation ability.
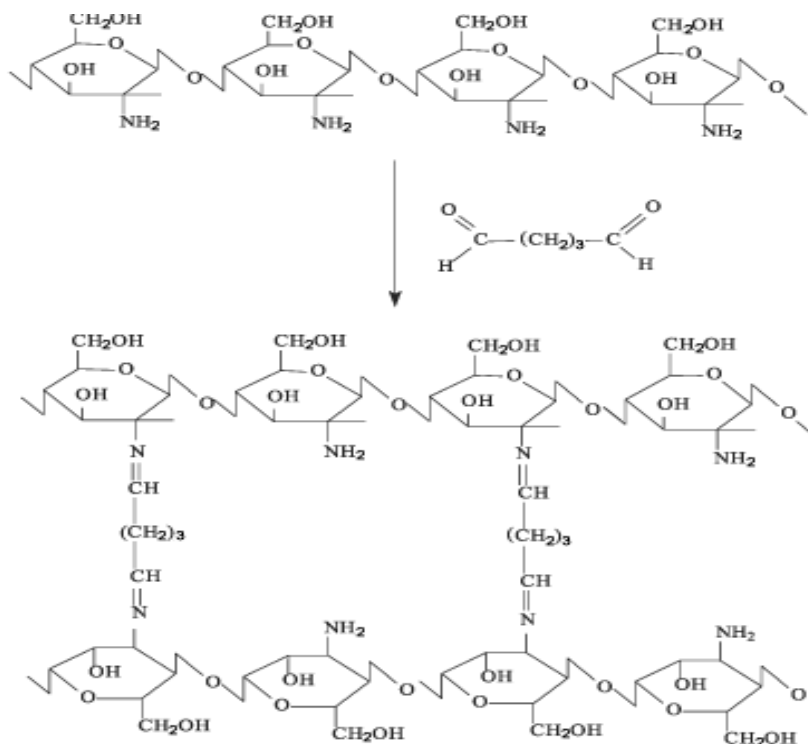
Figure 2.7. Crosslinking of chitosan molecules with glutaraldehyde

2.3.2.2. Titanium Dioxide as a Support Material

Titanium dioxide (TiO_2) also known as titania is a semi-conductor metal oxide that serves both as photocatalyst and catalyst support material in the treatment of toxic and non-biodegradable environmental contaminants. TiO_2 becomes one of the favourable candidates as a support for metal nanoparticles in heterogeous catalysis based upon its strong interaction with metal support, chemical and thermal stability, mechanical resistance and non-toxic, non-corrosive nature amongst all other metal oxide support materials [5]. There are different studies in literature that deal with the fabrication of catalysts based on the functionalized titania and gold for the reduction reactions. As a support, titania is produced in different sizes and forms such as thin films, powder, crystals. Deshmukh *et al.* snythesized nano-sized titania supported AgNps by a in-situ sol-gel method followed by reduction of silver salt that is proved to be an perfect catalyst towards conversion of 4-NP [83].

Yazid *et al.* developed sphere-formed titania supported Au nanoparticles in very small sizes by deposition-precipitation method that were found to have a noticeable effect on catalytic activity for the rapid conversion of 4-NP [68]. Dobrowolska *et al.* produced and mixed amine-functionalized SiO_2 and TiO_2 cores with Turkevich AuNPs. They reported that when compared to SiO_2, the higher amount of hydroxyl groups on the TiO_2 particle surface may result in higher amount of amine groups after derivatization step and thus supply more anchoring groups for AuNP binding which may further provide better catalytic performances within 4-Nitrophenol reduction. [84] The vast majority of studies concentrated on the production of TiO_2 in extremely small sizes as a support material and decoration with metal nanoparticles by homogenous deposition-precipitation method. However, these catalysts are impractical for column studies, industrial applications and tend to agglomerate, obstruct the growth control of nanoparticles.
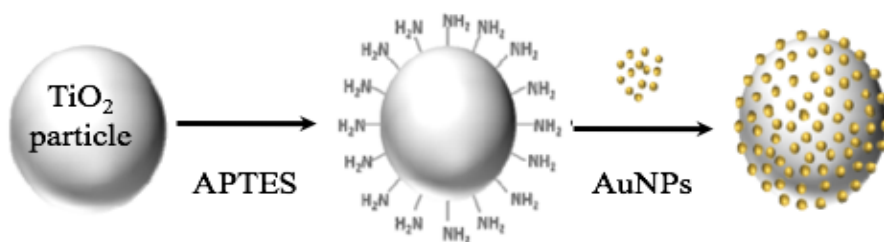
Figure 2.8. Amine derivatization and AuNP decoration of metal oxide spheres

Each form of titania can be synthesized in a broad size range from few nanometers to several micrometers. The chemical and physical properties of titania depend on the conditions of preparation method. The preparation processes could be seperated into two groups, gas-phase and solution preocesses. Unfortunately, the gas-phase methods have a main drawback which is high energy consumption. On the other hand, solution methods, usually used in the synthesis of powder form, are advantageous for having possibility to control stoichiometry. As a prominent, simple, cost-effective solution method, in one step sol-gel method, the solid product is formed by gelation. It is described as a process that involves formation of materials via a sol, gelation of the sol and elimination of solvent. A sol is a stable suspension of colloidal solid particles in a liquid formed by the hydrolysis of a precursor and a gel is a solid network formed by agglomeration of colloidal solid particles [85].

Many metal-oxide catalysts and catalyst supports are obtained by using sol-gel method. Titania can be produced by alkoxide or non-alkoxide sol-gel routes depending on the precursor. In an alkoxide sol-gel route, the sol is obtained by the interaction of metal alkoxide solutions/metal salts and solvents (water or alcohols) in significant ratios, and then gelation is occurred by the consecutive chemical reactions and electrochemical interactions of surface charges in solution, the network structure called gel is formed [86]. Titanium isopropoxide, titanium ethoxide and titanium n-butoxide are commonly used metal alkoxide precursors in sol-gel synthesis of titania, while the methanol, ethanol or propanol are used as solvents. In 2005, Mine *et al.* introduced a titania synthesis method in which a second solvent, acetonitrile, was used together with ethanol for the hydrolysis of titanium isopropoxide precursor. They observed that the presence and increasing concentrations of acetonitrile led to the generation of particles having smoother surface with high monodispersity in particle size. They also reported that the amount and size of prepared particles related to the rate of hydrolysis and condensation of precursor, the way of addition of precursor and method of mixing [87].
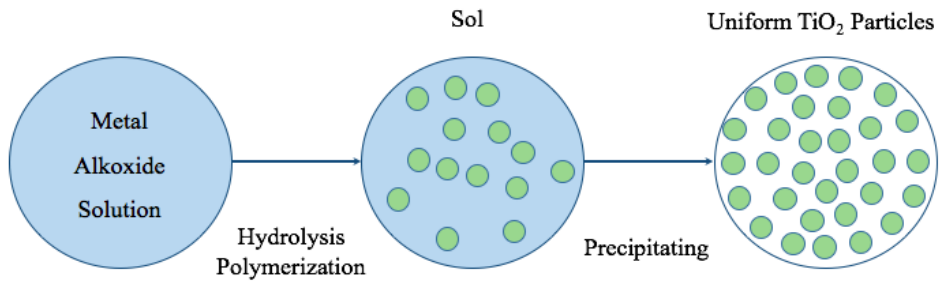
Figure 2.9. Synthesis of TiO$_2$ powder from a colloidal sol

3. EXPERIMENTAL METHODS

3.1. Plasmon-Enhanced Heterogeneous Catalyst Design

3.1.1. Synthesis of AuNP as Promising Plasmonic Catalyst

In our study, gold nanoparticles are synthesized by using two different procedures. These procedures are both based on the principle of reduction of Au^{+3} ions by a reducing agent. In Turkevich method, citrate ions serve as a reductant in the reduction of Au^{+3} ions and as a stabilizer in the stabilization of produced gold nanoparticles in water. In Martin method, the gold nanoparticles having relatively smaller sizes are synthesized as a result of the reduction of $HAuCl_4$ by $NaBH_4$ in water.

3.1.1.1. Materials

Auric chloride ($HAuCl_4.3H_2O$), sodium borohydride ($NaBH_4$), trisodium citrate ($Na_3C_6H_5O_7$) are used in the synthesis of gold nanoparticles (Sigma Chem. Co., USA). In order to prepare $NaBH_4$ and $HAuCl_4$ solutions, NaOH purchased from Sigma Chem. Co., USA and hydrochloric acid (HCl, % 37 w/w) purchased from Merck KGaA, Germany are used respectively. DDI water (R_w: 18 MΩ cm, Direct-Q 3 UV, Millipore, USA) is used along the synthesis.

3.1.1.2. Synthesis of AuNP by Turkevich Method

The prepared solution of $HAuCl_4$ (10^{-3}, 24 mL) is stirred magnetically at 300 rpm and heated until it starts boiling. Afterwards 2.0 mL sodium citrate solution (1.75 % (w/v)) is added into the boiling solution and the solution left to boil for 15 minutes. As it continues stirring, light yellow color of solution starts darkening. The color turns into deep red after 5 minutes which is a proof of the completion of the reduction of Au^{+3} ions by citrate. The boiling proceeds for 10 more minutes and after that the solution is separated from the heating element but was continued to be stirred magnetically in order to prevent aggregation. The solution cools down to room temperature. The final solution involves 10-20 nm AuNPs in size. The size of obtained AuNPs depends on the ratio between the amount of Au^{+3} ions and the amount of citrate ions in the solution.

3.1.1.3. Synthesis of AuNP by Martin Method

The aqueous stock solution of 50 mM gold chloride anions is prepared by dissolving certain amount of $HAuCl_4.3H_2O$ in 50 mM HCl solution. In parallel, the preparation of aqueous stock solution of 50 mM borohydride anions is made by dissolving

certain amount of reducing agent, $NaBH_4$ in 50 mM NaOH solution. In order to prepare 0.50 mM Au^0 solution, 100 μL of $AuCl4^-/H^+$ solution is added into 10 mL water in a glass beaker and the solution is started to be stirred magnetically at 300 rpm. Then 300 μL of $BH4^+/OH^-$ solution is injected all at once and following the injection, the hydrogen release is observed by the immediate color change. It should be noted that the conservation of volume of gold ions to borohydride ions ratio (1:3) is important for the size of gold nanoparticles. The light yellow color of solution turns into Turkey red thus proves the completion of reduction of gold nanoparticles. The final solution includes 2-5 nm gold nanoparticles in size. Martin Method enables the controlled production of smaller particles.

3.1.2. Synthesis of AuNP Decorated Chitosan Microgel Beads

3.1.2.1. Materials

The chitosan with low molecular weight (≥75 DA), acetic acid (%99 (w/w), dichloromethane (DCM), Tween-20 as a stabilizer are used in the preparation of chitosan solution (Aldrich Chem. Corp., USA). Glutaraldehyde solution (GA, 50 wt % in H_2O) is used as crosslinking agent, cethyltrimethylammonium bromide (CTAB) is used as a stabilizer in the chemical modification of chitosan (Sigma Chem. Co., USA). DDI water (R_w: 18 MΩ cm, Direct-Q 3 UV, Millipore, USA) is used along the synthesis.

3.1.2.2. Synthesis of Bare Chitosan Microgel Beads as a Support Material

The first step of microgel bead production is to prepare chitosan solution. It is prepared by the dissolution of chitosan powder (0.4 g) and Tween-20 (0.8 mL) in the dilute acetic acid solution (10 mL, 0.01 M). The solution is stirred magnetically at a rate of 300 rpm at room temperature within 24 hours. In the end of the period, dichloromethane (1 mL) is added into the chitosan solution followed by a probe-type sonication along 2 minutes. The final solution is then vortexed along 30 seconds and placed in ultrasonic bath for a minute. The second step of microgel bead production is the chemical modification of chitosan by cross-linking of functional amino groups in its structure in the presence of amine reactive cross-linking agent. The chitosan solution is injected dropwise into the stirring glutaraldehyde solution (10%, 50 mL) by a syringe pump at a flow rate of 0.003 mL/min. The stabilization of microspheres is ensured by the addition of CTAB (0. 25 g) into the glutaraldeyde solution. As a consequence, spherical water-swellable matrix structures having smooth surfaces are formed. The microspheres are removed from glutaraldeyhde solution at the end of 24 hours and are rinsed with distilled water several

times. The excess amount of crosslinker may change the pH of reaction medium. The monodisperse hydrogel beads, 3 mm in size, are obtained by applying this procedure.

3.1.2.3. Decoration of Chitosan Microgel Beads with Turkevich AuNPs and Martin AuNPs

The decoration of microgel beads with AuNps is provided by the addition of same amounts of beads into the two separate AuNP solutions that are previously prepared by Turkevich and Martin methods and then stirring the solutions magnetically at a rate of 300 rpm within 6 hours. In order to evaluate the influence of Au loading on catalytic activity, different amounts of beads added into same volume of AuNp solutions, respectively. The decoration of beads with AuNPs is achieved by the adsorption of AuNPs to the beads via the primer amine groups of chitosan. Table 3.1. involves the experimental conditions of decoration process.

Table 3.1. The experimental conditions for decoration of chitosan microgel beads with gold nanoparticles that are synthesized with Turkevich ve Martin Methods

Turkevich Method / Martin Method	
Amount of Chitosan Microgel Beads (g)	AuNP Loading on Chitosan Microgel Beads (%w/w)
1.6	2.5
0.8	5
0.4	10

Experimental Conditions: Volume of Turkevich AuNP solution: 24 mL; Volume of Martin AuNp solution: 80 mL; Stirring: 300 rpm, 6 hours

3.1.3. Synthesis of AuNP Decorated Polydisperse Titanium Dioxide Spheres
3.1.3.1. Materials

In the preparation of low sized polydisperse titanium spheres titanium tetra isopropoxide is used as a metal alkoxide, dodecylamine (DDA) as a stabilizer, methanol and acetonitrile are used as solvents (Sigma Chemical Co., USA). In order to provide amine functionalization of titanium spheres, triethylamine (TEA) and aminopropyltriethoxysilane (APTES) are used as functionalizers and isopropyl alcohol is

used as a solvent (Sigma Chem. Co., USA). DDI water (R_w: 18 MΩ cm, Direct-Q 3 UV, Millipore, USA) is used along the synthesis.

3.1.3.2. Synthesis of Bare Titanium Dioxide Spheres as Support Material

The sol-gel method is applied to synthesize low-sized polydisperse titanium spheres. The preparation of solvent environment that includes methanol (50.5 mL) and acetonitrile (24.5 mL) originates the first step of the procedure. It is followed by an addition of dodecylamine (DDA, 0.14 g) as a stabilizer and distilled water (0.09 mL) as a reactant respectively. Titanium isopropoxide (0.5 mL) as a metal alkoxide is added to the solution dropwise after stirring at a rate of 300 rpm at room temperature for 10 minutes. For the formation of sol, the final solution is left to be stirred at a rate of 300 rpm for 24 hours. In the course of that period, hydrous titanium oxide spheres are formed by the hydrolysis of precursor. TiO_2 spheres are precipitated and washed with reprepared solvent environment and isopropanol by centrifugation for several times to remove excess isopropoxide ions. Afterwards the spheres are dried at 60 ^{0}C and weighed. The amount of synthesized TiO_2 spheres changes depending on the ratio between the amounts of titanium isopropoxide and distilled water.

3.1.3.3. Derivatization of Titanium Dioxide Spheres with Aminopropyltriethoxysilane

The attachment of functional amine groups to the polydisperse bare TiO_2 spheres is performed by using Aminopropylethoxysilan. TiO_2 spheres (0.04 g) are dispersed in the medium prepared by the sonication of isopropanol (18 mL), APTES (2 mL) and TEA (0.3 mL). The dispersion is added into a sealed glass reactor which is then placed in temperature-controlled shaking water bath. The amine derivatization process continues for 24 hours at 80 ^{0}C, the spheres are washed with isopropanol by centrifugation (9000 rpm, 10 minutes) in order to remove excess APTES. The spheres are rinsed with distilled water for few times and precipitated by centrifugation. The amount of the derivatized bare TiO_2 spheres is measured by gravimetric analysis.

3.1.3.4. Decoration of Titanium Dioxide Spheres with Turkevich AuNPs and Martin AuNPs

The decoration of microgel beads with AuNps is provided by the injection of same amount of amine attached titanium spheres into the AuNP solutions that are prepared by Turkevich and Martin methods and then stirring the solutions magnetically at a rate of 300 rpm for 6 hours. In order to evaluate the influence of Au loading on catalytic activity,

different amounts of spheres are added into same volume of AuNp solutions. The decoration of spheres with AuNPs is achieved by the adsorption of AuNPs to the spheres via the amine groups of functionalized TiO_2. Table 3.2. shows the experimental conditions of decoration process.

Table 3.2. The experimental conditions for the decoration of TiO_2 spheres with gold nanoparticles that are synthesized with Turkevich ve Martin Methods

Turkevich Method / Martin Method	
Amount of Amine Functionalized TiO_2 Spheres (g)	AuNP loading on TiO_2 Spheres (%w/w)
0.08	1
0.04	2
0.02	4

Experimental Conditions: Volume of Turkevich AuNP solution: 9,6 mL; Volume of Martin AuNP solution: 20 mL; Stirring: 300 rpm, 6 hours

3.2. Characterization Studies

The surface morphologies, size distribution properties and elemental analysis of bare and gold nanoparticle decorated chitosan microgel beads, bare and gold nanoparticle decorated TiO_2 spheres are both indicated by the micrographs from scanning electron microscopy and energy dispersive x-ray spectroscopy (SEM-EDX; QUANTA 400F Field Emission, FEI, Japan). The samples of bare microgel beads and AuNP/beads are prepared by freeze-drying of beads at -80 ^{o}C in order to preserve their structural properties. The samples of bare TiO_2 and AuNP/TiO_2 spheres are prepared by the dispersion of certain amounts of dried spheres in an aqueous sodium dodecyl sulfate (SDS) solution (%0.1 w/v) by sonication. A drop of 0.2 mL of dispersion was injected onto a carbon tape and dried at room conditions. The dried samples are then coated with gold/platinum by physical vapor deposition method. The size distribution properties of gold nanoparticles obtained by Turkevich and Martin Methods are indicated by the images from high contrast transmission electron microscope (CTEM; FEI Tecnai G2 Spirit BioTwin) due to the ability of analyzing at high resolution at nano level. The samples of gold nanoparticles are

prepared by dispersion of certain amounts of dried nanoparticles in distilled water. A very small drop of dispersion is injected onto a grid and dried at room conditions. The specific surface areas of bare and gold nanoparticle decorated chitosan microgel beads, bare and gold nanoparticle decorated TiO_2 spheres are measured by surface area and pore size analyzer (Quantachrome, Nova 2200E, UK) using the BET isotherm. The analyses are made at 77 K following the degassing of all samples under vacuum at 250 ^{o} C for 6 h. BET specific surface area was calculated from nitrogen adsorption data between the relative pressure range of 0.05 and 0.2. The chemical structure of bare and gold nanoparticle decorated chitosan microgel beads, bare and gold nanoparticle decorated TiO_2 spheres are determined by X-ray diffraction spectroscopy (XRD, Rigaku Ultima-IV, USA). Diffraction patterns were collected in the range of 0º − 90º (2θ) with a step size of 0.02º. The presence and concentration of AuNPs and 4-nitrophenol molecules were determined by UV-Vis spectrophotometer (GENESYS 10S UV-Vis, Thermo Scientific, USA). Each batch of AuNPs were analyzed by spectral scan in the range of 400 and 800 nm for uniform size distribution and to identify the molecules by their characteristic peaks.
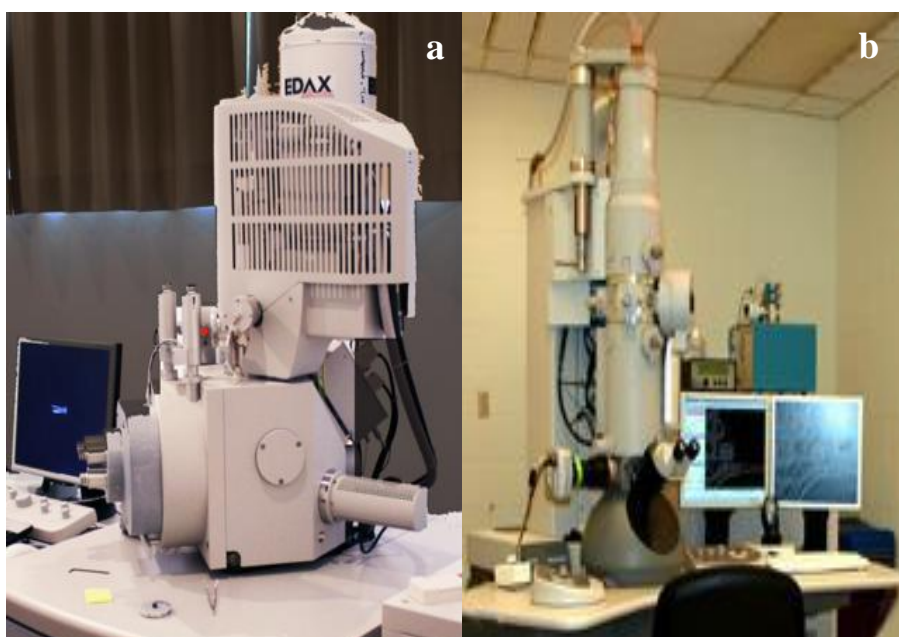
Figure 3.1. The equipment used for the characterization of bare chitosan microgel beads, bare TiO$_2$ spheres, gold nanoparticles and heterogeneous catalysts a) QUANTA 400F Field Emission SEM-EDAX b) CTEM, FEI Tecnai G2 Spirit BioTwin c) Surface Area and Pore Size Analyzer, Quantachrome Nova 2200 d) XRD, Rigaku Ultima IV e) UV-Vis Spectrophotometer, GENESYS 10S, Thermo Scientific

3.3. Plasmon-Enhanced Heterogeneous Catalysis of 4-Nitrophenol

3.3.1. Materials

In the plasmonic catalysis process 4-Nitrophenol is chosen as a target molecule and sodium borohydride (NaBH$_4$) is used as a reductant (Aldrich Chem. Corp., USA). DDI water (R$_w$: 18 MΩ cm, Direct-Q 3 UV, Millipore, USA) is used along the synthesis.

3.3.2. Reduction of 4-Nitrophenol by the Turkevich AuNP and Martin AuNP Decorated Chitosan Microgel Beads

The catalytic activities of chitosan microgel beads decorated with Turkevich AuNPs and Martin NPs (10 mg, AuNP loading: 5 % w/w) are both investigated within the reduction of 4-NP to 4-AP at room temperature. For this purpose, $NaBH_4$ (0.2 g) is added to a batch reactor that contains the aqueous solution of 4-Nitrophenol (7.5 ppm, 24 mL). The solution is stirred magnetically at a rate of 300 rpm at room temperature until the hydrogen release is completed. In order to measure the initial concentration of 4-Nitrophenol, 2 mL of sample is taken from the solution. Then AuNP decorated chitosan microgel beads (10 mg) are added into the reaction medium. For the determination of the change in 4-Nitrophenol concentration with time, the samples are taken after certain periods of time, diluted with distilled water and taken into a quartz glass. The quartz glass is placed in UV-vis spectrophotometer and 4-Nitrophenol concentration is measured by the absorption of sample at wavelength of 400 nm.
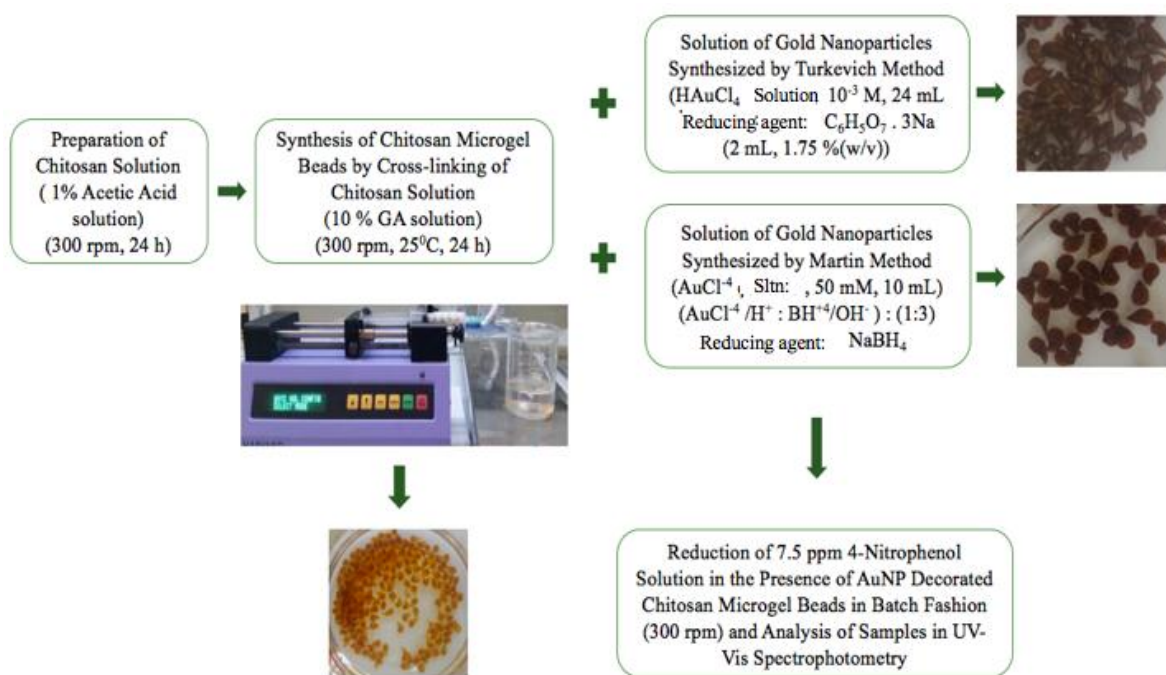
Figure 3.2. Steps of AuNP/ Chitosan microgel bead synthesis and 4-Nitrophenol reduction a) Harvard Apparatus PHD ULTRA 4400 Syringe Pump that added chitosan solution into the glutaraldehyde solution dropwise b) Bare chitosan microgel beads c) Turkevich AuNP decorated chitosan microgel beads d) Martin AuNP decorated chitosan microgel beads

The catalytic activities of chitosan microgel beads decorated with Turkevich AuNPs and Martin AuNPs are investigated by changing catalyst amount and initial 4-Nitrophenol

concentration. The details of experimental conditions in the reduction of 4NP to 4AP via AuNP decorated chitosan microgel beads are given in Table 3.3.

Table 3.3. The experimental conditions for the reduction of 4-NP by chitosan microgel beads that are decorated with Martin AuNPs

Experimental Conditions	Parameter	Range
7.5 ppm, 25^0C	Catalyst Amount	5,10, 20 mg
10 mg catalyst, 25^0C	Initial 4-NP Concentration	3.75, 7.50, 15.00 ppm

Volume of Reaction: 24 mL, Amount of $NaBH_4$: 0.2 g

3.3.3. Reduction of 4-Nitrophenol by the Turkevich AuNP and Martin AuNP Decorated Titanium Dioxide Spheres

The catalytic activities of TiO_2 spheres decorated with Turkevich AuNPs and Martin NPs (12.5 mg, Au loading: 2% w/w) are investigated within the reduction of 4-Nitrophenol (7.5 ppm, 24 mL) to the 4-Aminophenol at room temperature. For this purpose, $NaBH_4$ (0.2 g) is added to a batch reactor that contains the aqueous solution of 4-Nitrophenol (7.5 ppm, 24 mL). The solution is stirred magnetically at a rate of 300 rpm at room temperature until the hydrogen release is completed. In order to measure the initial concentration of 4-Nitrophenol, 2 mL of sample is taken from the solution. Then AuNP decorated chitosan microgel beads (10 mg) are added into the reaction medium. For the determination of change in 4-Nitrophenol concentration with time, the samples are taken after certain periods of time, centrifuged at 13000 rpm for 5 seconds for solid separation. The supernatant is diluted with distilled water and taken into a quartz glass. The quartz glass is placed in UV-vis spectrophotometer and 4-Nitrophenol concentration is measured by the absorption of sample at wavelength of 400 nm.
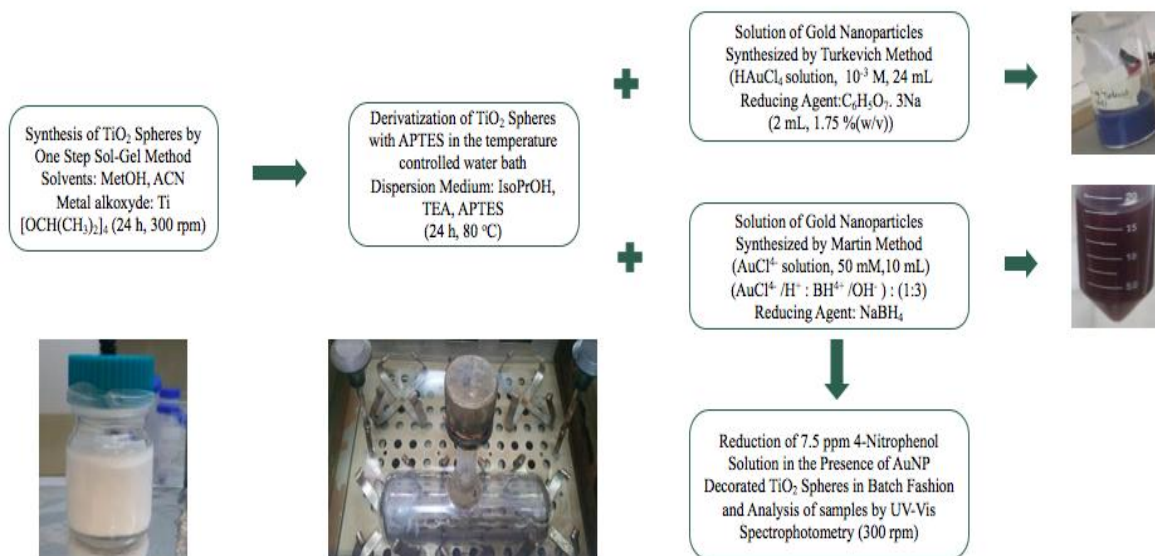
Figure 3.3. Steps of AuNP/TiO$_2$ sphere synthesis and 4-Nitrophenol reduction a) Solution of bare TiO$_2$ spheres obtained by one-step sol-gel method b) Temperature controlled water bath and a reactor c) Turkevich AuNP decorated TiO$_2$ spheres d) Martin AuNP decorated TiO$_2$ spheres

The catalytic activities of TiO$_2$ spheres decorated with Turkevich AuNPs and Martin AuNPs are investigated by changing catalyst amount and initial 4-Nitrophenol concentration. The details of experimental conditions of the reduction of 4-NP to 4-AP via AuNP decorated TiO$_2$ spheres are given in Table 3.4.

Table 3.4. The experimental conditions for the reduction of 4-NP by TiO$_2$ spheres that are decorated with Martin AuNPs

Experimental Conditions	Parameter	Range
7.5 ppm 4-NP, 25^{0}C	Catalyst Amount	2.5, 6.25, 12.5, 25 mg
1 mg catalyst, 25^{0}C	Initial 4-NP Concentration	3.75, 7.50, 15.00, 30.00 ppm

Volume of Reaction: 24 mL, Amount of NaBH$_4$: 0.2 g

3.3.4. Recovery and Reusability of Catalyst

The reusability of chitosan microgel beads and TiO$_2$ spheres decorated with Martin AuNPs are investigated respectively by the fact that Martin AuNPs, having smaller size and narrow size distribution, has shown the highest catalytic activity in the plasmonic catalysis of 4-NP. At the end of the complete reduction of 4-Nitrophenol, AuNP/chitosan

beads (10 mg catalyst, 2.5% loading, 7.5 ppm initial 4-Nitrophenol concentration, 25^0C for Martin AuNP decorated chitosan microgel beads) are recovered by easy filtration of the solution and rinsed with distilled water at the end of each experiment. At the end of the complete reduction of 4-Nitrophenol via AuNP/TiO_2 spheres (12.5 mg catalyst, 2% loading, 7.5 ppm initial 4-Nitrophenol concentration, 25^0C for Martin AuNP decorated TiO_2 spheres) the suspension is centrifuged at 9000 rpm for 5 minutes and the precipitated TiO_2 catalyst particles are rinsed with distilled water. The recovered catalyst particles are reused in the reduction of 4-Nitrophenol that is repeated under the same experimental conditions. 4-Nitrophenol reduction and catalyst recovery are repeated for 3 times.

4. RESULTS & DISCUSSION

4.1. Synthesis and Characterization of Plasmonic Catalyst

4.1.1. Synthesis and Characterization of AuNPs Synthesized by Turkevich and Martin Methods

The TEM images of AuNPs obtained by Turkevich and Martin Methods are given in Figure 4.1. The gold nanoparticles obtained by Turkevich Method in which $HAuCl_4$ molecules are reduced by citrate ions are found to be 10-12 nm in size. On the other hand, the gold nanoparticles obtained by Martin Method in which $HAuCl_4$ molecules are reduced in the presence of $NaBH_4$ are found to be between 3-5 nm in size. The images reveal that the gold nanoparticles are synthesized in expected sizes having narrow size distributions.
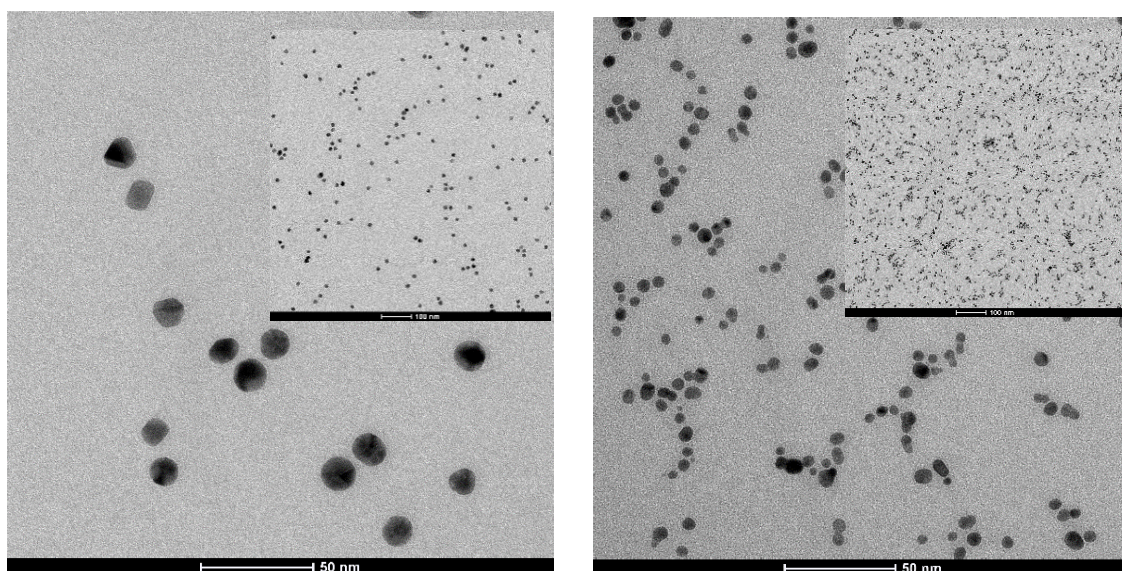
Figure 4.1. SEM images of gold nanoparticles that are synthesized by a) Turkevich Method b) Martin Method

Surface plasmon resonance is a special phenomenon that serves as an essential tool for monitoring the morphological property of AuNPs. Surface plasmon band intensity and peak are directly related to type of metal, particle size, shape, structure and composition of surrounding which mainly influences the electron charge density on the particle surface [88]. The characteristic surface plasmon peaks of gold nanoparticles that are different in size can be seen in the technical document arranged by Sigma-Aldrich. The document indicates that as the particle size increases from 5 nm to 100 nm, the peak shifts from 515 to 572 nm.
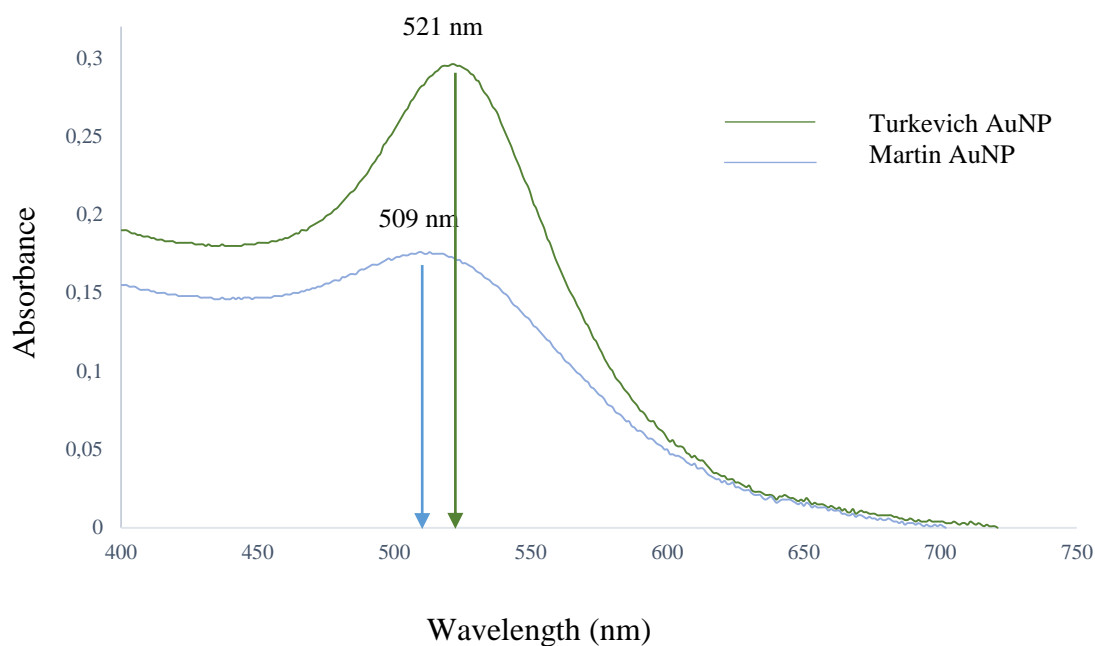
Figure 4.2. UV-Vis spectra of AuNP solutions obtained by Turkevich and Martin Methods

The UV-Vis spectrum of synthesized Turkevich and Martin AuNP solutions are given in Figure 4.2. The surface plasmon bands for the Turkevich AuNPs 3-5 nm in size and Martin AuNPs 10-12 nm in size are observed at 521 and 509 nm in the spectrums, respectively. The results are compatible with the ones indicated in the technical document arranged by Sigma-Aldrich.

4.2. Synthesis and Characterization of Support Materials Decorated with Turkevich AuNPs and Martin AuNPs

4.2.1. Synthesis and Characterization of Bare and AuNP Decorated Chitosan Microgel Beads

The chitosan microgel beads are generated by the addition of chitosan solution dropwise into the 20% glutaraldehyde solution. The decoration of cross-linked bare chitosan beads with Turkevich and Martin AuNPs is materialized by firm contact between the functional amine groups of chitosan microgel beads and AuNPs synthesized in different sizes, respectively. In order to present an example of surface morphologies of gold nanoparticle decorated chitosan microgel beads, the SEM images of Martin AuNP decorated beads with an Au loading of 2.5% are taken. The SEM images of bare and AuNP decorated chitosan microgel beads are given in Figure 4.3.
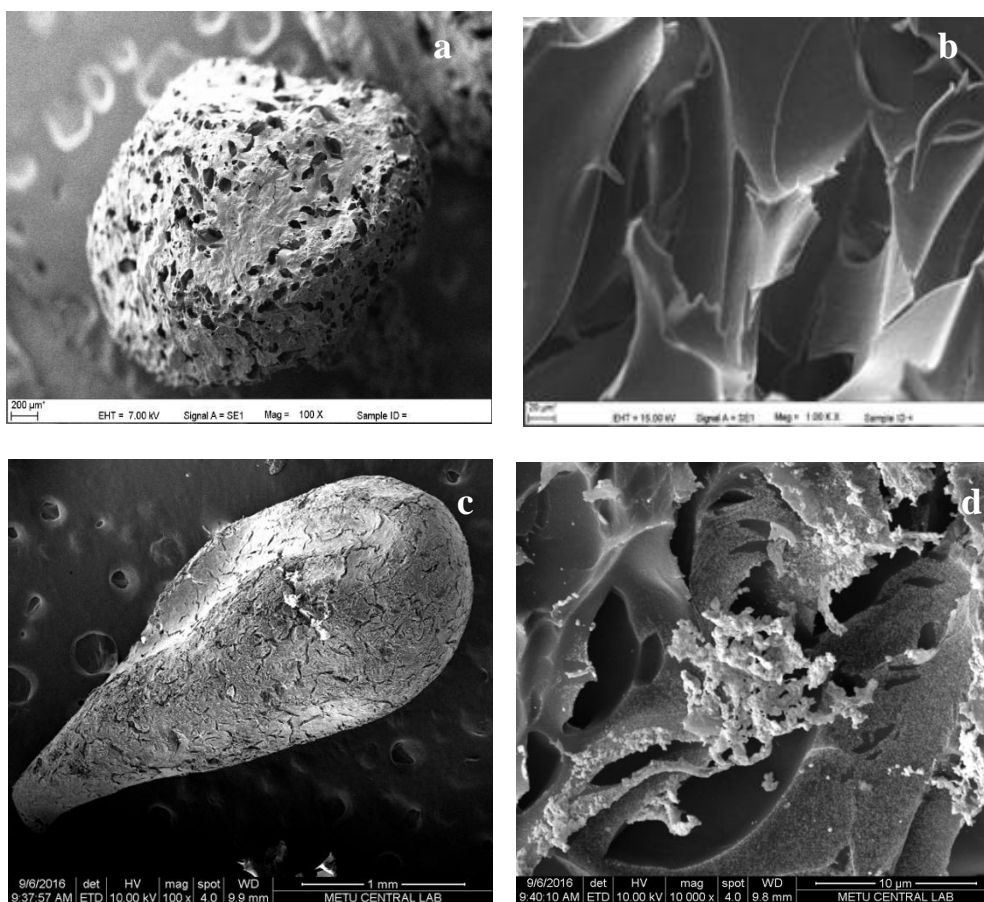
Figure 4.3. SEM photographs of a-b) bare chitosan microgel bead 100x, 10000x, c-d) Martin AuNP decorated chitosan microgel bead (2.5 % (w/w%) Au loading) 100x, 10000x

Therefore, the difference between the morphologies seen in the SEM images of bare chitosan microgel beads and Martin AuNP decorated chitosan microgel beads has an evidentially confirmed value for the successful decoration of gold nanoparticles on the chitosan microgel bead surface. The gold content of resulting beads is found as 2.32% (w/w%) from EDX analysis. Both dispersed particles and small aggregates on the surface of the chitosan microgel beads could be seen. The degree of agglomeration can be associated with the higher surface energy and collision frequency of AuNPs at higher concentrations. As the concentration of gold salt decreases, the number of colliding gold nanoparticles lowers in a constant volume. Thus, a decrease is seen in agglomeration which can further give rise to the generation of monodisperse and uniform gold nanoparticles at low concentrations.

The size and specific surface area (SSA) of bare chitosan microgel bead are shown in the Table 4.1. The drying method of particles has an influence on the surface area

measurements. Therefore, the lower surface area value of chitosan microgel beads may be explained by the treatment of beads by freeze-drying method before characterization. The value obtained by using BET isotherm is found to be compatible with the literature values.

Table 4.1. The size properties and SSA of bare chitosan microgel spheres

Support Material	Diameter (mm)	Specific Surface Area (m^2/g)
Bare chitosan microgel beads	3 mm	1,289

The structures of bare chitosan microgel beads, Turkevich and Martin AuNP decorated chitosan microgel beads were analyzed by X-Ray Diffaraction spectroscopy (XRD). The patterns, in the 2θ range of 3-90°, are given in Figure 4.4.
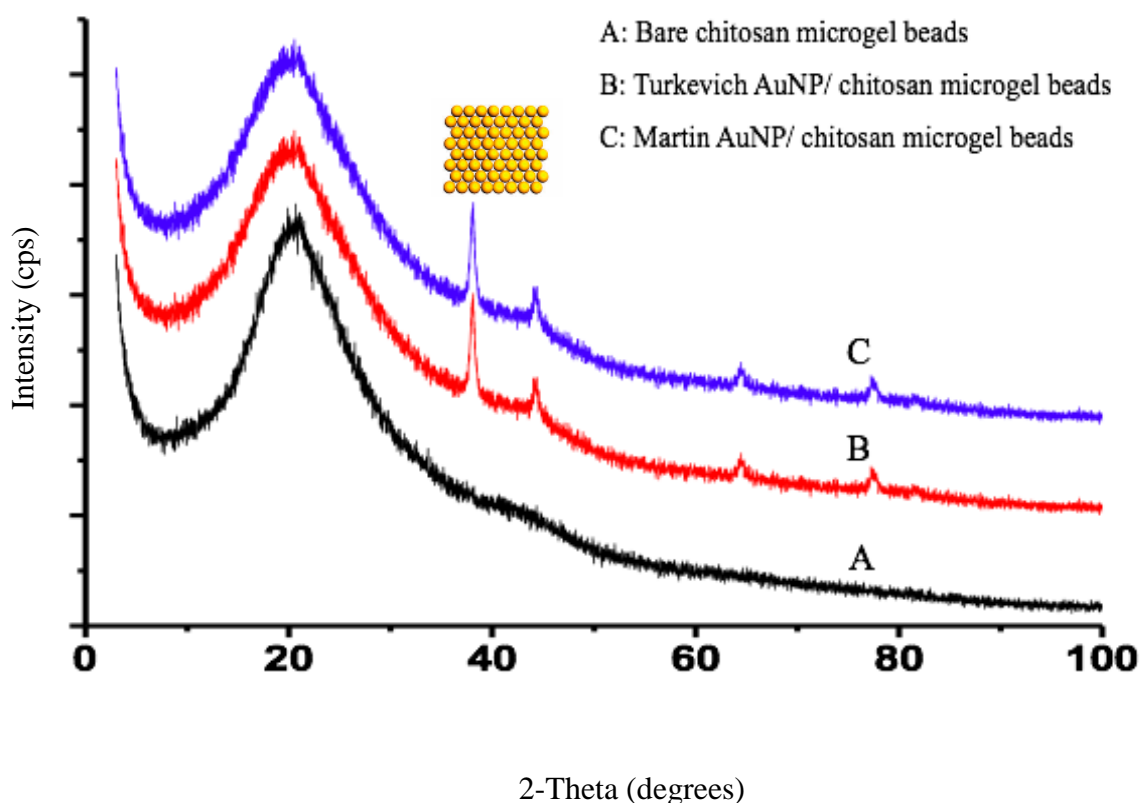
Figure 4.4. XRD patterns of bare chitosan microgel beads, Turkevich and Martin AuNP decorated chitosan microgel beads

The peak at 2θ values of about 20° in the pattern of bare chitosan microgel beads is the characteristic peak that demonstrates the semi-crystallinity of chitosan [89]. After the decoration of beads with AuNPs, the characteristic peaks of bare chitosan broaden due to the presence of AuNPs. The patterns of Turkevich AuNP and Martin AuNP decorated microgel beads reveal new diffraction peaks at 2θ values of about 38 ∘, 44 ∘, 65 ∘ and 77 ∘, which correspond to the Bragg's reflections (111), (200), (220) and (311) of face centered cubic structure of AuNPs, respectively. All that peaks confirm the decoration of AuNP particles on the chitosan gel matrix. However, the appearance of an additional peak at 2θ value of 82° in the pattern of both Turkevich and Martin AuNP decorated chitosan microgel beads can be explained by the occurrence of impurities in the medium that may cause pH change, thus aggregation of gold nanoparticles [90]. The peak intensity reflects the order of gold particle size [91].

4.2.2. Synthesis and Characterization of Bare and AuNP Decorated Titanium Dioxide Spheres

The bare TiO$_2$ spheres are synthesized by simple one-step sol-gel method in the presence of metal alkoxide salt as a precursor and methanol/acetonitrile as solvent system. Afterwards, the amine functionalized titania spheres are obtained by a firm contact between hydroxyl groups of bare TiO$_2$ spheres and methoxysilane groups of Aminotriethoxysilane. In order to prove the success of the amine functionalization the elemental analysis is applied to the spheres. The gold content of resulting TiO$_2$ spheres is found to be 1,98% (w/w%) from EDX analysis. The reaction with APTES enables the attachment of gold nanoparticles to the TiO$_2$ spheres through the functional amine groups. The decoration process is occurred by the addition of derivatized TiO$_2$ spheres into the solutions of AuNPs synthesized by Turkevich and Martin methods, respectively. The size properties and surface morphologies of AuNP decorated TiO$_2$ spheres are revealed by the SEM analysis after drying the spheres in an oven for several hours. SEM images of Martin AuNP decorated beads with an Au loading of 2% are taken in order to present an example of surface morphologies of gold nanoparticle decorated TiO$_2$ spheres. The SEM images of bare and AuNP decorated chitosan microgel beads are given in Figure 4.5.
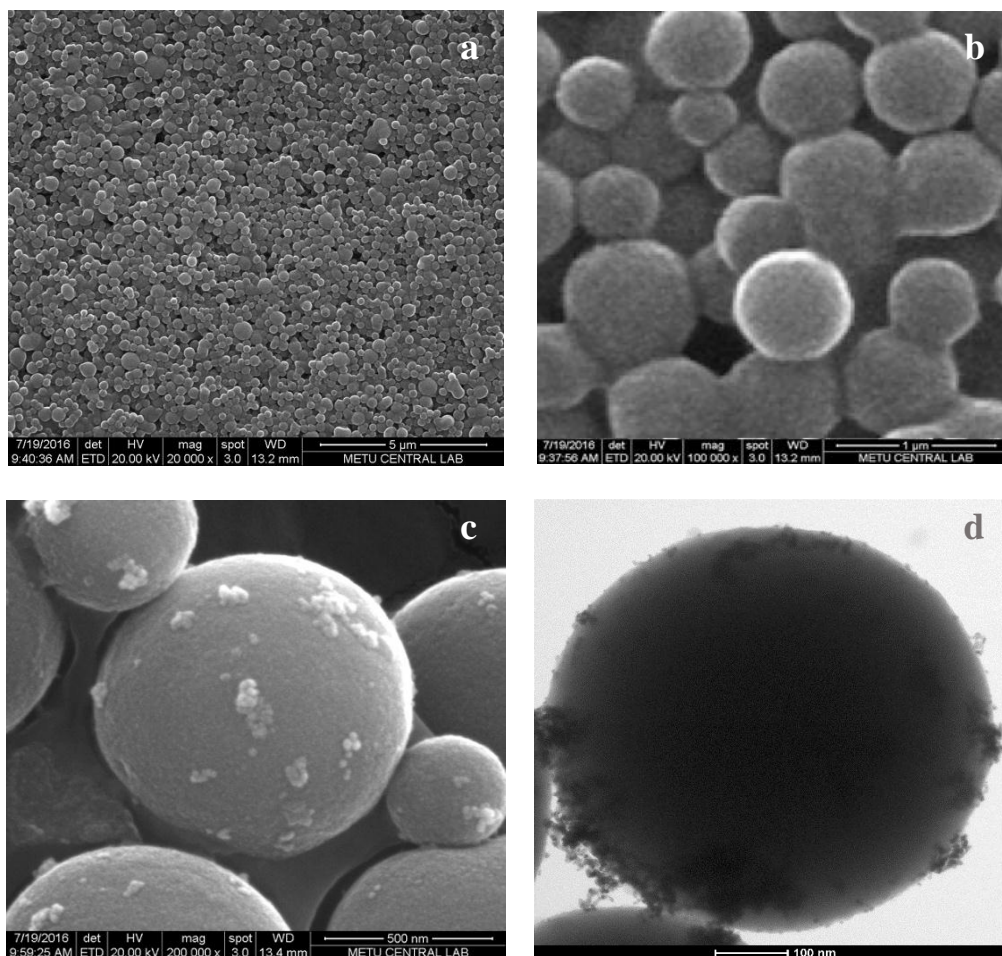
Figure 4.5. SEM photograps of a-b) bare TiO$_2$ spheres 20000x, 100000x, respectively c) Martin AuNP decorated TiO$_2$ spheres (2% (w/w%) Au loading) 200000x d) TEM image of Martin AuNP decorated TiO$_2$ sphere (2% (w/w%) Au loading)

Since the gold atoms are heavier than Ti and O atoms in AuNP/chitosan catalyst, AuNPs are appeared to be brighter in Scanning Electron Microscopy [92]. The surface functionalization and then decoration of TiO$_2$ spheres by amine attachment and AuNP adsorption, respectively, are proved to be successful considering the existence of nano-sized particles on the surface of the TiO$_2$ spheres that can be seen in the SEM and TEM images of AuNP decorated titania spheres. Figure 4.5. also indicates that the titania spheres sythesized by the one-step sol-gel method are different in size which refers to polydispersity. The usage of acetonitrile as a second solvent leads up the formation of uniform spherical particles with smoother surfaces as it was reported by Mine *et al.* By increasing the amount of acetonitrile, the monodispersity can be increased but it also leads to a decrease in the sizes of particles [87]. Furthermore, the TEM image reveals homogeneous distribution of AuNPs on the outer surface of TiO$_2$ spheres. The average

size, coefficient of variation for size distribution and specific surface area (SSA) of bare titania spheres with 2% Au loading are given in Table 4.2.

Table 4.2. The size and SSA of bare TiO_2 spheres

Support Material	Diameter (nm)	CV (%)	Specific Surface Area (m^2/g)
Bare TiO_2 spheres	920	%17	277,4

The average size is calculated as $920 \pm 0,156$ nm based on 100 particles from a sample. The high surface area value calculated by BET isotherm has appeared in the range that refers to mesoporousity. The mesoporousity of $AuNP/TiO_2$ catalyst can enhance the catalytic activity due to the high amount of accessible sites at the interface between AuNPs and TiO_2 support [93].

The structures of bare titania spheres, Turkevich and Martin AuNP decorated titania spheres were analyzed by X-Ray Diffaraction (XRD). XRD patterns and the patterns in the 2θ range of 3-90° are given in Figure 4.6.
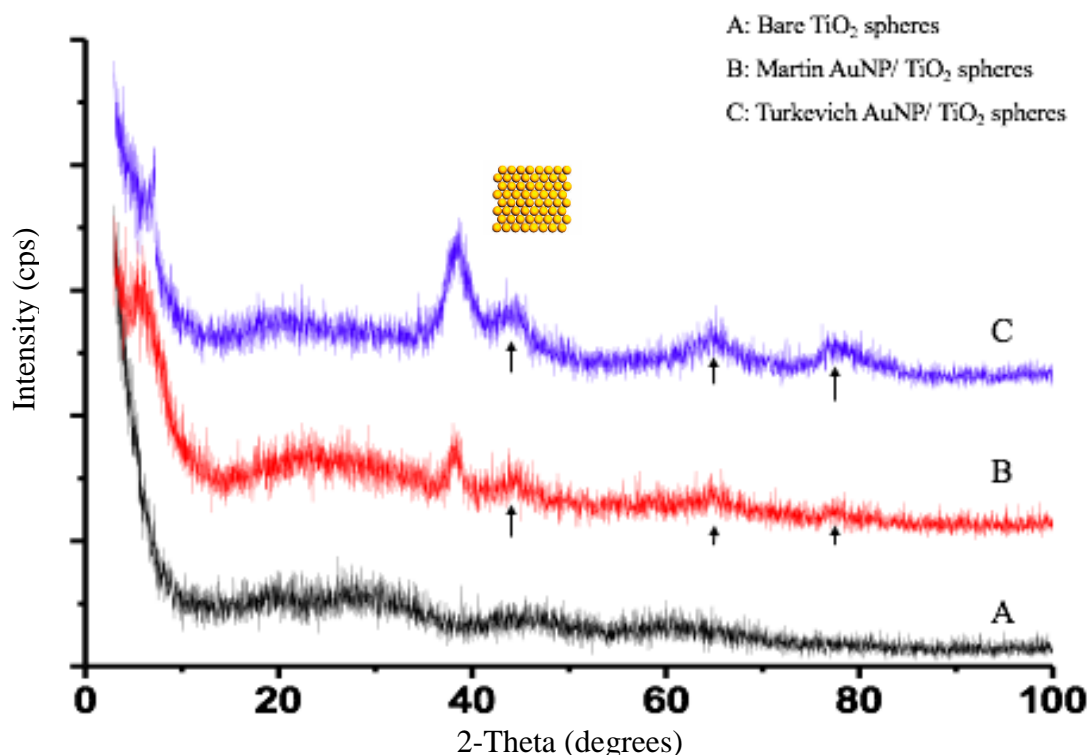
Figure 4.6. XRD patterns of bare TiO_2 spheres, Turkevich and Martin AuNP decorated TiO_2 spheres

44

In addition to the anatase and rutile peaks of titania, the characteristic peaks at 2θ: 38°, 44°, 65° and 77° of face-centered cubic structure AuNPs are seen in the XRD patterns of TiO$_2$ spheres decorated with Turkevich and Martin AuNPs. The results prove that the gold nanoparticles, synthesized in two different sizes, successfully interacted with the TiO$_2$ spheres. The intensities of the peaks decreased in the Turkevich AuNP decorated TiO$_2$ spheres when compared to Martin AuNP decorated TiO$_2$ spheres. These results are compatible with the results obtained by Petkov *et al.* and Moreau *et al.* who reported that the intensity of characteristic peaks of metallic gold decreases as the size of AuNPs decreases [94, 95]. There are no other peaks observed in the XRD pattern that signify the impurities. This indicates the high purity of obtained AuNP particles.

4.3. Plasmon- Enhanced Heterogeneous Catalytic Activity Runs

4.3.1. Reduction Mechanism of 4-Nitrophenol

The reduction of 4-NP to 4-AP by excess amount of sodium borohydride is the model reaction for the evaluation of catalytic performances of metal NPs. The reaction is based on the principle of the generation of 4-Nitrophenolate ions after the addition of NaBH$_4$ as a reductant into 4-Nitrophenol solution showing an absorption peak at 317 nm. The UV-vis absorption peak of 4-Nitrophenol shifts from 317 nm to 400 nm, thus the color of solution changes from light yellow to dark yellow by the addition of NaBH$_4$. The changes indicate the formation of 4-Nitrophenolate ions in the reaction environment. Unfortunately, the peak at 400 nm remains unaltered for a long period despite the excess amount of NaBH$_4$. It could be explained by the kinetic barrier arose from large potential difference between 4-nitrophenolate and BH$_4^-$ ions [49]. Gold nanoparticle as a plasmonic catalyst serves as an electronic relay system to pass through the kinetic barrier, thus has capability to catalyze the formation of 4-Aminophenol effectively.
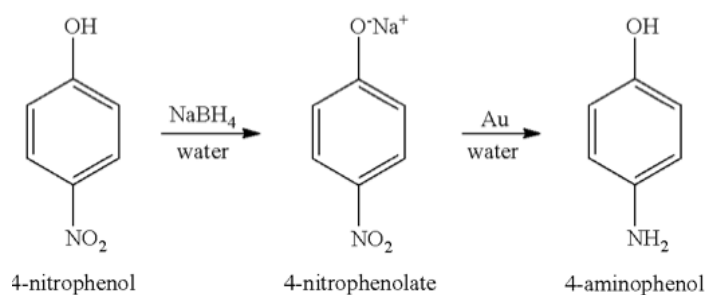
Figure 4.7. Reduction steps of 4-NP to 4-AP

The following studies involve the application of chitosan microgel beads supported and TiO$_2$ spheres supported AuNPs obtained by two different methods and thus in different sizes. The effect of AuNP loading, amount of catalyst, initial 4-Nitrophenol concentration on the catalytic activity and stability of catalysts are evaluated. Since the concentration of NaBH$_4$ greatly exceeds that of 4-NP, the reduction rate can be assumed to be independent of NaBH$_4$ concentration [96]. As Deshmukh *et al.* got appreciable reduction rates within 3 minutes at room temperature, the 4-Nitrophenol reduction was conducted in water at room temperature in which the reactants are often soluble, and the catalyst is stable during the reaction [83].

4.3.2. Plasmonic Catalysis of 4-Nitrophenol in the Presence of AuNP Decorated Chitosan Microgel Beads

The catalytic activities of Turkevich and Martin AuNP decorated chitosan microgel beads were evaluated within the reduction of 4-Nitrophenol by using UV-Vis absorption spectroscopy. Figure 4.9. shows the time-dependent UV-Vis spectra along the reduction of 4-Nitrophenol solution (7.5 ppm, 24 mL) in the presence of Turkevich AuNP decorated chitosan microgel beads (5 mg) by using excess amount of NaBH$_4$ at room temperature.
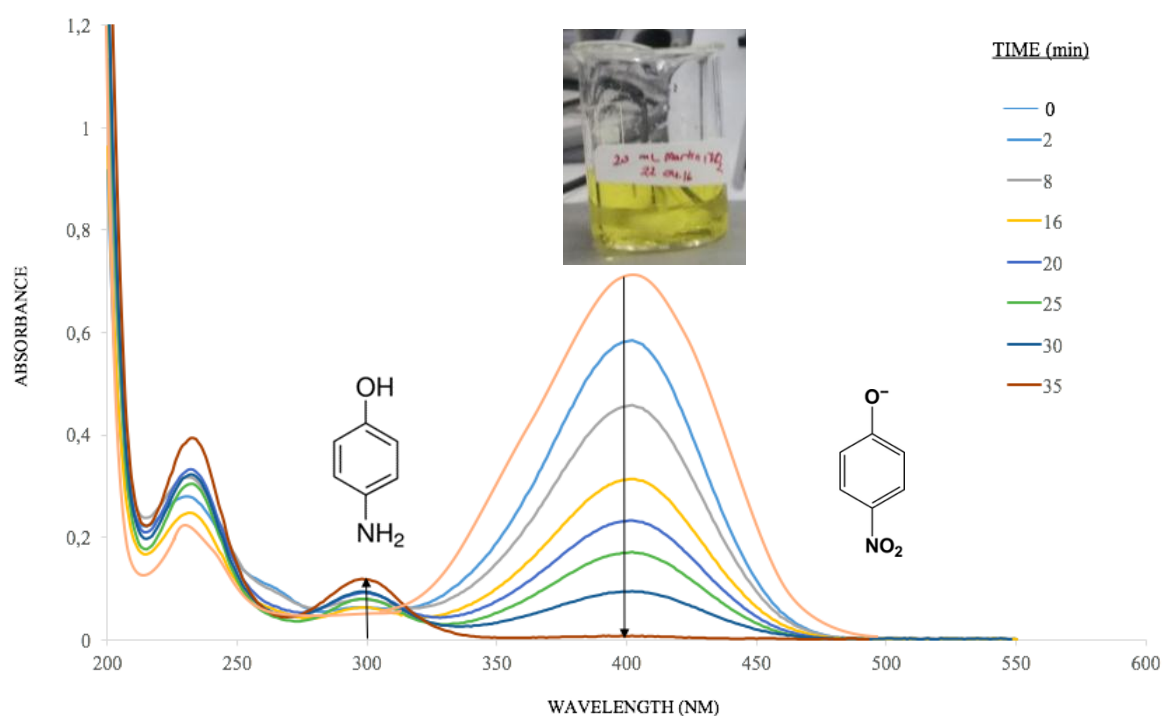
Figure 4.8. UV-vis spectrum of 4-NP reduction in time (Conditions: Turkevich AuNP decorated chitosan microgel beads, Catalyst Amount: 10 mg, Au loading (w/w %): 2,5 %, Initial 4-NP concentration: 7.5 ppm, volume of solution: 24 mL, Temperature: 25^{0}C)

The absorption peak at 400 nm indicates the occurance of 4-Nitrophenolate anions that are formed by the addition of $NaBH_4$. The decrease in the peak intensity of 4-Nitrophenolate peak at 400 nm and the continuous increase in the intensity of the peak at 300 nm are attributed to the generation of 4-Aminophenol by AuNP decorated chitosan microgel beads. The peak at 400 nm eventually disappears (the complete reduction of 4-Nitrophenol is achieved) within 35 min at given conditions. The concentration of 4-Nitrophenol is calculated according to the decrease in the absorbance peak at 400 nm, which is directly proportional to the reduction in 4-NP concentration. The complete reduction is achieved within 12 minute in optimum experimental conditions.

4.3.2.1. Effect of AuNP Size and Loading

The influence of Au loading on the plasmonic catalytic reduction rate of 4-Nitrophenol was observed within the reduction of 4-Nitrophenol solution (7.5 ppm, volume of solution: 24 mL) in the presence of chitosan microgel beads decorated with increasing amounts of Au loading (1,25%, 2,5 %, 5 %, 10 %, 20% (w/w %), catalyst amount: 10 mg). This set of experiments was applied both in the presence of Turkevich AuNP and Martin AuNP decorated chitosan microgel beads. The changes in 4-Nitrophenol concentration in time for increasing amounts of Au loading in the presence of chitosan microgel beads decorated with gold nanoparticles that are different in size are given in Figure 4.9 and 4.10.

Figure 4.9. The effect of Au loading on the reduction rate of 4-NP in the presence of chitosan microgel beads decorated with AuNPs synthesized by Turkevich Method (Conditions: Catalyst amount: 10 mg, Initial 4-Nitrophenol concentration: 7.5 ppm, volume of solution: 24 mL, Temperature: 25 ^{0}C)

Figure 4.10. The effect of Au loading on the reduction rate of 4-NP in the presence of chitosan microgel beads decorated with AuNPs synthesized by Martin Method (Conditions: Catalyst amount: 10 mg, Initial 4-Nitrophenol concentration: 7.5 ppm, volume of solution: 24 mL, Temperature: 25 ^{0}C)

The results from Figure 4.9. show that the increase in the amounts of Au loading leads to a significant change up to the value of 2,5%. However, in the higher loading amounts of Turkevich AuNPs, no changes are seen in the rate of 4-Nitrophenol reduction. Similar results are obtained in the presence of higher loading amounts of Martin AuNPs. The results may be explained by lowering the amount of free functional groups, thus lowering the sorption capacity of chitosan microgel beads [97]. The figures also demonstrate that the time needed for the complete reduction of 4-NP solution decreases from 35 minutes to 12 minutes with Martin AuNP decorated beads due to the higher redox potential of low size NPs. Therefore, Martin AuNP decorated chitosan microgel beads with a loading amount of 2,5% are employed in further experiments conducted to investigate the effects of other parameters on the catalytic activity.

4.3.2.2. Effect of Catalyst Amount

The influence of amount of catalyst on the plasmonic catalytic reduction rate of 4-NP is observed within the reduction of 4-NP solution (7.5 ppm, 24 mL) in the presence of increasing amounts of AuNP decorated chitosan microgel beads (5 mg, 10 mg, 20 mg, Au Loading (w/w %): 2,5 %). This set of experiments is applied in the presence of Martin AuNP decorated chitosan microgel beads. The changes in 4-Nitrophenol concentration in the course of reduction reaction using increasing amounts of chitosan microgel beads decorated with gold nanoparticles that are different in size are given in Figure 4.11.

Figure 4.11. The effect of catalyst amount on the reduction rate of 4-NP in the presence of chitosan microgel beads decorated with AuNPs synthesized by Martin Method (Conditions: Au Loading (w/w %): 2,5%, Initial 4-NP concentration: 7.5 ppm, Volume of solution: 24 mL, Temperature: 25 ^{0}C)

The results indicate that the increase in the amount of catalyst leads to an increase in the reduction rate of 4-NP. However, in the presence of amounts of Martin AuNP/ chitosan catalyst higher than 10 mg, there are no significant changes were seen in the percentage of conversion. The complete reduction takes place along 12 minutes in the presence of 10 mg catalyst, while it continues within 16 minutes as the catalyst amount is doubled. These results are compatible with the results obtained by Zhang *et al.* [53]. This

can be explained by the external mass transfer limitation between spheres that blocks the adsorption of 4-Nitrophenol molecules through the catalyst surface in the usage of larger amounts of catalyst [2]. Therefore, 10 mg of Martin AuNP decorated chitosan microgel beads were used in further experiments that were performed in order to evaluate the effects of other parameters on the catalytic activity.

4.3.2.3. Effect of Initial 4-Nitrophenol Concentration

The influence of initial 4-NP concentration on the catalytic reduction rate of 4-NP was observed within the reduction of different concentrations of 4-Nitrophenol solutions (3.75 ppm, 7.5 ppm, 15 ppm, volume of solution: 24 mL) in the presence of AuNP decorated chitosan microgel beads (10 mg, Au Loading (w/w %): 2,5 %). This set of experiments is applied in the presence of Martin AuNP decorated chitosan microgel beads. The changes in 4-Nitrophenol concentration in the course of time at increasing initial concentrations of 4-NP in the presence of chitosan microgel beads decorated with gold nanoparticles that are different in size are given in Figure 4.12.
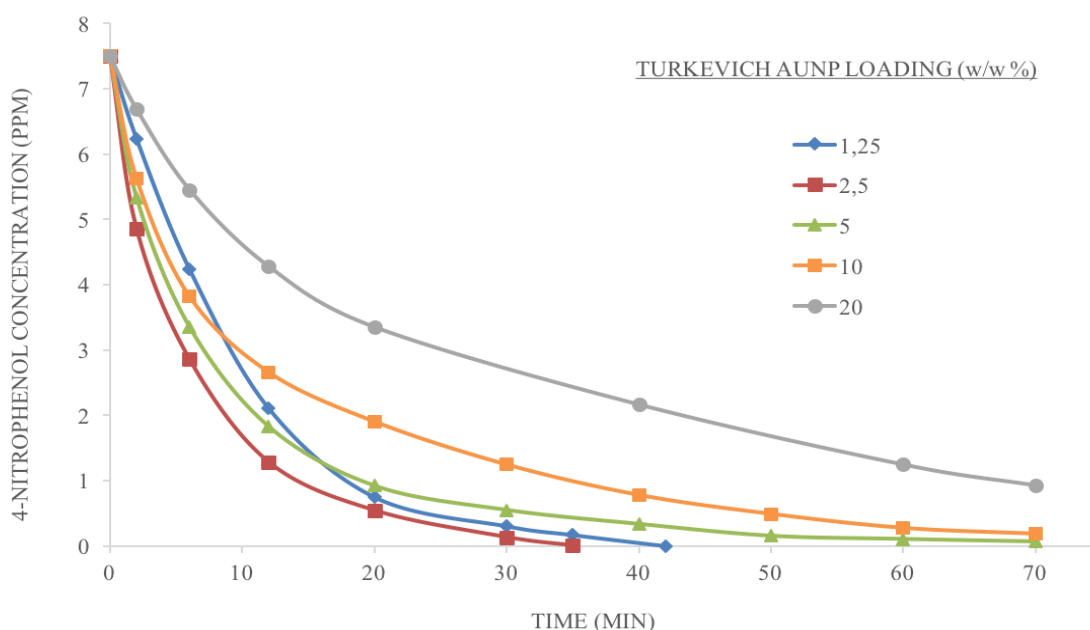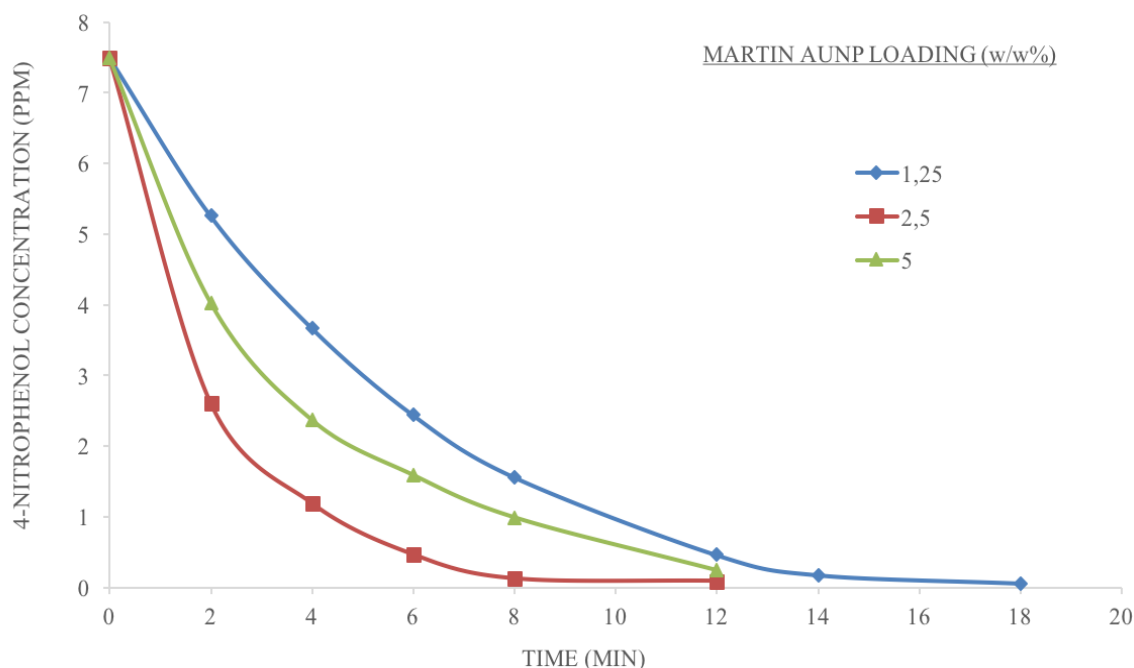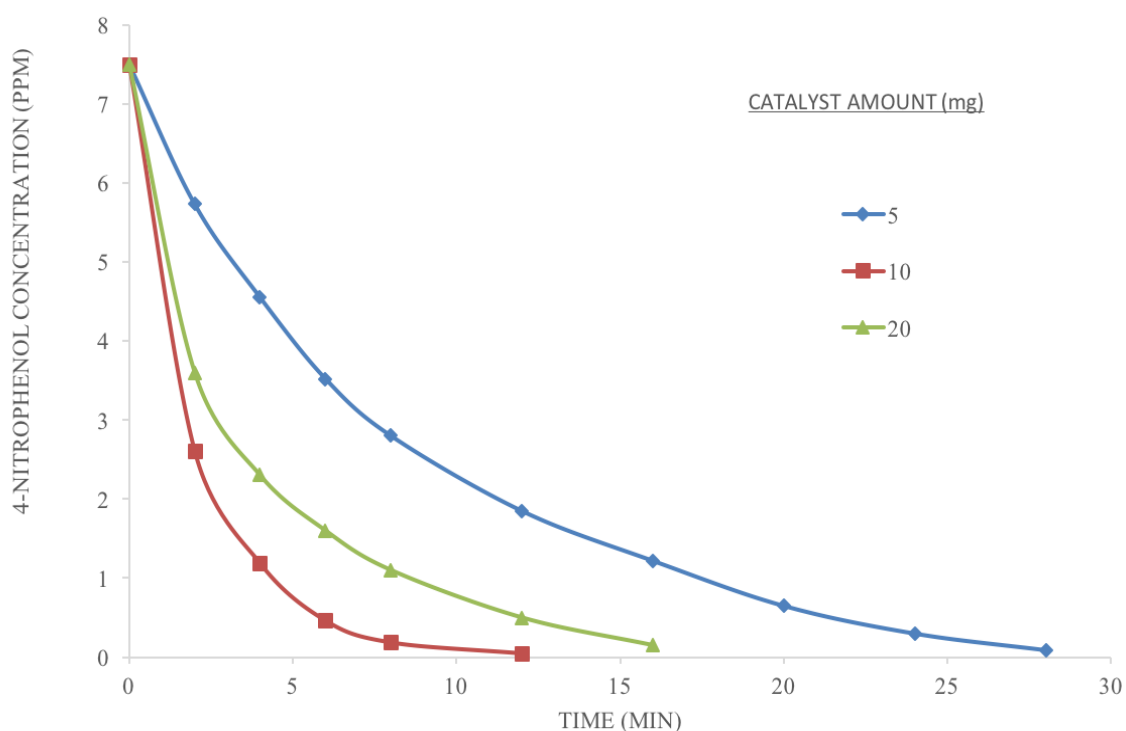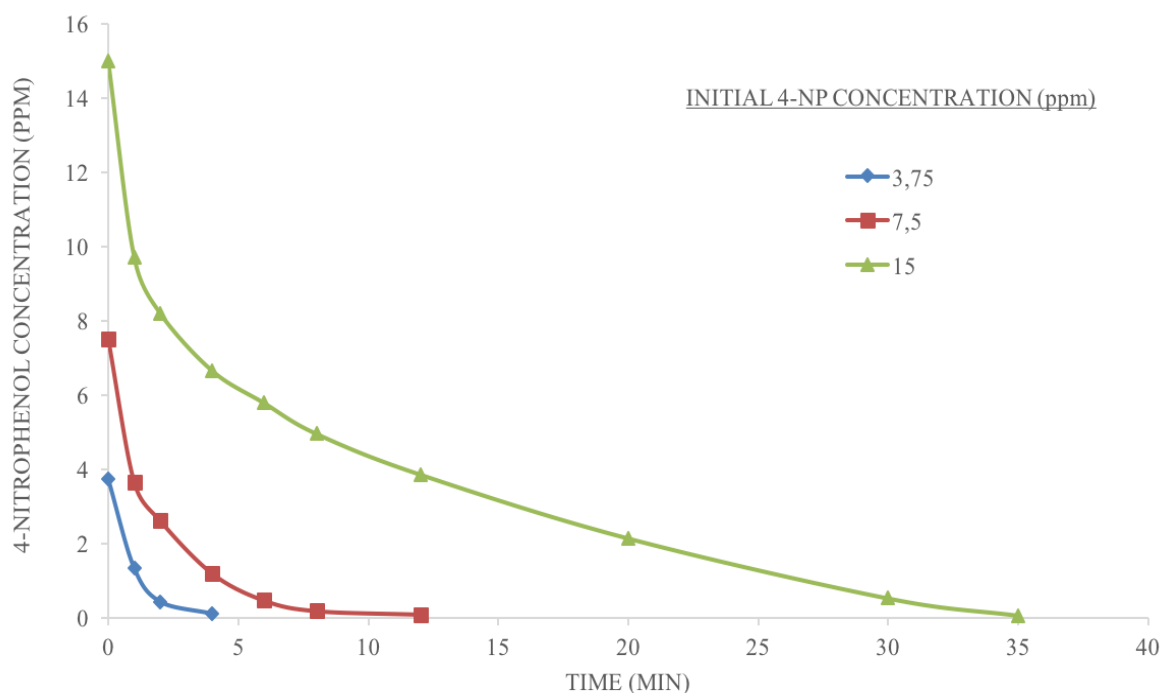

Figure 4.12. The effect of initial 4-NP concentration on the reduction rate of 4-NP in the presence of chitosan microgel beads decorated with AuNPs synthesized by Martin Method (Conditions: Catalyst amount: 10 mg, Au Loading (w/w %): 2,5 %, Volume of solution: 24 mL, Temperature: 25 ^{0}C)

The results of three different concentrations of 4-Nitrophenol are given in Figure 4.12. It demonstrates that increasing concentrations of 4-NP in the presence of Martin AuNP decorated chitosan microgel beads as catalyst lead to an increase in complete reduction time. Since the surface of NP becomes saturated with 4-Nitrophenol molecules, remarkable decreases in the reactivity of BH_4^- on the surface of the NP and in the rate of electron transfer to the NP surface are occurred [52].

4.3.2.4. Recovery and Reusability

The recovery and reusability studies were performed only for the Martin AuNP decorated chitosan microgel beads that show the highest plasmonic catalytic activity for the 4-NP reduction amongst other catalysts. In order to investigate the reusability of Martin AuNP decorated chitosan microgel beads, the reduction reaction was repeated for three times under the same experimental conditions (catalyst amount: 10 mg, Au loading (w/w %): 2.5 %, initial 4-NP concentration: 7.5 ppm, volume of solution: 24 mL, temperature: 25^0C). The beads were recovered easily by filtration after each experiment, rinsed and added into the fresh mixture of the reactants. The percentage of removal within each repetition is shown in Figure 4.13.
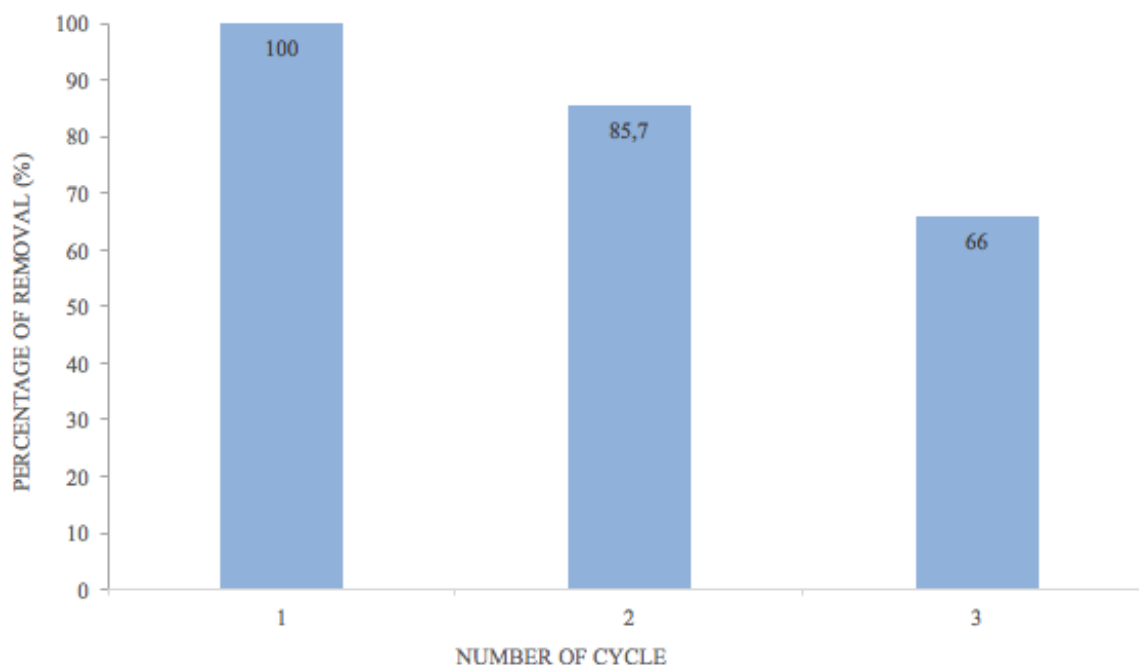
Figure 4.13. The reusability of Martin AuNP decorated chitosan microgel beads used in the reduction of 4-Nitrophenol (Conditions: catalyst amount: 10 mg, Au loading (w/w %): 2,5 %, initial 4-NP concentration: 7.5 ppm, volume of solution: 24 mL, temperature: 25^0C)

Figure 4.13. shows that the percentage of conversion of 4-Nitrophenol has decreased by 44% after 3 cycles in the presence of Martin AuNP decorated chitosan microgel beads. Since the catalytic performance of a catalyst depends on the active sites on its surface, the decrease in catalytic activity through the cycles can be explained by the deactivation of active sites on the surface of gold nanoparticles. Moreover, the loss of catalytic activity of metal NPs/chitosan beads can also be associated with the interactions between chitosan and the metals, as the diffusion of reactants onto the chitosan matrices is affected by the charge and network of chitosan. Martin AuNP decorated chitosan microgel beads can easily adsorb 4-Aminophenol that may result in poisoning of the catalyst with loss of activity [78].

As one of the latest studies employing a different form of chitosan as a catalyst support material in the catalytic conversion of 4-Nitrophenol, Wei *et al.* introduced a method in which $AuCl_4$ ions were reduced to zero-valent AuNPs by chitosan itself without any additional reducing agent under thermal treatment within 12 hours. Since the pH was found to have a significant effect on in-situ preparation of AuNPs in supramolecular hydrogels, the pH is adjusted to 5.6 as an optimum value. Under the optimum conditions, the reduction reaction was almost completed within 5 minutes. However, the catalyst was only effective for the first cycle and the recovery remained as a difficulty [78].

As another one of the latest studies employing a bead form of different material as a catalyst support material in the catalytic conversion of 4-NP, Pal *et al.* introduced Au embedded hydrogel beads. The beads are prepared by the incubation of calcium alginate beads with $HAuCl_4$ solution for 3 hours and then irradiation with UV light source for 40 minutes. The separate preparation and then deposition of AuNPs led to a control over NP size. Under optimum reaction conditions, 92% of 4-Nitrophenol was converted to 4-Aminophenol within 50 minutes. Although the recovery of the catalyst 2 mm in size was simple, the catalyst was only effective for the first cycle [98]. When compared to these recent advances, Au/chitosan hydrogel beads were found to be more promising catalyst towards the reduction of 4-Nitrophenol due to the enhancement in reduction rates under optimum conditions and ease of deposition of AuNPs which allows controlled growth of NPs without a need of pH adjustment and high temperatures.

4.3.3. Plasmonic Catalysis of 4-Nitrophenol in the Presence of AuNP Decorated TiO$_2$ Spheres

The catalytic activities of Turkevich and Martin AuNP decorated titania spheres were evaluated within the reduction of 4-Nitrophenol solution by UV-Visible absorption spectroscopy. Figure 4.14 demonstrates the time-dependent UV-Vis spectrum along the reduction of 4-NP solution (7.5 ppm, 24 mL) in the presence of Turkevich AuNP decorated titania spheres (2 mg) by using excess amount of NaBH$_4$ at room temperature.
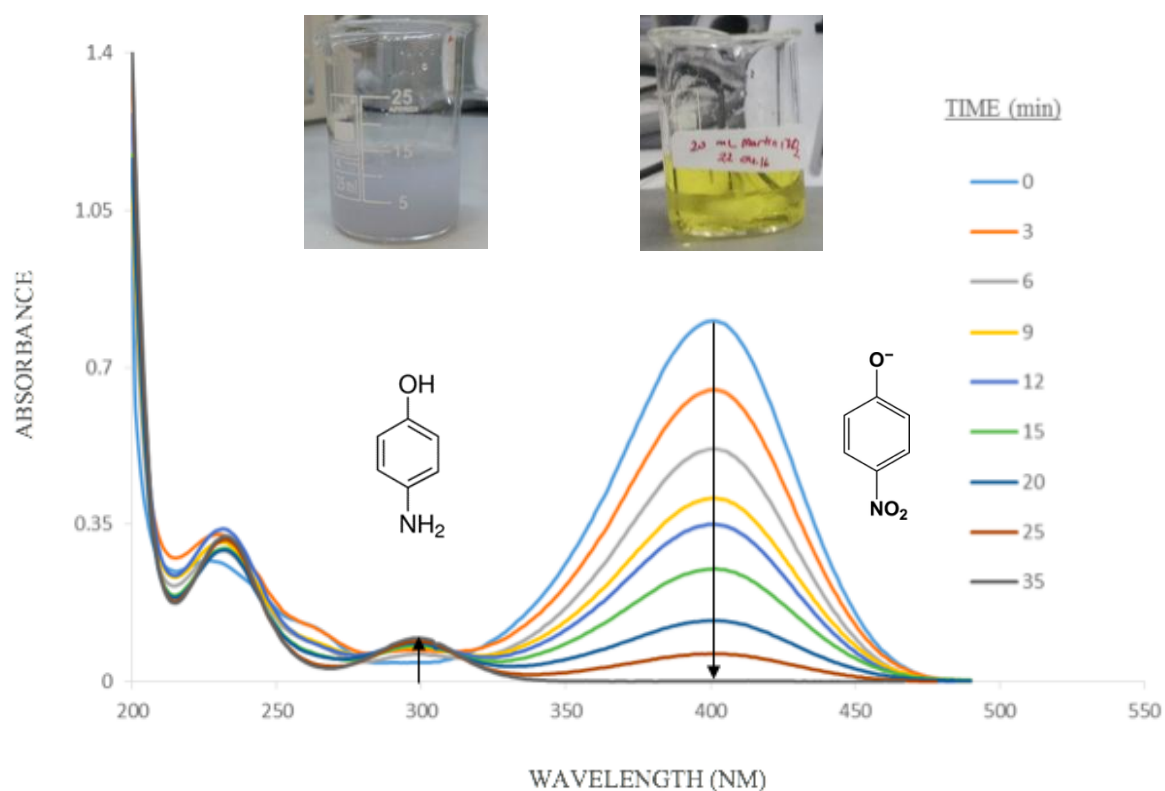
Figure 4.14.UV-vis spectrum of 4-NP reduction at different times (Conditions: Catalyst: Turkevich AuNP decorated TiO$_2$ spheres, Catalyst Amount: 12.5 mg, Au loading (w/w %): 2%, Initial 4-NP concentration: 30 ppm, 24 mL, Temperature: 25^0C)

The absorption peak at 400 nm indicates the occurrence of 4-Nitrophenolate anions that are formed by the addition of NaBH$_4$. The decrease in the intensity of the 4-Nitrophenolate peak at 400 nm and the continuous increase in the intensity of the peak at 300 nm are attributed to the generation of 4-AP by AuNP decorated TiO$_2$ spheres. The peak at 400 nm eventually disappears within 35 minutes at given conditions. The complete reduction is achieved within 1 minute in optimum experimental conditions.

4.3.3.1. Effect of AuNP Size and Loading

The influence of Au loading on the plasmonic catalytic reduction rate of 4-NP was observed within the reduction of 4-NP solution (7.5 ppm, volume of solution: 24 mL) in the presence of TiO_2 spheres decorated with increasing amounts of Au loading (1 %, 2 %, 4 % (w/w %), catalyst amount: 12.5 mg). This set of experiments were applied both in the presence of Turkevich AuNP and Martin AuNP decorated TiO_2 spheres. The changes in 4-Nitrophenol concentration in time at increasing amounts of Au loading in the presence of TiO_2 spheres decorated with gold nanoparticles that are different in size are given in Figure 4.16.

Figure 4.15. The effect of Au loading on the reduction rate of 4-NP in the presence of TiO_2 spheres decorated with AuNPs synthesized by Turkevich and Martin Methods (Conditions: Catalyst amount: 12.5 mg, Initial 4-NP concentration: 7.5 ppm, Volume of solution: 24 mL, Temperature: 25 ^{0}C)

The results from the figure above show that the increase in the amounts of Au loading leads to a significant change up to the value of 2%. However, in the higher loading amounts of Turkevich AuNP and Martin AuNP, no changes could be seen in the rate of reduction of 4-NP. The catalytic activity mostly depends on the total surface area of AuNPs in catalyst system. As the loading of AuNP increases, the number of gold nanoparticles on titania support increases initially, thus the total surface area increases. The

results are compatible with the results obtained by Li *et al.* who reported that the sizes of gold nanoparticle grow larger, as the Au loading increases further than a significant value, leading up to a decrease in the catalytic activity of Au/TiO$_2$ catalyst [43]. The figure also demonstrates that the time needed for the complete conversion of 4-NP solution decreases from 4 minutes to 1 minute with Martin AuNP decorated beads due to the fact that low size NPs facilitate the electron transfer. Therefore, Martin AuNP decorated TiO$_2$ spheres with a loading amount of 2% are used in further experiments that are conducted to evaluate the effects of other parameters on the catalytic activity.

4.3.3.2. Effect of Catalyst Amount

The influence of catalyst amount on the catalytic reduction rate of 4-NP was observed within the reduction of 4-NP solution (7.5 ppm, 24 mL) in the presence of increasing amounts of AuNP decorated TiO$_2$ spheres (1.25 mg, 2.5 mg, 6.25 mg, 12.5 mg, Au Loading (w/w %): 2 %). This set of experiments were applied both in the presence of Turkevich AuNP and Martin AuNP decorated TiO$_2$ spheres. The changes in 4-Nitrophenol concentration in the course of reduction reaction using increasing amounts of TiO$_2$ spheres decorated with gold nanoparticles that are different in size are given in Figure 4.17.

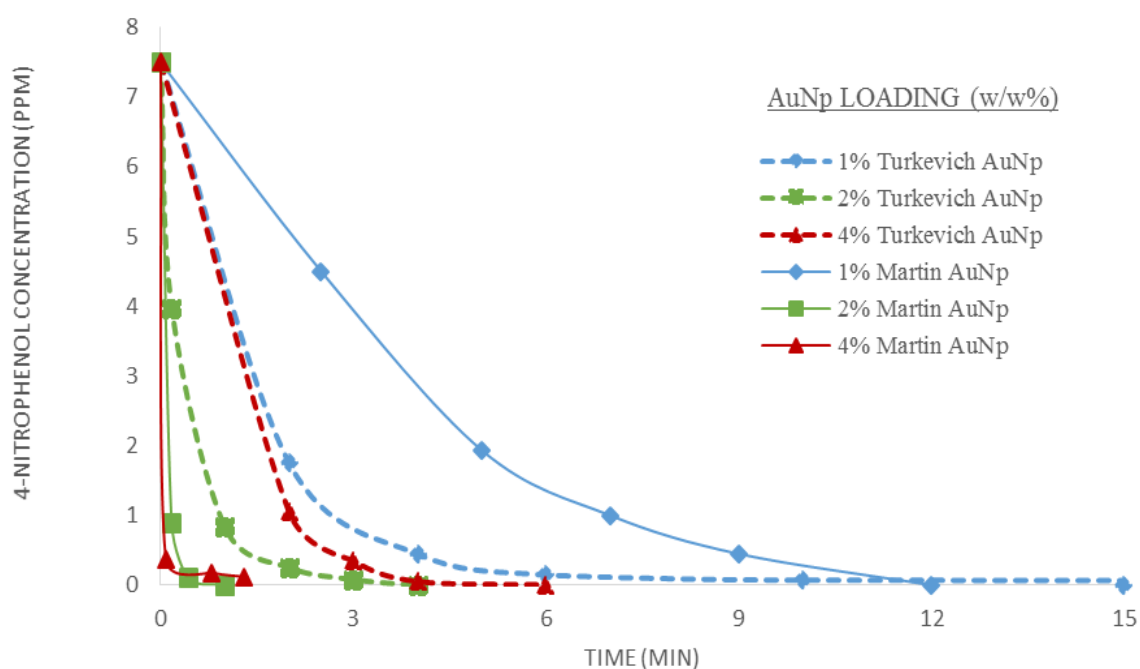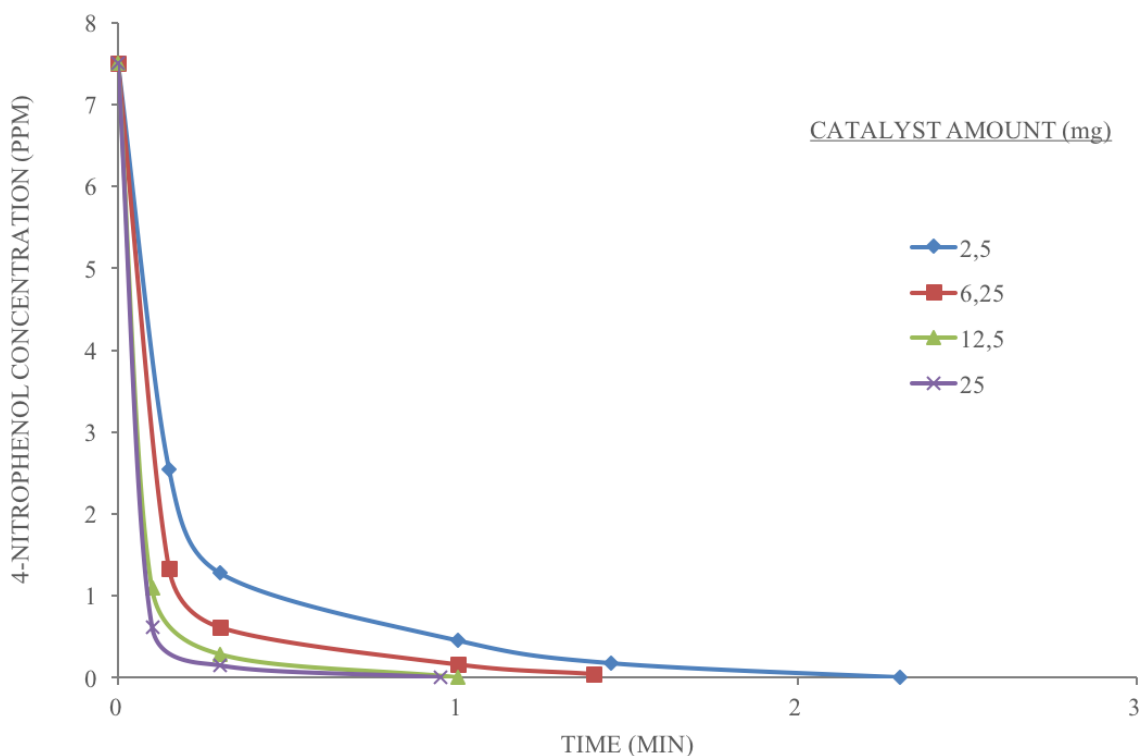**Figure 4.16.** The effect of catalyst amount on the reduction rate of 4-NP in the presence of TiO$_2$ spheres decorated with AuNPs synthesized Martin Method (Conditions: Au Loading (w/w %): 2%, Initial 4-NP concentration: 7.5 ppm, Volume of solution: 24 mL, Temperature: 25 ^{0}C)

The results indicate that the increase in the amount of catalyst leads to an increase in the reduction rate of 4-NP. However, in the presence of amounts of Martin AuNP/ TiO$_2$ catalyst higher than 12.5 mg, there are no significant changes seen in the reduction rate. The complete reduction takes place along 60 seconds in the presence of 12.5 mg catalyst, while it reduces only to 58 seconds as the catalyst amount is doubled. The results are corroborated by the results obtained by Desmukh *et al.* who explained the reason for this tiny decrease by the aggregation of solid particles in the usage of larger amounts of catalyst [83]. The decrease in the reduction rate is also attributed to the lower dispensability of the catalyst in the reaction mixture. Therefore, 12.5 mg of AuNP decorated TiO$_2$ spheres were used in further experiments that are conducted to evaluate the effects of other parameters on the catalytic performance.

4.3.3.3. Effect of Initial 4-Nitrophenol Concentration

The influence of initial 4-NP concentration on the catalytic reduction rate of 4-NP was observed within the reduction of different concentrations of 4-NP solutions (3.75 ppm ,7.5 ppm, 15 ppm, 30 ppm, volume of solution: 24 mL) in the presence of AuNP decorated TiO$_2$ spheres (1.25 mg, Au Loading (w/w %): 2 %). This set of experiments were conducted both in the presence of Turkevich AuNP and Martin AuNP decorated TiO$_2$ spheres. The changes in 4-Nitrophenol concentration in the course of time at higher initial concentrations of 4-NP by TiO$_2$ spheres decorated with Martin gold nanoparticles that are different in size are given in Figure 4.18
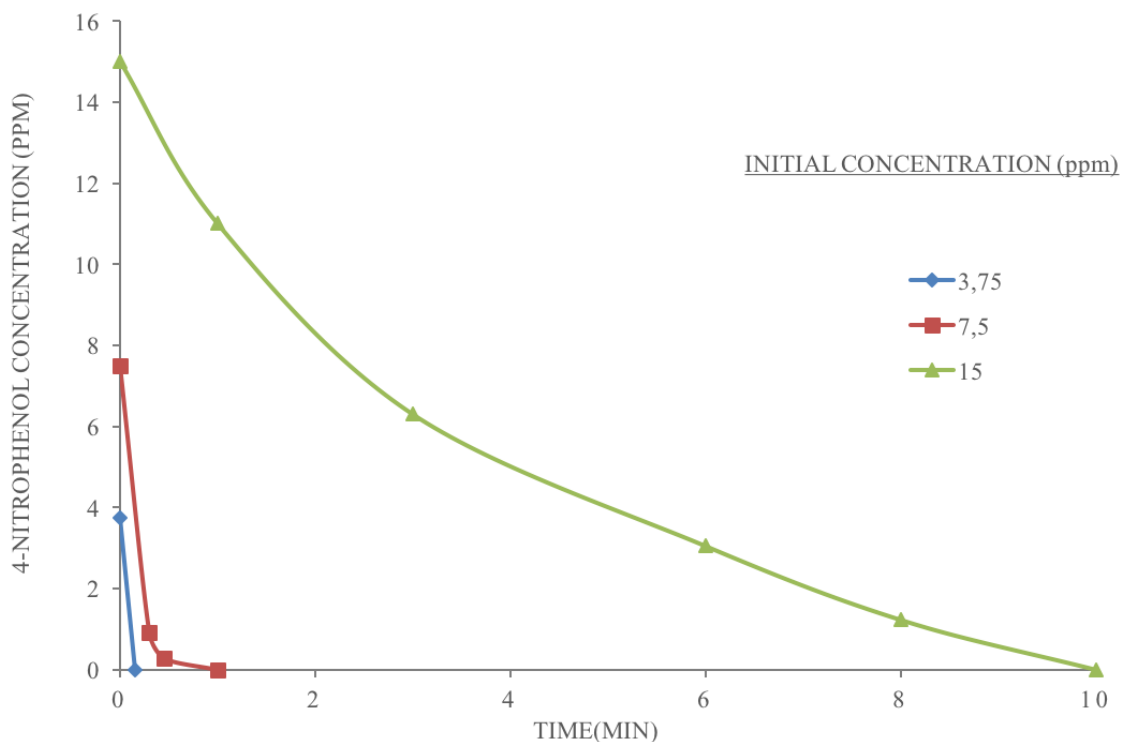
Figure 4.17. The effect of initial 4-NP concentration on the reduction rate of 4-NP in the presence of TiO$_2$ spheres decorated with AuNPs synthesized by Martin Method (Conditions: Catalyst amount: 12.5 mg, Au Loading (w/w %): 2%, Volume of solution: 24 mL, Temperature: 25 ^{0}C)

Figure 4.17. indicates that the increasing concentrations of 4-Nitrophenol in the presence of Martin AuNP decorated TiO$_2$ spheres as catalyst lead to an increase in complete reduction time. There is a competitive adsorption of substrate and reductant on the nanoparticle surface [52]. Therefore, the increase in complete conversion period is attributed to the the amount of BH$_4^-$ ions that remains unchanged while the amount of 4-Nitrophenolate ions keeps on increasing. Thus the required time for the transfer of electrons into the metal surface by reductant increases [3].

4.3.3.4. Recovery and Reusability

The recovery and reusability studies were performed only for the Martin AuNP decorated TiO$_2$ spheres that showed the highest plasmonic catalytic activity in the conversion of 4-NP. In order to investigate the reusability of Martin AuNP decorated TiO$_2$ spheres the reduction reaction was repeated for three times under the same experimental conditions (catalyst amount: 12.5 mg, Au loading (w/w %): 2%, initial 4-NP concentration: 7.5 ppm, volume of solution: 24 mL, temperature: 25^{0}C). The spheres are recovered by

centrifugation (9000 ppm, 1 min) at the end of each experiment, rinsed and redispersed in a fresh mixture of the reactants. The percentage of removal within each repetition is shown in Figure 4.19.
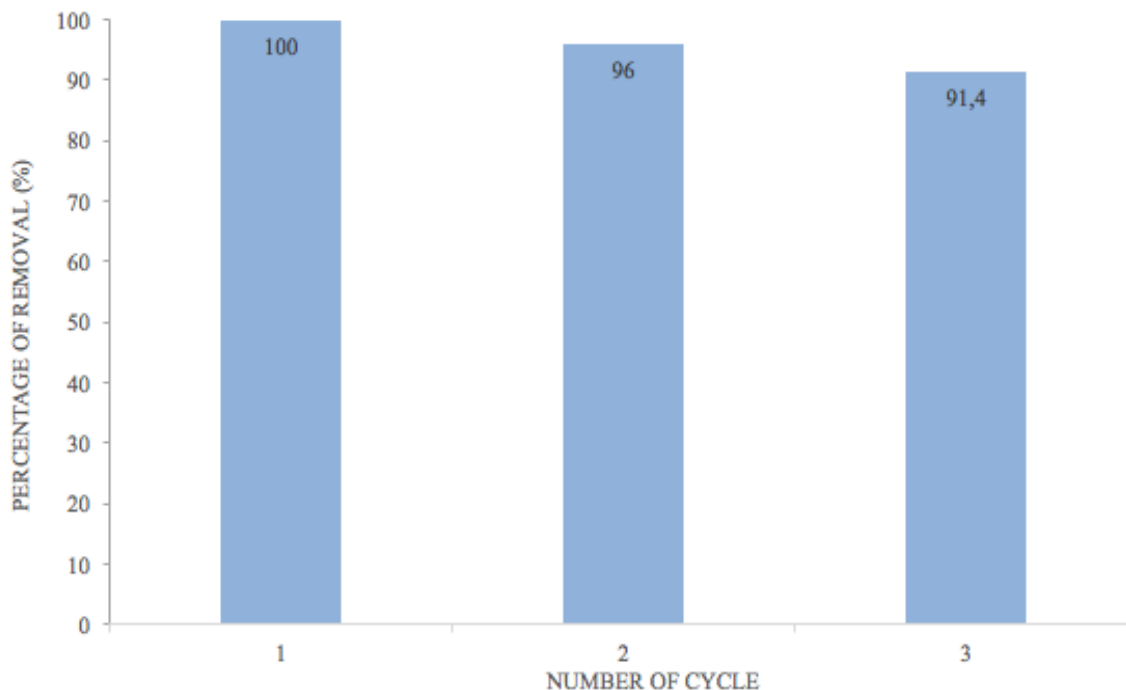
Figure 4.18. The reusability of Martin AuNP decorated TiO_2 spheres used in the reduction of 4-Nitrophenol (Conditions: catalyst amount: 12.5 mg, Au loading (w/w %): 2%, initial 4-NP concentration: 7.5 ppm, volume of solution: 24 mL, temperature: 25^0C, reaction time: 1 min)

The stability and reusability of catalysts have a great importance for practical applications. As it has been presented in the previous studies the catalytic activity decreases continuously while the recycling studies continues [69, 99]. As seen in Figure 4.18. the reduction efficiency slightly decreases by 8.6 % over the 3 successive cycles. This decrease can be attributed to the loss of Martin AuNP decorated TiO_2 spheres during the separation by centrifugation after each cycle. This slight decrease might also be explained by the absorption of 4-Aminophenol on catalyst surface [99].

As one of the latest studies employing TiO_2 spheres having small sizes as a catalyst support material in the catalytic conversion of 4-NP, Yazid *et al.* introduced AuNP deposited nonporous TiO_2 spheres 100 nm in size which are prepared by deposition-precipitation (DP) method. It was found that in DP method the pH has a crucial effect on

AuNP size distribution and AuNP loading. Under optimum conditions, the complete reduction of 4-Nitrophenol is achieved within 2.5 minutes [68].

Hao *et al.* introduced mesoporous AuNP/TiO$_2$ nanofibers as a catalyst support material which were prepared by in-situ synthesis of AuNPs in metal-alkoxide precursor solution, followed by an electrospinning of resulting solution for 12 hours. The electrospun composite nanofibers are then calcined at 500^{0}C. Finally, the mesoporous AuNP/TiO$_2$ hybrid nanofibers, 200 nm in size, are formed. followed by calcination at 500^{0}C. Under the optimum conditions, the complete reduction of 4-Nitrophenol via novel mesoporous nanocomposite fibers is achieved wihin 16 minutes [69]. When compared with these recent advances, Au/TiO$_2$ spheres, in specific shape and sizes, are found to be more promising catalyst towards the conversion of 4-NP to 4-AP due to the enhancement in reduction rates under optimum conditions and ease of deposition of AuNPs which allows controlled growth of NPs without a need of pH adjustment and high temperatures.

5. CONCLUSION

In the scope of this thesis, novel catalysts were fabricated which enable the elimination of toxic pollutants as 4-Nitrophenol by means of heterogeneous catalytic reduction in aqueous environment. Plasmon-enhanced catalytic reduction process was preffered for providing complete conversion without producing toxic by-products, having ease of operation and measurement of both 4-NP and 4-AP, for being cost-effective and energy-saving, time saving and environmentally friendly. The sizes of AuNPs and the interaction between NPs and support material are the most important parameters in the enhancement of catalytic activity. The production of novel catalysts was achieved by the immobilization of the plasmonic gold nanoparticles into the novel forms of chitosan and titanium dioxide support materials, respectively. The plasmonic catalytic activities of fabricated catalysts were investigated within the reduction of 4-NP in the presence of $NaBH_4$ as a reducing agent. In these runs, the effects of type of support material, size of nanoparticle as perfomance enhancing parameters and loading amount of nanoparticle, catalyst amount and initial 4-Nitrophenol concentration as operational parameters were evaluated in batch fashion.

The conclusions obtained from the synthesis, characterization and catalytic activity measurements of the titania based catalysts were given below:

- ✓ Chitosan microgel beads, 3 mm in size with the SSA area of 1.3 m^2/g, were synthesized by crosslinking reaction in which glutaraldehyde serves as a cross-linker. Titanium dioxide (TiO_2) spheres as second support material, were obtained by one-step sol-gel method. The TiO_2 spheres, in the size range of 0.7-1.2 μm with the SSA of 277.4 m^2/g were synthesized within the hydrolysis of titania precursor, titanium isopropoxide in a solvent medium including methanol and acetonitrile. After the reproduction of TiO_2 spheres, it appeared that the amount and size of obtained particles depend on the rate of hydrolysis and condensation of precursor and the way of addition.

- ✓ In order to decorate TiO_2 spheres with AuNPs, the spheres were derivatized by APTES resulted in the amine functionalization of TiO_2. Since chitosan has functional amine and hydroxyl groups originally, there is no need for an additional derivatization step. Support materials and gold nanoparticles with different sizes were prepared separately. The AuNPs, obtained by Turkevich Method in which $HAuCl_4$ molecules were reduced by citrate ions, were found to be 10-12 nm in size.

On the other hand, the gold nanoparticles, obtained by Martin Method in which $HAuCl_4$ molecules were reduced in the presence of $NaBH_4$, were found to be between 3-5 nm in size. The gold nanoparticles directly were deposited onto the beads and spheres. The characteristic peaks of face centered cubic gold (2Θ: 38°, 44°, 64° and 77°) from XRD results and percentages of gold contents from EDX analysis indicated that both Turkevich and Martin AuNPs were successfully deposited onto the bead and sphere surfaces, individually.

✓ The plasmonic catalytic activities of Turkevich and Martin AuNP decorated chitosan microgel beads and TiO_2 spheres were investigated by the reduction of 4-NP to 4-AP by changing the Au loading, catalyst dosage and initial 4-NP concentration. Significant enhancements in plasmonic catalytic activities of Martin AuNP decorated chitosan microgel beads and TiO_2 spheres, in which the AuNP size is smaller, were seen when compared with Turkevich AuNP decorated chitosan microgel beads and TiO_2 spheres. These results were found to be compatible with the results from previous studies, reported that the rate of reduction increases by decreasing AuNP size and thus increasing total surface area [100].

✓ The complete reduction of 4-Nitrophenol having initial concentration of 7.5 ppm was achieved within 12 minutes in the presence of 10 mg Martin AuNP decorated chitosan microgel beads as catalyst (2.5% (w/w%) AuNP loading). The results were found to be comparable with the results from literature studies that have been conducted in the presence of catalysts supported with flakes of chitosan [78] or the catalysts supported with bead forms of different materials such as alginate, PMMA, PVA etc. [77, 96, 101].

✓ The recovery and reusability studies indicated that the catalysts, having a high capacity, were suitable for reuse for the reduction of 4-Nitrophenol. However, the percentage of conversion of 4-Nitrophenol decreased by 44% after 3 cycles in the presence of Martin AuNP decorated chitosan microgel beads that can be explained by the deactivation of active sites on the surface of gold nanoparticles or the adsorption of 4-Aminophenol by the free functional groups of chitosan. The catalytic activites of chitosan in each cycle can be enhanced by the optimization of desorption conditions of generated 4-Aminophenol.

✓ The complete reduction of 4-Nitrophenol having initial concentration of 7.5 ppm was achieved within 60 seconds in the presence of 12.5 mg Martin AuNP decorated

TiO$_2$ spheres as catalyst (2% (w/w%) AuNP loading). The catalyst synthesis was repeated and the catalyst was found to be suitable for resue for the reduction of 4-Nitrophenol without a considerable capacity loss which is smaller than 10% for 3 subsequent cycles. These results were found to be comparable with the results from literature studies that were conducted in the presence of plasmonic catalysts supported with extremely low-sized and/or highly porous TiO$_2$ spheres [68, 102] or with different forms of TiO$_2$ [83, 92].

✓ In the light of forementioned results, it is suggested to perform studies to evaluate the catalytic activity of novel Au/chitosan beads within the plasmon-enhanced catalytic reduction of 4-Nitrophenol in continuous fashion. The particles are applicable for column studies owing to their milimetric sizes and low-cost. Since chitosan is a biopolymer, the large amounts of wastes of chitosan based catalysts do not pose a considerable threat for the environment.

✓ It is also recommended to evaluate the photocatalytic activity of novel TiO$_2$ spheres and AuNP/TiO$_2$ spheres within the photocatalytic degradation of 4-Nitrophenol or other organic contaminants.

REFERENCES

[1]   Harrison, M.A.J., Barra, S., Borghesi, D., Vione, D., Arsene, C., Olariu, R.J., Nitrated phenols in the atmosphere: a review, *Atmospheric Environment*, 39(2), 231-248, **2005**.

[2]   Wunder, S., Polzer, F., Lu, Y., Mei, Y., Ballauff, M., Kinetic analysis of catalytic reduction of 4-Nitrophenol by metallic nanoparticles immobilized in spherical polyelectrolyte brushes, *The Journal of Physical Chemistry C*, 114(19), 8814-8820, **2010**.

[3]   Torkamani, F. , Azizian, S., Green and simple synthesis of Ag nanoparticles loaded onto cellulosic fiber as efficient and low-cost catalyst for reduction of 4-nitrophenol, *Journal of Molecular Liquids*, 214, 270-275, **2016**.

[4]   Zhao, P., Feng, X., Huang, D., Yamg., G., Astruc, D., Basic concepts and recent advances in nitrophenol reduction by gold- and other transition metal nanoparticles, *Coordination Chemistry Reviews*, 287, 114-136, **2015**.

[5]   Bagheri, S., Julkapli, N.M., Abd Hamid, S., Titanium dioxide as a catalyst support in heterogeneous catalysis, *Scientific World Journal*, 2014, 7274-7296, **2014**.

[6]   Mourya, V.K., Inamdar, N.N., Chitosan-modifications and applications: Opportunities galore, *Reactive and Functional Polymers*, 68(6), 1013-1051, **2008**.

[7]   Güney, E., *Genel Ortam* Kirlenmesi, Palme Yayıncılık, Ankara, **2008**.

[8]   Viessman Jr., W., Hammer, J., *Water Supply and Pollution Control*, 6th edition, Addison Wesley Longman, Inc., Canada, **1998**.

[9]   UNESCO, World Water Assessment Programme (WWAP), *The United Nations World Water Development Report 4: Managing Water Under Certanty and Risk*, Paris, **2012**.

[10]   Gündüz, T., *Çevre Sorunları*, 2nd edition, Gazi Kitabevi, Ankara, **2004**.

[11]   Martín-Hernández, M., *Comparative Stundy on the Treatment of a High-Strength p-Nitrophenol Wastewater*, PhD Thesis, Universitat Autonoma de Barcelona Departament d'Enginyeria Quimica, Spain, **2005**.

[12]   Agency, U.E.P., *Code of Federal Regulations,* Washington, DC., **1987**.

[13]   Nuhoglu, A., Yalcin, B., Modelling of phenol removal in a batch reactor, *Process Biochemistry*, 40(3–4), 1233-1239, **2005**.

[14]   Ju, K.S., Parales, R.E., Nitroaromatic Compounds, From Synthesis to Biodegradation, *Microbiology and Molecular Biology Reviews*, 74(2), 347-362, **2010**.

[15]   Michalowicz, J., Duda, W., Phenols-Spurces and Toxicity, *Polish Journal of Environmental Studies*, 16(3), 347-362, **2007**.

[16]   Ramteke, L.P., Gogate, P.R., Removal of ethylbenzene and p-nitrophenol using combined approach of advanced oxidation with biological oxidation based on the use of novel modified prepared activated sludge, *Process Safety and Environmental Protection*, 95, 146-158, **2015**.

[17]   Akbal, F., Gurel, L., Bahadir, T., Guler, İ., Bakan, G., Buyukgungor, H., Multivariate Statistical Techniques for the Assessment of Surface Water Quality at the Mid-Black Sea Coast of Turkey, *Water, Air, & Soil Pollution*, 216(1), 21-37, **2011**.

[18]   Loos, R., Gawlik, B.M., Locoro, G., Rimaviciute, E., Contini, S., Bidoglio, G., EU-wide survey of polar organic persistent pollutants in European river waters, *Environmental Pollution*, 157(2), 561-568, **2009**.

[19]   Wennrich, L., Efer, J., Engewald, W., Gas chromatographic trace analysis of underivatized nitrophenols, *Chromatographia*, 41(5), 361-366, **1995**.

[20]   European Comission, *Proposal for a Directive of The European Parliament and of The Council on Environmental Quality Standards in the field of water policy and amending Directive 200/60/EC*, 397, Brussels, **2006**.

[21]   World Health Organization, *Concise International Chemical Assessment Document 20: Mononitrophenols*, Geneva, **2000**.

[22]   Eichenbaum, G., Johnson, M., Kirkland, D., Evans, D., Tonell, A., Assessment of the genotoxic and carcinogenic risks of p-nitrophenol when it is present as an impurity in a drug product, *Regulatory Toxicology and Pharmacology*, 55(1), 33-42, **2009**.

[23]   Registry, A.f.T.S.a.D., *Toxicological Profile for Nitrophenols: 2-Nitrophenol and 4-Nitrophenol*, Atlanta, GA, **1992**.

[24]   Liu, F., Wu, Z., Wang, D., Yu, J., Jiang, X., Chen, X., Magnetic porous silica–graphene oxide hybrid composite as a potential adsorbent for aqueous removal of p-nitrophenol, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 490, 207-214, **2016**.

[25]   Ando, N., Matsui, Y., Kurotobi, R., Matsushita, T., Ohno, K., Comparison of natural organic matter adsorption capacities of super-powdered activated carbon and powdered activated Carbon, *Water Research*, 44(14), 4127-4136, **2010**.

[26]   Roostaei, N., Tezel, F.H., Removal of phenol from aqueous solutions by adsorption, *Journal of Environmental Management*, 70(2), 157-164, **2004**.

[27]   Busca, G., Berardinelli, S., Resini, C., Arrighi, L., Technologies for the removal of phenol from fluid streams: A short review of recent developments, *Journal of Hazardous Materials*, 160(2–3), 265-288, **2008**.

[28]   Yang, Q., Chen, X., Jiang, X., Liquid–Liquid Microextraction of Nitrophenols Using Supramolecular Solvent and Their Determination by HPLC with UV Detection, *Chromatographia*, 76(23), 1641-1647, **2013**.

[29]   Tomei, M.C., Annesini, M.C., Luberti, R., Cento, G., Senia, A., Kinetics of 4-Nitrophenol biodegradation in a sequencing batch reactor, *Water Research*, 37(16), 3803-3814, **2003**.

[30]   Arena, F., Italiano, C., Raneri, A., Saja, C., Mechanistic and kinetic insights into the wet air oxidation of phenol with oxygen (CWAO) by homogeneous and heterogeneous transition-metal catalysts, *Applied Catalysis B: Environmental*, 99(1–2), 321-328, **2010**.

[31]   Yadav, A., Teja, A.K., Verma, N., Removal of phenol from water by catalytic wet air oxidation using carbon bead – supported iron nanoparticle – containing carbon nanofibers in an especially configured reactor, *Journal of Environmental Chemical Engineering*, 4(2), 1504-1513, **2016**.

[32]   Jing, G., Luan, M., Chen, T., Progress of catalytic wet air oxidation technology, *Arabian Journal of Chemistry*, 9(2), 1208-1213, **2016**.

[33]   Levec, J., Pintar, A., Catalytic wet-air oxidation processes: A review, *Catalysis Today*, 124(3–4), 172-184, **2007**.

[34]   Stüber, F., Font, J, Eftaxias, A., Paradowska, M., Suarez, M.E., Fortuny, A., Bengoa, C., Fabregat, A., Chemical Wet Oxidation for the Abatement of Refractory Non-Biodegradable Organic Wastewater Pollutants, *Process Safety and Environmental Protection*, 83(4), 371-380, **2005**.

[35]   Dong, X., et al., Study on catalytic and non-catalytic supercritical water oxidation of p-nitrophenol wastewater, *Chemical Engineering Journal*, 277, 30-39, **2015**.

[36]   Zhang, A., Gan, Z., Lu, X., Jin, W., Yu, Y., Zhang, M., Heterogeneous Fenton-like catalytic removal of p-nitrophenol in water using acid-activated fly ash, *Journal of Hazardous Materials*, 201–202, 68-73, **2012**.

[37]   Li, L., Feng, Y., Liu, Y., Wei, B., Guo, J., Jio, W., Zhang, Z., Zhang, Q., Titanium dioxide nanoparticles modified by salicylic acid and arginine: Structure, surface properties and photocatalytic decomposition of p-nitrophenol, *Applied Surface Science*, 363, 627-635, **2016**.

[38]   Xie, F., Xu, Y., Jia, C., Zhang, P., Alternate pulses of ultrasound and electricity enhanced electrochemical process for p-nitrophenol degradation, *Ultrasonics Sonochemistry*, 28, 199-206, **2016**.

[39]   Zhang, Y., Yang, N., Murugananthan, M., Yoshihara, S., Electrochemical degradation of PNP at boron-doped diamond and platinum electrodes, *Journal of Hazardous Materials*, 244-245, 295-302, **2013**.

[40]   Kulkarni, M., Chaudhari, A., Biodegradation of p-Nitrophenol by P. putida, *Bioresource Technology*, 97(8), 982-988, 2006.

[41]   Salehi, Z., Yoshikawa, H., Mineta, R., Kawase, Y., Aerobic biodegradation of p-nitrophenol by acclimated waste activated sludge in a slurry bubble column, *Process Biochemistry*, 46(1), 284-289, **2011**.

[42]   Shen, J., Xu, X., Jiang, X., Mu, Y., Wang., L., Coupling of a bioelectrochemical system for p-nitrophenol removal in an upflow anaerobic sludge blanket reactor, *Water Research*, 67, 11-18, **2014**.

[43]   Li, B., Hao, Y., Shao, X., Tang, H., Wang, T., Zhu, J., Yan, S., Synthesis of hierarchically porous metal oxides and Au/TiO$_2$ nanohybrids for photodegradation of organic dye and catalytic reduction of 4-Nitrophenol, *Journal of Catalysis*, 329, 368-378, **2015**.

[44]   Satoh, T., Suzuki, S., Reduction of organic compounds with sodium borohydride-transition metal salt systems, *Tetrahedron Letters*, 10(52), 4555-4558, **1969**.

[45]   Pradhan, N., Pal, A., Pal, T., Silver nanoparticle catalyzed reduction of aromatic nitro compounds, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 196(2–3), 247-257, **2002**.

[46]   Esumi, K., Miyamoto, K., Yoshimura, T., Comparison of PAMAM–Au and PPI–Au Nanocomposites and Their Catalytic Activity for Reduction of 4-Nitrophenol, *Journal of Colloid and Interface Science*, 254(2), 402-405, **2002**.

[47]   Henglein, A., Small-particle research: Physicochemical properties of extremely small colloidal metal and semiconductor particles, *Chemical Reviews*, 89(8), 1861-1873, **1989**.

[48]   Zhang, P., Shao, C., Zhang, Z., Mu, J., Guo, Z., Liu, Y., In situ assembly of well-dispersed Ag nanoparticles (AgNPs) on electrospun carbon nanofibers (CNFs) for catalytic reduction of 4-nitrophenol, *Nanoscale*, 3(8), 3357-3363, **2011**.

[49]   Ghosh, S.K., Mandal, M., Kundu, S., Nath, S., Pal, T., Bimetallic Pt–Ni nanoparticles can catalyze reduction of aromatic nitro compounds by sodium borohydride in aqueous solution, *Applied Catalysis A: General*, 268(1–2), 61-66, **2004**.

[50]   Gu, S., Lu, Y., Albrecht, M., Ballauff, M., Kinetic analysis of the reduction of 4-nitrophenol catalyzed by Au/Pd nanoalloys immobilized in spherical polyelectrolyte brushes, *Physical Chemistry Chemical Physics*, 17(42), 28137-28143, **2015**.

[51]   Youzhi, G., Yang, H., Yiping, Z., Li, C., Fanyong, Y., Fabrication of thermosensitive hydrogel-supported Ni nanoparticles with tunable catalytic activity for 4-nitrophenol, *Journal of Materials Science*, 51(6), 3200-3210, **2016**.

[52]   Antonels, N.C., Meijboom R., Preparation of well-defined dendrimer encapsulated ruthenium nanoparticles and their evaluation in the reduction of 4-nitrophenol according to the Langmuir-Hinshelwood approach, *Langmuir*, 29(44), 13433-13442, **2013**.

[53]   Zhang, R., Zheng, P., Ma, X., Preparation and catalytic properties of magnetic rectorite-chitosan-Au composites, *Journal of Alloys and Compounds*, 690, 381-389, **2017**.

[54]   Mahmoud, M.A., Garlyyev, B., El-Sayed, M.A., Determining the Mechanism of Solution Metallic Nanocatalysis with Solid and Hollow Nanoparticles: Homogeneous or Heterogeneous, *Journal of Physical Chemistry C*, 117(42), 21886-21893 **2013**.

[55]   Shin, K.S., Choi, J., Park, S.C., Jang, J.H., Kim, K., Facile Synthesis and Catalytic Application of Silver-Deposited Magnetic Nanoparticles, *Catalysis Letters*, 133(1), 1-7, **2009**.

[56]   Haruta, M., Kobayashi, T., Sano, H., Yamada, N., Novel Gold Catalysts for the Oxidation of Carbon Monoxide at a Temperature far Below 0 °C, *Chemistry Letters*, 16(2), 405-408, **1987**.

[57]   Jin, Z., Xiao, M., Bao, Z., Wang, P., Wang, J., A General Approach to Mesoporous Metal Oxide Microspheres Loaded with Noble Metal Nanoparticles, *Angewandte Chemie International Edition*, 51(26), 6406-6410, **2017**.

[58]   Martin, M.N., Basham, J.I., Chando, P., Eah, S., Charged gold nanoparticles in non-polar solvents: 10-min synthesis and 2D self-assembly, *Langmuir*, 26(10), 7410-7417, **2010**.

[59]   Brust, M., Walker, M., Bethell, D., Schiffrin, D., Whyman, R., Synthesis of thiol-derivatised gold nanoparticles in a two-phase Liquid-Liquid system, *Journal of the Chemical Society Chemical Communications*, 7, 801-802, **1994**.

[60]   Panigrahi, S., Basu, S., Praharaj, S., Pande, S., Jana, S., Pal, A., Ghosh, K., Pal, T., Synthesis and size-selective catalysis by supported gold nanoparticles: Study on heterogeneous and homogeneous catalytic process, *Journal of Physical Chemistry C*, 111(12), 4596-4605, **2007**.

[61]   Turkevich, J., Stevenson, P.C., Hillier, J., A study of the nucleation and growth processes in the synthesis of colloidal gold, *Discussions of the Faraday Society*, 11, 55-75, **1951**.

[62]   Deraedt, C., Salmon, L., Gatard, S., Ciganda, R., Astruc, D., Sodium borohydride stabilizes very active gold nanoparticle catalysts, *Chemical Communications*, 50(91), 14194-14196, **2014**.

[63]   Hu, H., Xin, J., Hu, H., Wang, X., Miao, D., Liu, Y., Synthesis and stabilization of metal nanocatalysts for reduction reactions - a review, *Journal of Materials Chemistry A*, 3(21), 11157-11182, **2015**.

[64]   Wei, L., Brunelli, N.A., Didas, A.S., Ping, E.W., Jones, C.W., Aminopolymer–Silica Composite-Supported Pd Catalysts for Selective Hydrogenation of Alkynes, *ACS Catalysis*, 3(8), 1700-1708, **2013**.

[65]   Raveendran Shiju, N. Guliants, V., Recent developments in catalysis using nanostructured materials, *Applied Catalysis A: General,* 356, 1-17, **2009**.

[66]   Holden, M.S., Nick, K.E., Perry, C.C., Synthesis and Catalytic Activity of Pluronic Stabilized Silver-Gold Bimetallic Nanoparticles, *RSC Advances*, 4(94), 52279-52288, **2014**.

[67]   Li, M., Chen, G., Revisiting catalytic model reaction p-nitrophenol/NaBH4 using metallic nanoparticles coated on polymeric spheres, *Nanoscale*, 5(23), 11919-11927, **2013**.

[68]   Yazid, H., Adnan, R., Farrukh, M.A., Gold nanoparticles supported on titania for the reduction of p-nitrophenol, *Indian Journal of Chemistry*, 52, 184-191, **2013**.

[69]   Hao, Y., Shao, X., Li, B., Hu, L., Wang, T., Mesoporous TiO2 nanofibers with controllable Au loadings for catalytic reduction of 4-nitrophenol, *Materials Science in Semiconductor Processing*, 40, 621-630, **2015**.

[70]   Liu, W., Yang, X., Xie, L., Size-controlled gold nanocolloids on polymer microsphere-stabilizer via interaction between functional groups and gold nanocolloids, *Journal of Colloid and Interface Science*, 313(2), 494-502, **2007**.

[71]   Guibal, E., Heterogeneous catalysis on chitosan-based materials: a review, *Progress in Polymer Science*, 30(1), 71-109, **2005**.

[72]   Dutta, K., Dutta, J., Tripathi, V.S., Chitin and chitosan: Chemistry, properties and applications, *Journal of Scientific &Insutrial Research*, 63, 20-31, **2004**.

[73]   Crini, G., Badot, P.M., Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature, *Progress in Polymer Science*, 33(4), 399-447, **2008**.

[74]   Grem, I.C.d.S., Lima, B.N.B., Carneiro, W.F., Mansur, C.R.E., Chitosan microspheres applied for removal of oil from produced water in the oil industry, *Polímeros*, 23, 705-711, **2013**.

[75]   Zhang, M., Helleur, R., Zhang, Y., Ion-imprinted chitosan gel beads for selective adsorption of Ag+ from aqueous solutions, *Carbohydrate Polymers*, 130, 206-212, **2015**.

[76]   Zhao, X., Li, Q., Zhang, X., Su, H., Lan, K., Chen, A., Simultaneous removal of metal ions and methyl orange by combined selective adsorption and photocatalysis, *Environmental Progress & Sustainable Energy*, 30(4), 567-575, **2011**.

[77]   Kuroda, K., Ishida, T., Haruta, M., Reduction of 4-nitrophenol to 4-aminophenol over Au nanoparticles deposited on PMMA, *Journal of Molecular Catalysis A: Chemical*, 298(1–2), 7-11, **2009**.

[78]   Wei, D., Ye, Y., Jia, X., Yuan, C., Qian, W., Chitosan as an active support for assembly of metal nanoparticles and application of the resultant bioconjugates in catalysis, *Carbohydrate Research*, 345(1), 74-81, **2010**.

[79]   Wu, X., Wu, X.W., Huang, Q., Shen, J., Zhang, H., In situ synthesized gold nanoparticles in hydrogels for catalytic reduction of nitroaromatic compounds, *Applied Surface Science*, 331, 210-218, **2015**.

[80]   Vincent, T., Guibal, E., Chitosan-supported palladium catalyst. 5. Nitrophenol degradation using palladium supported on hollow chitosan fibers, *Environmental Science& Technology*, 38(15), 4233-4240, **2004**.

[81]   Shen, X., Shamshina, J., Berton, P., Gurau, G., Rogers, R., Hydrogels based on cellulose and chitin: fabrication, properties, and applications, *Green Chemistry*, 18(1), 53-75, **2016.**

[82]   Ahmed, E.M., Hydrogel: Preparation, characterization, and applications: A review, *Journal of Advanced Research*, 6(2), 105-121, **2015**.

[83]   Deshmukh, S.P., Dhokale, R.K., Yadav, H.M., Achary, S.N., Delekar, S.D., Titania–supported silver nanoparticles: An efficient and reusable catalyst for reduction of 4-nitrophenol, *Applied Surface Science*, 273, 676-683, **2013**.

[84]   Dobrowolska, P., Krajewska, A., Gajda-Raczka, M., Bartosewicz, B., Nyga, P., Jankiewicz, B.J., Application of Turkevich Method for Gold Nanoparticles Synthesis to Fabrication of SiO2@Au and TiO2@Au Core-Shell Nanostructures, *Materials*, 8(6), 2849-2862, **2015**.

[85]   Brinker, C.J., Scherer, G.W., *Sol-gel Science*, Academic Press., **1990**.

[86]   Toygun, Ş., Könecoglu, G., Kalpakli, Y., General Principles of Sol-Gel, *Sigma Journal of Engineering&Natural Sciences*, 31(4): p. 456-476, **2013**.

[87]   Mine, E., Hirose, M., Nagao, D., Kobayashi, Y., Konno, M., Synthesis of submicrometer-sized titania spherical particles with a sol–gel method and their application to colloidal photonic crystals, *Journal of Colloid and Interface Science*, 291(1), 162-168, **2005**.

[88]   Ghosh, S.K., Pal, T., Interparticle coupling effect on the surface plasmon resonance of gold nanoparticles: from theory to applications, *Chemical Reviews*, 107(11), 4797-4862, **2007**.

[89]   Yadollahi, M., Farhoudian, S., Namazi, H., One-pot synthesis of antibacterial chitosan/silver bio-nanocomposite hydrogel beads as drug delivery systems, *International Journal of Biological Macromolecules*, 79, 37-43, **2015**.

[90]   Panigrahi, S., Basu, S., Praharaj, S., Synthesis and size-selective catalysis by supported gold nanoparticles: study on heterogenous and homogenous catalytic process, *Journal of Physical Chemistry C*, 111(12), 4596-4605, **2007**.

[91]   Fong, T.S., Johan, M.R., Ahmad, R.B., Synthesis and Characterization of Gold-Titanium-Mesoporous Silica Nanomaterials, *International Journal of Electrochemical Science*, 7, 4716-4726, **2012**.

[92]   Wang, X., Zhao, Z., Ou, D., Tu, B., Cui, D., Wei, X., Cheng, M., Highly active Ag clusters stabilized on TiO2 nanocrystals for catalytic reduction of p-nitrophenol, *Applied Surface Science*, 385, 445-452, **2016**.

[93]   Denkwitz, Y., Geserick, J., Hörmann, U., Plzak, V., Kaiser, U., Hüsing, N., Behm, R.J., Mesoporous Au/TiO2 Catalysts for Low Temperature CO Oxidation, *Catalysis Letters*, 119(3), 199-208, **2007**.

[94]   Yan, W., Petkov, V., Mahurin, S.M., Overbury, S.H., Dai, S., Powder XRD analysis and catalysis characterization of ultra-small gold nanoparticles deposited on titania-modified SBA-15, *Catalysis Communications*, 6(6): 404-408, **2005**.

[95]   Moreau, F., Bond, G.C., Taylor, A.O., Gold on titania catalysts for the oxidation of carbon monoxide: control of pH during preparation with various gold contents, *Journal of Catalysis*, 231(1), 105-114, **2005**.

[96]   Lu, Y., Spyra, P., Mei, Y., Ballauff, M., Pich, A., Composite Hydrogels: Robust Carriers for Catalytic Nanoparticles, *Macromolecular Chemistry and Physics*, 208, 254-261, **2007**.

[97]   Park, S.I., Kwak, I.S., Won, S.W., Yun, Y.S., Glutaraldehyde-crosslinked chitosan beads for sorptive separation of Au(III) and Pd(II): opening a way to design reduction-coupled selectivity-tunable sorbents for separation of precious metals, *Journal of Hazardous Materials*, 248-249, 211-218, **2013**.

[98]   Saha, S., Pal, A., Kundu, S., Basu, S., Pal, T., Photochemical Green Synthesis of Calcium-Alginate-Stabilized Ag and Au Nanoparticles and Their Catalytic Application to 4-Nitrophenol Reduction, *Langmuir*, 26(4), 2885-2893, **2010**.

[99]   Lin, F.H., Doong, R.A., Highly efficient reduction of 4-nitrophenol by heterostructured gold-magnetite nanocatalysts, *Applied Catalysis A: General*, 486, 32-41, **2014**.

[100]   Lin, C., Tao, K., Hua, D., Ma, Z., Zhou, S., Size effect of gold nanoparticles in catalytic reduction of p-nitrophenol with $NaBH_4$, *Molecules*, 18(10), 12609-12620, **2013**.

[101]   Gupta, V.K., Yola, M.L., Eren, T., Kartal, F., Caglayan, M.O., Atar, N., Catalytic activity of Fe@Ag nanoparticle involved calcium alginate beads for the reduction of nitrophenols, *Journal of Molecular Liquids*, 190, 133-138, **2014**.

[102]   Ismail, A.A., Hakki, A., Bahnemann, D.W., Mesostructure Au/TiO_2 nanocomposites for highly efficient catalytic reduction of p-nitrophenol, *Journal of Molecular Catalysis A: Chemical,* 358, 145-151, **2012**.

CURRICULUM VITAE

Credentials

Name, Surname: Gökçe ERDEM

Place of Birth: Ankara

Marital Status: Single

E-mail: gokcerdem57@gmail.com

Address: 19. Sokak No:40 Emek Mahallesi/ANKARA

Education

MSc: Hacettepe University Chemical Engineering Department

BSc: Gazi University Chemical Engineering Department

High School: TED Ankara College Foundation Private High School

Foreign Languages

English: Advanced

German: Intermediate

Work Experience

07/2012- 08/2012   TÜPRAŞ, KIRIKKALE (Internship)

08/2011- 09/2011   Turkey Sugar Factories, Inc., Sugar Institute, ANKARA (Internship)

Areas of Experiences

Microparticle and Nanoparticle Synthesis

Biopolymers

Wastewater Treatment Technologies

Projects and Budgets

"Design of Hydrogel Supported Photocatalyst for Continous Oxidation of Phenolic Compounds", Hacettepe University Scientific Research Project (BAP No: FHD-2015-7738)

Publications

-

Oral and Poster Presentations:

1) Erdem, Gökçe; Yavuz Ersan, Hülya; Tuncel, Ali; Optimization of A New Chitosan Based Catalyst for Degradation of Textile Dyes, *4th Nanomedicine World Congress and 2nd International NanoBioTechnology Symposium,* Muğla, Türkiye, 2015

2) Erdem, Gökçe; Hamaloğlu, Kadriye Özlem; Yavuz Ersan, Hülya; Tuncel, Ali; Synthesis of a Metal-Oxide Sphere Based Plasmonic Catalyst for The Degradation of p-Nitrophenol, *12th National Chemical Engineering Congress,* İzmir, Türkiye, 2016

HACETTEPE UNIVERSITY
GRADUATE SCHOOL OF SCIENCE AND ENGINEERING
THESIS/DISSERTATION ORIGINALITY REPORT

HACETTEPE UNIVERSITY
GRADUATE SCHOOL OF SCIENCE AND ENGINEERING
TO THE DEPARTMENT OF CHEMICAL ENGINEERING

Date: 18/01/2017

Thesis Title / Topic: Synthesis Of Chitosan And Titanium Dioxide Based Plasmonic Catalysts for the Catalytic Reduction of Phenolic Compounds

According to the originality report obtained by myself/my thesis advisor by using the *Turnitin* plagiarism detection software and by applying the filtering options stated below on 18/01/2017 for the total of 72 pages including the a) Title Page, b) Introduction, c) Main Chapters, d) Conclusion and e) Bibliography sections of my thesis entitled as above, the similarity index of my thesis is 7 %.

Filtering options applied:
1. Bibliography/Works Cited excluded
2. Quotes excluded
3. Match size up to 5 words excluded

I declare that I have carefully read Hacettepe University Graduate School of Sciene and Engineering Guidelines for Obtaining and Using Thesis Originality Reports; that according to the maximum similarity index values specified in the Guidelines, my thesis does not include any form of plagiarism; that in any future detection of possible infringement of the regulations I accept all legal responsibility; and that all the information I have provided is correct to the best of my knowledge.

I respectfully submit this for approval.

Date and Signature

Name Surname:	GÖKÇE ERDEM
Student No:	N13223321
Department:	Chemical Engineering Department
Program:	Chemical Engineering
Status:	☑ Masters ☐ Ph.D. ☐ Integrated Ph.D.

18/01/2017

ADVISOR APPROVAL

APPROVED.

Prof. Dr. Hülya YAVUZ ERSAN
(Title, Name Surname, Signature)