SynThesis Of Advanced Functional Nanomaterials For Sustainable Water Treatment Technologies

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SYNTHESIS OF ADVANCED FUNCTIONAL NANOMATERIALS FOR SUSTAINABLE WATER TREATMENT TECHNOLOGIES

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Dedication

This dissertation is dedicated:

…to my parents for their love and affection…

…to my lovely wife, Anu, for her love, inspiration, and support…

… to my son, Aureus, for bringing good fortune in our family…

… and to my friends and colleagues who have inspired me while carrying out research and working on this dissertation.
SYNTHESIS OF ADVANCED FUNCTIONAL NANOMATERIALS FOR SUSTAINABLE WATER TREATMENT TECHNOLOGIES

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Abstract

Water is the most essential resource for the sustenance of life. Water is also necessary for agriculture, industry, household, and environmental conservation. However, due to large population growth and industrial expansion, access to clean water is becoming increasingly difficult around the world. Current water treatment technologies have not changed in over one hundred years and require a large infrastructure due to their low efficiencies and large-scale needs. In this context, the utilization of advanced functional nanomaterials and the adaptation of nanotechnology could potentially allow for miniaturizing water treatment and develop decentralized solutions for rural areas. This dissertation presents the design, synthesis, characterization, and functional evaluation of functional nanomaterials such as noble metal nanoparticles, metal oxide nanoparticles, and polymeric nanoparticles for sustainable water treatment technologies.

In Chapter 2, sodium squarate mediated novel method for the synthesis of gold nanoparticles (AuNPs) of about 22 nm in size is reported. The AuNPs were supported on cellulose fibers (CF) by mixing the AuNPs solution with the cellulose fibers. The AuNPs and its nanocomposites with CF exhibited excellent catalytic activity towards the reduction of 4-nitrophenol (4-NP) with sodium borohydride (NaBH₄). The AuNPs were further utilized for the selective and naked-eye observable sensing of spectroscopically silent heavy metals *viz.* chromium (III) and lead (II) in water.

Chapter 3 demonstrates the ability of sodium rhodizonate as a bifunctional reducing as well as a stabilizing agent for the synthesis of a series of noble metal nanoparticles *viz.* gold (Au), silver (Ag), platinum (Pt), and palladium (Pd). Transmission electron microscopy revealed that the Pt, Au, Ag, and Pd NPs had the average core diameter of about 2, 8, 26, and 39 nm,
respectively. The ability of these nanoparticles towards the catalytic reduction of 4-NP with NaBH₄ and the dual-catalytic oxidation of formic acid followed by the reduction of methyl orange (MO) was studied.

Chapter 4 further studies the ability of sodium rhodizonate for the preparation of AuNPs of controlled size in water. At room temperature, the method can generate AuNPs with an average size of ~11 nm, whereas at 80 °C, it can generate AuNPs with an average size of ~7 nm. The rhodizonate-stabilized AuNPs were supported on CF and the CF-supported AuNPs were utilized for the catalytic reduction of 4-NP and organic dyes such as methyl orange (MO), methylene blue (MB) in water. The method was further extended to the synthesis of bimetallic (Au-Ag) nanoparticles and nanoporous gold nanoparticles.

In Chapter 5, a facile method to prepare macroporous cellulose fibers supported PtNPs (PtNPs@KWP) is reported. The PtNPs@KWP exhibited excellent catalytic activity as well as cyclic stability towards the reduction of organic pollutant in the presence of hydrogen (H₂) gas and FA. The FA and H₂ gas were utilized as the clean and alternative reducing agents. The catalytic reduction of hexavalent chromium [Cr(VI)] to trivalent chromium [Cr(III)] was also studied using FA as the reducing agent.

In chapter 6, a novel method for the synthesis of fullerene (C₆₀) stabilized AuNPs is reported. The AuNPs were supported on titanium dioxide (TiO₂) and the nanocomposites exhibited enhanced photocatalytic degradation of MO and catalytic reduction of 4-NP in water. Both the photocatalytic degradation of MO and the catalytic reduction of 4-NP were influenced by the size and the weight percent of the AuNPs loading. Furthermore, the photocatalytic generation of hydroxyl radical (•OH) was studied through the terephthalic acid photoluminescence tests.
A novel and facile method for the synthesis of zinc oxide nanoparticles (nZnO) is demonstrated in Chapter 7. The transmission electron microscopy (TEM) images revealed the spherical shape of the nZnO with an average size of 35 nm. The band gap and the specific surface area of the nZnO were measured to be about 3.32 eV and 80.11 m²/g, respectively. The nZnO was utilized for the photocatalytic degradation of MO and MB in water under the ultraviolet (UV-B) light and sunlight irradiation. Almost a complete degradation of MO and MB was obtained within 30 min of UV-B light irradiation. Under the sunlight irradiation, more than 95 % of the MO solution undergone degradation within 30 min period of time. The photocatalytic generation of •OH was further studied by the terephthalic acid fluorescence tests.

Sucrose mediated facile method for the preparation of high-surface-area Cobalt (Co), Nickel (Ni), and Copper (Cu) sponges is reported in Chapter 8. The Co, Ni, and Cu sponges were found to have highly porous morphology having specific surface areas of 17.39, 8.84 and 2.72 m²/g, respectively. The powder X-ray diffraction spectroscopy (XRPD) pattern demonstrated the crystalline metallic nature of the sponges and the thermogravimetric analysis (TGA) revealed the presence of a trace amount of carbon in the sponges. The catalytic activity of the metal sponges was studied by the reduction of organic pollutants viz. 4-NP, MO, and MB in water. It was found that the Cu sponge was much faster in the reduction of 4-NP, MO, and MB, which was followed by the Co and Ni sponges, respectively.

Chapter 9 reports the preparation of a regenerable adsorbent viz. sulfonated resorcinol-formaldehyde (RF-SO₃H) microspheres for the adsorptive removal of anionic and cationic organic pollutants from water. The equilibrium adsorption capacity was measured to be 710 mg/g and 511 mg/g for MO and MB, respectively. The adsorption of MO and MB from tap water matrix was also performed and shown to maintain similar adsorption capacity as in
deionized water. In addition, a packed glass column was prepared to demonstrate the continuous adsorption of MO and MB under flow conditions.

The findings of the above-mentioned works, especially the novel synthesis methods of the nanostructured materials, may promote further studies in the synthesis of a variety of metallic, mixed metallic nanoparticles, their oxides, and composites. Moreover, the nanomaterials, synthesized in this study, could potentially be useful in the area of electrocatalysis, energy storage, photothermal therapies, solar harvesting, photothermal distillations, drug deliveries, and so on.
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Chapter 1: Synthesis, Properties, and Potentials of Nanomaterials for Water Treatment

1.1. Introduction

Particles having at least one dimension ranging from 1 to 100 nm are called nanoparticles.\(^1\) Particles in the nanometer size regime exhibit exotic size and shape-dependent physical, chemical, and optical properties in contrast to the macroscale or bulk size materials.\(^2,3\)

For example, bulk or macroscopic gold is shiny yellow in color and is one of the most chemically inert materials, whereas; gold nanoparticles (AuNPs) can generate a variety of color in the visible spectrum depending on the particles size and shape. Also, gold nanoparticles have extremely high catalytic activity. Due to the nanometer size range, nanomaterials possess very high specific surface area and surface energy. For instance, 1 mg particles of 1 nm\(^3\) size has an equal surface area of 1 kg particles of 1 mm\(^3\) size. Due to these extraordinary properties, nanomaterials have drawn tremendous attention in a wide variety of applications such as adsorption, photo/electro/chemical catalysis, energy storage, drug delivery, photothermal therapy, solar distillation, surface enhanced Raman spectroscopy, and so on. Some of the intriguing properties of the nanomaterials are discussed in more details as follows. Later, some commonly employed methods for the preparation of nanomaterials, their potentials in water treatment technologies, and the summary of the thesis objectives and contributions are discussed.

1.1.1. Optical Properties of Nanoparticles

Nanoparticles demonstrate size- and shape-dependent extraordinary optical properties. For instance, gold and silver nanoparticles demonstrate a wide range of color in the visible range of spectrum based on the size and shape of the particles. A strong absorption band in the visible spectrum is observed due to the phenomena called the localized surface-plasmon resonance (LSPR) absorption band.\(^4\) The LSPR band originates from the collective oscillation of
conduction electrons of the nanoparticles upon the interaction with electromagnetic radiation. In details, when light strikes a gold nanoparticle, the electromagnetic field of the incident beam start to oscillate the electron cloud of the nanoparticles collectively at the same frequency as the incident light. The LSPR absorption could occur in any nanomaterial which an adequate density of free electrons. However, platinum and palladium nanoparticles do not show any LSPR band in the visible region of the electromagnetic radiation. The LSPR band of platinum and palladium nanoparticles are usually found in the ultraviolet range, unlike the gold and silver nanoparticles. Figure 1.1 shows the typical image of gold, silver, platinum, and palladium nanoparticles solutions in water, the principle of localized surface-plasmon resonance (LSPR) absorption, and the UV-visible absorption spectra of the AuNPs solution.

Figure 1.1: a) Typical image of Au, Ag, Pt, and PdNPs solutions in water, b) principle of the surface-plasmon resonance, and c) UV-visible absorption spectrum of AuNPs in water.

Plasmonic nanoparticles, such as AuNPs and AgNPs, possess high molar absorption coefficient (10^8 to 10^{10} M^{-1}cm^{-1}), which is comparable to organic dyes. Therefore, plasmonic NPs are a good candidate for the solar light harvesting related researches viz. the plasmonic sensitization of the solar cells, photothermal distillations, photothermal disinfection of water, etc. Moreover, the light absorption properties of NPs can be tuned by varying the size, shape, composition, and the degree of aggregation. For example, spherical shape AuNPs...
generate a single SPR absorption band in the visible range, whereas; rod-shaped AuNPs, also known as gold nanorods, produce two distinct absorption bands in the visible and the near or far infrared region. This absorption/optical properties of AuNPs can be utilized for the sensing of a variety of species such as organic or inorganic pollutants, biomolecules, microorganisms, etc. Gold nanorods, due to their infrared or near infrared light absorption properties, can potentially be utilized in the photothermal therapy for the tumor ablation. In addition to the light absorption properties, noble metal nanoparticles demonstrate the photoluminescence and light scattering properties. These properties are useful in biological imaging, surface enhanced resonance Raman, sensing and so on.

Like the noble metal nanoparticles, the band gap of the semiconductor type metal oxides nanoparticles viz. TiO$_2$, ZnO, and WO$_2$ can be tuned by varying the size, shape, and composition. The tunability of the band gap of the semiconductor-type metal oxides nanoparticles is highly important in the area of photovoltaics, electro/photochemical reactions, photocatalysis, etc.

1.1.2. Catalytic Properties of Nanoparticles

Nanoparticles, especially the noble and transition metal nanoparticles, possess unique chemical or catalytic properties. Their catalytic properties is typically observed at the nanoscopic size in contrast to the macroscopic size. As compared to the bulk material, the nanoparticles have a larger proportion of atoms at the edges and the corners, which are surrounded by fewer atoms, Figure 1.2. The exposed atoms at the edges and the corners have higher surface energy and thereby considered to be chemically/catalytically more reactive than the atoms in the bulk. Additionally, in the nanoscale size nanoparticles sometimes expose a
particular crystalline facet predominantly over other facet. Due to the exposure of a specific facet of the crystal metallic nanoparticles provide exotic catalytic properties as well.

![Exposed atoms at the corner and the edges](image)

Figure 1.2: Size-dependent extraordinary catalytic properties of the metal nanoparticles.

In order to become catalytically active, the surface of the nanoparticles needs to be exposed to the solvent or more accurately to the substrate. However, if the nanoparticles are exposed, they tend to aggregate and agglomerate to form bulk macroscopic particles due to their high surface energy.\(^{21}\) The aggregation and agglomeration of the nanoparticles reduce the specific surface area, increase the particle size, hinder the active sites and thereby impair the catalytic activity. Moreover, the utilization of the catalytic nanoparticles in solution is usually neither economically nor environmentally favorable because of the requirement of the energy-intensive processes for the separation of the nanoparticles and the loss of the nanoparticles during the separation process. Therefore, the catalytic nanoparticles are commonly supported on high surface area solid matrices, also known as catalyst support.

**1.1.3. Physical Properties of Nanoparticles**

The miniaturization of a material to the nanometer size range induce dramatic consequences for its physical properties too. For instance, the melting point of a solid substance decreases with the decrease in the size of that substance. This phenomenon is commonly known as “melting point depression”, which was shown by Sir William Thomson in 1871.\(^{20}\) Gold
nanoparticles is an ideal example to demonstrate this phenomenon. The melting point of bulk metallic gold is 1064 °C, however; for gold nanoparticles of 2-3 nm size it drops to 700 °C.\textsuperscript{21} The theoretical changes in melting point with respect to the radius of a particle can be calculated applying the Gibbs-Thomson equation.\textsuperscript{22,23}

\[
T_M(d) = T_{MB}(1 - \frac{4\sigma_{sl}}{H_f\rho_s d})
\]

Where: 
- \(T_M\) = Size-dependent melting temperature
- \(T_{MB}\) = Bulk melting temperature
- \(\sigma_{sl}\) = solid–liquid interface energy
- \(H_f\) = Bulk heat of fusion
- \(\rho_s\) = density of solid
- \(d\) = particle diameter

![Figure 1.3: Relationship between particle size and melting point of gold nanoparticles.](image)

A normalized Gibbs–Thomson equation for gold nanoparticles can be demonstrated as in Figure 1.3. Interestingly, the shape of the curve was found to be in general agreement with those obtained through experimentally.\textsuperscript{24,21} As shown in Figure 1.3, the melting point of gold nanoparticles can reach to even lower than room temperature (~23-25 °C) when the size decreases to less than about 1.4 nm. The change in the particles size can change other
fundamental physical properties of the materials as well such as the conductivity, electrical properties, refractive index, etc.

### 1.2. Methods for the Preparation of Nanoparticles

There are a number of methods for the preparation of different types of nanoparticles. However, all the methods can be broadly classified under two categories *viz.* top-down approaches and bottom-up approaches. In the top-down approach, macroscopic bulk material is cut down or subdivided into the nanoscopic size. For example, noble metal nanoparticles can be fabricated by shining high energy laser beam/ion beam on the bulk metal foil in water.\textsuperscript{25} The high energy ion beam/laser light transfers energy to the atoms on the surface target material, which eventually ejects atoms to yield nanoparticles to the environment. Likewise, plasmas can be used too to fabricate the nanoscale structures.\textsuperscript{26}

In contrary, the bottom-up techniques fabricate nanostructured materials from atomic or molecular precursors. Various chemical and physical techniques are available for the bottom-up synthesis of nanoparticles. For instance, the chemical vapor deposition (CVD) and atomic layer deposition (ALD) are some of the widely-employed bottom-up techniques for the fabrication of nanostructures.\textsuperscript{27,28} While there are many bottom-up techniques, the wet chemical synthesis method is one of the most widely accepted methods. In solution, the precursors react to form nanoparticles which are stabilized by using the stabilizing agents. In the synthesis of metallic nanoparticles, the reaction usually proceeds by the reduction of the metal ions to the zero-valent metal state and the subsequent stabilization by the stabilizing agents. Various reducing agents such as sodium borohydride, sodium citrate, and hydrazine are commonly used for this purpose.
1.2.1. Synthesis of Noble Metal Nanoparticles

Among many methods, two most widely used methods for the synthesis of AuNPs are I) the reduction followed by the stabilization of AuNPs by sodium citrate in water, also called as Turkevitch method, which was introduced in 1951\textsuperscript{29} and II) the Bi-phasic synthesis, where the reduction is carried out by NaBH\textsubscript{4} and the stabilization is provided by Thiols, published by Brust-Schiffrin in 1994.\textsuperscript{30} However, there are instances, where the utilization of other types of stabilizers and/or reducing agents has been reported.\textsuperscript{31,32,33,34} Majority of these methods require heat \textit{viz.} Turkevitch method, harsh reducing agent \textit{viz.} NaBH\textsubscript{4} in Brust-Schiffrin method, separate reducing and stabilizing agents, prolonged stirring/incubation time, multiple steps, post-synthesis separation and/or modifications, and organic solvents. However, for biological applications, chemical sensing of aqueous species, bio-imaging, and catalysis the requirements for water solubility of the NPs and the simplicity in synthesis without the use of harsh reagents is important. Also, the nanoparticles that are prepared following the above-mentioned methods may provide inefficient catalytic activity because of the presence of strong stabilizing agents \textit{viz.} alkanethiol, citrate on the surface. These stabilizing agents hinder the collision and contact between the substrate and the metal nanoparticles surface. Therefore, there is a need for a method for the synthesis of noble metal nanoparticles that have highly exposed and active surface to facilitate enhanced catalytic properties.

1.2.2. Synthesis of Metal Oxide Nanoparticles

As the noble metal nanoparticles, the semiconductor type metal oxides such as zinc oxide (ZnO) and titanium dioxide (TiO\textsubscript{2}) are some of the most extensively studied metal oxides nanoparticles.\textsuperscript{35} Due to their cheaper price, abundance, and high chemical and physical robustness they are used in a number of applications \textit{viz.} transparent electrodes of the dye-
sensitized solar cells,\textsuperscript{36} piezoelectric nanogenerators,\textsuperscript{37} sensing,\textsuperscript{38} as fillers in numerous products,\textsuperscript{39} UV light absorbers in personal care products,\textsuperscript{40} light emitting diodes (LED),\textsuperscript{41} ultraviolet (UV) photodetectors,\textsuperscript{42} and photocatalysis.\textsuperscript{43} As a photocatalyst, these metal oxides and their nanocomposites demonstrate excellent ability towards the degradation of organic pollutants in water under the UV and solar light illumination.\textsuperscript{44,45} Organic pollutants undergo degradation through the redox-processes driven by the electronic excitation between valence and conduction bands of the nanoparticles.\textsuperscript{46} Also, they have the ability to generate reactive oxygen species (ROS) under the UV light irradiation, which can degrade organic pollutants and inactivate or inhibit the growth of microorganisms in water.

Various chemical and physical methods have been reported for the synthesis of metal oxide nanoparticles thus far.\textsuperscript{47} Some of the commonly employed methods include the sol-gel,\textsuperscript{48} combustion,\textsuperscript{49} hydro/solvothermal,\textsuperscript{50} laser ablation,\textsuperscript{51} chemical vapor deposition,\textsuperscript{52} microemulsion techniques,\textsuperscript{53} and microwave-assisted synthesis.\textsuperscript{54} In addition, there are physical top-down techniques, such as mechanical or mechanochemical milling, where the bulk metal oxide is converted into nanoparticles.\textsuperscript{55} Recently, the combustion synthesis method has become a very popular and effective technique to synthesize metal oxide nanoparticles due to the versatility, simplicity, and rapidity of the process.\textsuperscript{56} In combustion synthesis, a mixture of metal salt as an oxidizer (e.g., metal nitrates) and fuels (e.g., urea, glycine, hydrazides) is heated to a high-temperature. When heated to a temperature, the mixture undergoes a self-sustained reaction to produce uniform metal oxide nanoparticles while burning away the fuel in the form of CO\textsubscript{2}, H\textsubscript{2}O, and other gases.
1.3. Potential of Nanomaterials for Water Treatment Technologies

Water is the most essential resource for life to exist. Water is also necessary for many other applications including but not limited to agriculture, industry, household, recreation, and environmental conservation. Although the supply seems abundant, there is only about 2.5% of the water on the Earth is fresh water, and over two-thirds of this is frozen in glaciers and polar ice caps. Therefore, the fresh water source on earth is not limitless. This limited amount of fresh water is necessary for the life to survive and for the industries, for agricultural fields, and for other applications. However, due to rapid industrialization and population growth, the freshwater resources are dwindling. The lack of wastewater treatment plant and the indiscriminate disposal of the wastewater in the environment is causing the contamination of the freshwater resources exponentially. For example, about 70% of the fresh water is utilized for agriculture and almost all of this water becomes contaminated with pesticides, hormones, nitrates, and other fertilizers after use. This huge portion of fresh water ends up in the river, lake, ponds, and other freshwater aquifers and cause the pollution of the whole water systems. Therefore, access to clean water is becoming increasingly difficult to almost anywhere in the world. It is estimated that, currently, over 650 million people around the world lack access to safe water and in every two minutes one child under the age of five die due to waterborne diseases, poor water quality, and inadequate sanitation. Therefore, there is an essential need for the development of an efficient, safe, reliable and affordable method for water treatment technologies. The current water treatment technologies have not changed in over one hundred years and require a large infrastructure due to their low-efficiencies and large-scale needs. In this context, the utilization of advanced functional nanomaterials and the adaptation of nanotechnology could potentially bring new opportunities. The nanomaterials can be utilized for water treatment, wastewater reuse, and
pollution treatment using emerging technologies or advances in conventional treatment technologies. For example, highly active nanoparticles/nanomaterials could be used for the removal or degradation of per- and polyfluoroalkyl substances (PFAS) and pharmaceuticals from water. Nanomaterials-enabled chemical, photocatalytic and electrocatalytic, adsorptive, and advanced oxidation processes can be employed for the efficient and selective degradation of pollutants in water without causing any secondary pollutions. The development of new catalytic nanoparticles may provide the decontamination of water and thus enabling the development of portable water treatment systems for small towns and off-grid rural communities around the world. This dissertation presents several novel and intriguing methods for the synthesis of functional nanomaterials having active surfaces (e.g. noble metal nanoparticles, metal oxide nanoparticles, and polymeric nanoparticles) and their applications in the catalytic, photocatalytic, and adsorptive water treatment technologies. Various emerging and existing water treatment processes such as catalytic, photocatalytic, and adsorptive processes have been studied to degrade or remove organic and inorganic pollutants from water.

1.4. Thesis Objectives and Contributions

The objective of this thesis is the development of experimental methodologies for the synthesis of metallic and non-metallic nanoparticles with applications focusing on sustainable water treatment technologies. Various noble metal nanoparticles (gold, silver, platinum, and palladium), transition metal nanoparticles (cobalt, nickel, and copper), metal oxide nanoparticles (ZnO), and polymeric nanoparticles (resorcinol-formaldehyde) were synthesized employing facile and large-scale adaptable synthesis techniques. The nanoparticles were utilized for the catalytic, photocatalytic, and adsorptive processes for the degradation and removal of organic and inorganic pollutants from water. Also, selective and naked-eye detectable sensing of Cr(III)
and Pb(II) in water was achieved by the use of gold nanoparticles. The summary of the research projects that have been included in this dissertation is given as follows.

Sodium squarate mediated novel method for the rapid synthesis of gold nanoparticles (AuNPs) in water is presented in Chapter 2. The AuNPs demonstrated good catalytic properties for the reduction of organic compounds in water. Also, the nanoparticles revealed interesting and selective sensing properties for Pb(II) and Cr(III) in water.

It was found that sodium rhodizonate could be utilized for the synthesis of gold, silver, platinum, and palladium nanoparticles in water. The ability of rhodizonate ion towards the reduction of noble metals and the formation of nanoparticles is reported in Chapter 3 and Chapter 4. The method generated nanoparticles of varying size with the variation of the reaction temperature. The nanoparticles have the ability to bind with various supports and to catalyze different types of chemical reactions. The method could be further extended to prepare bimetallic nanoparticles and high-surface-area nanoporous gold nanoparticles.

In Chapter 5, a facile method to prepare macroporous cellulose fibers supported PtNPs (PtNPs@KWP) is reported. The PtNPs@KWP exhibited excellent catalytic activity as well as cyclic stability towards the reduction of organic pollutant in the presence of hydrogen (H₂) gas and FA. The FA and H₂ gas were utilized as the clean and alternative reducing agents. The FA-induced catalytic reduction was found to be faster than the H₂ gas induced one. The PtNPs@KWP demonstrated excellent cyclic stability without leaching the PtNPs or the platinum ions in the solution for at least five cycles. The PtNPs@KWP was also utilized for the reduction of Cr(VI) to Cr(III) in water.

In chapter 6, a novel method for the synthesis of fullerene (C₆₀) stabilized AuNPs is reported. The AuNPs were supported on titanium dioxide (TiO₂) and the nanocomposites
exhibited enhanced photocatalytic degradation of MO and catalytic reduction of 4-NP in water. Both the photocatalytic degradation of MO and the catalytic reduction of 4-NP were influenced by the size and the weight percent AuNPs loading. Compared to the pristine TiO$_2$, the 4.76 weight % AuNPs loaded TiO$_2$ showed about twice and 132 times faster activity in the photodegradation of MO and the reduction of 4-NP, respectively. Further, the photocatalytic generation of hydroxyl radical (•OH) was confirmed through the terephthalic acid photoluminescence tests.

A novel and facile method for the synthesis of zinc oxide nanoparticles (nZnO) is demonstrated in Chapter 7. The nZnO was utilized for the photocatalytic degradation of MO and MB in water under the ultraviolet (UV-B) light and sunlight irradiation. Almost a complete degradation of MO and MB was obtained within 30 min of UV-B light irradiation. Under the sunlight irradiation, more than 95 % of the MO solution undergone degradation within 30 min period of time. The photocatalytic generation of •OH was further studied by the terephthalic acid fluorescence tests.

Sucrose mediated facile route for the preparation of high-surface-area Cobalt (Co), Nickel (Ni), and Copper (Cu) sponges are reported in Chapter 8. The Co, Ni, and Cu sponges were found to have highly porous morphology having specific surface areas of 17.39, 8.84 and 2.72 m$^2$/g, respectively. The powder X-ray diffraction spectroscopy (XRPD) pattern demonstrated the crystalline metallic nature of the sponges and the thermogravimetric analysis (TGA) revealed the presence of a trace amount of carbon in the sponges. The catalytic activity of the metal sponges was studied by the reduction of organic pollutants viz. 4-NP, MO, and MB in water. It was found that the Cu sponge was much faster in the reduction of 4-NP, MO, and MB, which was followed by the Co and Ni sponges, respectively.
Chapter 9 reports an improved method for the preparation of a regenerable adsorbent viz. sulfonated resorcinol-formaldehyde (RF-SO₃H) microspheres for the adsorptive removal of anionic and cationic organic pollutants from water. The equilibrium adsorption capacity was measured to be 710 mg/g and 511 mg/g for MO and MB, respectively. The adsorption of MO and MB from tap water matrix was also performed and shown to maintain similar adsorption capacity as in deionized water. In addition, a packed glass column was prepared to demonstrate the continuous adsorption of MO and MB under flow conditions.
Chapter 2: Sodium Squarate Mediated Novel Synthesis of Gold Nanoparticles and their Catalytic and Metal Sensing Properties

2.1. Introduction

Due to the extraordinary physical, chemical, and optical properties, gold nanoparticles (AuNPs) are one of the most versatile and widely studied nanomaterials.\textsuperscript{58} AuNPs are designed for numerous applications including but not limited to catalysis, photocatalysis, plasmonic photovoltaics, photothermal solar distillation, chemical sensing, biological and medical drug delivery systems, biomedicine, bioimaging, and photothermal therapy.\textsuperscript{59,60,61} Recently, the application of AuNPs for catalysis has garnered much attention.\textsuperscript{62} For example, the aldehyde–alkyne–amine (A\textsuperscript{3}) coupling, the reduction of nitro compounds into amines, the Suzuki–Miyaura Cross-Coupling, the production of hydrogen from carbon monoxide and steam, and the oxidation of glucose to gluconic acid are some of the important types of catalytic reactions to mention.\textsuperscript{63,64,65} However, in most cases, when AuNPs are used in solution, their aggregation leads to the gradual loss of their catalytic activity. Moreover, the separation, recovery, and reuse of the AuNPs from the reaction mixture becomes a real challenge. For this reason, AuNPs supported on a high-surface-area and solvent permeable solid matrix to obtain better cyclic stability and at the same time to minimize the cost. For instance, AuNPs have been supported on various types of cellulosic materials,\textsuperscript{66} mesoporous silica,\textsuperscript{67} Zeolites,\textsuperscript{68} and mesoporous carbon.\textsuperscript{69} Since cellulose is one of the most naturally abundant polymers, it has been a major type of matrix for the support of noble metal NPs.\textsuperscript{70} However, to achieve sufficient anchoring of AuNPs, the cellulose fibers are often functionalized with a number of groups.

In addition to the catalytic properties, AuNPs possess high molar absorption coefficient (10\textsuperscript{8} to 10\textsuperscript{10} M\textsuperscript{-1}cm\textsuperscript{-1}) in the visible spectrum due to the phenomenon called surface plasmon
resonance.\(^9\) Also, the color of the AuNPs solution can be tuned by changing the size, shape, composition, surface functionality, and the degree of aggregation of the nanoparticles. For example, a nicely dispersed AuNPs solution in water shows a redshift in the absorption spectrum after they get aggregated. This absorption/optical properties of AuNPs can be utilized for the sensing of a variety of species such as organic or inorganic pollutants, biomolecules, microorganisms, etc.\(^7\)

Herein, we report a novel method to prepare AuNPs that are reduced and stabilized by sodium squarate leading to SA-AuNPs. The SA-AuNPs easily binds to cellulose fibers (CF) to give nanocomposites (e.g. CF-AuNPs-2.94 and CF-AuNPs-1.96), which vary only in the weight percent of AuNPs loading, 2.94% and 1.96% by weight, respectively. The SA-AuNPs were thoroughly characterized with the help of UV-Visible spectroscopy, surface enhanced resonance Raman (SERS) spectroscopy, transmission electron microscopy (TEM), energy dispersive X-ray (EDX) spectroscopy, dynamic light scattering (DLS, and zeta potential measurements. The cellulose fibers-supported AuNPs were characterized with scanning electron microscopy (SEM), EDX, TEM, X-Ray powder diffraction (XRPD), and FTIR spectroscopy. Both the SA-AuNPs and the cellulose fibers-supported SA-AuNPs exhibited excellent catalytic activity for the reduction of 4-nitrophenol (4-NP) with NaBH\(_4\). A chromatographic column was packed with the cellulose fibers-supported AuNPs and used for continuous catalytic reduction of 4-NP to evaluate the stability of the catalyst. In addition to the catalytic properties, the metal mediated aggregation properties of the SA-AuNPs were utilized for the selective and sensitive colorimetric detection of Cr(III) and Pb(II) in water is demonstrated.
2.2. Materials and Methods

2.2.1. Materials

3,4-Dihydroxy-3-cyclobutene-1,2-dione [commonly known as squaric acid, (99%)], sodium hydroxide (NaOH ≥ 98%), hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O, 99.9%), 4-nitrophenol (4-NP) (O₂NC₆H₄OH ≥99%), sodium borohydride (NaBH₄, 99%), and cellulose fibers were obtained from Sigma-Aldrich, USA. Milli-Q water (>18.20 MΩ cm resistivity) was obtained from Milli-Q (Advantage A-10) water filter.

2.2.2. Synthesis of SA-AuNPs

An aqueous solution of 38.8 mM 5 mL sodium squarate was prepared by reacting (mixing) 22.12 mg (0.194 mmol) of squaric acid and 15.52 mg (0.388 mmol) sodium hydroxide in water. It is worthy to mention that squaric acid is not soluble in water; however, the conjugate base viz. sodium squarate is fairly soluble in water. Then, to a 100 mL round-bottomed flask containing 20 mL of 0.5 mM solution of hydrogen tetrachloroaurate trihydrate, 1 mL of 38.8 mM sodium squarate was added, all at once, while stirring vigorously.

Scheme 2.1: Synthesis of a) SA-AuNPs and b) cellulose fibers-supported AuNPs.
The reaction mixture turned into a deep burgundy color after a few seconds of stirring (Scheme 2.1a), indicating the formation of AuNPs. The stirring was continued for 30 min and the AuNPs solution was preserved under ambient conditions for further characterization, and catalytic applications. The as-prepared SA-AuNPs stock solution had a concentration of 0.0933 mg of Au per 1 mL of solution.

2.2.3. Preparation of Cellulose Fibers-supported SA-AuNPs

Depending upon the desired weight percent of AuNPs loading different quantities of SA-AuNPs solution and cellulose fibers were used. For example, to prepare cellulose fibers having 1.96% AuNPs by weight, referred to as CF-AuNPs-1.96, 196.04 mg of the cellulose fibers were added to 42 mL of the stock solution of SA-AuNPs. This mixture was then honk sonicated for 5 min, which caused SA-AuNPs to bind with the cellulose fibers leading to the decolorization of the SA-AuNPs solution, Scheme 1b. Composite CF-AuNPs-1.96 was then centrifuged out at a speed of 4000 rpm for 5 min, washed repeatedly with DI water, dried in a vacuum desiccator, and finally placed in an oven at 60 °C for overnight. In order to prepare 2.94% AuNPs loaded cellulose fibers, referred to as CF-AuNPs-2.94, 194.12 mg of the cellulose fibers were added to 63 mL of SA-AuNPs stock solution, which was followed by the aforementioned procedure.

2.3. Characterization of SA-AuNPs and the Nanocomposites

2.3.1. UV-Visible Spectroscopy of the SA-AuNPs

UV-Visible spectrum of the 6 times diluted SA-AuNPs solution in H₂O is shown in Figure 2.1. The SA-AuNPs solution in H₂O is also shown in the inset picture. A strong absorption band centered at 521 nm was observed, which is characteristic to the surface-plasmon resonance absorption band for the AuNPs. The molar absorption coefficient of the SA-AuNPs
stock solution was calculated to be 1.83×10^6 M\(^{-1}\)cm\(^{-1}\) considering the average particle size of about 21.01 nm.

Figure 2.1: UV-Visible absorption spectrum of the SA-AuNPs in H\(_2\)O and the digital photograph of the SA-AuNPs solution.

2.3.2. TEM Image and EDX Spectra of the SA-AuNPs

The size, shape, and dispersity of the SA-AuNPs were examined by the Transmission Electron Microscopy (TEM) image, Figure 2.2a. The TEM image of the SA-AuNPs in H\(_2\)O showed that the AuNPs were spherical in shape and well dispersed with little to no aggregation, Figure 2.2a. Further analysis revealed the core diameter of the SA-AuNPs ranging from 8 to 35 nm, with an average size of about 21.01 nm, Figure 2b.

Figure 2.2: a) Typical TEM image of the SA-AuNPs, b) size distribution of SA-AuNPs based on TEM image, and c) EDX spectrum of the SA-AuNPs.
The energy-dispersive X-ray (EDX) analysis was conducted on SA-AuNPs to determine the elemental composition of the SA-AuNPs, Figure 2c. The EDX spectrum showed a high abundance of gold as well as traces of C and O. This further indicates the stabilization of the AuNPs by the squarate ions.

2.3.3. SERS of the SA-AuNPs

Figure 2.3 shows the Raman scattering spectrum of the SA-AuNPs and the sodium squarate solution (1.8 mM) in water. It could be observed that the intensity of the characteristic peaks, originated from the sodium squarate solution (Figure 2.3a), is enhanced in the SA-AuNPs solution (Figure 2.3b). This enhancement in the signal of the sodium squarate indicates their binding on the AuNPs surface, which eventually provided the stability of the AuNPs in aqueous solution. The binding of the squarate ion with the AuNPs was also revealed by the small shift of the carbonyl peaks at 1573 cm\(^{-1}\) to a shoulder peak at 1556 cm\(^{-1}\). This effect eventually indicated that the squarate ion is structurally bonded with the surface of the AuNPs.

![Raman spectrum of a) sodium squarate solution and b) SA-AuNPs in water. * indicates the instrumental artifact at baseline.](image)

The Raman spectra of SA-AuNPs revealed two new peaks at 2129 and 2144 cm\(^{-1}\). These could be assigned to the characteristic peaks of carbon monoxide (CO) perpendicularly bound to
the AuNPs surface, which seems to be originated from the degradation of sodium squarate anion. Similar peaks were observed in other studies, where sodium squarate anion was bound to the gold and platinum electrode surfaces.72

2.3.4. DLS and Zeta Potential of the SA-AuNPs

Dynamic light scattering (DLS) was carried out on a 6 times diluted solution of SA-AuNPs in water to determine the size distribution of the nanoparticles in solution, Figure 2.4a. The average hydrodynamic diameter was observed to be about 44.21 nm, which is almost double the size obtained from the TEM analysis. This is because in solution the DLS gives the hydrodynamic size; whereas, the TEM image gives the size of the gold nanoparticle core only.

![Figure 2.4: a) Dynamic Light scattering and b) zeta potential of the SA-AuNPs in water.](image)

Zeta potential of the 6 times diluted of SA-AuNPs solution in water showed negative values of -32.6 mV, Figure 2.4b. This negative zeta potential signifies that the AuNPs surface had a net negative charge, which may be due to the binding of squarate anions on the AuNPs. This further explains the high dispersion stability of the SA-AuNPs in water due to the interparticle electrostatic repulsive forces.

2.3.5. SEM Images and EDS of the CF-AuNPs

Figure 2.5a and 2.5b show the typical SEM images of cellulose fibers before and after binding with the SA-AuNPs. The images demonstrated that the cellulose fibers had diameter of
about 25 micrometers with varying lengths. The cellulose fibers maintain the same morphology after binding with the SA-AuNPs.

The EDS spectral analysis of the pristine cellulose fibers and the CF-AuNPs-2.94 is shown in Figure 2.5c and 2.5d, respectively. The EDS spectrum of the pristine cellulose fibers showed the presence of carbon and oxygen, which are the constituents of the cellulose fibers. However, the EDS spectrum of the CF-AuNPs-2.94 showed an additional peak of gold, which indicated the presence of gold in the nanocomposites.

Figure 2.5. Typical SEM images of a) pristine CF and b) CF-AuNPs-2.94. EDX spectrum of c) pristine CF and d) CF-AuNPs-2.94.

2.3.6. TEM Image of the CF-AuNPs

Typical TEM image of the CF-AuNPs-2.94 is shown in Figure 2.6. The image was obtained by staining the nanocomposite with an aqueous solution of uranyl acetate before imaging. The TEM image showed a close proximity between the cellulose fibers and the SA-AuNPs, which further indicated that the SA-AuNPs were bound to the cellulose fibers by some kind of interactions.
Figure 2.6: TEM image of the CF-AuNPs-2.94.

2.3.7. XRPD Pattern of the CF-AuNPs

Figure 2.7 shows the X-Ray diffraction patterns of the cellulose fibers as well as the nanocomposites. Three main diffraction peaks originated at $2\theta = 14.5^\circ$, $16.4^\circ$ and $22.4^\circ$ corresponds to the cellulose $\text{I}_\alpha$ or cellulose $\text{I}_\beta$ allomorph. The XRD peaks that originates from these two allomorphs of cellulose usually locate very close to each other, which is difficult to distinguish. Therefore, it cannot be confirmed the type of cellulose allomorph from XRD pattern only.

Figure 2.7: XRD patterns of a) pristine CF, b) CF-AuNPs-2.94, and c) and CF-AuNPs-1.96.
However, the XRPD pattern of CF-AuNPs-2.94 and CF-AuNPs-1.96 and nanocomposites showed additional peaks at 37.7°, 43.8°, 64.1° and 77.2° corresponding to the Au 111, 200, 220, and 311 crystalline planes, respectively. This type of XRPD pattern indicated the presence of face-center cube (fcc) crystalline gold in the SA-AuNPs. Moreover, it can be observed that the intensity of the AuNPs peaks increased with the increase in the percent weight of AuNPs on the cellulose fibers.

2.4. Results and Discussion

2.4.1. Synthesis of the SA-AuNPs

The SA-AuNPs were prepared by mixing aqueous solutions of sodium squarate and chloroauric acid (HAuCl₄·3H₂O) at room temperature. The reaction mixture turned into a deep burgundy color after a few seconds of stirring indicating the formation of AuNPs. As no separate reducing and stabilizing agents were used, the formation of the gold nanoparticles could be attributed to the reduction followed by the stabilization by the squarate ions. To the best of our knowledge, the method is novel and has been reported for the first time in this report. Also, the method can be considered as one of the simplest methods among all other reported methods. All other methods for the synthesis of gold nanoparticles in water require longer time, heat, hazardous chemicals, separate reducing and stabilizing agents.

The cellulose fibers-supported AuNPs were prepared by mixing cellulose fibers with the SA-AuNPs solution, followed by honk sonication for five minutes. The nanoparticle solution of SA-AuNPs turned clear without any trace of plasmonic absorption at 521 nm, indicating that all the SA-AuNPs were taken up by the cellulose fiber. The advantage of this method is that the cellulose fibers did not require any functionalization to bind with the AuNPs and the method is pretty simple and fast.
2.4.2. Catalytic Reduction of 4-NP by the SA-AuNPs

The catalytic reduction of 4-NP to 4-AP is shown in Scheme 2.2. The reduction of 4-NP to 4-AP was monitored by UV-Visible spectroscopy. The amount of SA-AuNPs used in the catalysis experiments was 5.8 mole percent with respect to 4-NP. In a quartz cuvette, 0.2 mL of (0.001M) 4-NP aqueous solution was diluted with 0.8 mL of Milli-Q water. Afterwards, 0.5 mL of (0.1 M) freshly prepared NaBH₄ solution in water was added into the 4-NP solution. Later, 50 µL of the AuNPs stock solution was quickly added and mixed into the quartz cuvette.

![Scheme 2.2: The SA-AuNPs catalyzed reduction of 4-NP to 4-AP.](image)

The reaction course was monitored, every 30 seconds, by the gradual decrease in the absorbance of 4-nitrophenolate at 400 nm. The formation of a new absorption band centered at 310 nm is characteristic to the formation of 4-AP.

Figure 2.8 shows the time-dependent UV-Visible spectrum and the kinetics of the catalytic reduction of 4-NP to 4-AP. A continuous decrease in the absorbance centered at 400 with the lapse of reaction time was observed, Figure 2.8a. This decrease in absorbance is indicative to the reduction of 4-NP to 4-AP. The time dependent UV-Visible spectrum of the uncatalyzed reaction, where no AuNPs were used, showed negligible decrease in absorbance at 400 nm even after 16 min of reaction time. This signified that the AuNPs is the species that catalyzed the reaction. This further signified the robust nature of 4-NP to undergo reduction without the catalyst.
Figure 2.8b shows the kinetics of the catalytic reductions of 4-NP. A linear relationship between \(-\ln(C_t/C_0)\) and reaction time \((t)\) is indicative that the kinetics of the catalysis followed the Langmuir–Hinshelwood (LH) model, where \(C_0\) represents the initial concentration of 4-NP and \(C_t\) represents the concentration of 4-NP at time \((t)\). Moreover, the catalytic reactions, where \(-\ln(C_t/C_0)\) increases linearly with respect to time indicates that the course of the reaction follows pseudo-first-order kinetics, which eventually follows the equation \(kt = -\ln(C_t/C_0)\).

![Graph showing kinetics of catalytic reductions of 4-NP](image)

Figure 2.8: a) Time-dependent UV-Visible spectrum of 4-NP during the catalytic reduction and b) pseudo-first order kinetics of the catalyzed and uncatalyzed reactions.

As shown in Figure 2.8b, the apparent rate constant \((k_{app})\) of the catalytic reduction of 4-NP in the presence of SA-AuNPs was calculated to be \(5.365 \times 10^{-3} \text{ s}^{-1}\). Whereas, the apparent rate constant of the uncatalyzed reaction is calculated to be \(2.138 \times 10^{-4} \text{ s}^{-1}\).

2.4.3. Catalytic Reduction of 4-NP by the Nanocomposites

In a standard quartz cuvette, 3 mg of the nanocomposite of each type, was added to 2.5 mL of a 1 mM aqueous solution of 4-NP which was followed by a bath sonication for 5 min. Afterwards, 1 mL of freshly prepared 0.159 M solution NaBH₄ in water was added and mixed quickly. The reaction course was monitored by using the kinetics software of the UV-Visible
spectrophotometer. In this particular set up the spectrophotometer monitored the lowering of the absorbance of 4-nitrophenolate at 400 nm with respect to time at a time interval of 10 s.

Figure 2.9 shows the kinetics of the reduction of 4-NP to 4-AP catalyzed by CF-AuNPs-2.94 and CE-AuNPs-1.96, and pristine cellulose fibers as a control. The results showed that \( -\ln \left( \frac{C_t}{C_0} \right) \) increased with respect to the time, which indicated that the reaction course followed pseudo-first-order kinetics. The apparent rate constants of the catalytic reactions were calculated to be \( 4.280 \times 10^{-3} \text{ s}^{-1} \), \( 1.713 \times 10^{-3} \text{ s}^{-1} \) and \( 5.33 \times 10^{-5} \text{ s}^{-1} \), for CF-AuNPs-2.94, CE-AuNPs-1.96 and pristine cellulose fibers, respectively.

![Graph showing the kinetics of the reduction of 4-NP to 4-AP catalyzed by different catalysts](image)

Figure 2.9: Plot of \(-\ln(C_t/C_0)\) versus reaction time during the reduction of 4-NP catalyzed by a) CF-AuNPs-2.94, b) CF-AuNPs-1.96, and c) pristine CF.

It was observed that the cellulose fibers supported SA-AuNPs catalyzed reactions had induction periods of about 2 min and 7 min for CF-AuNPs-2.94 and CE-AuNPs-1.96, respectively. This induction period is usually observed in heterogeneous catalysis. Induction period can be defined as the time that a catalytic reaction takes to establish the adsorption and desorption equilibrium of the reactants and the products. During this induction period no reaction product can be obtained and after this time period the reaction products starts to appear.
2.4.4. Catalytic Reduction of 4-NP Through the Packed Reactor Column

In order to evaluate the practical applicability of the cellulose supported SA-AuNPs, a glass chromatographic column having dimensions I.D. x O.D x L = 20 x 26 x 457 mm was packed with the cellulose supported SA-AuNPs mixed with sand, Figure 2.10. In detail, 11 mL of SA-AuNPs stock solution (0.0933 mg/ml) was mixed with 500 mg of cellulose fibers followed by sonication for 5 min. The cellulose fibers bound SA-AuNPs was thoroughly mixed with 90 g of sea sand with particle size ranging from 125 to 500 micrometers. Afterwards, the column was filled by wet method and the column was packed about 19 cm. Cotton and coarse sea sand were used as the support at the bottom of the column. The top of the column was also filled with coarse sea sand for about 4 cm, Figure 2.10 (inset).

![Figure 2.10: UV-Visible spectrum of the inlet 4-NP and the eluent 4-AP solutions. Inset: An operating reactor column.](image)

The column was first washed with 500 mL of DI water. For the continuous catalysis reaction, 60 mg of NaBH₄ (1.586 mmol) was dissolved in 60 mL of 0.5 mM 4-NP solution with stirring. The freshly-prepared solution was then continuously fed into the column having the valve of the column completely open. The initial flow rate of the column was measured to be
about 2.25 mL/min. However, a gradual decrease in flow rate was observed because of the back-pressure created by the hydrogen gas that evolved from the NaBH₄. When the whole column was filled with the reaction solution, an average flow rate of 1.25 mL/min was observed. The eluted reaction solution looked clear with generation of micro bubbles, which indicated the excess NaBH₄ was coming out along with 4-AP. The UV-Visible spectrum of the eluted solution did not have any absorption band centered at 400 nm, which indicated the complete reduction of 4-NP, Figure 2.10. Moreover, a new absorption band was originated at 310 nm, which is the characteristic band for 4-AP, Figure 2.10. The column was used for 20 such successive reactions cycles over a period of 6 months and every time complete reduction of 4-NP was observed. No loss in the catalytic activity was found, which indicated the robustness of the nanocomposites.

2.4.5. Sensing of Cr(III) and Pb(II) by the SA-AuNPs

2.4.5.1. Selectivity to Cr(III) and Pb(II)

For the selectivity test, 200 µL solution of 5.89 µM concentration of different metal ion was added into the 1000 µL SA-AuNPs solution. The SA-AuNPs solution used for this study was 5 times diluted SA-AuNPs stock solution. A series of 20 metal ions were tested and it was found that only Cr(III) and Pb(II) changed the color of the SA-AuNPs solution, Figure 2.11.

Figure 2.11: Selectivity of the SA-AuNPs towards sensing Cr(III) and Pb(II) solution in water.
To further analyze the change in color of the SA-AuNPs, UV-Visible spectra was obtained on the SA-AuNPs solution after metal ion was added, Figure 2.12. It was found that the Cr(III) and Pb(II) shifted the SPR absorption band of the SA-AuNPs to red. For Cr(III) and Pb(II), new SPR absorption bands originated at 765 and 660 nm, whereas; the intensity of the SPR absorption of SA-AuNPs decreased at 525 nm.

![Figure 2.12: a) UV-Visible spectra of the SA-AuNPs solution after the addition of metal ions and b) extent of red shift of the LSPR band of the SA-AuNPs.](image)

When gold nanoparticles aggregates in solution, it causes an interparticle surface Plasmon coupling, which causes a color change from red to blue. This color change is widely employed in the development of colorimetric sensing of ions, small molecules or proteins. The extent of red shift was found to be highest for Cr(III) and then for Pb(II). For any other metals there was no shift in the SPR band at 525 nm was observed. This indicated the selectivity of the SA-AuNPs solution towards the Cr(III) and then for Pb(II) ions in water.

### 2.4.5.2. Sensitivity to Cr(III) and Pb(II)

Later, the sensitivity of SA-AuNPs towards the detection of Cr(III) and Pb(II) was studied by adding solutions of different analyte concentrations, Figure 2.13. For Cr(III) and
Pb(II), a new red-shifted peak originated and the peak shifted more to red with the increase in the analyte concentration. This extent of red shifting was more prominent for Cr(III) in compared to Pb(II), Figure 2.14. From the UV-Visible spectrum it could be observed that the SA-AuNPs could detect up to 375 ppb Cr(III) and 12 ppm Pb(II) in water.

Figure 2.13: UV-Visible spectra of the SA-AuNPs solution after varying concentration a) Cr(III) and b) Pb(II) ions were added.

To further understand the reason why the SA-AuNPs changes color in solution, TEM images were taken on the SA-AuNPs before and after the addition of Cr(III) solution, Figure 2.14. It was observed that the SA-AuNPs were nicely dispersed in solution before the addition of the Cr(III) ion, however; after the addition of the Cr(III) ion the SA-AuNPs undergone aggregation.

This aggregation caused the coupling of the LSPR band, which eventually shifted absorption band to the right direction as shown in the UV-Visible spectrum. This further caused the color change detectable by the naked eyes. For higher concentration of Cr(III), the aggregation of SA-AuNPs happened rally fast within about 5 min period of time, the SA-AuNPs eventually precipitated out from solution causing the decolorization of the solution.
2.5. Conclusion

A novel method for the preparation of gold nanoparticles (AuNPs) in water using sodium squarate as a reducing and stabilizing agent is reported. These nanoparticles were supported on the cellulose fibers to make active nanocomposites that exhibited excellent catalytic activity for the reduction of 4-NP with NaBH₄. A chromatography column was packed with the nanocomposites for the continuous catalytic reduction of 4-NP under the flow conditions. In addition to the catalytic properties, the SA-AuNPs demonstrated naked eye detectable selective sensing of Cr(III) and Pb(II) in water.
Chapter 3: Sodium Rhodizonate Mediated Novel Synthesis of Gold, Silver, Platinum, and Palladium Nanoparticles and their Catalytic Properties

3.1. Introduction

Noble metal nanoparticles possess unique size- and shape-dependent electrical, optical, chemical and physical properties. In particular, their size-dependent catalytic properties, which is typically observed at the nanoscopic size in contrast to the macroscopic size, has made them some of the most widely studied nanomaterials. As compared to the bulk material, the nanoparticles have a larger proportion of atoms at the edges and the corners, which are surrounded by fewer atoms. The exposed atoms at the edges and the corners are considered to be chemically more reactive than the atoms in the bulk. Recently, the catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) and the dual-catalytic oxidation of the formic acid followed by the reductive degradation of organic pollutants have drawn much attention. The catalytic reduction of 4-NP to 4-AP is not only a model reaction in academia but also the reduced product (4-AP) has industrial applications. For example, 4-AP is used as a photographic developer, corrosion inhibitor, antioxidant, precursor for the manufacture of analgesic and antipyretic drugs, an intermediate in the synthesis of paracetamol, etc. On the other hand, the dual-catalytic oxidation of the formic acid followed by the reductive degradation of organic pollutants is becoming an intriguing method in the area of hydrogen storage and the environmental remediation. The catalytic oxidation of formic acid generates H₂ and CO₂ gases. This reaction could be utilized as a clean and stable source of generating H₂ gas. Moreover, the in situ generated H₂ gas could be utilized to reductively degrade organic and inorganic pollutants in water viz. methyl orange, nitrate, and hexavalent chromium in water. The formic acid
induced reductive degradation of organic pollutants has benefit over other reducing agents \textit{viz.} \textit{NaBH}_4 as it does not produce any secondary pollutants. However, the catalytic reduction of the 4-NP and the dual catalytic oxidation of formic acid followed by the reductive degradation of MO commonly require noble metal nanoparticles as the catalysts.\textsuperscript{82}

There are number methods for the synthesis of noble metal nanoparticles, where a wide variety reducing and/or stabilizing agents are utilized. However, most of these methods cannot produce Au, Ag, Pt, and Pd nanoparticles following a common synthetic procedure. Further, some methods require multiple steps, harsh reducing agent \textit{viz.} \textit{NaBH}_4, organic solvents, prolonged stirring/incubation time, and separate reducing and stabilizing agents. Additionally, in the biological and medical drug delivery systems, chemical sensing of aqueous species, bio-imaging, and catalysis the requirement for the simplicity in the synthesis and water solubility is of the prime choice. Therefore, a generic and simple method for synthesis of noble metal nanoparticles using limited number of reagents is highly desired in the field of the noble metal nanoparticles research.

Herein, we report a general one-step method for the synthesis of Au, Ag, Pt, and PdNPs in water that are both reduced and stabilized by sodium rhodizonate. To the best of our knowledge, the ability of the rhodizonate ions for the synthesis of Au, Ag, Pt and PdNPs following a generic method has not been reported yet. The rhodizonate ion acts as a bifunctional reducing as well as stabilizing agent for the nanoparticles. UV-Visible spectroscopy, transmission electron microscopy (TEM), energy dispersive X-ray (EDX) spectroscopy, and the zeta potential measurements were used to characterize the NPs. The catalytic activities of the NPs were evaluated by two types of catalytic reactions. The first reaction studied here is the
reduction of 4-NP to 4-AP in water in the presence of excess NaBH₄. The second reaction we studied here is the dual-catalytic oxidation of the formic acid followed by the reduction of MO.

3.2. Materials and Methods

3.2.1. Materials

Sodium rhodizonate dibasic (97%), hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O, 99.9%), hydrogen hexachloroplatinate (IV) hydrate (H₂PtCl₆·3H₂O ≥99.9%), silver nitrate (AgNO₃), Palladium nitrate [Pd(NO₃)₂], 4-nitrophenol (O₂NC₆H₄OH ≥99%), sodium borohydride (NaBH₄, 99%), formic acid (CH₂O₂) and methyl orange (MO), were purchased from Sigma-Aldrich, USA. Milli-Q water (>18.20 MΩ cm resistivity) was obtained from Milli-Q (Advantage A-10) water filter system.

3.2.2. Synthesis of the NPs

All the nanoparticles were prepared following a same synthetic procedure, Scheme 3.1. Separate 0.5 mM stock solutions of metal precursors were prepared by dissolving a required amount metal salt in water. A separate 9.7 mM aqueous solution of sodium rhodizonate was prepared by dissolving 83.04 mg (0.388 mmol) of sodium rhodizonate in 40 ml of water. For a typical synthesis, in a 100 mL round-bottomed flask 20 mL of 0.5 mM aqueous solution of metal precursor was allowed to boil. Afterwards, 4 mL of 9.7 mM sodium rhodizonate was injected while vigorous stirring of the solution. The reaction mixture was further boiled for 20 min to make sure a complete reduction of the metal ions. The molar ratio of the sodium rhodizonate to the noble metal ions was 3.88 in all the syntheses. The NPs solutions were preserved under ambient conditions for further characterization and catalytic applications.
3.2.3. Catalytic Activity of the NPs

The catalytic activity of the nanoparticles was evaluated by two different types of reduction reactions, Scheme 3.2 and 3.3. The first reaction was the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in presence of excess NaBH₄, whereas the second reaction was the dual-catalytic oxidation of formic acid followed by the reduction of methyl orange.

For the reduction of 4-NP, in a standard quartz cuvette 1 mL of 4-NP aqueous solution (0.2 mM) was mixed with 50 µL of NPs stock solution. Afterwards, 0.5 mL of freshly prepared NaBH₄ aqueous solution (5mg NaBH₄ in 0.5 ml of water) was added into the quartz cuvette and
the reaction course was monitored, every 30 second, by using the UV-Visible spectrophotometer. The UV-Visible spectrophotometer monitored the time-dependent lowering of the absorbance of 4-nitrophenolate at 400 nm. It is worth mentioning that the 4-NP reacts with NaBH₄ to yield 4-nitrophenolate, which shows strong absorption band centred at 400 nm.

For the dual-catalytic oxidation of formic acid followed by the reduction of MO, in a standard quartz cuvette, 50 µL of NPs stock solution was added to 1.5 mL of 26.7 ppm aqueous solution of MO. Afterwards, 50 µL of formic acid was added and mixed quickly. The reaction course was monitored by the UV-Visible spectroscopy, which monitored the lowering of the absorbance of MO at 515 nm in every 30 s interval of time.

Scheme 3.3: Metal nanoparticles catalyzed oxidation of FA followed by the reduction of MO.

The percent reduction of 4-AP and MO was calculated using the following equation.

Percent reduction of 4-AP or MO = \(\frac{A_0 - A_t}{A_0} \times 100\%\)

where \(A_0\) and \(A_t\) represent the absorbance of 4-NP and MO at 400 and 515 nm, respectively at the beginning and at time (t) of the catalytic reduction.

The reaction kinetics was analyzed by the linear form of the pseudo-first-order kinetic model, which is expressed by the following equation.

Pseudo-first-order reaction rate equation, \(-\ln \left(\frac{C_t}{C_0}\right) = kt\)
where \( k \) (1/min) represents the pseudo-first-order rate constant of the catalytic reduction; \( C_0 \) and \( C_t \) represent the initial and time-dependent concentrations of 4-NP and MO, respectively.

### 3.3. Characterization of the NPs

#### 3.3.1. UV-Visible Spectroscopy of the NPs

The typical UV-Visible spectrum of the Au, Ag, Pt, and PdNPs are shown in Figure 3.1. Strong absorption bands centered at about 530 and 416 nm were observed for the Au and AgNPs, respectively. This type of absorption band is also known as the L-surface-plasmon resonance (SPR) absorption band, which is usually exhibited by the Au and Ag nanoparticles. The SPR band of the nanoparticles originates from the collective oscillation of conduction electrons upon interaction with electromagnetic radiation. It could be observed that the SPR band generated by AgNPs is about 100 nm blue shifted compared to the AuNPs. This is because of the fact that the Ag and Au have completely different atomic size, electronic structure and conductivity.

![Figure 3.1: UV-Visible absorption spectrum of the Au, Ag, Pt, and PdNPs in water.](image)

On the other hand, the Pt and PdNPs did not show any SPR band in the Visible region of the electromagnetic radiation. The SPR band of platinum and palladium nanoparticles are usually
found in the ultraviolet range, unlike the Au and AgNPs, which usually display SPR band in the
Visible region. Additionally, the size of the nanoparticles and their degree of aggregation usually
shift the SPR band. For example, gold nanoparticles less than 2 nm in size usually do not exhibit
the SPR band in the Visible region.84

3.3.2. TEM, HRTEM, EDS, and Zeta Potential of the NPs

The typical TEM images of the NPs with the corresponding size distributions are shown
in Figure 3.2. The TEM images show that the Au, Ag, and PtNPs are fairly spherical and well
dispersed in in water although some degree of aggregations could also be observed. It could be
observed that some of the AuNPs look like nanoprism and nanocube in shape. The AgNPs are
seen to be larger in diameter and have more faced morphology compared to the other NPs.

![Figure 3.2: Typical TEM images of the a) PtNPs, b) AuNPs, c) AgNPs, and d) PdNPs.
Corresponding size distributions of the NPs (e-h). Scale bar = 20, 20, 200 and 100
nm for the Pt, Au, Ag and PdNPs, respectively.](image)

The PdNPs are observed to be somewhat less spherical and amorphous in shape. Moreover, the PdNPs were found to be more aggregated compared to the Au, Ag, and PtNPs in solution. The corresponding size distribution histograms of the NPs reveal that the Pt, Au, Ag, and PdNPs have the average core diameter of about 2, 8, 26, and 39 nm, respectively. The
change in particles size could be attributed to the difference in the reduction potential of the metals and the stabilization ability of the rhodizonate ion towards the different noble metal ions studied here.

In order to determine the crystallinity as well as to analyze the nanoparticles qualitatively, high-resolution TEM analysis was carried out, Figure 3.3. HRTEM image can reveal the crystalline faces of the nanoparticles with atomic resolution. Moreover, the interlayer spacing, obtained from the HRTEM images, is usually utilized to characterize the different lattice planes of crystalline materials, which in turn is used for the qualitative analysis of the material.

![HRTEM images](image)

**Figure 3.3:** HRTEM images of the a) PtNPs, b) AuNPs, c) AgNPs, and d) PdNPs showing the characteristic (111) lattice spacing.

The interlayer spacing, shown in Figure 3.3a, is measured to be about 0.22 nm, which is the characteristic lattice spacing of the platinum Pt(111) planes.\(^5\) Similarly, the characteristic interlayer spacing of the Au(111), Ag(111), and Pd(111) planes were measured to be about 0.23, 0.24, and 0.22 nm, respectively, Figure 3.3b-d.\(^6\) Therefore, the HRTEM images confirmed the nanoparticles are crystalline and metallic in nature.

Energy-dispersive X-ray (EDX) analysis was conducted to determine the elemental composition of the nanoparticles. As a representative, the EDX spectrum was obtained from the AuNPs sample only, Figure 3.4a. The EDX spectrum revealed the presence of gold, carbon, and
oxygen in the nanoparticles sample. The presence of carbon and oxygen indicate the presence of rhodizonate ions that are bound to the AuNPs surfaces. This further indicates that the stabilization of the AuNPs by the excess rhodizonate ions present in the solution.

Figure 3.4: a) Energy dispersive X-ray (EDX) spectrum of AuNPs and b) Zeta potential of the AuNPs in water.

The zeta potential measurements were carried to determine the net charge on the NPs surface, Figure 3.4b. The net zeta potential was determined to be -32.7, -34.0, -20.5, and -7.46 for the Au, Ag, Pt, and PdNPs, respectively. The net negative values of the zeta potential further suggest the binding of the negatively charged rhodizonate ions on the nanoparticles surface and thereby yield a negative zeta potential. This indicates the dispersion stability of the NPs in water due to the interparticle electrostatic repulsive forces. Moreover, it could be observed that the PdNPs have the least net zeta potential value. This in turn indicates the poor dispersion stability of PdNPs in water in compared to the other NPs. This result is similar to the TEM studies, where the PdNPs were seen highly aggregated compared to the other NPs.

3.4. Results and Discussion

3.4.1. Synthesis of the NPs in Water

The Au, Ag, Pt, and PdNPs were facilely synthesized by mixing solutions of sodium rhodizonate and metal precursor solutions in water at an elevated temperature. The reaction mixture changed color immediately after the solutions were mixed together. This indicated the
formation of NPs by the naked eye visualization. The rhodizonate ions reduced the metallic ion to metallic NPs. Afterwards, the excess rhodizonate ions bound to the metallic ions situated on the surface of the nanoparticles by the coordination bond. As a result, the rhodizonate ions capped the NPs from further growth. Therefore, the rhodizonate ions acted as the bifunctional reducing as well as capping agent. The ability of rhodizonate ion to form coordination complexes with different metal ions has been reported before.\textsuperscript{87,88} However, its ability toward the reduction of Ag, Pt, and Pd ions to their metallic nanoparticles followed by their stabilization is not investigated until we reported here. Therefore, sodium rhodizonate could potentially be utilized as a soft reducing agent for various other organic syntheses, where reducing agent viz. NaBH\textsubscript{4} is too strong to use. Furthermore, the catalytic activity of the nanoparticles towards the reduction of 4-NP and the reductive degradation of MO is systematically studied and compared. The catalytic reduction of 4-NP is not only a model reaction that is commonly studied in academia but also the reduction product has some industrial applications. The catalytic oxidation of formic acid followed by the reductive degradation of MO, on the other hand, could be utilized as a green method to degrade organic pollutants in water, which could be an attractive alternative method in the area of environmental remediation.

3.4.2. Catalytic Reduction of 4-nitrophenol by the NPs

The time-dependent decrease in the absorbance of 4-NP centered at 400 nm with the corresponding kinetics of the catalytic reductions is shown in Figure 3.5. Figure 3.5a shows the continuous decrease in the absorbance of 4-NP at 400 nm during its catalytic reduction in presence of the AgNPs. The time-dependent percent reduction of the 4-NP, catalyzed by different NPs, is shown in Figure 3.5b. It could be observed that the Ag and AuNPs were faster catalyzing the reduction of 4-NP compared to the Pd and PtNPs. The un-catalyzed reaction,
where no NPs were used, shows negligible percent reduction of the 4-NP. This signifies the robust nature of 4-NP to undergo the reduction by NaBH₄ only. The slow catalytic activity of the PtNPs could be attributed to its strong stabilization by the rhodizonate ions in solution. However, the slow catalytic activity of the PdNPs could be attributed to its large particle size and high degree of aggregations in solution.

Figure 3.5: a) Time-dependent UV-Visible spectrum of the 4-NP during its reduction on the AgNPs, b) time-dependent percent reduction of the 4-NP catalyzed by different nanoparticles, and c) pseudo-first order kinetics of the corresponding catalyzed and un-catalyzed reductions.

The kinetics of the catalytic reduction of 4-NP, catalyzed by different NPs, is shown in Figure 3.5c. A linear relationship between the $-\ln(C_t/C_0)$ and reaction time (t) was observed. This suggests that the kinetics of the 4-NP reduction follows the Langmuir–Hinshelwood (LH) model. Moreover, the linear increase of $-\ln(C_t/C_0)$ with respect to the reaction time indicates that the reduction follows pseudo-first-order kinetics. The apparent rate constants ($k_{app}$) of the catalytic reduction of 4-NP in the presence of Ag, Au, Pt, and PdNPs were found to be 2.1482, 1.1167, 1.088 $\times 10^{-1}$, and 1.65 $\times 10^{-2}$ min⁻¹, respectively. Whereas, the apparent rate constant of the uncatalyzed reaction is calculated to be 8.0 $\times 10^{-4}$ min⁻¹. Moreover, it could be observed that the
induction time for the Ag and AuNPs catalyzed reaction is about zero, which indicate their excellent catalytic activity.

3.4.3. Catalytic Oxidation of Formic Acid Followed by the Reduction of MO

Figure 3.6 shows the time-dependent decrease in the absorbance of MO centered at 515 nm with the corresponding kinetics of the reduction. Likewise the 4-NP reduction, the –\ln(Ct/Co) vs time (t) is a straight line, which indicates that the reactions follow pseudo-first-order kinetics. The apparent rate constants of the reactions (k_{app}) were calculated to be 4.145, 1.25 \times 10^{-2}, 6.7 \times 10^{-3}, 9.0 \times 10^{-5} and 7.0 \times 10^{-5} min^{-1}, for PtNPs, PdNPs, AuNPs, AgNPs catalyzed and control experiments, respectively.

The un-catalyzed reaction, where no NPs were used, showed negligible percent reduction of the MO. The PtNPs demonstrated very fast and the Pd and AuNPs demonstrated moderate catalytic activity, whereas the AgNPs showed negligible activity under the experimental conditions. The Pt and the PdNPs are well-known catalysts for the oxidation of formic acid to generate CO$_2$ and H$_2$ gases.\(^8^9\) Afterwards, the in situ generated H$_2$ gas gets chemisorbed on the
NPs surface, which eventually reduces the MO and break the conjugation through the diazo (N=N) bond. As a result, the MO loses its color gradually. The slow catalytic activity of the PdNPs, in this study, could be attributed to their large particle size and high degree of aggregations in solution. Moreover, it could be observed that the induction period for the PtNPs catalyzed reaction is about 30 sec. This may happen due to the two steps catalysis reactions viz. the oxidation of formic acid and the reduction of the MO. Induction period is commonly observed in heterogeneous catalysis and it is a measure of the time that takes to reach the adsorption-desorption equilibrium between the reactants and products with the catalyst.

3.5. Conclusion

In conclusion, we report a facile method for the generation of Au, Ag, Pt and Pd nanoparticles in water that are both reduced and stabilized by sodium rhodizonate. The performance of these nanoparticles towards the catalytic reduction of 4-nitrophenol (4-NP) and methyl orange (MO) was systematically studied and compared. The results indicated that AgNPs followed by AuNPs exhibited significantly faster kinetics for the reduction of the 4-NP with NaBH₄ as compared to the Pt and the PdNPs. In contrary, the reduction of MO with formic acid catalyzed by the Pt and PdNPs was found to be faster as compared to the AuNPs and AgNPs. Sodium rhodizonate mediated synthesis of the Au, Ag, Pt and Pd nanoparticles represent a general route for functionally active catalysts with a wide range of potential applications.
4.1. Introduction

A major class of anthropogenic organic pollutants consists of dyes that are widely used by numerous industries.\textsuperscript{90} However, a large portion of these dyes is discharged into the environment, which is the key reason for the contamination of water by dyes. Like other organic pollutants, many dyes are well known to be toxic, carcinogenic and mutagenic to human beings and aquatic organisms. Moreover, many of these dyes are fairly stable and persistent in nature and thereby show resistance to natural degradation. The dyes also have high molar absorption coefficient and thereby, can intensely colorize a large amount of water, which is undesirable for municipal usage purposes. Therefore, the removal of organic dyes is an indispensable part of wastewater treatment.

Commonly employed methods for the treatment of organic pollutants from wastewater includes but not limited to adsorption,\textsuperscript{91} chemical precipitation,\textsuperscript{92} photocatalytic degradation,\textsuperscript{93} advanced oxidation processes,\textsuperscript{94} and the biological treatment.\textsuperscript{95} Removal of organic pollutants by adsorption and chemical precipitation does not destroy them rather transfer the pollutants from one phase to another. Photocatalytic degradation, on the other hand, can degrade organic pollutants to mineralization. However, the requirement of ultraviolet light, low quantum yield and slow rate of degradation limit their practical applicability. Biological treatments can also efficiently decompose the organic compounds using microorganisms such as algae, fungi, bacteria, and yeasts. However, some organic pollutants are highly resistant, toxic, and carcinogenic to microorganisms and that is why the typical biological treatment is practically ineffective in their decomposition.\textsuperscript{96} In this context, the catalytic reductive degradation of
organic pollutants has been reported as a relatively new and effective method of wastewater treatment technology.\textsuperscript{97} Catalytic reduction can effectively degrade organic pollutants at a faster rate with better stability and recyclability.\textsuperscript{98} Moreover, it has been reported that some pollutants in their reduced form become less toxic and thereby can be degraded by biological treatment.\textsuperscript{99} As for example, 4-nitrophenol (4-NP), which is a common industrial pollutant can be reduced into less toxic 4-aminophenol (4-AP). Therefore, chemical reduction followed by the biological treatment could be an effective method for the degradation of toxic and carcinogenic organic pollutants from water.\textsuperscript{100} In addition, the reduced form of some pollutants \textit{viz.} 4-AP also has industrial applications as a photographic developer, corrosion inhibitor, antioxidant, precursor for the manufacture of analgesic and antipyretic drugs, an intermediate in the synthesis of paracetamol, etc.\textsuperscript{101} Hence, the reduction of organic pollutants is an effective method not only in the context of pollutants treatment but also is an effective way of resources regeneration.

Most commonly used catalysts for the reductive degradation of organic pollutants are based on noble and transition metals.\textsuperscript{102} Moreover, owing to the high surface area, fast reactivity, recyclability, chemical and physical robustness supported noble metal nanoparticles-based catalysts are of the prime choice in this regard.\textsuperscript{103}

Herein, we report a novel method of generating AuNPs that are reduced and stabilized by sodium rhodizonate. The method was extended for the synthesis of Au-Ag alloy nanoparticles. From the Au-Ag alloy nanoparticles, Ag was selectively etched out to obtain porous AuNPs, which could potentially be used as an extremely active catalyst due to its ultra-high surface area and porous morphology. The AuNPs were supported on cellulose fibers (CF) and utilized for the catalytic reduction of 4-NP, MO, and MB in water. The CF-supported AuNPs catalysts provide convenience in handling, recovery, and reuse.
4.2. Materials and Methods

4.2.1. Materials

Sodium rhodizonate dibasic (97%), hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O, 99.9%), silver nitrate (AgNO₃, ≥99%), ammonium hydroxide solution (28% NH₃ in H₂O, ≥99.99% trace metals basis), 4-nitrophenol (O₂NC₆H₄OH, ≥99%), sodium borohydride (NaBH₄, 99%), methyl orange (MO), methylene blue (MB) and fibrous cellulose were purchased from Sigma-Aldrich, USA. Deionized water was obtained from Milli-Q (Advantage A-10) water filter system having resistance >18.20 MΩ cm.

4.2.2. Synthesis of AuNPs, Ag-AuNPs, and Porous AuNPs

In a typical synthesis, to a 100 mL round-bottomed flask containing 20 mL of 0.5 mM solution of HAuCl₄, 4 mL of 9.7 mM sodium rhodizonate was added, all at once, while stirring vigorously (Scheme 4.1). After a few seconds of stirring the reaction mixture turned into a deep burgundy color (Scheme 1), which indicated the formation of AuNPs. The AuNPs synthesized at room temperature (ca. RT= 23 °C) are hereafter denoted as AuNPs-RT. After 5 min of stirring the AuNPs-RT solution was preserved under ambient conditions for further characterization, application, and attachment with CF. As-prepared AuNPs stock solution had a concentration of 0.0821 mg of Au⁰ per 1 ml of the AuNPs solution. In order to synthesize AuNPs at 80 °C both of the solutions were preheated to 80 °C before mixing. The AuNPs synthesized at 80 °C is hereafter denoted as AuNPs-80C.
Scheme 4.1: Synthesis of AuNPs reduced and stabilized by sodium rhodizonate at a) room temperature (RT = 23 °C) and b) 80 °C.

For the preparation of Ag-AuNPs of 50-50 molar ratio of Ag and Au, to a 20 mL hot (80 °C) aqueous solution of 0.25 mM HAuCl₄ and 0.25 mM AgNO₃, 4 mL of 9.7 mM sodium rhodizonate was added. The mixture was heated for 10 min while stirring. Following the same procedure, Ag-AuNPs of different molar ratio of Ag and Au (ca. 75 % Ag-25 % AuNPs, 26 % Ag-75% AuNPs) were prepared. For the preparation of the nanoporous AuNPs, Ag was selectively etched out from the Ag-AuNPs. To etch out Ag, 28 % aqueous ammonium hydroxide solution was used. In details, in 1 mL Ag-AuNPs solution 1 mL ammonium hydroxide solution was added. This mixture was left stirring for 24 hours for the efficient etching of Ag.

4.2.3. Preparation of Cellulose Fibers-supported AuNPs

The AuNPs-RT was used for making the nanocomposites with CF. The nanocomposites are referred to as CF-AuNPs-2.87 and CF-AuNPs-0.98, where the values 2.87 and 0.98 represent the percentage weight of AuNPs loaded on the CF. Two different nanocomposites were prepared differing on the percentage of AuNPs loading and used to investigate the dependence of the rate of reduction on the amount of AuNPs loading.
Different quantities of AuNPs-RT stock solution and CF were used depending upon the weight percentage of gold loading. For example, to prepare nanocomposite CF-AuNPs-2.87, 200 mg of CF were added to 72 mL stock solution of AuNPs-RT. This mixture was then bath sonicated for 10 min, which caused AuNPs-RT to bind with the CF, Scheme 4.2.

The CF bound AuNPs-RT was then separated by centrifugation at a speed of 4000 rpm for 5 min. The centrifuged supernatant showed no plasmonic absorption band centred at 519 nm, which indicates that the AuNPs-RT were attached onto the CF with 100 percent loading efficiency. The centrifuged nanocomposites were washed repeatedly with DI water and eventually dried in a vacuum oven at 60 °C for overnight. In order to prepare nanocomposite CF-AuNPs-0.98, 200 mg of CF were added to 24 mL of AuNPs-RT stock solution and the aforementioned procedure was followed.

4.2.4. Catalytic Reduction of 4-NP, MO, and MB

In details, in a standard quartz cuvette, 3 mg of either CF-AuNPs-2.87 or CF-AuNPs-0.98 was added to 2.5 mL of 4-NP aqueous solution (1 mM), followed by the mixture was bath sonicated for 2 min to obtain uniform dispersion throughout. Afterwards, 1 mL of freshly prepared NaBH₄ aqueous solution (0.159 M) was added and mixed quickly. The reduction reaction course was monitored by using the kinetics software of the UV-Visible spectrophotometer, which monitored the lowering of the absorbance of 4-nitrophenolate at 400
nm in a certain interval of time. It is noteworthy to mention that the 4-NP reacts with NaBH₄ to yield 4-nitrophenolate, which shows strong absorption band centred at 400 nm.

In the reduction of MO and MB, 2 mg of either CF-AuNPs-2.87 or CF-AuNPs-0.98 was added with 10 mL of MO or MB having a concentration of 0.15275 mM (50 ppm) and 0.1563 mM (50 ppm), respectively. The mixture was bath sonicated for about 2 min. Afterwards, 50 mg (1.3217 mmol) NaBH₄ powder was quickly added into the above mixture and the reduction reaction course was monitored by the gradual decrease of the absorbance at 465 and 615 nm for the MO and MB, respectively. In order to investigate the adsorption ability of the nanocomposites control experiments were carried out, which showed no adsorption of either 4-NP, MO, or MB.

The time-dependent percent reduction of 4-NP, MO, and MB was calculated using the following equation.

\[
\text{Percent reduction} = \frac{A_0 - A_t}{A_0} \times 100 \%
\]

where \(A_0\) and \(A_t\) represent the absorbance of 4-NP, MO and MB at the beginning and at time (t) of the catalytic reduction.

4.3. Characterization the AuNPs and the Nanocomposites

4.3.1. UV-Visible Spectroscopy of the AuNPs

Figure 4.1 shows the UV-Visible spectrum of the AuNPs-RT and AuNPs-80C stock solutions in water. Strong plasmonic absorption bands centred at 519 nm and 514 nm were observed for the AuNPs-RT and AuNPs-80C, respectively.
It was observed that the plasmonic absorption band generated by AuNPs-RT was about 5 nm red shifted compared to the AuNPs-80C. This red shift in plasmonic absorption band of the AuNPs-RT happened because of the relatively bigger size of the AuNPs-RT compared to the AuNPs-80C.

4.3.2. TEM Images of the AuNPs

The typical TEM images of AuNPs with the corresponding size distribution histogram are shown in Figure 4.2. TEM images show that both the AuNPs-RT and AuNPs-80C are fairly spherical and well dispersed in solution with some aggregations. The corresponding size distribution histogram, Figure 4.2c, shows that the AuNPs-RT have an average core size of ~11 nm. On the other hand, the AuNPs-80C have an average core size of ~7 nm, Figure 4.2d. The average smaller particles size of the AuNPs-80C compared to the AuNPs-RT is also revealed by the UV-Visible experiment.
4.3.3. TEM Images of the Nanocomposites

A typical TEM image of CF-supported AuNPs nanocomposites viz. CF-AuNPs-2.87 is shown in Figure 4.3. The TEM image shows that AuNPs-RT are distributed all over the CF surfaces. This indicates that the AuNPs certainly have strong affinity for the CF, which caused them to bind together. Similar binding affinity of cellulose towards the noble metal nanoparticles was studied by Junhui et. al. The size distribution of the AuNPs-RT bound to the CF is also shown in the inset.
Figure 4.3: Typical TEM image of CF-AuNPs-2.87 showing the AuNPs bound on the CF. Inset: Size distribution of the AuNPs bound on the CF. Scale bar 200 nm.

4.3.4. SEM Images and EDS of the Nanocomposite

Typical SEM image of the CF-AuNPs-2.87 nanocomposite is shown in the inset of Figure 4.4 to show the fibers-like morphology of the CF.

Figure 4.4: EDX spectrum of CF-AuNPs-2.87. Inset: SEM images of the CF-AuNPs-2.87. The EDS spectrum performed on CF-AuNPs-2.87 shows the presence of high abundance of carbon, oxygen with relatively lower abundance gold, Figure 4.4. This further indicates the presence of AuNPs on the CF. In contrary, the pristine CF did not show any gold peak at all in the EDS spectrum.
4.3.5. XRPD of the Nanocomposites

The X-ray diffraction patterns of CF-AuNPs-2.87 and CF-AuNPs-0.98 are shown in Figure 4.5a and 4.5b, respectively. The diffraction peaks located at $2\theta = 14.5^\circ$, $16.4^\circ$ and $22.4^\circ$ corresponds to the 100, 010 and 110 crystalline faces of $\alpha$ cellulose $\beta$ allomorphs.

![XRD patterns of the a) CF-AuNPs-2.87 and b) CF-AuNPs-0.98.](image)

These two allomorphs of cellulose usually originate XRD peaks that are located very close to each other. This is why it is difficult to distinguish the cellulose allomorphs from XRD spectrum only. In addition, a set of new diffraction peaks at $37.8^\circ$, $43.4^\circ$, $64.2^\circ$ and $77.4^\circ$ was also observed, which corresponds to the 111, 200, 220 and 311 lattice planes of the face-centered cube (fcc) crystalline gold that originated from the AuNPs bound to the CF. In addition, it was observed that the relative intensity of the characteristic gold diffraction peaks increased with respect to the increase in AuNPs loading.

4.3.6. TEM Image of the Nanoporous AuNPs

A typical TEM image of the nanoporous AuNPs is shown in Figure 4.6. The image revealed the porous morphology of the AuNPs. The nanoporous AuNPs could be seen as aggregated and larger in particle size compared to the pure solid AuNPs. It could be assumed
that the high concentration of ammonium hydroxide induced the aggregation of the nanoporous AuNPs.

Figure 4.6: Typical TEM image of the nanoporous AuNPs.

4.4. Results and Discussion

4.4.1 Synthesis of AuNPs and their Binding Affinity with Cellulose Fibers

AuNPs were prepared by mixing HAuCl₄ solution with sodium rhodizonate and the reaction generated nanoparticles immediately. At room temperature (ca. 23 °C), this method generated AuNPs with an average size of ~11 nm, whereas at 80 °C, the method formed AuNPs with an average size of ~7 nm. The ability of rhodizonate ion to form coordination complexes with metal ions has been reported before. However, the ability of the rhodizonate ion towards the reduction and stabilization of gold ion has not been investigated to the best of our knowledge. The AuNPs synthesized at 80 °C had smaller average size compared to the one synthesized at room temperature. One explanation is that the faster rate of the reaction at the higher temperature may form more nucleation sites that in turn lead to the formation of smaller nanoparticles compared to room temperature.
When rhodizonate-stabilized AuNPs are exposed to CF and bath sonicated, they immediately bind to each other with 100 percent AuNPs loading ability. This indicates that the rhodizonate stabilizer is highly labile and exchangeable with the hydroxyl functional groups of CF. In contrast, AuNPs prepared with the use of stronger stabilizers such as citrate or alkanethiols do not readily adsorb on to cellulose, although there are procedures that utilize in-situ formation and binding of AuNPs with the CF.\textsuperscript{105}

### 4.4.2 Catalytic Reduction of 4-nitrophenol on the Nanocomposites

The time-dependent percent reduction of 4-NP to 4-AP and the corresponding kinetics of the reactions are shown in Figure 4.7a and 4.7b, respectively. The $-\ln(C_t/C_0)$ vs time (t) is a straight line, which indicates that the reactions follow pseudo-first order kinetics. The apparent rate constants ($k_{app}$) of the reactions, calculated from the slope of the trendlines, are calculated to be $1.03 \times 10^{-2}$ s$^{-1}$, $5.19 \times 10^{-3}$ s$^{-1}$ and $6.67 \times 10^{-5}$ s$^{-1}$, for the CF-AuNPs-2.87, CF-AuNPs-0.98 and pristine CF, respectively. Compared to the uncatalyzed reaction, where pristine CF was used with NaBH$_4$, the CF-AuNPs-2.87 and CF-AuNPs-0.98 catalyzed reactions are about 154 times and 78 times faster, respectively.

The normalized rate constants ($k_{nor}$), obtained by dividing the $k_{app}$ by the amount of AuNPs, are calculated to be 35.40 and 52.15 for the CF-AuNPs-2.87 and CF-AuNPs-0.98 respectively. Moreover, it was observed that the nanocomposites CF-AuNPs-2.87 and CF-AuNPs-0.98 catalyzed reactions had induction periods of about 1 min and 2 min, respectively. The induction period is typically observed in heterogeneous catalysis, which is the time it takes to achieve the adsorption and desorption equilibrium between the reactants and the products.\textsuperscript{106} The un-catalyzed reaction shows about 8 percent reduction of 4-NP after 20 min of reaction time, which in turn signifies the robust nature of 4-NP to undergo the reduction.
The UV-Visible spectrum of the 4-nitrophenolate and its reduced product *viz.* 4-AP solution is shown in Figure 4.7c. It is observed that the absorption band centred at 400 nm, which is the characteristic band for 4-nitrophenolate, diminished after the reduction. However, a new absorption band originated at 300 nm, which is the characteristic band for 4-AP.\textsuperscript{107}

The stability of the nanocomposite CF-AuNPs-2.87 was also investigated by carrying out the catalytic reduction of 4-NP for five successive cycles, Figure 7d. The percent reduction of 4-NP was measured after 8 min of catalysis in every cycle. It was observed that the CF-AuNPs-2.87 effectively reduces about 91 percent of the 4-NP to 4-AP on the 5\textsuperscript{th} cycle. Little drop of catalytic activity is also observed from the 1\textsuperscript{st} through 5\textsuperscript{th} cycle. This little loss of activity may have happened because of the gradual loss of the catalyst during the centrifugal separation prior to the use of next cycle.
4.4.3 Catalytic Reduction of MO and MB on the Nanocomposites

The time-dependent percent reductive decolorization of MO and MB along with their corresponding kinetics of the reduction is shown in Figure 4.8. Figure 4.8a shows that the reduction of MO catalyzed by CF-AuNPs-2.87 is faster than the one catalyzed by CF-AuNPs-0.98. The reduction follows the pseudo-first order type kinetics, Figure 4.8b. The apparent rate constants (k\text{app}) were found to be \(4.58 \times 10^{-3} \text{ s}^{-1}\), \(3.36 \times 10^{-3} \text{ s}^{-1}\) and \(1.27 \times 10^{-4} \text{ s}^{-1}\), for the CF-AuNPs-2.87, CF-AuNPs-0.98 and pristine CF, respectively. The reduction of MB catalyzed by CF-AuNPs-2.87 was found to be faster than the one catalyzed by the CF-AuNPs-0.98, Figure 4.8c. The apparent rate constants (k\text{app}) were calculated to be \(4.82 \times 10^{-3} \text{ s}^{-1}\), \(3.99 \times 10^{-3} \text{ s}^{-1}\) and \(1.20 \times 10^{-4} \text{ s}^{-1}\), for CF-AuNPs-2.87, CF-AuNPs-0.98 and pristine CF, respectively.

![Figure 4.8](image)

**Figure 4.8:** Time-dependent reductive decolorization of a) MO and c) MB, Pseudo-first order kinetics of the reductions of b) MO and d) MB.

It was observed that the rate of reduction depended upon the concentration of AuNPs, provided that the concentration of NaBH\textsubscript{4} and the size of the AuNPs remain constant. An
increase in the concentration of AuNPs increased the reduction rate and vice-versa. However, the normalized rate constant ($k_{\text{app}}$) decreased with the increase in the amount of AuNPs.

4.5. Conclusion

In conclusion, we demonstrate sodium rhodizonate as a novel reducing and stabilizing agent for the synthesis of gold nanoparticles, whose size depends on the temperature at which the synthesis is carried out. The same procedure could be extended to prepare Au-Ag bimetallic nanoparticles. From Au-Ag bimetallic nanoparticles, silver could be selectively etched out to prepare the nanoporous AuNPs. the Sodium rhodizonate-stabilized gold nanoparticles readily bound to cellulose fibers forming stable nanocomposites with high catalytic activity. The nanocomposites exhibited catalytic activity and cyclic stability towards the reduction of 4-nitrophenol and organic dyes such as methyl orange and methylene blue in water.
Chapter 5: Rapid Synthesis of Ultrasmall Platinum Nanoparticles Supported on Macroporous Cellulose Fibers for Catalysis

5.1. Introduction

Noble metal nanoparticles (NPs) demonstrate intriguing catalytic activity, which is mainly dependent on their size, shape, and the elemental composition. In the nanoscale size range (1-100 nm), particles have a larger proportion of exposed atoms at the edges and the corners, which are extremely catalytically reactive in comparison to the atoms in the macroscopic particles. As a result, the noble metal nanoparticles are extremely catalytically active, whereas the bulk noble metals are some of the most inert materials known.

For practical applications, NPs are often supported on high-surface area solid matrices due to the economic and environmental benignity. Solid catalyst support prevents the energy-intensive separation processes (e.g. ultrafiltration, ultra-centrifugation) of the NPs, avoids their loss, and restrains their aggregation and agglomeration. Additionally, catalyst support facilitates the easier handling, recovery, and reuse of the catalyst, which avoids the environmental pollution and minimizes the cost. In regard to the catalyst supports, cellulose fibers have drawn much attention because of its abundance, low-cost, strong binding (bonding and nonbonding) interactions, chemical and physical stability and the ease of functionalization. The porous structure and high oxygen density (e.g. ether and hydroxyl functional groups) makes cellulose fibers an interesting material as a support of the metallic NPs. Further, cellulose fibers supported metal NPs can be carbonized to obtain carbon supported metal NPs, which could provide exciting catalytic (e.g. electrocatalytic and chemical catalytic) properties.

Organic dyes are widely used in numerous industries (e.g. paper, pulp, textile, and plastics manufacturing) and their improper disposal is causing a serious environmental pollution.
Adsorption, photo/electro-catalysis, advanced oxidation processes, and sedimentation are some of the commonly employed methods for the removal of the organic pollutants. However, the catalytic processes (e.g. reductive and/or oxidative degradation) is becoming an intriguing and alternative method for the wastewater treatment technology.\textsuperscript{109} Catalytic processes can essentially degrade organic pollutants, whereas other methods may transfer the pollutants from one phase to another. For the catalytic reduction of organic pollutants, sodium borohydride (NaBH\textsubscript{4}) is the most commonly used reducing agent. However, the major drawbacks of NaBH\textsubscript{4} is that it causes secondary pollution by the generation of by-products. The removal of these secondary pollutants becomes even more challenging. Therefore, the development and utilization of a cleaner reducing agent could be beneficial in this purpose.

In this aspect, formic acid (FA) is gaining particular interest as an alternative reducing agent in terms of the environmental remediation. The catalytic oxidation of FA (also known as the decomposition of FA) generates H\textsubscript{2}, H\textsubscript{2}O, CO and CO\textsubscript{2} via dehydrogenation (HCOOH $\rightarrow$ H\textsubscript{2} + CO\textsubscript{2}) and dehydration (HCOOH $\rightarrow$ H\textsubscript{2}O + CO) pathways.\textsuperscript{110} The dehydrogenation route is an ideal way of H\textsubscript{2} gas production and the in situ generated H\textsubscript{2} gas could be utilized to reduce organic and inorganic pollutants. In addition to the FA, the utilization of commercially available H\textsubscript{2} gas could be a lucrative alternative to NaBH\textsubscript{4}. Although, neat H\textsubscript{2} gas is commonly utilized in organic chemistry for the hydrogenation of organic compounds, there are few reports for its utilization towards the reductive degradation of organic pollutants in water.\textsuperscript{111} Likewise, there are few reports for the utilization of FA towards the reductive degradation of organic pollutants in water. The FA and H\textsubscript{2} gas-induced catalytic reductions commonly require transition and/or noble metal NPs (e.g. Pt and Pd).\textsuperscript{112} In case of the FA, although transition metals can be utilized the low pH caused by the FA can dissolve the metals in aqueous solution. Therefore, the
utilization of noble metal NPs could be a beneficial approach due to their chemical and physical robustness against FA.

In this study, the synthesis of ultrasmall platinum NPs (PtNPs) is reported by employing sodium rhodizonate as a reducing and stabilizing agent. The PtNPs were supported on macroporous cellulose fiber, obtained from kimwipe paper (KWP), making kimwipe paper supported PtNPs (PtNPs@KWP). Cellulose fiber was chosen as the support because of its high binding affinity towards the PtNPs, good mechanical and chemical stability, availability, and potential functionalizibility. These PtNPs@KWP was then applied as a catalyst for the reductive degradation of MO in water using H₂ gas and FA. The H₂ gas and FA were utilized as the clean and alternative reducing agents to avoid the secondary pollution. Additionally, the catalytic reduction of Cr(VI) to Cr(III) in presence of FA was studied. The performance and stability of the PtNPs@KWP was further evaluated by carrying out the catalysis for multiple cycles in deionized and fresh drinking water matrices.

5.2. Materials and Methods

5.2.1. Materials

Sodium rhodizone dibasic (97%), hydrogen hexachloroplatinate (IV) hydrate (H₂PtCl₆ 3H₂O ≥ 99.9%), MO was purchased from Amresco and Kimtech KWP were purchased Fisher Scientific, USA. Formic acid was purchased from BDH Chemicals while H₂ gas (99.99%) was obtained from Matheson Tri-Gas. Potassium dichromate (ACS reagent, ≥99.0%) was purchased from Sigma Aldrich. Milli-Q water (> 18.20 MI cm resistivity) was obtained from Milli-Q (Advantage A-10) water filter system. The simulated fresh drinking water was prepared following the Nanotechnology Enabled Water Treatment (NEWT) protocol. In detail, 252 mg /L NaHCO₃, 147 mg /L CaCl₂•2H₂O, 124 mg /L MgSO₄•7H₂O, 95 mg/L Na₂SiO₃•9H₂O, 12 mg /L
NaNO₃, 2.2 mg/L, NaF, and 0.18 mg/L NaH₂PO₄·H₂O were dissolved in the deionized water to achieve the simulated FDW.

5.2.2. Synthesis of PtNPs and the Preparation of PtNPs@KWP

For the synthesis of PtNPs, 0.5 mM aqueous solution of H₂PtCl₆ and 9.7 mM aqueous solution of sodium rhodizonate were prepared separately. In a 100 mL round bottom flask, 20 mL of 0.5 mM aqueous solution of H₂PtCl₆ was brought to boil and then 5 mL of 9.7 mM sodium rhodizonate solution was injected into the H₂PtCl₆ solution with vigorous stirring (1200 rpm). The reaction mixture was further boiled for 5 min to ensure a complete reduction of the metal ions. When the reaction was complete, the reaction was allowed to cool to room temperature and a single sheet of KWP, weighing about 456 mg, was immersed into the flask whilst occasional shaking by hand for about 5 min. It was found that the PtNPs were bound to the KWP after the shaking, which could be easily seen by the color change of the KWP. The PtNPs bound KWP (PtNPs@KWP) turned grayish brown from the pristine white color of the KWP. The PtNPs@KWP was rinsed three times with deionized water and stored wet (without drying) under ambient conditions. Considering 100 % binding ability of the PtNPs on the KWP, the weight % of the PtNPs on the KWP was calculated to be 0.87 %.

5.2.3. Catalytic Activity of the PtNPs@KWP

Three different types of reactions were carried out to study the catalytic activity of the PtNPs@KWP. The first reaction was the reduction of MO in the presence of excess H₂ gas, where H₂ gas acted as the reducing agent. The second reaction was the dual-catalytic oxidation of FA and the concurrent reduction of MO. In this case, the decomposition of FA generated H₂ gas and the in situ generated H₂ gas was utilized for the reduction of MO. The third reaction was the FA-induced catalytic reduction of Cr(VI) to Cr(III).
5.2.3.1. **H$_2$ gas Induced Reduction of MO**

In a 125 mL Erlenmeyer flask, 100 mL of 20 ppm MO solution was taken. A full PtNPs@KWP was immersed into the solution. Afterward, H$_2$ gas was bubbled into the flask while gentle stirring of the reaction mixture by a stirring bar. The reaction flask was kept open during the H$_2$ gas bubbling. It was observed that the H$_2$ gas bubbling gradually decolorized the MO solution. The reduction of MO was concurrently monitored in every 2 minutes period of time by using an Ultraviolet-Visible (UV-Visible) spectrophotometer. About 1 mL aliquots were taken for UV-Visible analysis and the sample that was taken for UV-Visible analysis was reintroduced into the catalysis reaction flask. The UV-Visible spectrophotometer monitored the lowering of the characteristic absorbance of MO at 464 nm with respect to time.

**5.2.3.2. Formic Acid Induced Reduction of MO and Cr(VI)**

In a 125 ml Erlenmeyer flask, 100 mL of 20 ppm MO solution was added with a full PtNPs@KWP. Afterward, 50 μL of FA was added, mixed quickly and continuously stirred on a magnetic stirring plate. The addition of FA dropped the pH of the solution to ~3.0 and the characteristic absorption maxima of MO at 464 nm was found to redshift to 515 nm. Therefore, the reaction course was monitored by monitoring the absorbance of MO at 515 nm. In every 2 min, 1 mL sample was taken for UV-Visible analysis and after the analysis the samples were reintroduced into the reaction flask.

Same experimental procedure was followed for the catalytic reduction of Cr(VI) into Cr(III). In this case, 50 mL Cr(VI) solution of 20 ppm concentration was taken and 1 mL FA was added into the solution. UV-visible spectroscopy was used to monitor the reduction of Cr(VI) to Cr(III).
5.2.3.3. Catalytic Reduction of MO in Simulated Water

In order to investigate the efficiency and the real-life applicability of the PtNPs@KWP, the FA and the H₂ induced catalytic reductions of MO were carried out into simulated fresh drinking water (FDW). The simulated FDW contained different ions such as the carbonate, bicarbonate, chloride, phosphate, sodium, calcium, magnesium, etc. For the H₂ gas induced reduction, same procedure that was utilized for DI water was followed. However, for the FA acid induced catalytic reduction, it was observed that 50 uL FA in 100 mL of 20 ppm MO solution did not lower the pH to 3.0 as it did in the case of DI water. It was found that 200 uL of FA was needed to lower the pH of the MO solution in FDW to 3.0. Therefore, for the FA induced reduction of MO in FDW, 200 uL of FA was used in 100 mL of 20 ppm MO solution. 100 mL of 20 ppm MO solution. It is well known that the FA oxidation works efficiently at acidic pH.

5.3. Results and Discussions

5.3.1. Characterization of PtNPs and PtNPs@KWP

Various techniques such as Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDX), UV-Visible spectroscopy, X-ray powder diffraction spectroscopy (XRPD), X-ray photoelectron spectroscopy (XPS), and BET surface area analysis were utilized to thoroughly characterize the PtNPs and the PtNPs@KWP. For example, TEM and SEM revealed the morphology of the PtNPs and their successful attachment to the macroporous cellulose fibers of the KWP. The X-ray powder diffraction analysis demonstrated the crystalline nature of the PtNPs and the cellulose fibers. The BET surface area analysis provided the specific surface area, pore size and pore volume of the PtNPs@KWP. The XPS study provided the elemental and chemical composition of the PtNPs@KWP.
5.3.2. TEM Images and UV-Visible Spectrum of the PtNPs

The particles size, shape, size distribution, and the d-spacing of the PtNPs were studied by the HRTEM. Figure 5.1a shows the TEM images of the PtNPs before binding with the KWP. The PtNPs can be seen spherical in shape with the average diameter of 2.25 nm. The PtNPs were distributed as individual particles and in the form of small aggregations. Figure 1b and 1c show the KWP bound PtNPs with different magnifications. It can be seen that the PtNPs are distributed on the surface of the cellulose nanofibers of the KWP. Compared to the PtNPs in solution, the PtNPs on the KWP was found to be somewhat more aggregated.

HRTEM image of the PtNPs is shown in Figure 5.1d. The lattice spacing of 0.22 nm can be clearly seen, which corresponds to the d-spacing of the Pt (111) plane of face centered cubic (FCC) crystal structure of the PtNPs. This eventually confirmed the nanocrystalline structure of the PtNPs. Figure 5.1e shows the size distribution histogram of the PtNPs obtained from the TEM image and it can be seen that the PtNPs have the average diameter of about 2.25 nm.

Figure 5.1: TEM images of the a) PtNPs in water, b-c) TEM images of the PtNPs@KWP with different magnifications, d) HRTEM image of the PtNPs showing the d-spacing of the (111) crystalline plane, e) size distribution of the PtNPs, and f) UV-Visible spectrum of the PtNPs solution in water. Inset: Digital photograph of the PtNPs solution in water.
The UV-Visible spectrum as well as the digital photograph of the PtNPs solution in water is shown in Figure 5.1f. No surface plasmon resonance absorption (SPR) band was observed in the Visible range of the electromagnetic radiation. Sometimes the SPR band of PtNPs can be found in the ultraviolet region, which may have overlapped with the absorption band of the excess rhodizonate ion, in this case. As sodium rhodizonate is yellow in color it generated a strong absorption band and absorption tail in the UV (e.g. at 365 nm) and Visible regions of the spectrum, respectively (as shown in Figure 5.1f). Therefore, due to the presence of the excess rhodizonate ions, the PtNPs solution could be seen as yellowish brown in color (Figure 5.1f inset).

5.3.3. SEM Images and EDX of the PtNPs@KWP

The SEM images of the PtNPs@KWPs is shown in Figure 5.2a and 5.2b with varying magnifications. The SEM images revealed the fibrous morphology of the macroporous cellulose fibers obtained from the kimwipe paper. The fibers could be seen intertwined together with high aspect ratio. Morphology wise, the fibers were seen as flattened and elongated having width of about 20 µm, Figure 5.2b. The SEM image analysis further provided the porous morphology of the cellulose fibers as seen in Figure 5.2b.

![SEM images](image)

Figure 5.2: SEM images (a and b) showing the macroporous cellulose fibers network of the KWP with different magnifications, c) EDX spectra of the PtNPs@KWPs, and d) Photographs of the pristine KWP (left) and PtNPs supported KWP (right).
The EDX spectrum, performed on PtNPs@KWP, showed the presence of high abundance of carbon and oxygen with relatively lower abundance of platinum. The weak platinum intensity in the EDX spectrum could be attributed to the low platinum loading (ca. 0.87 wt %) on the KWP. This presence of platinum in the EDX spectrum further indicates the successful binding of the PtNPs with the KWP. The binding of the PtNPs on the KWP could also be seen by the naked eye observation. The pristine white KWP turned grayish brown in color, which resulted from the incorporation of the PtNPs into the KWP, Figure 5.2d.

5.3.4. XRPD Pattern and BET of the PtNPs@KWP

The PtNPs@KWP was further characterized by the XRPD analysis to reveal the crystalline property of the cellulose fibers and the PtNPs. As shown in Figure 5.3, diffraction peaks at $2\theta = 15.4^\circ$, 16.2$^\circ$ and 22.7$^\circ$ can be attributed to the 100, 010 and 110 crystalline faces of the cellulose Iα, or the 110, 110, and 200 crystalline faces of the cellulose Iβ allomorphs. The XRD patterns of these two allomorphs of cellulose are very similar and the XRD peaks are usually located very close to each other and thereby it is difficult to distinguish from XRD study only. In addition to the diffraction peaks of the crystalline cellulose fibers, three weak peaks located at 39.8$^\circ$, 46.4$^\circ$, and 67.7$^\circ$ were observed, which are characteristic to the (111), (200), and (220) diffraction planes of the crystalline Pt (0) nanoparticles, respectively. This type of XRD pattern further confirms the face-centered cube (fcc) crystalline structure of the PtNPs.114

Additionally, the PtNPs@KWP was characterized by the nitrogen gas adsorption studies to obtain the specific surface area. The Brunauer–Emmett–Teller (BET) specific surface area of the PtNPs@KWP was measured to be about 0.0816 m$^2$/g having pore volume of about 1.344 mm$^3$/g and pore size of about 145.449 Å, which is completely in agreement with other reports.115
Previous studies report that the specific surface area of native cellulose ranges from 0.6 to 1 m²/g having pore volumes of about 2 mm³/g.

![Figure 5.3: XRPD pattern of the PtNPs@KWP showing the crystallinity of the KWP (peaks marked as *) and the PtNPs (marked as ▼). Inset: shows the fcc crystalline structure of the PtNPs.](image)

5.3.5. High-resolution XPS of the PtNPs@KWP

High resolution X-ray photoelectron spectrum was obtained to analyze the qualitative elemental composition of the PtNPs@KWP. The XPS survey spectra of the PtNPs@KWP, shown in Figure 5.4a, indicated that the PtNPs@KWP is chemically composed of carbon, oxygen, and platinum. The high-resolution XPS spectra was obtained to further analyze the oxidation state of the elements. For example, two peaks of Pt 4f at 71.38 eV (Pt 4f⁷/₂) and 74.58 eV (Pt 4f⁵/₂), shown in Figure 5.4b, further indicated that the platinum is present mostly as Pt⁰. Additionally, a less intense peak of Pt 4f at 76.38 eV (Pt 4f⁵/₂) indicated the presence of Pt²⁺ species. It could be assumed that the Pt⁰ peaks originated from the metallic core of the PtNPs and Pt²⁺ peak originated from ionic surface of the PtNPs. Due to the presence of the Pt²⁺ on the surface, the excess rhodizonate ion could coordinate with them to stabilize the platinum nanoparticles.
Figure 5.4: XPS a) survey spectrum of the PtNPs@KWP, b) high-resolution spectrum of the Pt 4f and, c) high-resolution spectrum of the C 1s.

The presence of C-C, C-O, and O-C-O bonds were also observed from the high-resolution XPS of the C 1s, Figure 5.4c. These bonds can be attributed to the functionalities (e.g. alcohol, ether) that are present in the cellulose fibers.

5.3.6. Synthesis and Catalytic Activity of the PtNPs@KWP

The PtNPs were synthesized by mixing aqueous solutions of sodium rhodizonate and H$_2$PtCl$_6$ in water. The reaction mixture changed color from an orange to brownish yellow within 5 min period of heating, which indicated the formation of the PtNPs. The color of the H$_2$PtCl$_6$ solution changed from yellow to brown due to the reduction of the Pt$^{4+}$ to Pt$^{0}$ and the formation of PtNPs. On the other hand, the color of the rhodizonate ion changed from deep orange to light yellow due to its oxidation. Therefore, the resultant PtNPs solution appeared brownish yellow color as shown in Figure 2d. As sodium rhodizonate is the only species used for the synthesis of the PtNPs, it performed as the reducing as well as stabilizing agent. We assume that the excess rhodizonate ions coordinated to the ionic platinum (Pt$^{2+}$) at the surface of the PtNPs to stabilize them.

In our previous studies, we reported the use of conjugate base of oxocarbon acid (e.g. sodium rhodizonate and sodium squarate) as the bifunctional reducing and stabilizing agent for the fast synthesis of gold, silver, platinum, and palladium nanoparticles in water. Later, a
systematic mechanism for the reduction of Au$^{3+}$ to Au$^{0}$ by sodium squarate was proposed by Nathaniel E. Larm and colleagues.$^{118}$ Additionally, Shuangming Chen and colleagues proposed a mechanism for the reduction of Pt$^{4+}$ to Pt$^{0}$ in a methanol-water system.$^{119}$ Based on the findings of those mechanistic studies, we propose a mechanism for the reduction of Pt$^{4+}$ to Pt$^{0}$ in conjunction with the oxidation of sodium rhodizonate, Scheme 5.1. The overall mechanism for the reduction of Pt$^{4+}$ to Pt$^{0}$ can be split into three steps viz. the I) ligand exchange, II) $[\text{PtCl}_6]^{2-}$ reduction to $[\text{PtCl}_2]^{2-}$, III) loss of Cl$^-$ and the aggregation of the $[\text{PtCl}_2]^{2-}$ to form Pt$^{0}$ nanoclusters, and IV) hydrolysis of the oxidation product for rhodizonate. In the ligand exchange step, the enolate oxygen of the rhodizonate ion replace the Cl$^-$ from the $[\text{PtCl}_6]^{2-}$ by the nucleophilic substitution, Step I. After the ligand exchange, the rhodizonate ion donates electrons to the $[\text{PtCl}_6]^{2-}$ to reduce it into $[\text{PtCl}_4]^{2-}$. During this electron transfer process, the rhodizonate ion gets oxidized into the cyclic hexaketone compound and gets dissociated from the complex, Step II. The $[\text{PtCl}_4]^{2-}$ then may get further reduced to zerovalent Pt atoms viz. $[\text{PtCl}_2]^{2-}$ by two possible pathways viz. reduction by a second rhodizonate ion or by the disproportionation reaction.

Afterwards, the zerovalent Pt atoms in the form of $[\text{PtCl}_2]^{2-}$ aggregate together and lose Cl$^-$ ions to form PtNPs, Step III. The excess rhodizonate ions further stabilize the PtNPs by the coordination bond and thereby the nanoparticles do not grow further to the larger (micron) size particles. The oxidation product of the rhodizonate ion viz. the cyclic hexaketone is chemically labile and undergoes the hydrolysis to form alcohol derivatives, Step IV.
Scheme 5.1: Proposed mechanism for the reduction of [PtCl₆]²⁻ to metallic Pt.

The as-synthesized PtNPs were supported on KWP due to their macroporosity and chemical functionality. The KWP, consisting of highly pure and interweaved cellulose fibers, offer interconnected pores (shown by SEM image, Figure 2b) that can host nanostructured materials. In this study, when a piece of KWP was immersed in the aqueous PtNPs solution, the PtNPs were readily impregnated into the cellulose fibers through these pores. Moreover, due to the abundance of the polarized functionality (e.g. O-H and O-C-O) of the cellulose, we assume the PtNPs were also bound to KWP via electrostatic and non-bonding interactions. The electron-rich oxygen atoms of polar hydroxyl and ether groups of cellulose are considered to interact with electropositive transition metal cations.¹²⁰
The catalytic activity of the PtNPs@KWP towards the reductive degradation of MO by H₂ gas and FA is depicted in Scheme 5.2. In the FA-induced catalysis, the PtNPs@KWP simultaneously catalyzed the oxidation of FA (e.g. HCOOH → H₂ + CO₂) and the reduction of MO to the degradation products.¹²¹

Scheme 5.2: PtNPs@KWP catalyzed reduction of MO in the presence of H₂ gas and FA.

The oxidation of FA can be catalyzed by many homogeneous and heterogeneous transition metal compounds.¹²² However, the low pH caused by the FA usually dissolves the transition metal catalysts. Therefore, the utilization of noble metal nanoparticles (e.g. PtNPs) is important because of their chemical robustness and better catalytic activity. Additionally, the binding of the NPs on a solid support provides better handling and reuse for the purpose of practical applications.

5.3.7. Analysis of the Reaction kinetics

The concentration of FA and H₂ gas used in the catalysis were in much excess than the concentration of the substrate (MO) and thereby the concentration of FA and H₂ gas can be considered as constant. Therefore, pseudo-first-order kinetics with respect to MO could be applied to evaluate the reaction rate. The linear form of the pseudo-first-order kinetic model is expressed by equation 1.

\[
\text{Pseudo – first – order rate equation: } -\ln \frac{c_t}{c_0} = kt
\] (1)
Where \( k \) (1/min) represents the pseudo-first-order rate constant of the catalytic reduction; \( C_0 \) and \( C_t \) represent the initial and time-dependent concentration of MO.

The % reduction of MO was calculated using equation 2.

\[
\text{Reduction} \ (% ) = \frac{C_0 - C_t}{C_0} = \frac{A_0 - A_t}{A_0} \times 100\%
\]  

(2)

where \( C_0 \) and \( C_t \) represent the concentrations of MO (mg/L) at the beginning and at time \( t \), respectively. \( A_0 \) and \( A_t \) represent the absorbance of MO at concentrations \( C_0 \) and \( C_t \), respectively.

5.3.8. Catalytic Reduction of MO with H\(_2\) Gas

The time-dependent catalytic reduction of MO and the corresponding kinetics of the reductions is shown in Figure 5. The time-dependent UV-Visible shows the gradual decrease in the absorbance of MO centered at 464 nm and 275 nm, however, the origin of a new band at 245 nm suggests the formation of other compounds. The band at 464 nm originates due to the strong conjugation of the MO through the molecule and the band 285 nm is attributed to the azo bond (-N=N-) of the MO, which originated due to the \( \pi \rightarrow \pi^* \) electronic transition.\(^{123}\) However, the origin of the new absorption band at 245 nm, after the reduction of MO, corresponds to the degradation product of the MO \( \text{viz.} \) 4-aminobenzenesulfonate and the 4-N,N-dimethylanlinobenzene.\(^{124}\)
The time-dependent percent reduction of the MO, catalyzed by the PtNPs@KWP, is shown in Figure 5.5b. It was found that about 95% of the MO was reduced after 6 min of reaction and afterwards, the reduction became slow. However, after 10 min more than 99% of the MO was reduced. In contrary, the uncatalyzed reduction, where pristine KWP was used, demonstrated about 1.6% decolorization of MO after 10 min. Therefore, it could be concluded that the PtNPs bound to the KWP is responsible for the catalysis. The pseudo-first-order kinetics of the catalytic reduction is shown in Figure 5.5c. The apparent rate constants ($k_{app}$) of the PtNPs@KWP catalyzed reaction, obtained from the slope of the $\ln \left( \frac{C_t}{C_0} \right)$ vs time line, was calculated to be 0.529 min$^{-1}$. However, the $k_{app}$ of the uncatalyzed reaction was calculated to be 0.0017 min$^{-1}$. Therefore, it was found that the PtNPs@KWP catalyzed the reduction of MO 311 times faster than the uncatalyzed reaction.

5.3.9. Catalytic Oxidation of FA Followed by the Reduction of MO

Figure 6 shows the time-dependent decrease in the absorbance of MO centered at 515 nm with the corresponding kinetics of the reduction. It could be noted that the MO in acidic pH gives red shifted absorption maxima at ~ 515 nm due to the quinonoid benzene ring resonance system of the MO. The addition of 20 uL FA in 100 ml 20 ppm MO solution lowered the pH to ~ 3. From the time-dependent UV-Visible, it could be observed that within 6 min the MO was completely reduced to the corresponding reduced species. The absorption band at 515, 275, and 325 nm completely disappeared, however, a new band originated at 245 nm. The 285 and 325 nm absorption bands are corresponding to the azo bond (-N=N-) bond of the MO. As discussed
above, new absorption band at 250 nm corresponds to the degradation production of the MO viz. 4-aminobenzenesulfonate and the 4-N,N-dimethylaminobenzene.

Figure 5.6: a) Time-dependent UV-Visible absorption spectrum of MO solution during the catalysis, b) time-dependent percent reduction of MO, and c) pseudo-first-order kinetics of MO reduction.

As shown in Figure 6b, more than 99 % of the MO was reduced after 6 min of reaction, which is a little faster than the H₂ gas catalyzed reduction. This indicates that the in situ generated H₂ gas works faster than the H₂ gas bubbled catalysis. The uncatalyzed reduction demonstrated about 17% decolorization of MO after 10 min, which is due to the adsorption of MO on the KWP. Likewise, in the H₂ gas bubbled catalysis, the –ln (Ct/Co) vs time (t) is a straight line which indicates that the reactions follow pseudo-first-order kinetics. The k_{app} of the catalyzed reaction was calculated to be 0.891 min⁻¹, which is higher than the H₂ gas induced catalysis.

5.3.10. Catalytic Reduction of Cr(VI)

The catalytic reduction of Cr(VI) by FA on the PtNPs@KWP is shown in Figure 5.7. The time-dependent UV-Visible absorption spectrum of the K₂Cr₂O₇ solution during the catalysis is shown in Figure 5.7a. It could be observed that the characteristic absorption peaks of Cr(VI) at 350 and 240 nm diminished gradually with respect to the time of the reaction. The percent reduction of Cr(VI) is shown in Figure 5.7b.
Figure 5.7: a) Time-dependent UV-Visible absorption spectrum of K$_2$Cr$_2$O$_7$ solution during the catalysis, b) time-dependent percent reduction of Cr(VI), and c) pseudo-first-order kinetics of the reduction.

It was found that about 96 % Cr(VI) was reduced to Cr(III) after 21 min of reaction on the first cycle. However, on the 2$^{nd}$ and 3$^{rd}$ cycles the percent reduction after 21 min dropped to 60 and 34, respectively. The reason of this loss of activity could be attributed to the release or the dissolution of the platinum nanoparticles for the KWP, which could be observed in Figure 5.7d. The pseud-first-order kinetics of the catalytic reactions are shown in Figure 5.7c. The rate constants of the catalyzed reaction on the first cycle and the uncatalyzed reaction were calculated to be 0.135 and 0.002 min$^{-1}$, respectively.

5.3.11. Catalytic Reduction of MO in Simulated Water

The effectiveness and the applicability of the PtNPs@KWP was further determined by carrying out the catalysis in simulated FDW. The simulated FDW contained dissolved metallic and non-metallic ions (NaHCO$_3$, CaCl$_2$, MgSO$_4$, Na$_2$SiO$_3$, NaNO$_3$, NaF, NaH$_2$PO$_4$) and thereby the effect of these ions on the catalytic efficiency was further determined. Figure 5.8 shows the utilization of PtNPs@KWP for the catalytic reduction of MO in the presence of H$_2$ gas and FA in
FDW. The H₂ gas-induced catalysis reduced about 97% MO after 10 min, however; the FA-induced catalysis reduced about 99.8% MO after 10 min of reaction.

![Graph showing catalytic reduction of MO in simulated FDW by H₂ gas and FA on PtNPs@KWP.](image)

**Figure 5.8:** Catalytic reduction of MO in simulated FDW by H₂ gas and FA on PtNPs@KWP; a) percent reduction of MO, and b) pseudo-first-order kinetics of the reduction.

It could be observed that the PtNPs@KWP catalyzed reduction of MO in FDW was somewhat less active than the deionized water, which could be due to the presence of different ions in the simulated FDW. Likewise, for the catalysis in deionized water, the catalysis in FDW also followed the pseudo-first-order reaction kinetics, Figure 5.8b. The $k_{app}$ of the H₂ gas and the FA induced catalytic reduction of MO in simulated FDW are calculated to be 0.419 and 0.474 min⁻¹, respectively.

**5.3.12. Cyclic Stability of the PtNPs@KWP**

The cyclic stability of the catalyst is extremely important for the purpose of practical applications, especially when noble metals are used as the catalysts. In order to determine the stability, the PtNPs@KWP was used for at least five cycles for each type of the catalysis. For FA induced catalysis, the PtNPs@KWP was used for five consecutive cycles on the same day. The PtNPs@KWP was rinsed with DI water between the cycles. For the H₂ induced catalysis, a
separate PtNPs@KWP was used for five consecutive cycles on the same day and the catalyst was rinsed with DI water after every cycle.

![Graph](image)

**Figure 5.9**: Stability of the PtNPs@KWP for five consecutive cycles of catalysis. a) FA and b) H$_2$ gas induced catalytic reduction of MO.

During each cycle, the reaction achieved 99-100% reduction of MO in a span of ten minutes as can be seen in Figure 5.9. A comparison can be inferred between the FA and the H$_2$ gas induced catalytic reduction of MO where Figure 5.9a demonstrates that the FA has faster catalytic reducibility than H$_2$ gas shown in Figure 5.9b. The steep curve in Figure 8a indicates that during each cycle, the FA was able to catalytically reduce MO at a faster rate than the H$_2$ gas induced one.

The stability of the PtNPs@KWP was further studied by carrying out ICP-OES on the solution after the catalytic experiments. The goal was to determine if there was any leaching of the PtNPs in the solution during the catalytic experiments. For this, a single PtNPs@KWP was used for three cycles of H$_2$ gas and two cycles of FA induced catalytic reduction of MO solution. After each cycle of catalysis, the decolorized MO solution was stored, acidified, and analyzed by the ICP-OES. The ICP-OES results demonstrated that there was undetectable level (below 10 ppb) of platinum in each of the MO catalyzed solution. This confirmed that PtNPs were strongly
bound to the cellulose fibers, which did not detach or dissolve as platinum ions from the KWP. This eventually confirmed the robustness of the PtNPs@KWP towards the catalytic experiments that were carried out in this study.

5.3.13. Proposed Mechanism of the Catalytic Reduction of MO

The catalytic oxidation of FA has been demonstrated as a potential method of H₂ gas generation and thereby FA is considered as storage medium of H₂. The decomposition of FA occurs via several proposed reaction pathways when different catalysts are used. The first pathway is considered to begin with the dehydrogenation or decomposition of FA (COOH) to yield H₂ and CO₂, Equation 3.

\[
\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2 \quad [\Delta G^\circ = -32.9 \text{ kJmol}^{-1}] \quad (3)
\]

The in situ generated H₂ molecules can chemisorb on the surfaces of the PtNPs and then catalyze reduction of MO, which is equivalent to the H₂ gas bubbled catalytic reduction of MO. The second pathway is considered to happen with the decarbonylation or dehydration of FA (HCOOH) to produce CO and H₂O, Equation 4.

\[
\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O} \quad [\Delta G^\circ = -20.7 \text{ kJmol}^{-1}] \quad (4)
\]

The generated CO then adsorb to the PtNPs surface, which have the ability to reduce the organic and inorganic species while being oxidized into CO₂. The third pathway, also known as formate pathway, involves the formation of formate and its subsequent oxidation to CO₂ and the release of H₂ gas. Therefore, either way the FA decomposition can simultaneously reduce organic and inorganic species in the presence of PtNPs. Moreover, the benefit of the utilization of FA is that the decomposition product of FA viz. H₂, H₂O, CO₂ do not cause secondary pollution while reducing the organic pollutants in water.
5.5. Conclusion

In conclusion, we report a simple and fast method for the synthesis of ultrasmall PtNPs in water using sodium rhodizonate. The PtNPs were supported on macroporous cellulose fibers that was obtained from KWP. The cellulose fibers supported PtNPs demonstrated excellent catalytic property and superior stability towards the reduction of MO in the presence of FA and H₂ gas. The results of this study indicate that the FA and H₂ gas can be utilized as a clean and environmentally benign reducing agents for the reductive degradation of organic pollutants in water. Also, the PtNPs@KWP could also be efficiently utilized for the catalytic reduction of Cr(VI) to Cr(III) using FA as the environmentally friendly reducing agent. The findings of this study can be extended to the catalytic reduction of other organic and inorganic pollutants for the purpose of water treatment.
Chapter 6: Fullerene Stabilized Gold Nanoparticles Supported on Titanium Dioxide for Photocatalytic Degradation and Catalytic Reduction of Organic Pollutants

6.1. Introduction

Titanium dioxide (TiO$_2$) is the most widely used photocatalyst because of its strong oxidizing property, cheaper price, low toxicity, and high chemical as well as physical robustness.\textsuperscript{132} As a photocatalyst, TiO$_2$ is a wide band gap (3.2 eV for anatase, 3.0 eV for rutile phase) material\textsuperscript{133} and thereby requires the ultraviolet (UV) light for the exciton separation.\textsuperscript{134} This limits their widespread acceptance in practical applications.\textsuperscript{135} Therefore, to enhance the photocatalytic activity of the TiO$_2$, methods such as the doping with different types of metallic and non-metallic elements and the sensitization by different types of organic dyes have been employed.\textsuperscript{136,137}

In this regard, a relatively new and intriguing way for the photosensitization of TiO$_2$ involves the binding of plasmonic nanoparticles so as to achieve the plasmon-induced charge separation at TiO$_2$.\textsuperscript{138} A number of different types of metallic, bimetallic and semiconductor type nanoparticles have been reported to bind with TiO$_2$ to enhance the photocatalytic activity.\textsuperscript{139,140} However, the AuNPs is one of the most extensively used plasmonic nanoparticles as the AuNPs possess special size and shape-dependent tunable optical properties, high molar absorption coefficient ($10^8$ to $10^{10}$ M$^{-1}$cm$^{-1}$),\textsuperscript{9} good catalytic activity along with very high chemical, and physical stability.

In addition to the plasmonic sensitization, AuNPs are well known to catalyze a wide variety of chemical reactions.\textsuperscript{141} However, the utilization of the AuNPs in solution is neither economically nor environmentally favorable for multiple reasons including but not limited to the requirement of the energy-intensive processes for the separation of the AuNPs, the loss of the
AuNPs during the separation process, and most importantly the aggregation and the agglomeration of the AuNPs. The aggregation and agglomeration of the AuNPs reduce the specific surface area, increase the particle size, hinder the active sites and thereby impair the catalytic activity. Therefore, the AuNPs are commonly supported on high surface area solid matrices that are chemically as well as physically robust. In this context, TiO$_2$ has garnered much attention because of its sublime chemical, thermal, optical, and mechanical robustness.

Organic dyes $vìz.$ MO and nitro aromatic compounds $vìz.$ 4-NP are well known to be toxic, carcinogenic and mutagenic to human beings and aquatic organisms.$^{142}$ Moreover, the azo dyes and nitro aromatic compounds are fairly stable and persistent in nature and thereby are resistant to natural degradation. Therefore, their photocatalytic and the catalytic reductive degradation have drawn much attention in the area of environmental remediation. It is worthy to mention that the catalytic reduction of 4-NP to 4-AP has some industrial applications. For example, 4-AP is utilized as a photographic developer, an antioxidant, a corrosion inhibitor, an intermediate in the synthesis of paracetamol, a precursor for the manufacture of analgesic and antipyretic drugs, etc. On the other hand, the photocatalytic degradation of organic pollutants has benefits over other methods. For example, photocatalysis does not require any chemicals and thereby does not produce any secondary pollutants, the catalyst can often be used for multiple cycles without the loss of the activity and so on.

In this research, we report a simple method for the generation of AuNPs that are stabilized by fullerene (C$_{60}$). The C$_{60}$ stabilized gold nanoparticles (C$_{60}$-AuNPs) effectively bind to the TiO$_2$ nanoparticles yielding the nanocomposites hereafter called as (C$_{60}$-AuNPs-TiO$_2$). The nanocomposites were utilized in the photocatalytic degradation of methyl orange (MO) and the catalytic reduction of 4-nitrophenol (4-NP) in water. The TiO$_2$ supported C$_{60}$-AuNPs
demonstrated enhanced photocatalytic degradation of MO as well as the catalytic reduction of 4-NP compared to the TiO₂. The recyclability of the nanocomposites was examined for ten cycles and it was found that the catalyst is fairly active throughout the cycles.

6.2. Materials and Methods

6.2.1. Materials

All the chemicals were used as received. Fullerene (C₆₀) was purchased from SES research, while Gold(III) chloride trihydrate (HAuCl₄·3H₂O=99.999% trace metals basis), Sodium borohydride (NaBH₄ = 99%), Titanium(IV) dioxide nanopowder (TiO₂-P25) containing 80% Anatase and 20% Rutile phases with about 21 nm primary particle size (≥99.5% trace metals basis), 4-nitrophenol (O₂NC₆H₄OH ≥99%). Terephthalic acid [C₆H₄-(CO₂H)₂ = 98%], and N,N-Dimethylformamide (DMF = C₃H₇NO >99%) were acquired from Sigma-Aldrich, USA. Toluene (C₇H₈ =99.8%), Methanol (CH₄ O =99.8%) and Diethyl ether (C₄H₁₀O ≥99.0%) were purchased from BDH chemicals. Methyl Orange (C₁₄H₁₅N₃O₃S >98.0%) was obtained from TCI AMERICA. All water (>18.20 MΩ cm resistivity) used was obtained from Milli-Q (Advantage A-10) water filter. A portable tungsten halogen work light with 500W power was purchased from Home Depot as a source of light. The intensity of light was measured by using a digital Light Meter LX1330B. Syringe Filters with Polypropylene Housing and PTFE membrane material with 0.45μm pore size were obtained from VWR, which were used to filter the photocatalysis reaction mixture.

6.2.2. Synthesis of C₆₀-AuNPs

C₆₀-AuNPs were synthesized following the previously reported method with minor modifications. In detail, a C₆₀ solution was prepared by dissolving 6.0 mg of C₆₀ (0.0833 mmol) in 20 mL of toluene. A separate Au³⁺ solution was prepared by dissolving 20.0 mg
(0.0507 mmol) of the HAuCl₄·3H₂O in 20 mL of N,N-Dimethylformamide (DMF). Both the solutions were mixed together to obtain a new combined solution. As a reducing agent, a freshly prepared NaBH₄ solution in 10 mL methanol, having 21.0 mg (0.5551 mmol) of NaBH₄, was instantly added to the aforementioned solution while stirring vigorously. After 20 min of stirring, addition of 40 mL of diethyl ether induced the formation of a black precipitate that was isolated by centrifugation (5000 rpm, 5 min). The as- centrifuged wet C₆₀-AuNPs precipitate was dissolved in 30 mL of DMF by bath sonication for 30 min. A set of exactly four such reactions was carried out separately and the separate AuNPs solutions in DMF were combined together, which was used as a stock solution for the further use. The concentration of AuNPs in the stock solution was 0.3334 mg/mL.

In order to investigate the ability of the C₆₀ in the synthesis of the AuNPs, a control experiment was conducted without the use of C₆₀. It was found that the same synthetic procedure did not make AuNPs without the presence of the C₆₀. The reaction yielded lump of macroscopic size gold aggregates, which could never be dissolved in DMF by bath sonication. Therefore, it could be suggested that the C₆₀ mediated the AuNPs formation, which followed by mediate its attachment with the TiO₂.

6.2.3. Preparation of the AuNPs-C₆₀-TiO₂

Depending upon the wt % of the C₆₀-AuNPs loading on the TiO₂, different amount of C₆₀-AuNPs stock solution was used for the attachment with TiO₂. For example, to obtain 4.76 wt % of AuNPs loading on the TiO₂, 400 mg TiO₂ (P25) nanoparticles were added into a 60 mL C₆₀-AuNPs stock solution. Afterwards, the mixture was bath sonicated for about 10 min. The bath sonication facilitated the adsorption of the C₆₀-AuNPs on the TiO₂. The nanocomposite was recovered by centrifugation (4500 rpm, 5 min) followed by washing with methanol and de-
ionized water. The nanocomposites were dried in vacuum desiccators for overnight at 60 °C. Afterwards, the nanocomposites were finely ground by mortar and pestle, placed in a glass vial and heated to 470 °C on a hot plate for about 3 hours during which a more intensely blue color emerged. Following the aforementioned procedure two more C₆₀-AuNPs-TiO₂ nanocomposites were prepared, where the amount of AuNPs loading were 2.45 and 1.23 wt %, respectively.

In order to compare the photocatalytic activity of the 4.76 % C₆₀-AuNPs-TiO₂ nanocomposite, two different catalysts, named as 4.76 % AuNPs-TiO₂ (Control 1) and 4.76 % AuNPs-TiO₂ (Control 2), were also prepared following two different methods. The 4.76 % AuNPs-TiO₂ (Control 1) was prepared by making a suspension of Au³⁺ and TiO₂ (P25) in a 40 mL mixture of DMF and toluene (50:50) followed by the chemical reduction of Au³⁺ by the NaBH₄ (21 mg NaBH₄ in 10 mL MeOH). The 4.76 % AuNPs-TiO₂ (Control 2) was prepared by the UV photoreduction-deposition method. Both the catalysts were annealed at 470 °C following the above-mentioned method.

6.2.4. Methyl Orange Photodegradation Experiment

Screw-capped clear glass scintillation vial with 40 mL of capacity and dimensions of Diameter × Height = 28 mm × 98 mm was used as a reaction container. A 500W portable tungsten halogen lamp kept at a distance of about 15 inches away from the reaction vial was used as the light source. The intensity of light at the position of the vial was measured to be ~ 30000 lux. Methyl orange solution having concentration of 10 ppm (10 mg/L) was used for the photocatalytic experiments. In the photodegradation experiments, 20 mg of the catalyst was homogeneously dispersed in 20 mL of MO solution by 30 min of bath sonication in dark. The bath sonication facilitated the homogeneous dispersion of the catalysts as well as helped in the establishment of the adsorption-desorption equilibrium between the nanocomposites and MO.
The mixture was illuminated under the halogen lamp with stirring and at a regular interval of 40 min 1 mL sample was withdrawn. The photocatalytic experiment was carried out of 160 min. The sample was filtered through the syringe filter and UV-Visible spectroscopy was carried out on the filtrate to determine the percent degradation of the MO with time. It is worthy to mention that MO exhibits characteristic absorption band centered at 464 nm. For the cyclic stability experiments, the catalyst used in the first cycle was centrifuged and used in the same way for the subsequent cycles. However, the MO sample (1 mL each) was withdrawn at the beginning and after 180 min of light exposure to determine the percent degradation of MO. Sample was taken from the centrifuged (4000 rpm, 5 min) supernatant so as to minimize the loss of the catalyst.

6.2.5. Catalytic Reduction of 4-NP

For the reduction experiment, 10 mL of 4-NP aqueous solution (0.2 mM) was mixed with 3 mg of the TiO$_2$ supported AuNPs catalysts by 30 min of bath sonication. Afterwards, 1 mL of freshly prepared NaBH$_4$ aqueous solution (25 mg, 0.66 mmol) was added and the reaction course was monitored, every 10 seconds, by using the kinetics software of the UV-Visible spectrophotometer, which monitored the time-dependent lowering of the absorbance of 4-nitrophenolate at 400 nm.

6.3. Characterization of the C$_{60}$-AuNPs and its Nanocomposites with TiO$_2$

6.3.1. UV-Visible Spectroscopy of the C$_{60}$-AuNPs

The UV-Visible spectrum of the C$_{60}$-AuNPs solution in DMF is shown in Figure 6.1. A broad, weak, and shoulder type absorption band was observed at around 500 nm, which is characteristic of the surface-plasmon resonance (SPR) absorption band of the AuNPs with very small size.
Figure 6.1: UV-Visible absorption spectrum of the C$_{60}$-AuNPs in DMF with the corresponding digital photograph of the C$_{60}$-AuNPs solution (inset).

The SPR band originated from the collective oscillation of conduction electrons of the AuNPs upon the interaction with electromagnetic radiation. As a result, the AuNPs in solution demonstrate color in the Visible range of the electromagnetic radiation. Moreover, the color of the AuNPs could be tuned with the variation of its size and shape. The photograph of the C$_{60}$-AuNPs solution in DMF is shown in the inset picture.

6.3.2. TEM, HRTEM, and AFM images of the C$_{60}$-AuNPs

The size, shape, and the dispersity of C$_{60}$-AuNPs were examined by using the Transmission Electron Microscopy (TEM) and the Atomic Force Microscopy (AFM), Figure 6.2. The TEM image (Figure 6.2a) revealed that the C$_{60}$-AuNPs were fairly dispersed in solution having a range of core diameter from 1.5 to 11 nm and an average of 5 nm. Some C$_{60}$-AuNPs were also seen to have some degree of aggregation. The HRTEM image of C$_{60}$-AuNPs (Figure 6.2b) revealed the crystalline structure of C$_{60}$-AuNPs with interlayer spacing of 2.31 Å, which is the characteristic lattice spacing of the Au (111) lattice planes.$^{145}$
Figure 6.2: a) Low-magnification and b) high-resolution TEM images of the C\textsubscript{60}-AuNPs; c) size distribution of C\textsubscript{60}-AuNPs based on the TEM image; d) typical and e) 3-dimensional AFM images of the C\textsubscript{60}-AuNPs.

The typical and three-dimensional AFM images (Figure 6.2d-e) further confirmed the size, shape and the morphology of the C\textsubscript{60}-AuNPs, which in complete agreement with the TEM image analysis. For example, the three-dimensional AFM image showed that the C\textsubscript{60}-AuNPs were mostly about 5 nm in height.

6.3.3. TEM and HRTEM Images of the AuNPs-C\textsubscript{60}-TiO\textsubscript{2}

A typical TEM image of the C\textsubscript{60}-TiO\textsubscript{2}-AuNPs is shown in Figure 6.3a. It can be seen that AuNPs are of darker contrast compared to the TiO\textsubscript{2} nanoparticles, which is due to the large difference in atomic mass between the gold and the titanium. The heavier and bigger atoms usually absorb more electrons compared to the lighter and the smaller atoms\textsuperscript{146} Therefore, heavier atoms appeared to be blacker than the lighter atom on TEM images. Therefore, the presence of relatively smaller and darker C\textsubscript{60}-AuNPs was clearly seen on the TiO\textsubscript{2} support. In contrary, the TiO\textsubscript{2} nanoparticles were observed as comparatively bigger and less dark with an average diameter of about 21 nm.
Figure 6.3: a) Typical TEM image of the C$_{60}$-AuNPs-TiO$_2$, b) HRTEM image, and c) the selected area electron diffraction (SAED) pattern of the C$_{60}$-AuNPs-TiO$_2$. Inset: Size distribution the AuNPs supported on the TiO$_2$.

Morphology-wise, the C$_{60}$-AuNPs are more spherical while the TiO$_2$ nanoparticles are more faceted. Figure 6.3b showed a high magnification HRTEM image of the marked area in. The measured d-spacing of 2.33 Å on TiO$_2$ nanoparticle corresponds to the (112) planes, and the 2.04 Å d-spacing on AuNPs corresponds to the (200) planes. The selected area electron diffraction (SAED) pattern with some major reflections labeled is shown in Figure 6.3c. The size distribution of the C$_{60}$-AuNPs loaded on the TiO$_2$ is shown in Figure 6.3a (Inset). It was found that the average size of the AuNPs increased in the nanocomposites compared to the AuNPs in solution. This increase in the size of the AuNPs is observed because of the coalescence of the AuNPs during the heating of the composites at 470 °C.

6.3.4. XRPD Pattern of the C$_{60}$-AuNPs-TiO$_2$

The XRPD pattern of the C$_{60}$-AuNPs-TiO$_2$ and TiO$_2$ are shown in Figure 6.4a and 6.4b, respectively. It revealed that the pure TiO$_2$ is composed of the anatase and rutile crystalline forms. The characteristic diffraction peaks corresponding to the anatase and rutile crystalline forms are indexed as A and R in the Figure 4b, respectively.
Figure 6.4: XRPD patterns of the a) C₆₀-AuNPs-TiO₂ and b) the pristine TiO₂.
However, the XRPD of C₆₀-AuNPs-TiO₂ showed additional diffraction peaks located at the 2θ values of 38.06°, 44.4°, 64.6° and 77.9°, which could be identified as the 111, 200, 220 and 311 planes of the crystalline gold nanoparticles, respectively.¹⁴⁷ This type of diffraction pattern indicated the face-center cube (fcc) crystal structure of the AuNPs.¹⁴⁸ The diffraction peaks of the crystalline gold are indexed as Au in the XRPD spectrum, Figure 6.4a.

6.3.5. Diffuse-reflectance Spectrum of the C₆₀-AuNPs-TiO₂

The UV-Visible diffuse-reflectance spectrum, carried out on the C₆₀-AuNPs-TiO₂ and the TiO₂, is shown in Figure 6.5. The C₆₀-AuNPs-TiO₂ nanocomposites exhibited a broad absorption band ranging from 500 to 650 nm and centered at 570 nm, Figure 5b. This type of absorption band is attributed to the surface plasmon resonance band of AuNPs bound to the TiO₂ surface. On the other hand, TiO₂ did not show any significant absorption band above 400 nm, Figure 6.5a. TiO₂ is strongly absorptive in the UV region of the spectrum, which is because of the fact that the TiO₂ consists of both the anatase and rutile phases and they have absorption edges of 387 and 418 nm, respectively. Moreover, compared to the UV-Visible spectra of the C₆₀-AuNPs solution in DMF (Figure 6.1), the plasmonic absorption band of C₆₀-AuNPs-TiO₂ is red-shifted and became broader.
Figure 6.5: UV-Visible diffuse reflectance spectra of a) TiO$_2$ (P25), and b) C$_{60}$-AuNPs-TiO$_2$.

This is considered to happen because of the i) high refractive index of anatase TiO$_2$ (2.52), ii) the plasmon coupling between the AuNPs and TiO$_2$ nanoparticles, iii) and the increase in the AuNPs size during the annealing step.$^{149,150}$ The increase in the size distribution of the AuNPs in the nanocomposite is also observed in the TEM image, Figure 6.3a (inset). Therefore, the DRS results indicated that the AuNPs converted TiO$_2$ into a Visible light absorptive nanocomposite.

6.3.6. SEM Image and EDX Spectra of the C$_{60}$-AuNPs-TiO$_2$

The typical SEM image and the corresponding EDX spectra of the C$_{60}$-AuNPs-TiO$_2$ are shown in Figure 6.6. The SEM image (Figure 6.6a) showed the morphology of the C$_{60}$-AuNPs-TiO$_2$ whereas, the EDX analysis shows the qualitative and quantitative elemental composition of the C$_{60}$-AuNPs-TiO$_2$.

EDX spectrum of the C$_{60}$-AuNP-TiO$_2$ showed the presence of a high abundance of Titanium with comparatively less amount of gold and carbon, Figure 6.6b. Furthermore, the EDX spectrum was used for the quantitative elemental analysis, which showed that there was about 4.56 % wt AuNPs loaded on the TiO$_2$. 

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6.3.7. High-Resolution XPS Analysis of the C₆₀-AuNP-TiO₂

High-resolution XPS analysis was performed to reveal the qualitative elemental composition as well as the oxidation state of the AuNPs on the catalyst. The X-ray photoelectron spectra (Figure 6.7a) presented the Au 4f₅/₂ and Au 4f₇/₂ doublet with binding energies of 86.82 and 83.17 eV, respectively. These values of binding energies indicated that the AuNPs are deposited as metallic gold on the TiO₂.¹⁵¹

The Ti 2p₁/₂ and Ti 2p₃/₂ binding energies were observed at 558.58 and 464.32 eV (Figure 7b), which is in agreement with the reported literature values obtained for TiO₂ (P25).¹⁵² The presence of trace fullerene was also confirmed by the XPS analysis, which showed the presence
of carbon C1s core level peak at around 285 eV, Figure 6.7c. The result is consistent with previously reported observations, where fullerene (C60) was deposited on gold surface.153

6.4. Results and Discussion

6.4.1. Synthesis of C60-AuNPs and its Nanocomposite with TiO2

Commonly employed methods to bind metallic nanoparticles on TiO2 involve the UV light induced photoreduction-deposition, the chemical deposition-precipitation, and the use of linker to tether the nanoparticles and TiO2.154 However, these methods suffer from a common drawback, which is the aggregation or clustering of the nanoparticles on the TiO2. Also, in many cases, the AuNPs deposited TiO2 composite is heated to an elevated temperature to make an active form of the catalyst.155 During this heating treatment the AuNPs melt and fuse together to make larger size nanoparticles, which is not expected.24 It is also worthy to mention that the AuNPs more than 10 nm in diameter gradually loses the catalytic activity and those beyond 20 nm loses complete catalytic activity.156 Therefore, it is a challenge to have higher AuNPs loading on TiO2 having particle size less than 10 nm.

The method demonstrated in this report can prepare catalytically active nanocomposites of the AuNPs and TiO2 following a facile method, where the C60-AuNPs bind with the TiO2 without any modification on the surface of the AuNPs or the TiO2. The average size of the AuNPs in the composites was found to be about 8 nm, which is necessary to prepare photocatalytically active nanocomposites. We assume that the C60 fullerene played threefold role in the preparation of the nanocomposites. Firstly, it mediated the synthesis of AuNPs with an average particle size of about 5 nm. Secondly, the as synthesized C60-AuNPs facilely bound the TiO2 without any functionalization of the AuNPs or the TiO2 surface. Therefore, C60 facilitated
the binding of the AuNPs with the TiO₂. Thirdly, C₆₀ prevented the agglomeration of the AuNPs during the heat treatment and thereby prevented the further growth of the AuNPs on the TiO₂.

6.4.2. Photocatalytic Degradation of Methyl Orange

Photocatalytic generation of the ROS by the C₆₀-AuNP-TiO₂ nanocomposites was evaluated by the decolorization of methyl orange (MO) in water. The % MO decolorization with respect to the time of light exposure was calculated using the following equation:

\[
\% \text{ MO degradation} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100\% = \left( \frac{A_0 - A_t}{A_0} \right) \times 100\%
\]

where, \( C_0 \) represents the initial concentration of MO, \( C_t \) represents the concentration of MO at time \( t \), \( A_0 \) represents the absorbance of MO at the beginning of the photocatalysis, and \( A_t \) represents the absorbance of MO at time \( t \).

The time-dependent UV-Visible spectrum for the photocatalytic degradation of MO is shown in Figure 8. The degradation of MO catalyzed by 4.76 % C₆₀-AuNPs-TiO₂ showed that the characteristic absorbance of MO at 464 nm decreased rapidly in the first 120 min of reaction time and afterwards the degradation of MO slowed down. It was also observed that a new absorption band originated at 350 nm, which is attributed to the formation of the degradation products of MO.¹⁵⁷

Figure 6.8 showed the % MO degradation with respect to the time of the photocatalytic reaction. For the 4.76 % C₆₀-AuNPs-TiO₂ catalyzed reaction, the % degradation of MO was found to be more than twice fast up to 160 min compared to the pristine TiO₂. About 95 % of the MO degraded at 160 min whereas; it was about 47% for the TiO₂.
Figure 6.8: a) Time-dependent UV-Visible of the MO solution during its photocatalytic degradation, b) Time-dependent percent degradation of MO, and c) Pseudo-first order kinetics of the photodegradation of MO catalyzed by different catalysts.

Under the irradiation of light for 240 min and without the catalyst, MO did not undergo any degradation. This signified the robustness of MO under the light irradiation only. This further proved that the degradation of MO happened due to the presence of the catalysts. Moreover, the 4.76 % C60-AuNPs-TiO2 nanocomposite, in the absence of the light, did not show any adsorption as well as degradation of the MO even after 240 min. Therefore, it could be suggested that the degradation of MO happened due to the presence of light and the catalyst at the same time.

In compared to the 4.76 % AuNPs-TiO2 (Control 1 & 2) the photocatalytic activity of the 4.76 % C60-AuNPs-TiO2 nanocomposite was found to be much faster, Figure 8b. The poor photocatalytic activity of the 4.76 % AuNPs-TiO2 (Control 1 & 2) nanocomposites is considered
to happen because of the formation of larger size AuNPs on the TiO$_2$ during the reduction and/or the annealing process.

The kinetics of the photocatalytic degradation of MO by different catalysts is shown in Figure 6.8c. This showed that $-\ln(C_t/C_0)$ vs. the time graph followed the linear trends, which further indicated that the kinetics of the degradation of MO followed the Pseudo-first order reaction mechanism. The pseudo-first order rate equation is represented as follows:

$$kt = -\ln(C_t/C_0) \quad (1)$$

where $k$ represents the rate constant (min$^{-1}$) of the reaction, $C_t$ and $C_0$ represent the concentration of the MO at time $t$ and at the beginning of the reaction, respectively.

Moreover, a linear relationship between $-\ln(C_t/C_0)$ and reaction time ($t$) is indicative that the kinetics of the reaction followed the Langmuir–Hinshelwood (LH) model. The apparent rate constant ($k_{app}$) of the photocatalytic degradation of MO by the 4.76 % $C_{60}$-AuNPs-TiO$_2$, obtained by using equation 1, was calculated to be $2.03 \times 10^{-2}$ min$^{-1}$. Whereas, the apparent rate constant for the TiO$_2$ (P25) catalyzed reaction was calculated to be $3.70 \times 10^{-3}$ min$^{-1}$. From the values of rate constants, it is observed that the 4.76 % $C_{60}$-AuNPs-TiO$_2$ catalyzed reaction is 5.49 times faster than the one catalyzed by the TiO$_2$.

6.4.3. Recyclability of the Photocatalyst

The recyclability of the 4.76% $C_{60}$-AuNPs-TiO$_2$ was evaluated by carrying out the photocatalytic degradation of MO for 10 consecutive cycles. Figure 6.9 showed the activity of the catalyst for 10 cycles and it was observed that the catalyst was fairly active even after 10 cycle of use. However, the activity of the catalyst decreased very slowly. This decrease in activity may have happened due to the loss of some catalyst during the sampling of the MO solution from the reaction mixture.
The stability of the catalyst was further investigated by TEM image and EDX spectroscopy. The TEM image of the catalyst, after the 10 cycles of use, showed that the AuNPs were intact without any change in the morphology (Figure 6.10c). The EDX spectra also demonstrated the presence of Titanium, Gold, Carbon and Oxygen in the nanocomposite, which in turn demonstrated the robustness of the catalyst towards the multiple cycle of application.

Figure 6.9: a) Cyclic stability of the C_{60}-AuNPs-TiO2 for 10 consecutive cycles; b) Typical TEM image, and c) EDX spectra of the C_{60}-AuNPs-TiO2 after 10 cycles of catalysis.

6.4.4. Generation of Hydroxyl Radical in the Photocatalytic Processes

The generation of hydroxyl radicals (•OH) by the 4.76 % C_{60}-AuNPs-TiO2 nanocomposites was further monitored by the photoluminescence (PL) technique using terephthalic acid (TA) as the probing molecule. TA reacts with the •OH radical resulting a highly fluorescent product of 2-hydroxyterephthalate that has an intense fluorescence emission band centered at 425 nm with an excitation wavelength of 315 nm, Figure 6.10a. Moreover, it is well established that the fluorescence intensity of 2-hydroxyterephthalate is directly proportional to the amount of the •OH radicals produced at the interface of water and the catalyst.\textsuperscript{158}
Figure 6.10: a) Reaction of terephthalate with \textbullet\ OH radical to form 2-hydroxyterephthalate, b) time-dependent PL spectra of the 2-hydroxyterephthalic catalyzed by the C\textsubscript{60}-AuNPs- TiO\textsubscript{2} (4.76 wt % Au), and c) the kinetics of the photogeneration of the \textbullet\ OH measured by PL experiment.

The detailed experimental procedure was similar to that of the photocatalytic MO degradation test. In this case, MO was replaced by 20 mL of 5 \times 10^{-3} M sodium terephthalate solution, which was prepared by reacting terephthalic acid with stoichiometric amount of NaOH in water. Figure 6.10b showed the time-dependent fluorescence emission spectrum of 2-hydroxyterephthalate. It showed that the intensity of PL emission band centered at 425 nm increased linearly with the lapse of time of light exposure.

Therefore, the PL results suggested that the C\textsubscript{60}-AuNPs-TiO\textsubscript{2} photocatalyst generated hydroxyl radicals under the light irradiation. These highly active hydroxyl radicals in turn have the ability degrade the organic pollutants in water. However, it could be observed that the C\textsubscript{60}-AuNPs-TiO\textsubscript{2} generated hydroxyl radical at a slower rate compared to the pristine TiO\textsubscript{2}, which is
opposite to the results observed for the methyl orange degradation tests. One possible explanation could be the oxidative degradation of the methyl orange by the hole generated on the AuNPs surface. Moreover, methyl orange could also act as a photosensitizer and in that case the C$_{60}$-AuNPs-TiO$_2$ acted as a better catalyst compared to the pristine TiO$_2$.

6.4.5. Catalytic Reduction of 4-NP

The ability of the TiO$_2$ supported AuNPs catalyst was further evaluated by the catalytic reduction of the 4-NP into 4-AP in water with the presence of excess NaBH$_4$, Figure 11a. The UV-Visible spectrum for the catalytic reduction of the 4-nitrophenolate to 4-aminophenolate, catalyzed by the 4.76 % C$_{60}$-AuNPs loaded TiO$_2$ is shown in Figure 6.11b. Absorption band centered at 400 nm, characteristic to the 4-nitrophenolate, was found to disappear after the catalytic reduction. However, a new absorption band originated at about 300 nm, which is considered as the characteristic absorption band of the 4-aminophenolate.

The percent catalytic reduction of 4-NP to 4-AP is shown in Figure 6.11c. It was found that the speed of the catalytic reduction was proportional to the amount of AuNPs loading on the TiO$_2$. For example, the 4.76 % C$_{60}$-AuNPs loaded TiO$_2$ demonstrated faster catalytic activity compared to the 2.45 % C$_{60}$-AuNPs loaded one. Likewise, the catalytic reduction of 4-NP in presence of the 4.76 %-C$_{60}$-AuNPs-TiO$_2$ was found to be faster comparing to the 4.76 %-AuNPs-TiO$_2$ (Control 2). The slow catalytic activity of the 4.76 %-AuNPs-TiO$_2$ (Control 2) could be attributed to the larger size as well as the aggregation of the AuNPs on the TiO$_2$. The un-catalyzed reaction, on the other hand, showed negligible reduction of the 4-NP, which signified the robust nature of 4-NP to undergo the reduction by the NaBH$_4$ only.
The kinetics of the catalytic reduction of 4-NP is shown in Figure 6.11d. A linear relationship between the $-\ln(C_t/C_0)$ and reaction time ($t$) was observed, which suggested that the kinetics of the 4-NP reduction followed the Langmuir–Hinshelwood (LH) model. Moreover, the linear increase of $-\ln(C_t/C_0)$ with respect to the reaction time is indicative that the reduction followed pseudo-first-order kinetics. The apparent rate constants ($k_{app}$), of the catalytic reduction of 4-NP in the presence of 4.76, 2.45, and 1.35 percent, C$_{60}$-AuNPs loaded TiO$_2$ were found to be 0.630, 0.183, and 0.083 min$^{-1}$, respectively. Whereas, the apparent rate constants of the uncatalyzed and the one catalyzed by the 4.76 %-AuNPs-TiO2 (Control 2) reactions were calculated to be 0.0048 and 0.040 min$^{-1}$. Therefore, the reductions catalyzed by the 4.76, 2.45, and 1.35 percent, C$_{60}$-AuNPs loaded TiO$_2$ were found to be about 131, 38, and 17 times faster than the uncatalyzed reaction. Also, the reductions catalyzed by the 4.76, 2.45, and 1.35 percent,
C₆₀-AuNPs loaded TiO₂ were found to be about 16, 4.6, and 2.1 times faster than the 4.76 %-AuNPs-TiO₂ (Control 2) catalyzed reaction. Moreover, it could be observed that the induction time decreased with the increase in the AuNPs loading on the TiO₂. Therefore, from this study it could be suggested that the TiO₂ supported AuNPs, prepared by the method motioned in this work, could potentially be utilized for the photocatalytic degradation of MO as well as the catalytic reduction of 4-NP and other organic species.

6.5. Conclusion

In conclusion, we report a facile method to prepare fullerene (C₆₀) stabilized gold nanoparticles (AuNPs) and a simple way to bind them onto the TiO₂ surface. The TiO₂ supported gold nanoparticles demonstrated enhanced photocatalytic activity to degrade methyl orange in water. It was found that the 4.76 % wt. AuNPs supported on TiO₂ is more than twice as active for the photodegradation of MO compared to the pristine TiO₂. The photogeneration of the hydroxyl radical was also confirmed by the photoluminescence of the 2-hydroxyterephtalic acid. Further, the cyclic stability of the photocatalyst was demonstrated for multiple cycles and it was found that the catalyst was fairly active throughout the cycles. The catalytic activity of the C₆₀-AuNPs-TiO₂ was further studied by the reduction of the 4-NP to 4-AP and it was found that the TiO₂ supported AuNPs, prepared following the method reported here, this study is about 16 times more active compared to the one prepared by UV-irradiation deposition method having the same AuNPs loading. Therefore, the TiO₂ supported AuNPs, prepared by the method motioned in this work could potentially be utilized for the enhanced photocatalytic degradation of MO as well as the catalytic reduction of 4-NP and other organic species in water.
Chapter 7: Sucrose Mediated Fast Synthesis of Zinc Oxide Nanoparticles for the Photocatalytic Degradation of Organic Pollutants in Water

7.1. Introduction

Zinc oxide (ZnO) is one of the most extensively studied semiconductor type metal oxides. As a semiconductor material, ZnO has wide-bandgap of 3.37 eV and an exciton binding energy of 60 meV. In addition to the semiconductor property, ZnO has intriguing piezoelectric, oxidizing, antibacterial, and photocatalytic properties. As a photocatalyst, ZnO and its nanocomposites demonstrate excellent ability towards the degradation of organic pollutants in water under the UV light illumination. Organic pollutants undergo degradation on the ZnO surface through the redox-processes driven by the electronic excitation between valence and conduction bands. Also, ZnO has the ability to generate reactive oxygen species (ROS) under the UV light irradiation, which can degrade organic pollutants and inactivate or inhibit microorganisms in water.

Recently, the photocatalytic degradation of organic pollutants has drawn tremendous attention because of its advantages over other methods viz. adsorption, precipitation, filtration, coagulation, biological treatment, etc. For instance, photocatalytic processes usually do not require chemicals and do not produce any secondary pollutants; photocatalytic processes have the ability to degrade hazardous organic pollutants to mineralization; whereas, most of the other techniques transfer the pollutants from one place to another. Moreover, the photocatalyst can be used for multiple cycles without the loss of the activity. As ZnO demonstrates excellent photocatalytic activity, it could potentially be used as an efficient and viable photocatalyst for the degradation of organic pollutants in water. However, the photocatalytic activity of ZnO is obtained when the particles are in the nanoscopic size range (1-100 nm) in contrast to the
macroscopic or bulk size. Therefore, there is a need for the synthesis of high-quality zinc oxide nanoparticles (nZnO) via a facile method that avoids the use of harsh chemicals and rigorous experimental procedures.

Various chemical and physical methods have been reported for the synthesis of nZnO thus far.\textsuperscript{47} In addition, there are physical top-down techniques, such as mechanical or mechanochemical milling, where the bulk ZnO is converted into nZnO.\textsuperscript{55} A large number of methods for the synthesis of nZnO require expensive and hazardous substrates, rigorous experimental conditions, tedious techniques, and sophisticated instruments. Moreover, sometimes the nZnO are not efficient enough for the desired photocatalytic applications. Therefore, it is important to develop a simple, fast, and low-cost method for the synthesis of high-quality and photocatalytically active nZnO. Recently, the combustion synthesis has become a very popular and effective technique to synthesize metal oxide nanoparticles due to the versatility, simplicity, and rapidity of the process.\textsuperscript{56} In combustion synthesis, a mixture of metal salt as an oxidizer (e.g., metal nitrates) and fuels (e.g., urea, glycine, hydrazides) is heated to a high-temperature. When heated to a temperature, the mixture undergoes a self-sustained reaction to produce uniform metal oxide nanoparticles while burning away the fuel in the form of CO\textsubscript{2}, H\textsubscript{2}O, and other gases. Utilizing the combustion synthesis technique many types of single and mixed metal oxides nanoparticles have been prepared.\textsuperscript{164} For the synthesis of nZnO, different types of organic compounds, plant extracts have been used as fuels.\textsuperscript{165} However, there are some drawbacks of these methods. For example, the plant extracts containing metallic and nonmetallic impurities can modify the desired properties of the nZnO by doping it with the metallic and non-metallic elements. Also, the utilization of plant extracts for the large-scale synthesis of engineered nanoparticles may not be a viable method and it is still under questions.\textsuperscript{166} Other
organic compounds, such as urea and thiourea, usually make nZnO doped with nitrogen and sulfur, which may be undesired and can alter the desired catalytic property of the nZnO. Therefore, for the preparation of high-quality nZnO through the combustion synthesis method, a highly pure and cheap fuel is necessary. In this regard, sucrose could potentially be used as fuel because of its low price and availability in the form of high purity. To the best of our knowledge, there is no report for the synthesis of nZnO utilizing sucrose as the fuel in the combustion synthesis. Additionally, there is no report for the synthesis of nZnO that can be completely performed using a hot-plate within 30 min period of time.

Herein, we report a simple and fast method for the synthesis of nZnO by rapidly heating a paste of zinc nitrate hexahydrate [Zn(NO₃)₂.6H₂O] and sucrose (C₁₂H₂₂O₁₁) at 500 °C on the hot plate. The as-synthesized nZnO was thoroughly characterized by the high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX), powder X-ray diffraction spectroscopy (XRPD), X-ray photoelectron spectroscopy (XPS), UV-Visible absorption spectroscopy, BET surface area analysis, and Fourier transform infrared spectroscopy (FTIR). The nZnO demonstrated very good performance towards the photocatalytic degradation organic pollutants viz. methyl orange (MO) and methylene blue (MB) in water under the UV-B light and sunlight irradiation. The photocatalytic generation of hydroxyl radical (•OH) was confirmed through the terephthalic acid photoluminescence tests. The reproducibility of the synthesis method and the stability of the nZnO were also studied to evaluate the potential application of the nZnO for the photocatalytic water treatment.
7.2. Materials and Methods

7.2.1 Materials

Unless otherwise mentioned, all chemicals were used as received. Sucrose (C_{12}H_{22}O_{11} >99.5%), zinc nitrate hexahydrate [Zn(NO_3)_2.6H_2O ≥ 98%), sodium hydroxide (NaOH ≥ 98%) and Terephthalic acid [C_8H_6O_4 = 98%] were purchased from Sigma-Aldrich. Methyl Orange (C_{14}H_{15}N_3O_3 >98.0%) and methylene blue (C_{16}H_{18}ClN_3S >98%) were obtained from TCI AMERICA and Consolidated Chemical, respectively. Fisher Scientific 11-600-49sh Isotemp Analog Hot Plate Stirrer was used as the heating source for the synthesis of nZnO. Throughout the nZnO synthesis period, the hot plate was preheated to its highest capacity and the hot plate surface temperature was measured to be about 500 °C. Ultraviolet box reactor (UVP Ultraviolet Crosslinker, Model CL-1000), having UV-B fluorescent tube lamps, was used for the photocatalytic degradation of MO and MB. The UV reactor shined the light from top only. The intensity of light on the surface of the reaction was measured to be 21,500 lux. The intensity of light was measured by using a digital Light Meter LX1330B. The UV-B lamp generated light of 302 nm wavelength, as specified by the vendor of the lamp. Syringe Filters with Polypropylene Housing and PTFE membrane material with 0.45μm pore size were obtained from VWR, which were used to filter the reaction mixture. Milli-Q water (> 18.20 MΩ.cm resistivity) was obtained from Milli-Q (Advantage A-10) water filter system. The simulated fresh drinking water (FDW) was prepared following the Nanotechnology Enabled Water Treatment (NEWT) protocol. In detail, 252 mg /L NaHCO_3, 147 mg /L CaCl_2.2H_2O, 124 mg /L MgSO_4.7H_2O, 95 mg/L Na_2SiO_3.9H_2O, 12 mg /L NaNO_3, 2.2 mg /L, NaF, and 0.18 mg /L NaH_2PO_4.H_2O were dissolved in the deionized water to achieve the simulated FDW.
7.2.2. Synthesis of nZnO

Fisher Scientific 11-600-49sh Isotemp Analog Hot Plate Stirrer was used as the heating source for the synthesis of nZnO. Throughout the nZnO synthesis period, the hot plate was preheated to its highest capacity. Although the hot plate was heated to its highest capacity, the temperature was measured to be about 500 °C at the surface of the hot plate. In detail, in 150 ml glass beaker (Kimax), 1200 mg (3.51 mmol) sucrose and 3569.88 mg (12 mmol) Zn(NO₃)₂·6H₂O salt were mixed with 3 ml deionized water. The beaker was put on the preheated hot plate. Within 1-2 minutes the mixture turned into a viscous solution and immediately after the viscous solution started to decompose generating brownish yellow gases. After 3-4 min, blackish brown foam was obtained from the decomposition of zinc nitrate salt. Since the decomposition of zinc nitrate salt formed NO₂ and NOₓ gases, the hot plate was placed in a fume hood with proper ventilation. Afterward, the blackish brown hot foam/powder was transferred from the beaker to the same bare hot plate. The powder was stirred by a spatula. While heating at this high temperature in air, the blackish powder turned into yellowish-white powder of nZnO. The carbon in the powder combusted away in the form carbon dioxide. After 20 min of heating on the hot plate, the nZnO powder was allowed to cool down. For cooling, the hot plate was turned off and normal ambient cooling was utilized. The amount of nZnO obtained was about 810 mg, which was stored under ambient condition for the characterization as well as the photocatalytic applications.

7.2.3. Methyl Orange and Methylene blue Photodegradation Experiments

Photocatalytic degradation of MO and MB was carried out in a glass beaker (Pyrex) with 150 mL of capacity and dimensions of Diameter × Height = 28 mm × 98 mm. Methyl orange and methylene blue solutions having the concentration of 3 and 6 ppm (mg/L) were used for the
photocatalytic experiments. In the photodegradation experiments, 25 mg of the catalyst was homogeneously dispersed in 25 ml of MO or MB solution by 10 min of bath sonication in dark. The bath sonication facilitated the homogeneous dispersion of the nZnO as well as helped in the establishment of the adsorption-desorption equilibrium between the nZnO and the dye. The mixture was illuminated under the UV-lamps in the box reactor while stirring of the mixture. At a regular interval of 5 min, 1 mL sample was withdrawn and filtered through a syringe filter for UV-Visible spectroscopic analysis. The characteristic absorption maxima of MO and MB centered at 464 nm and 665 were used for the calculation of percent degradation, respectively. Same experimental conditions were utilized for the photocatalysis of MO under the sunlight illumination. Direct sunlight was utilized for the photocatalysis of MO in deionized and FDW matrices. For the cyclic stability experiments, the catalyst used in the first cycle was centrifuged and used in the same way for the subsequent cycles for the degradation of MO. The sample was taken from the centrifuged (4000 rpm, 5 min) supernatant so as to minimize the loss of the catalyst.

7.2.4. Photoluminescence Test for the Determination of Hydroxyl Radicals

The detail experimental procedure was similar to that of the photocatalytic MO or MB degradation tests. In this case, 25 ml of $5 \times 10^{-3}$ M sodium terephthalate solution was used instead of the MO or MB solution. A stock solution of $5 \times 10^{-3}$ M sodium terephthalate was prepared by reaction of a required amount of terephthalic acid with stoichiometric amount of NaOH in water. In every 5 min, 1 mL sample was withdrawn and filtered through the syringe filter. The fluorescence spectroscopy was carried out on the filtrate with an excitation wavelength of 315 nm to determine the fluorescence emission intensity of hydroxy terephthalate at 425 nm.
7.3. Results and Discussion

7.3.1 Mechanism for the Synthesis of nZnO

Due to the versatile applications of nZnO, there is a need for the synthesis of high-quality nZnO employing a simple and fast method. This report demonstrates a fast method for the preparation of photocatalytically active nZnO by rapidly heating a paste of Zn(NO$_3$)$_2$.6H$_2$O and sucrose at 500 °C on the hot plate, Figure 7.1. Based on the previous studies, the proposed mechanism for the formation of nZnO can be explained as follows: while heating on the hot plate, the mixture of Zn(NO$_3$)$_2$.6H$_2$O and sucrose dissolve and become concentrated to form a uniform viscous paste, Figure 1a. While further heating, the Zn(NO$_3$)$_2$.6H$_2$O starts to decompose rapidly to form NO$_2$ (brownish gas), N$_2$, CO$_2$, H$_2$O, and other nitrogenous gases, which blow the melted viscous paste and cause it to swell to form the blackish brown color foam, Figure 1b. Meanwhile, the sucrose undergoes partial carbonization through the dehydration and polymerization. The resulting foam-like composite is considered to contain nZnO embedded in partially carbonized sucrose foam, Equation 1.

\[
C_{12}H_{22}O_{11} \text{(s)} + Zn(NO_3)_2.6H_2O \text{(s)} \rightarrow C_{\text{foam}} + ZnO \text{(s)} + N_2(g) + H_2O(g) + NO_x(g) \quad (1)
\]

\[
C_{\text{foam}} + ZnO \text{(s)} \rightarrow ZnO \text{(s)} + CO_2(g) \quad (2)
\]
Further heating of this partially carbonized foam with the embedded nZnO at elevated temperature causes the oxidation of the carbon to CO$_2$ leaving nZnO, Equation 2, Figure 7.1c-e. It was observed that the nZnO looked yellowish white (Figure 7.1d) in color when hot and it turned to white when cooled down to room temperature (Figure 7.1e). Due to the oxygen vacancies in the ZnO crystal when hot it appears the color yellowish white and when cooled down to the room temperature it appears white color because of the filling up of the oxygen vacancy. The advantage of the method is that the experimental conditions are simple, fast and scalable. Moreover, the methodology does not require any expensive or hazardous reagents and the. The method can potentially be adapted to prepare a wide variety of other metal and mixed oxide nanoparticles.

The rapid industrialization and increasing population growth are posing a continual threat to the environment by polluting the air, water, and soil with numerous organic and inorganic contaminants. In regard to the aquatic environment, freshwater sources are being contaminated with numerous organic pollutants that are reported to be toxic, carcinogenic and mutagenic to human beings and aquatic organisms. As a result, freshwater water is not only becoming increasingly scarce but also hazardous to human health almost everywhere in the world. The utilization of nZnO for the photocatalytic degradation of organic pollutants in water could be considered as a viable and sustainable method for the purpose of water treatment. Therefore, a facile synthesis method of nZnO, as reported in this study, could accelerate the overall photocatalytic water treatment processes.
7.3.2. TEM and HRTEM Images of the nZnO

Transmission Electron Microscopy (TEM) images were obtained to visualize the size, shape, and the dispersity of the as-synthesized nZnO. The TEM images (Figure 7.2b and 7.2c) revealed that the nZnO are predominantly spherical in shape and highly monodisperse with the smooth surface. It could be observed that the nZnO tended to aggregate, which could be attributed to the high surface area of nZnO. The size distribution histogram, obtained by measuring the size of more than 100 randomly picked nanoparticles by the ImageJ software, demonstrated that the nZnO have an average size of about 35 nm, Figure 7.2d. Although the size of the nZnO varied from 15 to 55 nm, the majority of the particles were in the size range of 32 to 40 nm. A digital photograph of the nZnO is shown in Figure 7.2a.

![Figure 7.2](image.png)

Figure 7.2: a) Digital photograph of the nZnO in a glass vial; b-c) TEM images of nZnO with varying magnifications, d) size distribution of the nZnO, e) HRTEM image of the nZnO, and f) Fast Fourier Transform (FFT) image of the nZnO.

The crystalline nature of the nZnO was further analyzed by the High-Resolution Transmission Electron Microscopy (HRTEM), Figure 7.2e. Clear lattice fringes can be seen, which indicates the highly crystalline structure of the nZnO. The interplanar spacing of 2.8 Å further corresponds to the (100) lattice plane of the nZnO. The crystalline nature of the nZnO
surface was also characterized by the fast Fourier Transformation (FFT) analysis obtained from the HRTEM image of the nZnO, Figure 7.2f. The FFT analysis not only confirmed a good crystallinity but also determined the hexagonal wurtzite type crystalline structure of the nZnO.  

7.3.3. SEM Image and the EDX Spectrum of the nZnO

The morphology and the elemental composition of the as-prepared nZnO was further studied by the SEM image and EDX spectrum, Figure 7.3. As shown in Figure 7.3a, the nZnO particles were seen to be aggregated with powder-like morphology. A porous morphology of the nZnO was also found from the SEM image.

![SEM Image and EDX Spectrum of the nZnO](image)

Figure 7.3: a) Typical SEM image of the nZnO, b) EDX spectral image of the nZnO, and c) SEM EDX elemental mapping image of the nZnO.

To determine the qualitative information of the nZnO, the EDX spectrum was obtained, Figure 3b. The EDX spectrum generated strong peaks corresponding to zinc and oxygen indicating a high purity the as-synthesized nZnO. A small peak corresponding to carbon originated from carbon tape that was used as the substrate for the analysis. The SEM backscattered electron image of the nZnO and the X-ray EDS elemental mapping image of the
nZnO is shown in Figure 7.3c. As the EDS spectral analysis, the EDS elemental mapping image showed the presence and abundance of zinc and oxygen in the nZnO sample. This further confirmed the purity of the nZnO that was synthesized in this report.

### 7.3.4. XRPD Pattern and the BET Surface Area of the nZnO

The X-ray Powder Diffraction (XRPD) spectrum was obtained to determine the crystalline properties as well as the crystallite particles size of the nZnO. As shown in Figure 7.4, the diffraction pattern and the sharp peaks clearly indicate the crystalline nature of the as-prepared nZnO. Moreover, the diffraction peaks at $2\theta = 31.66^\circ$, $34.20^\circ$, $36.10^\circ$, $47.36^\circ$, $56.47^\circ$, $62.63^\circ$, $66.20^\circ$, $67.81^\circ$, $68.99^\circ$, $72.40^\circ$, and $76.90^\circ$ are characteristic to the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and 202 lattice planes of the nZnO. This type of XRPD pattern is characteristic to the polycrystalline hexagonal wurtzite crystal structure of the nZnO (Zincite, JCPDS 5-0664). From the XRPD pattern, it could be observed that the intensity of the ZnO (101) diffraction peak is somewhat stronger than the other peaks. This indicates that the nZnO have a preferential orientation towards (101) crystallographic direction. The absence of any other undesired peaks in the XRPD pattern indicates the high purity of the nZnO, which is also confirmed by the EDX elemental analysis.

![Figure 7.4: XRPD patterns showing the hexagonal wurtzite crystal structure of the nZnO.](image-url)
The average crystallite size of nZnO was further calculated by utilizing the Debye-Scherrer’s formula (Equation 3) from the XRD peak width of (101)\textsuperscript{174}.

\[ d = \frac{k\lambda}{\beta \cos(\theta)} \]  

(3)

where \( d \) is the crystallite size, \( k \) is the shape factor (0.9), \( \lambda \) is the wavelength of Cu Kα X-ray radiation (1.54 Å), \( \theta \) is the Bragg diffraction angle, and \( \beta \) is the full width at half maximum of the respective diffraction peak. Applying the Debye-Scherrer formula, the average crystallite size of the nZnO was found to be 28.9 nm. The crystallite size, obtained from the XRPD analysis, was found to have somewhat deviated from the average particle size measured by the TEM analysis. The crystallite size, measured from the XRPD analysis, is assumed to be the size of a coherently diffracting domain and it is not necessarily the same as particle size determined from the TEM images.

The nZnO was further characterized by the nitrogen gas adsorption studies to obtain the specific surface area, pore size and the pore volume. The Brunauer–Emmett–Teller (BET) specific surface area of the nZnO was measured to be about 80.11 m²/g, which is comparable or higher than the reported values\textsuperscript{175,176}. Additionally, the BJH pore volume and pore diameter of the nZnO were measured to be about 0.098 cm³/g and 54.48 Å, respectively.

7.3.5. UV-Visible and FTIR Spectrum of the nZnO

The UV-Visible spectrum of the nZnO suspension in ethanol (0.125 mg/mL) and the nZnO thin film on glass substrate is shown in Figure 7.5a. The nZnO in suspension and in the form of thin film generated similar UV-Visible absorption spectrum. In both cases, a sharp absorption band centered at 375 nm was obtained. The absorption band at 375 nm is characteristic to the intrinsic band-gap absorption of the nZnO due to the excitation of electrons from the valence
band to the conduction band (O2p→Zn3d).\textsuperscript{177} Based on the absorption band at 375 nm, the band-gap energy was calculated according to Equation 4.

\[ E = \frac{hc}{\lambda} \]  \hspace{1cm} (4)

where \( E \) is the energy (J), \( h \) is Planck's constant \((h = 6.626 \times 10^{-34} \text{ J s})\), \( c \) is the speed of light \((2.998 \times 10^8 \text{ m s}^{-1})\) and \( \lambda \) is the wavelength of the maximum absorption (375 nm).\textsuperscript{178}

Figure 7.5: a) UV-Visible absorption spectra of the nZnO thin film and nZnO suspension in ethanol and b) the FTIR spectra of the nZnO.

A band-gap energy of 3.32 eV was obtained for the nZnO, which is similar to the band-gap energy of the zinc oxide reported elsewhere.\textsuperscript{179} Moreover, Figure 5a shows that there are significant absorptions in the visible range and an absorption tail reaching to 800 nm. The origin of this absorption and tail could be assigned to the scattering of the light by nZnO in colloidal suspension or in the thin film. Therefore, from the UV-Visible spectrum, it is confirmed that the nZnO has a high absorption coefficient in the UV region (<400 nm) of the electromagnetic radiation.

The FTIR spectra of the nZnO is shown in Figure 7.5b. A strong peak at 415 cm\(^{-1}\) was observed, which is characteristic to the Zn-O stretching vibrational mode of the hexagonal ZnO nanoparticles.\textsuperscript{180} This further confirms the formation of ZnO nanoparticles by this method. A less
intense peak at ~3400 cm\(^{-1}\) can be attributed to the O-H stretching vibrations originated from the chemically bound OH group or the adsorbed moisture on the nZnO surface.

### 7.3.6. High Resolution XPS Analysis of the nZnO

The elemental composition and the purity of the nZnO were characterized by the XPS analysis. From the XPS survey spectrum, it was found that the nZnO was mainly consisting of Zn and O while having a trace of C, Figure 7.6a. Binding energies characteristic to the ZnO, Zn (2s, 2p, 3s, 3p, 3d), Zn LMM, Zn LMN, O KLL, and O 1s, were observed in the XPS spectrum.\(^\text{181}\)

![XPS spectra](image)

Figure 7.6: a) XPS survey spectrum of the nZnO, and high-resolution XPS spectrum of the b) Zn 2p, c) O 1s, and d) Zn 3p electrons.

The Zn2p3/2 and Zn2p1/2 peaks at 1022.5 eV and 1045.6 eV can be assigned to Zn element in ZnO, respectively. The Zn3p3/2 and Zn3p1/2 binding energy of the nZnO sample can be attributed to the peaks at 88.1 eV and 91.1 eV, respectively.\(^\text{182}\) The binding energy of O1s can be attributed to the peak at about 531 eV. The high-resolution XPS spectrum of O1s can be resolved into two peaks at 531.2 and 532.8 eV, which are characteristic to the Zn-O and the OH
on the surface of ZnO. The OH group may have originated from the breaking of Zn-O-Zn bond and the formation of Zn-OH bond, during the high-temperature synthesis under the ambient conditions. Therefore, from the XRD and XPS analyses, it could be inferred that the as-synthesized nZnO was highly pure.

### 7.3.7. Photocatalytic Degradation of MO and MB by UV Light

The photocatalytic performance of the nZnO was evaluated by the degradation of MO and MB in water under UV and sunlight illumination. As mentioned above, the photocatalysis of MO and MB was done in deionized water (DIW) and simulated fresh drinking water (FDW) matrices. The time-dependent percent degradation of MO and MB was calculated by using Equation 5. The UV-Visible spectroscopy was utilized to monitor the degradation of MO and MB.

\[
\text{Percent degradation} = \frac{C_0 - C_t}{C_0} \times 100\% = \frac{A_0 - A_t}{A_0} \times 100\% \tag{5}
\]

where \(C_0\) and \(C_t\) represent the initial and time-dependent concentrations of MO and MB, \(A_0\) and \(A_t\) represent the initial and time-dependent absorbance of MO and MB, respectively.

Figure 7a shows the time-dependent UV-Visible spectrum of 6 ppm MO solution in DIW during its photocatalytic degradation in the presence of nZnO. As shown in Figure 7.7a, the concentration of MO gradually decreased with respect to the time of photocatalysis. The absorption maxima at 464 and 275 nm disappeared almost completely after 30 min of catalysis, which suggested the degradation of MO in water.

The time-dependent percent degradation of 3 and 6 ppm MO solution is shown in Figure 7b. It was found that the 3 ppm MO solution in DIW completely decolorized within 15 min of photocatalysis, whereas it took about 25 min to completely decolorize the 6 ppm MO solution in DIW. It is typical that it takes longer time to degrade pollutants of higher concentration
compared to the lower concentration. The percent degradation of MO in FDW was found to be little slower compared to the one in DIW. For example, it took about 40 min to completely degrade the 6 ppm MO solution in FDW; whereas it took about 25 min in DIW. The presence of dissolved ions could be attributed to this slower photocatalytic activity. Also, it was observed that the extent of MO adsorption was higher in DIW compared to the FDW, Figure 7.7b. In the absence of the nZnO, the MO solution did not undergo any decolorization under the UV light irradiation, which indicated the robustness of MO against the photodegradation. Moreover, in the absence of light, nZnO showed less than 10 % decolorization of the MO solution (6 ppm in DIW) after 30 min (data not shown here), which is mainly due to adsorption. On the other hand, a complete decolorization of MO solution (6 ppm in DIW) was observed after 30 min in the presence of nZnO and UV light (Figure 7b), which indicated that the degradation of MO happened photocatalytically.

The time-dependent UV-Visible spectra and the percent degradation of MB is shown in Figure 7.7d and 7.7e. Both 3 and 6 ppm MB solution almost complete decolorization in about 30 min period of photocatalysis. The MB solution, in the absence of the nZnO, did not show any degradation under the UV light irradiation. Therefore, it confirmed that the nZnO was responsible for the degradation of MB under the UV light irradiation.

The experimental result for the photocatalytic degradation of MO and MB by nZnO was further analyzed by the Pseudo-first order kinetic model. The pseudo-first order rate equation is represented as follows:

\[ k_t = \ln(C_t/C_0) \]  

where \( k \) represents the rate constant (min\(^{-1}\)) of the reaction, \( C_t \) and \( C_0 \) represent the concentration of the MO and MB at time t and at the beginning of the reaction, respectively.
Figure 7.7: Time-dependent UV-Visible spectrum of a) MO and d) MB solution during the photocatalytic degradation, Time-dependent percent degradation of b) MO and e) MB, and Pseudo-first order kinetics of the degradation of c) MO and f) MB.

As shown in Figure 7.7c and 7.7f, the \(-\ln(C_t/C_0)\) vs. the time (t) graph followed the linear trends, which suggested that the kinetics of the MO and MB degradation followed the Pseudo-first order reaction mechanism. A linear relationship between \(-\ln(C_t/C_0)\) and reaction time (t) further indicate that the photocatalytic reaction followed the Langmuir–Hinshelwood (LH) model.\(^{184}\) The apparent rate constants (\(k_{\text{app}}\)) of the photocatalytic degradation of MO was calculated to be \(2.49 \times 10^{-1}\), \(1.95 \times 10^{-1}\), \(2.90 \times 10^{-1}\), and \(1.04 \times 10^{-1}\) min\(^{-1}\), respectively for 3 ppm MO in DIW, 6 ppm MO in DIW, 3 ppm MO in FDW, and 6 ppm MO in FDW solution. Likewise, the rate constants of MB degradation were calculated to be \(1.26 \times 10^{-1}\), \(1.15 \times 10^{-1}\), \(1.23 \times 10^{-1}\), and \(9.64 \times 10^{-2}\) min\(^{-1}\), respectively for 3 ppm MB in DIW, 6 ppm MB in DIW, 3 ppm MB in FDW, and 6 ppm MB in FDW solution.
7.3.8. Photocatalytic Degradation of MO by Sunlight

The photocatalytic performance of the nZnO was further evaluated by the degradation of 6 ppm MO solution in DIW and FDW by the sunlight irradiation. As shown in Figure 8a-c, the nZnO effectively degraded 6 ppm MO solution in DIW and FDW matrices and the percent degradation reached to almost to 100 within 30 min of sunlight irradiation. The degradation of MO in DIW was found to be faster compared to the FDW matrix, Figure 7.8b and 7.8c. Also, no degradation of MO solution was found in the absence of nZnO. The performance of the nZnO under sunlight irradiation can be attributed to the presence of 4-5 % of UV light in solar radiation.

![Figure 7.8](image)

Figure 7.8: a) Time-dependent UV-Visible spectrum for the photocatalytic degradation of 6 ppm MO in DIW under sunlight irradiation, b) Time-dependent percent degradation of 6 ppm MO solution in DIW and FDW, and c) Pseudo-first order kinetics of the degradation of MO.

Also, the fast-catalytic activity under sunlight irradiation was due to the extremely high intensity of the sunlight in compared to the UV light used in this study. The average intensity of the UV light in the box reactor was about 22,000 lux; whereas, the sunlight had an average intensity of about 100,000 lux. The sunlight irradiated photocatalytic degradation of MO followed the pseudo-first-order reaction kinetics and the rate constants ($k_{app}$) were calculated to be $1.71 \times 10^{-1}$ and $1.13 \times 10^{-1}$ for the 6 ppm MO in DIW and 6 ppm MO in FDW, respectively.
The photocatalytic activity of the nZnO for the degradation of MO and MB, studied in this report, is summarized in Table 1.

Table 7.1: Photocatalytic degradation of MO and MB by nZnO.

<table>
<thead>
<tr>
<th>Pollutants</th>
<th>Concentration</th>
<th>Water Matrix</th>
<th>Light source</th>
<th>Rate constant (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MO</td>
<td>3 ppm</td>
<td>DIW</td>
<td>UV</td>
<td>2.49 × 10⁻¹</td>
</tr>
<tr>
<td>MO</td>
<td>6 ppm</td>
<td>DIW</td>
<td>UV</td>
<td>1.95 × 10⁻¹</td>
</tr>
<tr>
<td>MO</td>
<td>3 ppm</td>
<td>FDW</td>
<td>UV</td>
<td>2.90 × 10⁻¹</td>
</tr>
<tr>
<td>MO</td>
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<td>FDW</td>
<td>UV</td>
<td>1.04 × 10⁻¹</td>
</tr>
<tr>
<td>MB</td>
<td>3 ppm</td>
<td>DIW</td>
<td>UV</td>
<td>1.26 × 10⁻¹</td>
</tr>
<tr>
<td>MB</td>
<td>6 ppm</td>
<td>DIW</td>
<td>UV</td>
<td>1.15 × 10⁻¹</td>
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<td>MB</td>
<td>3 ppm</td>
<td>FDW</td>
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<td>1.23 × 10⁻¹</td>
</tr>
<tr>
<td>MB</td>
<td>6 ppm</td>
<td>FDW</td>
<td>UV</td>
<td>9.64 × 10⁻²</td>
</tr>
<tr>
<td>MO</td>
<td>6 ppm</td>
<td>DIW</td>
<td>Sun</td>
<td>1.71 × 10⁻¹</td>
</tr>
<tr>
<td>MO</td>
<td>6 ppm</td>
<td>FDW</td>
<td>Sun</td>
<td>1.13 × 10⁻¹</td>
</tr>
</tbody>
</table>

From the above photocatalysis experiments, it could be concluded that the as-prepared nZnO is highly active in the degradation of organic compounds viz. MO and MB in DIW as well as FDW matrices. Therefore, it could be suggested that the nZnO could effectively be used for the photocatalytic degradation of organic compounds in water by the use of both the UV and the sunlight.

7.3.9. Stability of the nZnO and the Validation of the Method of nZnO Preparation

The cyclic stability of the nZnO was determined by conducting the photocatalytic degradation of MO for 5 cycles over a period of two weeks. A mixture of 25 ml MO solution (6 ppm) and 25 mg nZnO was irradiated for 30 min under UV light.
Figure 7.9: a) Cyclic stability of the nZnO for 5 cycles of MO degradation and b) Photocatalytic activity of nZnO prepared in three independent trials.

Afterward, the mixture was centrifuged at 4500 rpm for 10 min to obtain the clear supernatant, which was analyzed by UV-Visible spectroscopy to determine the percent degradation of MO. The centrifuged nZnO was used similarly for the following cycles. Figure 7.9a shows the photocatalytic activity of the nZnO for 5 cycles. The results reveal that the nZnO is fairly active throughout the cycles over the period of study. In every cycle, the nZnO degraded more than 96 percent of the MO. Therefore, from this study, it could be suggested that the nZnO, synthesized in this study, could potentially be utilized as a robust and long lasting photocatalyst for the degradation of organic pollutants from wastewater.

In order to validate the synthesis methodology, the nZnO was prepared in three independent trials was utilized for the degradation of 6 ppm MO solution in DIW. As can be seen from Figure 7.9b, the nZnO prepared in all three trials have the similar activity for the degradation of 6 ppm MO in solution. This results further validated the robustness of the methodology for the synthesis of nZnO.
Figure 7.10: a) Photocatalytic activity of nZnO prepared from Zn(NO$_3$)$_2$.6H$_2$O obtained from Sigma-Aldrich and the Fisher Scientific, and b) comparison of the photocatalytic activity of the nZnO with the commercial zinc oxide nanoparticles.

The robustness of the synthesis methodology was further evaluated by preparing nZnO from zinc nitrate salts obtained from two different vendors viz. the Sigma-Aldrich and the Fisher Scientific. The nZnO, prepared from the zinc nitrate salts of Sigma-Aldrich and the Fisher Scientific, were utilized for the degradation 6 ppm MO solution in DIW and compared, Figure 7.10. It was observed that the nZnO, synthesized from the Zn(NO$_3$)$_2$.6H$_2$O obtained from the Sigma-Aldrich and the Fisher Scientific, had a similar activity for the degradation of 6 ppm MO solution in DIW, Figure 7.10. Therefore, it could be concluded that a highly photocatalytically active nZnO can be prepared, following the method mentioned in this study, irrespective to the vendors of Zn(NO$_3$)$_2$.6H$_2$O. Additionally, the photocatalytic performance of the nZnO, prepared in this study, was compared with the commercially available zinc oxide nanoparticles obtained from Sigma-Aldrich, Figure 7.10b. It was found that the photocatalytic activity of the commercial zinc oxide nanoparticles was much faster compared to the nZnO. The difference in the performance could be because of the difference in the particle size, shape, crystallinity, and the purity of the commercial zinc oxide nanoparticles and the nZnO.

7.3.10. Determination of the ROS Generation in the Photocatalytic Process
The photocatalytic generation of hydroxyl radicals (•OH) was determined by the terephthalic acid (TA) photoluminescence (PL) technique. The sodium salt of terephthalic acid reacts with the photocatalytically generated •OH to form 2-hydroxyterephthalate, which demonstrate strong fluorescence emission band centered at 425 nm when excited at a wavelength of 315 nm, Figure 7.11. Qualitatively, the stronger the fluorescence intensity, the higher the amount of the •OH generation at the interface of water and the catalyst.

![Figure 7.11: The reaction of terephthalate with •OH radical to form 2-hydroxyterephthalate.](image)

The results of the TA photoluminescence tests are shown in Figure 7.12. Figure 7.12a shows the time-dependent fluorescence emission spectrum of 2-hydroxyterephthalate catalyzed by the nZnO; whereas Figure 7.12b shows the time-dependent fluorescence emission spectrum of 2-hydroxyterephthalate solution under UV light illumination (without the nZnO). For the nZnO catalyzed reaction, it could be seen that the fluorescence emission intensity increased at a much higher rate compared to the uncatalyzed reaction.
Figure 7.12: a) Time-dependent fluorescence spectra of the 2-hydroxyterephthalate solution catalyzed by the nZnO, b) time-dependent fluorescence spectra of the 2-hydroxyterephthalate solution only (without the nZnO), and c) fluorescence emission intensity at 425 nm versus time graph.

Figure 7.12c shows the fluorescence intensity of 2-hydroxyterephthalate at 425 nm with respect to the time of photocatalytic reaction. It can be seen that the fluorescence intensity for the nZnO catalyzed reaction increased very rapidly up to 10 min and afterward it became slow gradually. The gradual slowing of the fluorescence intensity could be attributed to the gradual decrease in the concentration of TA in the solution and thereby limiting the reaction between the •OH and the TA. However, at the end of 30 min the fluorescence intensity was still increasing. In compared to the uncatalyzed reaction, the nZnO catalyzed reaction generated a much higher amount of •OH, which can be seen from Figure 7.12c. The nZnO catalyzed reaction generated about 38 times more •OH compared to the uncatalyzed reaction. This result is complying to the photocatalytic degradation of MO and MB that is discussed above. Moreover, the TA fluorescence results indicate that the nZnO can generate hydroxyl radicals under the UV-B light illumination. The photocatalytic generated highly reactive and short-lived •OH have the ability to non-selectively degrade the organic pollutants in water.

Based on the findings of this study and the results of the previous mechanistic studies, the photocatalytic degradation of organic compounds on nZnO occurs as shown in Figure 7.13. The photons of the incident light couple with the oscillating valance band (VB) electrons in the nZnO, causing the excitation of electrons (e−) to the conduction band (CB) while leaving holes (h+) on valance band (VB). These holes (h+) on the VB then oxidize organic or inorganic species. Holes (h+) on the VB can also oxidize the hydroxyl (OH−) ions to hydroxyl radicals (•OH), which can non-selectively and effectively degrade organic pollutants in water.

![Figure 7.13: Proposed mechanism for the photocatalytic generation of ROS by the nZnO followed by the degradation of organic pollutants.](image)

On the other hand, the excited electrons (e−) on the CB have the ability to generate reactive oxygen species (ROS) such as superoxide radical anions (O2−) and hydroxyl radicals (•OH) in water. These short-lived, very active, and nonspecific ROS eventually initiate a series of reactions, which can degrade persistent and harmful organic pollutants. The successive degradation of organic pollutants may lead to the mineralization, which is the formation of harmless gases viz. CO2 and H2O.
7.4. Conclusion

In conclusion, we report a simple and fast method for the synthesis of nZnO of about 35 nm in size by heating a paste of zinc nitrate hexahydrate and sucrose on the hot plate. The as-prepared zinc oxide nanoparticles exhibited good photocatalytic activity for the degradation of MO and MB in water. The nZnO were found to be almost equally active in degrading MO and MB in deionized as well as simulated fresh drinking water matrices. The photocatalytic generation of hydroxyl radical was also confirmed by the terephthalic acid photoluminescence tests. The stability of the nZnO was studied for 5 cycles over a period of two weeks, which demonstrated no loss of the catalytic activity. The method described in this study can be utilized for the synthesis of nZnO, which in turn could potentially be applied for the photocatalytic degradation of organic pollutants in water. The significance of this report is the simplicity and robustness of the method for the synthesis of nZnO, which could be adapted for the synthesis of a wide variety of other metal and mixed metal oxides nanoparticles for a wide spectrum of applications.
8.1. Introduction

In chemical process industries, catalyst plays a key role by the transformation of raw materials into valuable products. A large portion of the world economy is directly or indirectly associated with the performance of catalysts. It is considered that about 30% of the gross domestic product in European economies and the processing of over 80% of all manufactured products somehow is associated with catalytic processes.\textsuperscript{186} Thus the development of catalyst is immensely important to make sure a global economic success and a sustainable society with fundamental aspects such as energy, food, and water.

In this regard, transition and noble metal-based catalysts are some of the most widely used ones due to the availability, cheaper price, stability, and the extraordinary catalytic properties of these metals.\textsuperscript{187} These catalysts are applied in a variety of chemical transformations such as hydrogenations,\textsuperscript{188} dehydrogenations,\textsuperscript{189} alkylation,\textsuperscript{190} amination,\textsuperscript{191} and coupling reactions.\textsuperscript{192} Recently, the application of catalysts for sustainable environmental remediation has garnered much attention.\textsuperscript{193} For example, the catalytic degradation of organic pollutants,\textsuperscript{194} catalytic reduction of nitrates\textsuperscript{195} and hexavalent chromium,\textsuperscript{196} catalytic dehydrohalogenation of halogenated compounds,\textsuperscript{197} and advanced oxidation processes (e.g. Fenton process)\textsuperscript{198} are some of the important types of catalytic reactions that are of special interests. Catalytic processes for environmental remediation have advantages over other methods. For example, the tunability in the reaction kinetics by tuning the morphology and the composition of the catalysts, the reusability, and cyclic stability. Therefore, the development of a self-supported and high-surface-area (e.g. porous metals) catalyst based on the facile method and cheap and readily available metals is highly desirable. In terms of the metal, the transition metals are of prime choice due to
their comparatively low price, availability, and intriguing catalytic properties. For example, porous Ni for the selective hydrogenation of carbonates into formic acid\textsuperscript{199} and the use of Raney\textsuperscript{®} Ni and Raney\textsuperscript{®} Co for the hydrogenation of the organic compounds are some of the catalysts to mention. The porosity increases the surface area and opens the active sites of metal, which are extremely important for the better performance of the catalysts. The porosity further facilitates elevated mass transport due to their higher surface areas, which is an important property for a catalyst to perform efficiently.\textsuperscript{200}

The commonly employed method for the preparation of self-supported porous metal includes the templated synthesis, where solid template such as alumina, pumice, sugar crystal, NaCl crystal, and polymer nanoparticles are used as the sacrificial materials.\textsuperscript{201} Morphology-wise, the template can be porous or solid in nature and the morphology of the final porous metal is dependent on the morphology of the template. If the template is porous (such as porous alumina or pumice), the metal salt precursor is impregnated into the pores of the template. Thermal or chemical reduction of the metal ion into the porous supports followed by the removal of the porous template make the porous metals. The porous metals prepared by this method usually have extraordinary higher specific surface area than the pure metal powders or foils. The synthesis of the metal sponges or porous metals by the templated method has some drawbacks such as the requirement of multiple steps of synthesis and the necessity of the washing off the templates after the synthesis. In addition to the templated synthesis, there are template-free synthesis methods where the porous metals could be synthesized by the direct chemical and electrochemical reduction of the metal slats.\textsuperscript{202} For example, Katla and colleagues reported the synthesis of porous gold, silver, platinum, and palladium nanosponges simply by the chemical reduction of the metal salts by sodium borohydride in aqueous solution.\textsuperscript{203} However, these
methods are limited to the synthesis of a small amount of materials and may not be adapted to the large scale synthesis for the practical applications. Therefore, the development of a method for the synthesis of porous metals that does not require a template and can prepare a large amount of catalyst (porous metals) by a simple procedure with the adaptability for industrial-scale production can be very lucrative in this area of research.

Herein, we report a facile method for the preparation of self-supporting and high-surface-area transition metal (e.g. cobalt, nickel, and copper) sponges by heating a paste of metal salt and sucrose. The synthesis requires heating in two steps. In the first step, a mixture of metal nitrate salt and sucrose was heated at ~180 °C in the presence of air for about 30 min to obtain a foam-like substance. In the second step, the foam-like substance was heated at 600 °C under argon to obtain the metal sponges. The utilization of sucrose as a soft sacrificial template for the preparation of metal sponges provides multiple advantages. For example, sucrose has reductive alcohol groups capable of reducing metal ions, which facilitates the nucleation and the growth of metallic clusters. Additionally, sucrose is a bio-derived organic compound having a cheaper price, sucrose is readily available, and it is not associated with any kind of chemical hazards. To the best of our knowledge, the method presented here is novel and extremely simple in the sense of not requiring any harmful solvents and chemicals while at the same time avoiding multiple steps. Therefore, it could be readily extended to the fabrication of macroporous frameworks of various other transition metals, metal oxides, and their hybrid nanocomposites. Additionally, the method could be adapted for the industrial-scale production of the high-surface-area metal, metal oxide porous structures and their nanocomposites for numerous applications. The as-prepared metal sponges have been applied for the catalytic reduction of anthropogenic organic pollutants viz. 4-NP, MO, and MB in water. The reduction of 4-NP to 4-aminophenol (4-AP) is important
with respect to the environmental remediation because of the toxic and carcinogenic nature of the 4-NP. Additionally, the 4-AP has usefulness as a photographic developer, corrosion inhibitor, precursor for the synthesis of paracetamol, etc. On the other hand, the catalytic reduction of MO and MB can be considered as an intriguing method towards their reductive degradation for the purpose of water treatment.

8.2. Materials and Methods

8.2.1. Materials

All the chemicals were used as received. Sucrose (>99.5%), Co(NO₃)₂.6H₂O (99.999% trace metals basis), Ni(NO₃)₂.6H₂O (99.999% trace metals basis), 4-nitrophenol (O₂NC₆H₄OH ≥ 99%), and sodium borohydride (NaBH₄ = 99%) were purchased from Sigma-Aldrich. Methyl Orange (C₁₄H₁₅N₃O₃S >98.0%) and methylene blue were obtained from TCI AMERICA and EMD Millipore Corporation, respectively. Milli-Q water (> 18.20 MΩ cm resistivity) was obtained from Milli-Q (Advantage A-10) water filter system.

8.2.2. Preparation of the Co, Ni, and Cu Sponges

All of the three metal sponges were prepared following the same experimental procedures. In detail, 400 mg sucrose and 4 mmol corresponding metal nitrate hydrate salt was mixed in a 100 mL glass beaker. The mixture was slowly melted on a hotplate heated at 120 °C. After heating and mixing on the hot plate for a while, a uniform viscous mixture was obtained. Then, the viscous mixture was immediately put in an oven, that was preheated to ~180 °C, for about 20 min. After this heating period a foam-like substance consisting of decomposed metal nitrate salts and sucrose was obtained. Since the decomposition of metal nitrate salts formed NO₂ and NOx gases, the furnace was placed in a fume hood with proper ventilation. Afterwards, the foam was annealed at 600 °C for 1 h in a tube furnace, under the flow of Argon, at a heating rate
of 10 °C/min. For cooling, normal cooling rate of the furnace was utilized. After the furnace was completely cooled to room temperature the metal sponges were taken out from the furnace, which was stored under ambient condition for the characterization and catalytic applications. For the synthesis of copper sponge, a minor modification was conducted. The mixture of sucrose and copper nitrate salt was first ground by a mortar and pestle and then the mixture was put into the oven at ~180 °C for the formation of foams.

**8.2.3. Catalytic Activity of the Co, Ni, and Cu Sponges**

The catalytic properties of the metal sponges were evaluated by the reduction of 4-nitrophenol (4-NP), methyl orange (MO), and methylene blue (MB) in water, Scheme 8.1. Excess sodium borohydride (NaBH₄) was used as the reducing agent. As NaBH₄ spontaneously decomposes in water, it is usually used in excess. The reduction of 4-NP, MB, and MO was monitored by the gradual decrease of their characteristic absorbance at 400, 464, and 665 nm, respectively with aid of UV-Visible spectrophotometer.

![Scheme 8.1: Metal sponges catalyzed reduction of 4-NP, MO, and MB in water.](image)

For the reduction of 4-NP, 10 mL of 4-NP aqueous solution (0.2 mM) was mixed with 10 mg of the metal sponges by 10 min of bath sonication in a glass scintillation vial. Afterwards, 1 mL of freshly prepared NaBH₄ aqueous solution (50 mg NaBH₄ in 1mL water) was added into
the reaction mixture and the reaction course was monitored by using the UV-Visible spectrophotometer.

For the catalytic reduction of MB and MO, same experimental procedure was followed except the concentration of MB and MO solution used was 15 ppm and 25 mg NaBH₄ in 1 mL water used as the reducing agent. The time dependent decolorization/reduction of MB and MO was monitored by their characteristic absorbance at 665 and 464 nm, respectively.

8.3. Results and Discussion

8.3.1. Mechanism of the Metal Sponges Synthesis

The Co, Ni, and Cu metal sponges were synthesized by heating a paste consisting of metal nitrate salt and sucrose (commonly known as table sugar), Scheme 8.2. The heating was performed in three steps. First, a mixture of the sucrose and metal nitrate salt was slowly melted on a hot plate at 120 °C to obtain a uniform viscous paste. Then, the paste was immediately heated at ~180 °C in a box furnace in the presence of air to obtain a foam-like composite. The foam-like composite consisted of partially carbonized sucrose and partially decomposed metal salts, Equation 1. When heated at this temperature, the nitrate salts started to decompose to generate different gases (Equation 1), which caused the sticky mixture to blow up in the form of foam-like composite during the heating process. The generation of the gases induced the porosity of the foam-like composite and eventually in the metal sponges.

\[
C_{12}H_{22}O_{11} (s) + Co(NO_3)_2.6H_2(s) \rightarrow C_{\text{foam}} + CoO (s) + N_2(g) + H_2O (g) + NO_x(g) \quad (1)
\]

\[
C_{\text{foam}} + CoO (s) \rightarrow Co (s) + CO_2(g) \quad (2)
\]
Finally, the foam-like composite was further heated at 600 °C in presence of argon to obtain the porous metal with the presence of a trace amount of carbon, Equation 2. When heated at 600 °C in argon atmosphere, the partially decomposed metal salt (metal oxide mostly) undergone carbothermal reduction forming porous metallic frameworks. In the carbothermal reduction, the carbon gets oxidized to form CO$_2$ gas while reducing metal oxides to zero valent metals. The generation of CO$_2$ gas may have caused additional porosity of the metallic sponges. Incomplete oxidation may have left behind trace of carbon in the porous metal catalysts.

The advantage of the method is that the experimental conditions is simple, fast, and adaptable to industrial scale. Moreover, the method does not require any expensive or hazardous reagents, experimental conditions, and post-synthesis modifications or treatments. The method could be adapted for the industrial-scale production of the high-surface area metal, metal oxide porous structures and their nanocomposites for numerous applications. We also assume that the method can be employed to prepare metals of different pore size and surface area by varying the experimental conditions and parameters such as metal precursor to the sucrose molar ratio, heating temperature and rate, etc.

**8.3.2. Characterization of the Metal Sponges**

The metal sponges were thoroughly characterized in terms of the morphology, crystallinity, specific surface area, and the thermal stability analyses. The SEM and TEM
images were taken to study the nanoscale morphology of the metal sponges. The elemental compositions of the metal sponges were qualitatively and quantitatively determined by the SEM-EDS analysis. The crystallinity and specific surface area and thermal stability of the metal sponges were investigated by the XRPD, BET surface area analysis, and the thermal gravimetric analysis.

8.3.2.1. SEM Images of the Metal Sponges

The SEM image analysis revealed the porous morphology of the as-synthesized cobalt, nickel, and copper sponges, Figure 8.1. For instance, the SEM image of the Co sponge (Figure. 1a,1b) demonstrated a self-supported three-dimensional interconnected network consisting of thin filaments. The filaments were seen to be nanoassembled and entangled together to form a 3 dimensional-interconnected structure. Further magnification revealed that the filaments were not uniform in terms of size and shape, Figure 8.1b. The filaments were often seen to have many branches indicating their formation during the foam formation and/or carbothermal reduction step of synthesis. A porous morphology with a high volume of void space was also observed from the SEM images. This void space and the porous structure induced the high specific surface area of the metal sponges, which is very important for the purpose of catalysis.

Similarly, the SEM images of the Ni and Cu sponges revealed the porous morphology, Figure 8.1c-f. The porosity and void spaces of the Ni and Cu sponges can be clearly seen in the SEM images. However, the Ni and Cu sponges were found to be less porous and filamentous as compared to the Co sponge. This indicate the less surface area of the Ni and Cu sponges compared to the Co sponge, which is further supported by the BET surface area analysis. Morphology-wise, the Ni and Cu sponges were seen to be more like two-dimensional sheet like structure with perforations.
Figure 8.1: Typical SEM images of the cobalt, nickel, and copper sponges with different magnifications.

8.3.2.2. EDX Spectrum of the Metal Sponges

The EDX spectrum was carried out to determine the qualitative and quantitative elemental analysis of the metal sponges, Figure 8.2. For example, Figure 1a demonstrates EDX peaks that are corresponding to cobalt, oxygen, and carbon. A high intensity of the cobalt peak indicates that the sponge is consisting of mostly cobalt metal, whereas; less intense peaks of carbon and oxygen indicates that there is some amount of carbon and oxygen in the cobalt sponge. Oxygen peak may have arisen from the protective oxide layer on the metal sponges. Likewise, the EDS spectrum of the nickel, and copper sponges showed a high abundance of nickel and copper with comparatively low abundance of carbon and oxygen. The strong cobalt, nickel, and copper peaks indicate that the sponges are mostly metallic in nature. However, the carbon and oxygen peaks indicate that the sponges have some percentage of carbon too. The crystalline metallic nature of the metal sponges was further analyzed by the XRPD analysis (discussed below).
Figure 8.2: EDX spectrum of the a) cobalt, b) nickel, and c) copper sponges.

The percent elemental composition of the metal sponges, obtained from the EDS analysis, is also shown in Figure 8.2. It was found that the Co sponge had about 3.5 % C, 0.6 % oxygen, and 95.8 % metallic cobalt. The Ni sponge was composed of about 4.8 % C, 0.1 % oxygen, and 95.1 % metallic nickel, whereas; the Cu sponge was composed of about 12.4 % C, 1.0 % oxygen, and 86.6 % metallic copper.

8.3.2.3. TEM Images of the Metal Sponges

The TEM image analysis was further performed to characterize the morphology of the metal sponges. Typical TEM images of the metal sponges with different magnifications are shown in Figure 8.3. From the TEM images it was found that the metal sponges had two different morphologies. For example, the Co sponge was seen have two different morphologies viz. the sponge-like and the particle-like morphologies that are shown in Figure 8.3a and 8.3b, respectively. Further analysis revealed that the sponge like morphology (Figure 8.3a) consisted of filamentous metal nanowire of varying dimensions and it was mostly observed where there was no carbon film associated.
We assume that the sponge-like morphology may have formed due to the fusion and aggregation of the smaller nanoparticles during the high-temperature heating steps of the synthesis. However, the particles like morphology was observed where there was carbon film, Figure 8.3b. The carbon film was originated from carbonization of sucrose and the metallic nanoparticles were seen to have varying particle sizes. We assume that the carbon film may have coated the metallic nanoparticles and prevented their further growth and aggregation leading to the sponge like morphology. Like the Co sponge, the Ni and Cu sponges demonstrated two types of morphologies. The average thickness of the Co, Ni, and Cu filaments in the sponges were calculated to be 56, 230, and 120 nm, respectively. The average size of the Co, Ni, and Cu nanoparticles in the sponges were calculated to be 9.5, 21, and 41 nm, respectively.

8.3.2.4. XRPD Pattern of the Metal Sponges

The X-Ray powder diffraction patterns were obtained to determine the crystalline properties of the metal sponges. The XRPD pattern of the Co sponge is shown in Figure 8.4a.
The diffraction peaks located at $2\theta = 44.1^\circ$, $51.5^\circ$ and $75.8^\circ$ can be attributed to the 111, 200, and 220 crystalline faces of the metallic cobalt.\(^{205}\) Moreover, this type of diffraction peaks corresponds to the face-centered-cube (fcc) crystalline phase of the metallic cobalt.\(^{206}\) The absence of any other undesired peaks indicate that the cobalt sponge is highly pure with crystalline metallic property and it has low or undetectable amount of cobalt oxides on it. This result is compatible with the EDS studies that were discussed above.

Similarly, the XRD pattern of the Ni and Cu sponges are shown in Figure 8.4b and 8.4c. The XRPD patterns of the Ni ($2\theta = 44.3^\circ$, $51.7^\circ$ and $76.1^\circ$) and Cu ($2\theta = 43.9^\circ$, $50.1^\circ$ and $73.8^\circ$) sponges correspond to the face-centered cube (fcc) phase of the crystal lattice.\(^{207}\) Additionally, the highly intense peaks of the Ni and Cu sponges without having additional peaks indicate their high purity, crystallinity, and the presence of no or undetectable amount of oxide layer on them.

![XRPD pattern of the a) cobalt, b) nickel, and c) copper sponges.](image)

Figure 8.4: XRPD pattern of the a) cobalt, b) nickel, and c) copper sponges.
The Debye-Scherrer’s Formula (Equation 3) was employed to determine the average crystallite size of the metal sponges. The XRPD peak corresponding to the (111) crystalline face was utilized in this regard.

\[ d = \frac{k \lambda}{\beta \cos(\theta)} \]  

(3)

where \( d \) is the crystallite size, \( k \) is the shape factor (0.9), \( \lambda \) is the wavelength of Cu K\( \alpha \) X-ray radiation (1.54 Å), \( \theta \) is the Bragg diffraction angle, and \( \beta \) is the full width at half maximum of the respective diffraction peak.

Employing the Debye-Scherrer formula, the average crystallite size of the Co, Ni, and Cu sponges where calculated to be 38.9, 25.6, and 27.3 nm, respectively. It could be observed that the crystallite sizes of the metal sponges, obtained from the XRPD analysis, were different from the average particle size measured by the TEM analysis. This because of the fact that the crystallite size is the size of a coherently diffracting domain of a crystal in a particle and it is not necessarily be same as the particle size determined from the TEM images.

8.3.2.5. Surface Area Analysis of the Metal Sponges

The specific surface area, pore size, and pore volume of the metal sponges were measured using nitrogen gas adsorption analysis. Table 1 shows the BET surface area, pore size, and pore volume of the metal sponges obtained from the N\(_2\) adsorption experiments. As can be seen from the BET analysis that the cobalt sponge had the greatest surface area ca. 17.3935 m\(^2\)/g, while copper has the least surface area of the three at 2.7280 m\(^2\)/g. The Ni sponge had the BET surface area of about 8.85 m\(^2\)/g.

The difference in surface can be correlated to the porosity and void spaces of the metal sponges, shown in the SEM images, Figure 8.1. correlates to the pore volume and pore diameter. Observing the SEM image, the difference in porosity is observable.
Table 8.1: BET surface area, pore volume, and pore diameter of the Co, Ni, and Cu sponges.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Average pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous Co</td>
<td>17.3935</td>
<td>0.006750</td>
<td>67.731</td>
</tr>
<tr>
<td>Porous Ni</td>
<td>8.8472</td>
<td>0.003236</td>
<td>74.118</td>
</tr>
<tr>
<td>Porous Cu</td>
<td>2.7280</td>
<td>0.004188</td>
<td>66.102</td>
</tr>
</tbody>
</table>

The SEM images revealed that the Co sponge had much higher porosity and void space compared to the Ni and Cu sponges and thereby the Co sponge demonstrated the highest BET surface area. The comparative pore volume and average pore diameter of the metal sponges are also given in Table 8.1.

8.3.2.6. Thermogravimetric Analysis of the Metal Sponges

In order to further quantify the percent amount of carbon in the metal sponges the thermal gravimetric analysis was carried out. As shown in Figure 8.5, the metal sponges lost less than 5% weight what heated to about 800 °C.

Figure 8.5: Thermal decomposition profile of the cobalt, nickel, and copper sponges. This indicated that percent weight of carbon in the metal sponges. From the results of this study it was found that the Co, Ni, and Cu sponges had only about 4.2, 1.7, and 1.8 weight percent carbon in the sponges.
8.4. Catalytic Activity of the Metal Sponges

The catalytic activity of the Co, Ni, and Cu sponges was studied by their ability to reduce 4-NP, MO, and MB in water with NaBH₄ at the unadjusted pH. The reduction of 4-NP, MO, and MB with NaBH₄ was monitored by the UV-Visible spectroscopy by the lowering of their characteristic absorption bands at 400, 464, and 665 nm, respectively. The reaction could be observed by the naked-eye too by the decolorization of the inherent color of the substrates. The experimental results of the catalytic reactions were analyzed by the pseudo-first-order rate equation, which is expressed as follows:

\[- \ln(C_t/C_0) = kt. \quad (4)\]

where \(C_0\) and \(C_t\) represent the initial and time-dependent concentrations of the substrates, respectively. The time-dependent percent reduction of 4-NP, MO, and MB was calculated by using the following equation:

\[
\text{Percent reduction} = \frac{C_0 - C_t}{C_0} \times 100\% = \frac{A_0 - A_t}{A_0} \times 100\% \quad (5)
\]

where \(A_0\) and \(A_t\) represent the the initial and time-dependent absorbance of 4-NP, MO and MB at 400, 464, and 665 nm, respectively.

To study the mechanism of the reaction, the Langmuir–Hinshelwood model was utilized. Langmuir–Hinshelwood model suggests that the reaction proceeds through the concomitant adsorption of the reducing agent and the substrate on the catalyst surfaces to complete the reaction.

8.4.1. Catalytic Reduction of 4-NP

The catalytic reduction of 4-NP by the metal sponges is shown in Figure 8.6. The reaction was studied upto 10 min period of time and within which the reaction proceeded to more than completion. The reaction was monitored by the time-dependent UV-Visible absorption
spectrum of 4-nitrophenolate. A representative UV-Visible absorption spectrum of 4-nitrophenolate is shown in Figure 8.6a. A gradual decrease in the absorbance at 400 nm is characteristic to the reduction of 4-NP; whereas the increase in the absorbance at 300 nm is characteristic to the formation of 4-AP, which could be clearly observed from Figure 6a.

Figure 8.6: a) Time-dependent UV-Visible spectrum of the 4-NP during the catalytic reduction on Cu sponge, b) Time-dependent percent reduction of 4-NP catalyzed by different metal sponges, and c) Pseudo-first order reaction kinetics of the catalytic reduction of 4-NP.

The time-dependent percent reduction of 4-NP by the metal sponges is shown in Figure 8.6b. It was found that the Cu sponge was the most active in doing the reduction, which was followed by the Co, and Ni sponges, respectively. Cu sponge took about 1 min to completely reduce the 4-NP into 4-AP, whereas Co and Ni sponges took about 6 min and 10 min to reduce more than 95 % of the 4-NP, respectively. In contrast, the reduction of 4-NP in the absence of catalyst showed negligible amount of reduction, which indicated the robustness of 4-NP to undergo reduction without the catalyst.

The kinetics of the catalytic reduction of 4-NP by the Co, Ni, and Cu sponges is shown in Figure 8.6c. The experimental results followed a linear relationship when \(-\ln(C_t/C_0)\) was plotted against reaction time (t) (Equation 4). This suggested that the reduction followed the pseudo-first order kinetics, which makes sense as NaBH₄ was used in a large excess in the reaction. The
apparent rate constant \((k_{\text{app}})\) of the reduction of 4-NP was obtained directly from the slope of the straight line of the \(-\ln(C_t/C_0)\) vs. time \((t)\) graph. For the Co, Ni, and Cu sponge the \(k_{\text{app}}\) was calculated to be \(1.31 \times 10^{-2} \text{ s}^{-1}\), \(9.10 \times 10^{-3} \text{ s}^{-1}\) and \(1.04 \times 10^{-1} \text{ s}^{-1}\), respectively. The \(k_{\text{app}}\) of the uncatalyzed reaction was calculated to be \(6.0 \times 10^{-5} \text{ s}^{-1}\), which is much slower than the Co, Ni, and Cu sponges catalyzed reactions.

The linear behavior of the \(-\ln(C_t/C_0)\) vs. time \((t)\) graph indicated that all the reaction followed the Langmuir–Hinshelwood (LH) model. This further suggested that the reduction of 4-NP happened through the simultaneous adsorption of the sodium borohydride and the 4-nitrophenolate on the surface of the metal sponges.

8.4.2. Catalytic Reduction of MO

The reduction of MO with NaBH\(_4\) using the metal sponges as catalysts is shown in Figure 8.7. The gradual decrease in absorbance at 464 nm and 275 nm corresponds to the reduction of MO and the gradual increase in absorbance at 245 nm corresponds to the formation of 4-aminobenzenesulfonate and 4-N,N-dimethylaminobenzene, Figure 8.7a. The time-dependent percent reduction of MO to 4-aminobenzenesulfonate and 4-N,N-dimethylaminobenzene by the metal sponges is shown in Figure 8.7b. The Cu sponge showed higher activity for the reduction of MO than the Co and Ni sponges. In the absence of catalyst, a minor reduction of MO was observed, however it is insignificant in comparison to the metal sponges catalyzed ones. The kinetics of MO reduction by the metal sponges is shown in Figure 8.7c demonstrating a linear relationship following the LH model, which also suggests a pseudo-first order kinetics as NaBH\(_4\) was used in excess. The \(k_{\text{app}}\) for the Co, Ni, and Cu sponge was calculated to be \(1.67 \times 10^{-2} \text{ s}^{-1}\), \(3.8 \times 10^{-3} \text{ s}^{-1}\) and \(1.58 \times 10^{-1} \text{ s}^{-1}\), respectively. The \(k_{\text{app}}\) of the uncatalyzed reaction was calculated to be \(2.0 \times 10^{-4} \text{ s}^{-1}\), which is many times slower than the metal sponge catalyzed reactions.
The kinetics of MO reduction by the metal sponges is shown in Figure 8.7c demonstrating a linear relationship following the LH model, which also suggests a pseudo-first order kinetics as NaBH₄ was used in excess. The $k_{\text{app}}$ for the Co, Ni, and Cu sponge was calculated to be $1.67 \times 10^{-2}$ s⁻¹, $3.8 \times 10^{-3}$ s⁻¹ and $1.58 \times 10^{-1}$ s⁻¹, respectively. The $k_{\text{app}}$ of the uncatalyzed reaction was calculated to be $2.0 \times 10^{-4}$ s⁻¹, which is many times slower than the metal sponge catalyzed reactions.

### 8.4.3. Catalytic Reduction of MB

The catalytic reduction of MB on the metal sponges is shown in Figure 8.8. Like 4-NP and MO, the reaction of MB was monitored by its reductive decolorization. During the catalysis, a gradual decrease in the characteristic absorbance of MB at 300 and 665 nm was observed, Figure 8a. The deep blue colored MB turned into a colorless reduced product viz. leucomethylene blue.

The time-dependent percent reduction of MB by different metal sponges is shown in Figure 8.8b. Out of the three sponges, it was found that the Cu sponge had the most catalytic activity, which was followed by the Co, and Ni sponges, respectively. The Cu sponge took about 1 min to completely reduce the MB, whereas Co and Ni sponges took about 6 min and 10 min to
reduce more than 95 % of the MB, respectively. When doing a control experiment without the catalyst, about 10 % reduction of MB was observed, which indicated that the metals sponges were responsible for its catalytic reduction.

Figure 8.8: a) Time-dependent UV-Visible spectrum of MB during the catalytic reduction on Ni sponge, b) Time-dependent percent reduction of MB catalyzed by different metal sponges, and c) Pseudo-first order kinetics of the catalytic MB reduction reactions.

The kinetics of the catalytic reduction of MB is shown in Figure 8.8c. The experimental results followed a linear relationship when $-\ln(C_t/C_0)$ was plotted against reaction time (t) (Equation 4). This suggested that the reduction followed the pseudo-first order kinetics and Langmuir–Hinshelwood (LH) model. For the Co, Ni, and Cu sponges the $k_{app}$ was calculated to be $1.13 \times 10^{-2}$ s$^{-1}$, $1.08 \times 10^{-2}$ s$^{-1}$, and $4.24 \times 10^{-2}$ s$^{-1}$, respectively. The $k_{app}$ of the uncatalyzed reaction was calculated to be $1.0 \times 10^{-4}$ s$^{-1}$, which indicates the robustness of MB to undergo reduction without the catalysts.

One may assume that the 4-NP, MO, and MB may have adsorbed during the catalysis. To avoid this confusion, control experiments were carried out where the mixture of substrates (4-NP, MO, and MB solutions) and the metal sponges were bath sonicated for 10 min. Afterwards, the percent adsorption was calculated. For all three metal sponges, less than 5 percent adsorption was obtained.
The catalytic activity of the metal sponges towards the reduction of 4-NP, MO, and MB is summarized in Table 2.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Substrate</th>
<th>Rate constant (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co sponge</td>
<td>4-NP</td>
<td>1.31×10⁻²</td>
</tr>
<tr>
<td>Ni sponge</td>
<td>4-NP</td>
<td>9.10×10⁻³</td>
</tr>
<tr>
<td>Cu sponge</td>
<td>4-NP</td>
<td>1.04×10⁻¹</td>
</tr>
<tr>
<td>No catalyst</td>
<td>4-NP</td>
<td>6.0×10⁻⁵</td>
</tr>
<tr>
<td>Co sponge</td>
<td>MO</td>
<td>1.67×10⁻²</td>
</tr>
<tr>
<td>Ni sponge</td>
<td>MO</td>
<td>3.8×10⁻³</td>
</tr>
<tr>
<td>Cu sponge</td>
<td>MO</td>
<td>1.58×10⁻¹</td>
</tr>
<tr>
<td>No catalyst</td>
<td>MO</td>
<td>2.0×10⁻⁴</td>
</tr>
<tr>
<td>Co sponge</td>
<td>MB</td>
<td>1.13×10⁻²</td>
</tr>
<tr>
<td>Ni sponge</td>
<td>MB</td>
<td>1.08×10⁻²</td>
</tr>
<tr>
<td>Cu sponge</td>
<td>MB</td>
<td>4.24×10⁻²</td>
</tr>
<tr>
<td>No catalyst</td>
<td>MB</td>
<td>1.0×10⁻⁴</td>
</tr>
</tbody>
</table>

### 8.4.4. Stability of the Metal Sponges

The cyclic stability of the metal sponges was determined by carrying out the catalytic reduction of 4-NP for five cycles, Figure 8.9. For Co, Ni, and Cu sponges, the percent conversion
of 4-NP to 4-AP was calculated after 6, 10, and 1 min of catalytic reduction, respectively. The percent conversion of 4-NP to 4-AP was calculated using the Equation 5. After every cycle, the catalyst was separated by either centrifugation (for copper sponge) or magnetic decantation (for Ni and Co sponges), washed with deionized water and was used for the following cycles.

![Cyclic stability of the metal sponges](image)

Figure 8.9: Cyclic stability of the metal sponges towards the reduction of 4-NP to 4-AP by a) Cobalt sponge, b) Nickel sponge, and c) Copper sponge.

Figure 8.9 shows that results for the cyclic stability of the metal sponges for the 4-NP reduction. It showed that all three metal sponges are highly stable towards reduction of 4-NP throughout the cycles. It showed that the Co and Cu sponges could effectively reduce more than 98 % of the 4-NP on every cycle of the reaction. Whereas, the Ni sponge reduced up to 96 % 4-NP on every cycle. No drop of catalytic activity was observed throughout the cycles. Therefore, from this study it could be concluded that the Co, Ni, and Cu sponges could potentially be used as a highly stable and efficient catalyst for the reduction of 4-NP in water.

8.5. Conclusion

In conclusion, we report a simple method for the preparation of porous cobalt, nickel, and copper sponges by heating a mixture of sucrose and metal nitrate salts. The metal sponges were found to have high porosity with particles and filamentous morphology. All three metal sponges demonstrated excellent catalytic activity for the reduction of 4-nitrophenol, methyl orange, and
methylene blue with NaBH$_4$ in water. Excellent cyclic stability of the sponges indicated their robustness and potential application in a variety of other catalytic reactions. Also, from the synthesis methodology perspective, the procedure demonstrated in this study could be adapted for the preparation of a wide variety of transition and mixed metal sponges for numerous applications.
Chapter 9: Sulfonated Resorcinol-formaldehyde Microspheres for the Adsorptive Removal of Organic Pollutants from Water

9.1. Introduction

A major portion of industrial pollutants from the manufacture of paper, plastic, leather, food, cosmetic, textile and pharmaceutical involve organic dyes in water. During the dyeing process, approximately 10 to 15% of the dyes are often dumped into the environment without treatment and end up in ponds, lakes, canals, rivers, and the sea. Dumping untreated water not only pollutes the usable water resources but also causes the loss of the dying material. Therefore, adsorbents with the ability of regeneration may allow for the re-use of the filter as well as the re-utilization of the dyes in the manufacturing industry, while promoting environmental conservation.

Many dye molecules are fairly stable and persistent in nature and thereby show resistance to natural degradation. Moreover, many of those molecules are toxic, carcinogenic, and mutagenic to humans and aquatic organisms. Organic dyes have high molar absorption coefficient and diminish sunlight penetration into water, which impairs photosynthesis and results in reduced amounts of dissolved oxygen in the water, thus impacts the whole ecosystems. Conventional methods used for the removal or degradation of organic pollutants in wastewater include adsorption, membrane filtration, ion exchange, chemical precipitation, photocatalytic degradation, advanced oxidation processes, electrochemical oxidation, chemical reduction, and the biological treatment. However, the adsorptive removal of dyes from contaminated water is simple to employ, less energy consuming, and does not cause secondary pollution. Therefore, adsorptive removal is one of the most widely employed methods for the removal of organic dyes from wastewater.
Currently, adsorbents for water treatment are mostly based on organic polymers, inorganic geopolymers or composites of both. Some examples are activated carbon,\textsuperscript{218} porous carbon,\textsuperscript{219} graphene and graphene derivatives,\textsuperscript{220} carbon nanotubes,\textsuperscript{221} zeolites,\textsuperscript{222} clay,\textsuperscript{223} mesoporous silica,\textsuperscript{224} layered double hydroxide,\textsuperscript{225} metal organic frameworks (MOF),\textsuperscript{226} nanostructured Fe\textsubscript{3}O\textsubscript{4},\textsuperscript{227} ZnO,\textsuperscript{228} and Ni/CoO.\textsuperscript{229} However, organic polymer-based adsorbents, including both the biopolymers and synthetic polymers, have drawn much attention because of their abundance, chemical and physical stability, ease of functionalization, biodegradability and renewability. For example, chitosan, starch, polystyrene, polyacrylic acid, and phenol-formaldehyde polymer have been used for the adsorptive removal of pollutants from wastewater.\textsuperscript{230,231,232} In most of these cases, the polymeric adsorbents are reported as bulk amorphous materials without a particular shape or morphology and may not have a high surface area.

Herein we report a simple method for the synthesis of sulfonated resorcinol-formaldehyde (RF-SO\textsubscript{3}H) microspheres with an average diameter of 200 to 350 nm that exhibit high adsorption capacity of organic dyes from water and have the ability to be regenerated. FTIR, TGA, SEM, EDS, and TEM characterized the RF-SO\textsubscript{3}H microspheres. MO and MB were used as the target pollutants because of their anionic and cationic charge, respectively. Moreover, MO and MB are widely used in industry, have carcinogenic and mutagenic properties, and are fairly resistant to natural degradation.

9.2. Materials and Methods

9.2.1. Materials

Resorcinol (ACS reagent, \textgeq 99.0 \%) and formaldehyde solution 37\% (stabilized with about 10\% methanol), ammonium hydroxide with 28.0 \% (w/w NH\textsubscript{3}) and
cetyltrimethylammonium bromide (95%), also known as CTAB were purchased from Sigma-Aldrich. Concentrated sulfuric acid (95-98 %) was purchased from BDH chemicals. Methyl orange and methylene blue were obtained from Amresco Inc. and EMD Millipore Corporation, respectively. Sand was purchased from J.T. Baker. Deionized water with a resistance of about 18.2 MΩ.cm at 25 °C was obtained from Milli-Q water purifier facilities from the lab.

9.2.2. Synthesis of RF-SO$_3$H Microspheres

In a 250 mL round-bottomed flask, 175 mg CTAB was dissolved in 75 mL of DI water. In this CTAB solution 2 mL of NH$_4$OH was added. A solution of 1.250 g of resorcinol in 85 mL of DI water, prepared separately, was added into the CTAB solution with vigorous stirring. The reaction mixture turned into a white suspension, which was bath sonicated for 10 min. Afterwards, 1.250 mL of the formaldehyde solution (37 %) was added into the above suspension with vigorous stirring. This mixture was refluxed for 24 hours with continuous stirring, which yielded reddish-brown precipitate of resorcinol-formaldehyde microspheres also referred to as RF-microspheres, Scheme 9.1. The product was vacuum filtered and washed with DI water and eventually dried in a vacuum oven at 60 °C for 12 hours. About 1.70 g (% Yield = 90) of the product was obtained.

In order to sulfonate, 20 mL of concentrated H$_2$SO$_4$ (95-98 %) was added to 1.6 g of the RF-microspheres in a 100 mL round bottomed flask. The mixture of H$_2$SO$_4$ and the RF-microspheres turned into a deep reddish-brown color, which was refluxed for 3 hours while stirring, Scheme 9.1. The reaction was cooled down to room temperature and 80 mL ice-cooled water was added with proper safety and precautions. The product was filtered by vacuum, washed with copious amount of deionized water to wash off any excess H$_2$SO$_4$.  

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Scheme 9.1: Synthesis of RF-SO$_3$H microspheres with possible structure.

The resulting sulfonated RF-microspheres (RF-SO$_3$H) were dried in vacuum oven at 60 °C for 12 hours, which was finely ground in a porcelain mortar and pestle. The amount of the RF-SO$_3$H microspheres was about 1 g.

9.2.3. Adsorption Experiments

All adsorption experiments were carried out under ambient conditions. The adsorption of MO was determined in two different pH conditions viz. 3.66 and 8.20. About 10 mg of the adsorbent was added into 40 mL of MO solutions with various concentrations viz. 50, 100, 200, 250, and 300 ppm. Then, the mixture was homogenized by bath sonication for 30 minutes. In order to achieve the equilibrium of adsorption, the mixtures were stirred for about 12 hours. Afterwards, 1 mL of the mixture was filtered through a 0.25 μm PTFE syringe filter to obtain a clear filtrate. The adsorption capacity was calculated from the difference between the initial and final dye concentrations, which was obtained from the UV-Visible measurements. The batch adsorption of MB was determined by following the same experimental procedure. However, 10 mg adsorbent was used for 20 mL MB solution. The adsorption capacity was calculated following the same method as MO.
The time-dependent adsorption capacity was obtained by adding 10 mg of the RF-SO$_3$H microspheres in 20 mL of 50 ppm dye solutions at pH 3.5 (both for the MO and MB). Bath sonication was carried out for first 5 min, which was followed by continuous stirring on magnetic stirrer. Afterwards, 1 mL of the mixture was withdrawn, and syringe filtered at different time interval for UV-Visible analysis.

The pH dependent experiments for the adsorption of MO was performed by dispersing 10 mg of the RF-SO$_3$H microspheres in 20 mL of 50 ppm MO solutions at different pH. The mixture was bath sonicated for about 30 min period of time. After bath sonication, 1 mL of the reaction mixture was syringe filtered for UV-Visible analysis. In case of MB adsorption, 10 mg of the RF-SO$_3$H microspheres was dispersed in 20 mL of 200 ppm MB solutions by bath sonication for about 30 min period of time. The mixture was left stirring for 12 hours and then the sample was taken. The pH of the solution was adjusted by using 1M NaOH or HCl and the amount of NaOH or HCl used was less than 50 μL to maintain the constant volume in every experiment.

Different desorbing solvents or mixture of solvents were added to 10 mg of the RF-SO$_3$H microspheres, which was pre-adsorbed with MO and MB. For the pre-adsorption of MO, 10 mg of the RF-SO$_3$H was added to 20 mL of 100 ppm MO solution at pH 3.66. The mixture was bath sonicated for 30 min. Afterwards, the mixture was stirred for 12 hours and then the RF-SO$_3$H microspheres adsorbed with MO was centrifuged out and dried. This dried adsorbent was added in 20 mL of desorbing solvents and the mixture was bath sonicated for 30 min to achieve efficient desorption. After 30 min of bath sonication, 1 mL sample was filtered through syringe filter to calculate the % desorption of MO. However, for the desorption of MB, different solvents were added to 10 mg of the RF-SO$_3$H microspheres, which was pre-adsorbed with MB from a 20...
mL of 20 ppm MB solution by 30 min of bath sonication and 12 hours of stirring. To achieve efficient desorption of MB, the solvents had 0.01M of dissolved NaOH.

The equilibrium adsorption capacities were calculated using the following equations:

\[
\text{Equilibrium adsorption capacity, } Q_e = \frac{C_0 - C_e}{m} \times V
\]  

(1)

The % dye adsorption was calculated using the following equation:

\[
\% \text{ adsorption} = \frac{C_0 - C_t}{C_0} = \frac{A_0 - A_t}{A_0} \times 100\%
\]  

(2)

where \(C_0\) and \(C_e\) represent the concentrations of the dyes (mg/L) at the beginning and at equilibrium, respectively. \(A_0\) and \(A_t\) represent the absorbance of the dyes at concentrations \(C_0\) and \(C_t\), respectively. \(m\) represents the mass of the adsorbent (g) and \(V\) represents the volume of dye solution (L).

A chromatographic column having the dimensions of I.D. x O.D x L = 20 x 26 x 457 mm was packed to about 17 cm with the mixture of RF-SO₃H microspheres and sand. In detail, 900 mg of the RF-SO₃H microspheres was homogeneously mixed with 90 g of sea sand by a ceramic mortar and pestle for few minutes of grinding. Afterwards, the column was filled by dry filling method. Cotton and coarse sea sand were used as the supports at the bottom and the top of the column, respectively.

The column was first washed with 100 mL of DI water. MO solution having a concentration of 20 ppm and pH 3.5 was fed into the column and allowed to pass under the gravity. The flow rate varied from 5 to 6.8 mL/min. In the continuous adsorption of MB, 20 ppm solution at pH 3.5 for the first cycle and pH 10.15 for the second cycle was fed into the column. Sample was taken in every 200 mL of the filtered water and UV-Visible spectrum was taken on it to measure the % dye adsorbed during the filtration.
As long as trace of dye was detected in the filtered water the filtration was discontinued and the regeneration of the column was carried out. For the regeneration of the column after the MO adsorption, a mixture of acetone and water (50:50) was used with or without the adjustment of pH. A total of about 500 mL solvent was fed into the column for the complete regeneration. However, for the regeneration after the MB adsorption, reagent alcohol or a mixture of reagent alcohol and water (99:1) with a concentration of 0.01 M NaOH was used. A total of about 500 mL of solvent was used for an efficient regeneration. After the regeneration the column was washed with 200 mL of DI water before running the next cycle of adsorption.

9.3. Results and Discussion

The RF-microspheres were synthesized in gram scale in the form of precipitate using resorcinol and formaldehyde monomers. The polymerization was catalyzed by NH₄OH while CTAB templated the microspheres formation via the hydrophobic effect in water. Resorcinol-formaldehyde based polymer is used in this study because of its high thermal and mechanical stability, ease of large-scale synthesis and functionalization to sulfonic acid group.

The RF-SO₃H microspheres showed high and fast adsorption capability towards MO and MB from deionized as well as tap water matrices. The adsorption of MO and MB from tap water was performed to investigate the interference of the coexisting ions on adsorption. It was found that the RF-SO₃H microspheres maintain similar adsorption capacity in tap water. Further, a packed column was made to investigate the potential practical applicability along with the stability and recyclability of the RF-SO₃H microspheres.
9.3.1. TEM Images of the RF and RF-SO$_3$H Microspheres

The TEM images of the RF and RF-SO$_3$H microspheres are shown in Figure 9.1. The RF-microspheres looked perfectly circular in shape with the size ranging from 360 to 700 nm in diameter, Figure 9.1a and 9.1d.

![TEM Images](image)

Figure 9.1: Typical TEM images of a) RF and b) RF-SO$_3$H microspheres. The size distributions of c) RF and d) RF-SO$_3$H microspheres. Scale bars: 1000 and 100 nm for Figure a and b, respectively.

Aggregations of some microspheres were also observed. TEM image also revealed the perfectly smooth surface of the RF-microspheres. In the contrary, the TEM images of RF-SO$_3$H microspheres revealed their spherical morphology with high surface roughness unlike the RF-microspheres, Figure 9.1b. The particle size also decreased, and more aggregations were observed compared. Similar result was observed in SEM analysis, which is discussed later.

9.3.2. SEM Images and EDX Spectrum of the RF and RF-SO$_3$H Microspheres

The typical SEM images of the RF and RF-SO$_3$H microspheres are shown in Figure 9.2. Like the TEM images, SEM images revealed that the RF-microspheres (Figure 9.2a) were perfectly spherical with smoother surfaces and are larger in size with less aggregations compared to the RF-SO$_3$H microspheres (Figure 9.2b). It is worthy to mention that surface roughness provides high surface area, which in turn increases the adsorption capacity of an adsorbent.$^{234}$
Figure 9.2. Typical SEM images of a) RF-microspheres and b) RF-SO$_3$H microspheres. c) EDX spectra of the RF-SO$_3$H microspheres.

The EDX analysis was carried out on the RF-SO$_3$H microspheres to investigate its elemental composition. The EDX spectrum revealed the presence of carbon, oxygen, and sulphur in the RF-SO$_3$H microspheres, Figure 9.2c. The presence of sulphur and oxygen indicated the presence of -SO$_3$H functional group in the RF-SO$_3$H microspheres.

**9.3.3. FTIR of the RF and RF-SO$_3$H Microspheres**

Fourier transform infrared (FTIR) spectroscopic analysis was conducted to investigate the presence of different functional groups, Figure 9.3. The FTIR spectra of the RF-microspheres showed the presence of O-H, aromatic and aliphatic C-H, aromatic ring C=C functional groups, which were confirmed by their stretching vibrations at 3226, 3076, 2924 and 1606 cm$^{-1}$, respectively.$^{235}$ The substituted aromatic ring and C-H rocking vibrations could be located at 1473 and 1380 cm$^{-1}$, respectively. Asymmetric bending vibration of $\sim$CH$_2$, the C-O stretching of ether, and the phenolic C–OH stretching could be assigned at $\sim$ 1430 cm$^{-1}$, 1045 cm$^{-1}$, and 1217 cm$^{-1}$, respectively. In addition, two peaks at $\sim$1171 cm$^{-1}$ and 1091 cm$^{-1}$ could be assigned to the bending vibrations of C–O. All of these characteristic vibrations in IR spectra indicate the presence of alcohol, benzene ring, methylene bridge and ether functional groups in the RF-microspheres, which is similar to other report.$^{236}$
The FTIR spectra of the RF-SO$_3$H microspheres showed additional peaks, which are attributed to the -SO$_3$H functional group, Figure 9.3b. New absorption peaks that originated at 1159, 1035, 807, and 620 cm$^{-1}$ are associated with the C–S and S=O functional groups. Peaks at 620 and 1035 cm$^{-1}$ originated from the stretching vibration of –SO$_3$H. The S=O stretching vibrations could be assigned at 1159 cm$^{-1}$. The FTIR spectrum combined with the EDS analysis eventually confirmed the presence of –SO$_3$H group in the RF-SO$_3$H microspheres.

### 9.3.4. TGA of the RF and RF-SO$_3$H Microspheres

Thermogravimetric analysis was carried out to investigate the thermal stability and the decomposition profile of the RF and RF-SO$_3$H microspheres. The TGA curve of the RF-microspheres (Figure 9.4a) showed the loss of free and absorbed water in the molecular space from 50 to 250 °C. Afterwards, the RF polymer started to decompose gradually with the increase in temperature. A complete decomposition of the RF-microspheres was observed at a temperature of about 675 °C and above.
Figure 9.4: TGA curves of a) RF-microspheres and b) RF-SO$_3$H microspheres.

In contrary, the RF-SO$_3$H microspheres showed some variation in the thermal decomposition, Figure 9.4b. The RF-SO$_3$H microspheres showed more resistance towards the thermal decomposition. The major decomposition of the polymer started from about 300 °C and a decomposition of about 96 % was observed at about 650 °C. The RF-SO$_3$H microspheres did not show complete decomposition even after 800 °C of heating. This may have happened because of the presence of impurities in it. The impurities may have come from the sulfonation as well as the grinding steps during the preparation of RF-SO$_3$H microspheres.

9.3.5. Adsorption Capacity of RF-SO$_3$H for MO and MB

The equilibrium adsorption capacity ($Q_e$) was calculated by using Equation 1. It was found that the $Q_e$ increased almost linearly up to the initial MO concentration of 300 ppm at pH 3.66 (Figure 9.5a). The $Q_e$ was calculated to be about 710 mg/g and 86 mg/g at an initial MO concentration of 300 ppm and pH 3.66 and 8.20, respectively. The % removal of MO decreased with the increase in initial MO concentration. About 74 % of the MO was adsorbed at an initial MO concentration of 300 ppm and at pH 3.66.
Unlike MO, the adsorption of MB was less pH dependent and the adsorption capacity at acidic and basic pH remained almost similar (Figure 9.5b). The $Q_e$ was measured to be 511 and 454 mg/g at the initial MB concentration of 400 ppm and pH of 8.25 and 4.25, respectively. The % removal of MB was found to be about 58 and 68 % at an initial concentration of 400 ppm and at pH 4.25 and 8.25, respectively.

The adsorption capacity of the RF-microspheres (before sulfonation) towards the MO and MB was also investigated under the same experimental conditions. It was found that the equilibrium adsorption capacity of the RF-microspheres was only about 25 mg/g and 66 mg/g towards MO and MB, respectively. This indicated that the higher adsorption capacity of the RF-SO$_3$H microspheres was because of the sulfonation of the RF-microspheres.

**9.3.6. Effect of pH on Adsorption**

The effect of pH on the adsorption of MO and MB is shown in Figure 9.6. It was found that the adsorption of MO was highly dependent on the pH of the solution. The MO adsorption capacity increased with the decrease in the solution pH, Figure 9.6a. This effect could be due to the protonation of the tertiary amine at acidic pH and the formation of ammonium ion that electrostatically binds to the sulfonate ion of the adsorbent.
In contrary, the adsorption trend of MB showed opposite trend, Figure 9.6b. The capacity of MB adsorption increased with the increase in pH of the solution. This opposite trend is possibly due to the acquirement of negative charge on the surface of the adsorbent (RF-SO$_3^-$), which caused the increase in the adsorption of MB due to an increase in the electrostatic attraction between the positively charged dye (MB) and the negatively charged adsorbent (RF-SO$_3^-$).

9.3.7. Adsorption Isotherms

Adsorption isotherm is the graphical representation of the amounts of dye adsorbed on a certain amount of adsorbent and the concentration of dyes at a constant temperature. Herein, two most commonly used adsorption isotherms viz. the Langmuir and the Freundlich isotherms were employed to understand the adsorption mechanism of MO and MB on the RF-SO$_3$H microspheres. The Langmuir adsorption isotherm model is based on the monolayer adsorption of adsorbate on the adsorbent. The linear form of the Langmuir adsorption isotherm model is expressed by the following equation.\(^\text{239}\)

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{K_l Q_m}$$

(3)
where $C_e$ represents the equilibrium concentrations of the dyes (mg/L), $Q_e$ and $Q_m$ represent the equilibrium and maximum dye adsorption capacity (mg/g) by the adsorbent, $K_L$ (L/mg) is the Langmuir constant, which is related to the affinity of the binding sites.

Freundlich adsorption isotherm model is based on both the monolayer and multilayer adsorptions of adsorbate on the adsorbent. The linear form of the Freundlich isotherm model is described as follows.\(^\text{240}\)

\[ \ln Q_e = \frac{1}{n} \ln C_e + \ln K_F \] (4)

where $K_F$ and $n$ are constants for a given adsorbate and adsorbent at a particular temperature.

The linear form of the Freundlich and Langmuir isotherm models (Equation 3 and 4) were applied on the experimental data. As shown in Figure 9.7, the adsorption of MO at pH 3.66 and 8.20 followed the Freundlich isotherm with the correlation coefficients ($R^2$) of 0.95377 and 0.95252, respectively. The linear form of Langmuir isotherm was also applied and the obtained correlation coefficients ($R^2$) values were 0.95852 and 0.68815, at pH 3.66 and 8.20, respectively. According to the Langmuir isotherm model, the maximum adsorption capacity of MO was calculated to be 833.13 mg/g and 65 mg/g at pH 3.66 and 8.20, respectively. It was observed that at pH 3.66 the adsorption of MO followed both the Langmuir and Freundlich isotherm models, which indicated that the MO adsorption on to the microspheres happened both by the monolayer and multilayer patterns. However, at pH 8.20, the adsorption followed the Langmuir isotherm much better than the Freundlich isotherm. This indicated that at pH 8.20, MO adsorbed mostly by monolayer pattern and because of this the adsorption capacity at pH 8.20 is much lower than the one at pH 8.20.
The adsorption of MB at pH 4.25 and 8.25 perfectly followed Langmuir isotherm model (Figure 9.7b) with the values correlation coefficients ($R^2$) of 0.99891 and 0.99541, respectively. This indicated that the adsorption of MB happened by monolayer type adsorption at both pH conditions and thereby, the adsorption capacity in both pH conditions was found almost similar. According to the Langmuir isotherm, the maximum adsorption capacity was calculated to be 454 and 500 mg/g at pH 4.25 and 8.25, respectively. The linear form of Freundlich isotherm model was also utilized, which showed the values of correlation coefficients ($R^2$) of 0.85137 and 0.79712, at pH 4.25 and 8.25, respectively. This further indicted the monolayer type adsorption of MB on the RF-SO$_3$H microspheres.

9.3.8. Adsorption Kinetics

The kinetics of the adsorption was evaluated by two most commonly used kinetic models viz. the pseudo-second-order and pseudo-first-order. The linear form of the pseudo-second-order model is expressed by the following equation.

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e}$$  \hspace{1cm} (5)

Linear form of the pseudo-first-order model is expressed by the following equation.
where $Q_e$ and $Q_t$ represent the adsorption capacities (mg/g) at equilibrium and at time $t$ (min); $K_1$ (1/min) and $K_2$ [g/(mg min)] are the rate constants of adsorption of the pseudo-first-order and pseudo-second-order kinetic models, respectively.

Figure 9.8a represents the time-dependent adsorption of MO and MB by the RF-SO$_3$H microspheres at the pH 3.5 for both the dyes. This shows the fast adsorption ability of the microspheres and it was found that about 99 % of the MB was adsorbed within 40 min, whereas for MO it was about 92 %. Figure 9.8b shows the linear form of the Pseudo-second-order kinetic model, which was obtained by using Equation 5. For both the MO and MB adsorptions, the relationship between the $t/Q_t$ vs. time was found to be linear having the values of correlation coefficients ($R^2$) equals 1.

This suggested that the adsorption of both the MO and MB perfectly followed the Pseudo-second-order kinetic model, which is quite similar to the previously reported results.$^{241}$ The perfect fit of the Pseudo-second-order kinetic model further suggested that the adsorption of both the dyes was favored by chemisorption. The values of Pseudo-second-order rate constants of adsorption were calculated as 1.2352 and 0.6757 [g/(mg min)] for MO and MB, respectively.
However the relationship between \( \log(Q_e - Q_t) \) vs. time (Equation 6) was found to be non-linear for both the MO and MB adsorptions (data not shown here). The correlation coefficients \( (R^2) \) of the trendlines were found to be 0.84167 and 0.47766 for MO and MB, respectively. This suggested that the adsorption kinetics of MO and MB poorly followed the Pseudo-first-order kinetic model.

**9.3.9. Desorption Studies**

The regeneration ability and reusability of the adsorbents is an important and desired property in the purpose of practical applications. Different solvents or mixture of solvents were employed for the efficient desorption of dyes from the RF-SO$_3$H microspheres, Figure 9.9. It was found that the mixture of acetone and water (50:50) desorbed about 45 % MO from the RF-SO$_3$H microspheres, Figure 9.9a.

![Figure 9.9: Effect of solvents to the desorption of a) MO and b) MB from the RF-SO$_3$H microspheres. Here, A = acetone, W = water, RA = reagent alcohol, EA = ethyl acetate, and MeOH = methanol.](image)

In order to achieve an efficient desorption of MB, different solvents were used with dissolved NaOH having concentration of 0.01 M. It was found that the mixture of reagent alcohol and water (99:1) effectively desorbed up to 70 % MB from the RF-SO$_3$H microspheres. None of the solvent without NaOH was found efficient to desorb MB.
9.3.10. Adsorption of MB from Tap Water

The adsorption capacity of the RF-SO$_3$H microspheres towards MB from the tap water is shown in Figure 10. It was found that the adsorption capacity was not influenced by the coexisting ions present in tap water. The maximum adsorption capacity towards MB was found to be 586 mg/g with 76 % removal efficiency at an initial dye concentration of 400 ppm and pH 6. This further suggests that the RF-SO$_3$H microspheres could potentially be used for the removal of cationic pollutants from water for practical applications.

![Figure 9.10: Adsorption capacity of RF-SO$_3$H microspheres for MB from tap water.](image)

9.3.11. Packed Column for Continuous Adsorption of MB

In order to investigate the potential practical applications and the stability of the RF-SO$_3$H microspheres, a glass column was packed with a mixture of RF-SO$_3$H microspheres and sand. The ability of the adsorbent column for the continuous adsorption of MB was investigated at pH 3.5 for the 1$^{\text{st}}$ cycle and at pH 10.15 for the 2$^{\text{nd}}$ cycle, respectively (Figure 9.11).

Acidic and basic pH were chosen to investigate the pH-dependent adsorption efficacy of the column. On the 1$^{\text{st}}$ cycle, the column filtered up to 10.2 L of MB solution with the removal efficiency of 98 % at the end. Whereas, on the 2$^{\text{nd}}$ cycle, it filtered up to 17 L MB solution with 98 % removal efficiency at the end. Before the 2$^{\text{nd}}$ cycle of adsorption, the adsorbent column was
regenerated with a mixture of reagent alcohol and water (99:1) with a NaOH concentration of 0.01M.

Figure 9.11: Percent MB adsorption vs. the volume of MB solution filtered through the adsorbent column. Inset: UV-Visible of the feed MB solution and the eluent.

9.4. Conclusion

A modified method for the preparation of sulfonated resorcinol-formaldehyde (RF-SO$_3$H) microspheres is reported. The ability of the RF-SO$_3$H to adsorb organic dyes such as methyl orange (MO) and methylene blue (MB) from water is reported. The equilibrium adsorption capacity of the RF-SO$_3$H microspheres was measured to be 710 mg/g and 511 mg/g for MO and MB, respectively. The RF-SO$_3$H microspheres were found to be equally effective in the adsorption of these dyes from tap water matrix. The effect of pH on the adsorption of MO and MB was studied and it was found that the adsorption capacity increased for MO in acidic pH and vice versa for MB. A packed glass column was prepared to demonstrate the continuous adsorption of MB under flow conditions.
Chapter 10: Conclusions and Future Directions

Novel and facile methods for the synthesis of gold, silver, platinum, and palladium nanoparticles were developed in this study. The nanoparticles were synthesized by employing sodium squarate and sodium rhodizonate as the bifunctional reducing and stabilizing agents. While sodium squarate could prepare only gold nanoparticles in water, sodium rhodizonate could prepare gold, silver, platinum, and palladium nanoparticles and their alloy nanoparticles in water. The specialty of these nanoparticles are I) they have catalytically active surfaces unlike the alkanethiol stabilized nanoparticles, II) they have ligand exchangeable surfaces and thereby the nanoparticles can bind to solid supports (e.g. cellulose fibers) without any modification of the supports or the nanoparticles. The catalytic reduction of organic pollutants viz. methyl orange, methylene blue, 4-nitrophenol, and inorganic pollutants viz. Cr(VI) was performed on these nanoparticles in the presence of sodium borohydride, formic acid, and hydrogen gas. While sodium borohydride is used ubiquitously, the use of formic acid and hydrogen gas is intriguing and highly beneficial in terms of water treatment as they do not cause any secondary pollution in water.

The squarate stabilized gold nanoparticles can potentially be utilized for photothermal therapy as they have self-aggregation properties in the presence of metal salts. We assume that the ionic concentration in the cell could aggregate the gold nanoparticles and would redshift the absorption maxima to the near/far infrared region. This infrared absorption ability of the aggregated nanoparticles could induce photothermal properties allowing applicability in photothermal therapy.

This study reported the preparation of the cellulose fibers-supported noble metal nanoparticles and their catalytic properties. The cellulose fibers-supported noble metal
nanoparticles can be carbonized to prepare carbon-supported nanoparticles, which could potentially be utilized for a number of catalytic and electrocatalytic reactions. The carbon-supported platinum and palladium nanoparticles could be interesting catalysts for the reduction of nitrates and oxyanions in water.

The photocatalysts such as zinc oxide nanoparticles and titanium dioxide-supported gold nanoparticles catalysts have shown the ability to generate reactive oxygen species and the degradation of organic pollutants in water under the solar light and ultraviolet light irradiation. The in situ generated reactive oxygen species could be utilized for the disinfection of water in resource-limited areas. Also, the sucrose mediated synthesis of zinc oxide nanoparticles can be extended to the synthesis of a wide variety of metal oxides and mixed metal oxides for a number of applications. The method for the preparation of porous metals can also be extended to prepare a wide spectrum of pure and mixed metal sponges for a number of catalytic applications.

The sulfonated resorcinol-formaldehyde microspheres demonstrated high adsorption capacity for methyl orange and methylene blue in water. The adsorbents can potentially be used for the removal of heavy metals and other organic pollutants from water. Also, the microspheres can be carbonized to prepare high surface area carbon nanoparticles that may provide exotic adsorptive and photothermal properties
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Appendix

Characterization Techniques

UV-Vis spectra were obtained by using Agilent Cary 50 Conc UV-Visible Spectrophotometer. Quartz cuvette of 10 mm path length was used as the sample holder for the UV-Vis studies. Transmission electron microscopy (TEM) and HRTEM experiments were performed using a Hitachi H-7650 and JEOL JEM3200FS Microscope. An acceleration voltage of 80 kV and 300 kV was used for the Hitachi H-7650 and JEOL JEM3200FS Microscope, respectively. Carbon filmed copper grids with 200 mesh (Electron microscopy sciences) were used for TEM imaging. For the TEM imaging, sample was drop casted onto the grid and air dried before imaging. Scanning Electron Microscopy (SEM) image and the Energy Dispersive X-ray (EDX) experiments were carried out using a Hitachi S-3400N Type II scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer. Carbon tape or mica surface was used as the substrate for the SEM imaging. Powder X-ray diffraction (XRPD) spectrum was obtained by using Bruker D8 Discover X-ray diffractometer with Cu Kα radiation (\(\lambda = 0.15418 \text{ nm}\)). Micromeritics ASAP 2020 Surface Area and Porosity Analyzer was used for the nitrogen adsorption isotherms and to obtain the specific surface area of the nZnO. The Raman analysis was carried out by using Kaiser Optical System RXN1 equipped with Invictus 785 nm diode laser and Andor back illuminated CCD detector with 80 mW laser power for 20 seconds under 40X objective. The Raman intensities were calculated after baseline correction with GRAMS/AI (7.00) software. Dynamic light scattering (DLS) was carried out by using Zetasizer Nano ZS90 with quartz cuvette of 10 mm path length. Zeta potential measurement was carried out using Zetasizer Nano ZS90 with Disposable folded capillary cell. Thermo ScientificTM Nicolet iS5 FTIR Spectrometer with attenuated total reflection (ATR) sampling
technique was used for FTIR spectroscopy. Thermogravimetric analysis was performed by using a Simultaneous Thermal Analysis Instrument (Model DSC/TGA Q600) under nitrogen atmosphere, scanning at 10 °C/min from 25 °C to 800 °C. Raman spectra were recorded on a micro-Raman LabRAM HR (Horiba Jobin Yvon, NJ, USA), equipped with a He-Ne laser (632.8 nm) was used as the excitation source. XPS data were collected using a Thermo Scientific Escalab 250Xi spectrometer with a six-channel detector. Photoelectrons were generated with a monochromatic Al Ka (1486.68eV) X-ray source.

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Vita

Md Tariqul Islam was born and raised in Gazipur, Bangladesh. He earned his Bachelor of Science with Honors in Applied Chemistry and Chemical Engineering from the University of Dhaka, Bangladesh in 2011. He joined the University of Texas at El Paso for his Doctoral Degree in Chemistry in Fall 2012. His research interests lie in the synthesis of advanced functional nanomaterials and their applications in sustainable water treatment, catalysis, and energy storage systems. Md Tariqul Islam has published 27 scientific research articles in peer-reviewed journals thus far. He is currently working on more than 5 manuscripts that are under review/preparation. He serves as an invited reviewer for more than ten renowned scientific journals. He also serves as a judge in scientific symposiums, presentations, and conferences. He also loves to volunteer as a science demonstrator in outreach activities.

Md Tariqul Islam was the recipient of a number of rewards, grants, and honors including State of Texas Public Education Grant for International Students, NSF-PREM Publication Award, Outstanding Panel Presentation Award at UTEP Graduate Research Expo, and the Bangladesh-Sweden Trust Fund Travel Grant.

When not in the lab, Md Tariqul Islam enjoys watching movies, traveling places, catching fish, playing cricket, and cheering for the Bangladesh Cricket Team.

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