T. R.
VAN YUZUNCU YIL UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCE
DEPARTMENT OF MECHANICAL ENGINEERING

APPLICATION OF ZERO VALENT NANO IRON ON BACTERIAL GROWTH

M.Sc.THESIS

PREPARED BY: Farooq Omar MOHAMMED
SUPERVISOR: Assist. Prof. Dr. Halil Ibrahim YAVUZ

VAN-2019

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ACCEPTANCE and APPROVAL PAGE

This thesis entitled "**APPLICATION OF ZERO VALENT NANO IRON ON BACTERIAL GROWTH**" presented by Farooq Omar Mohammed under supervision of Assist. Prof. Dr. Halil Ibrahim YAVUZ in the department of Mechanical Engineering has been accepted as a M. Sc. thesis according to Legislations of Graduate Higher Education on 06/08/2019 with unanimity / majority of votes members of jury.

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Farooq Omar Mohammed

ABSTRACT

APPLICATION OF ZERO VALENT NANO IRON ON BACTERIAL GROWTH

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M. Sc. Thesis, Department of Mechanical Engineering
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In This thesis, the aim of this study was to determine the positive and negative effects of the development of nanoparticle zero-valent iron (Fe) on bacteria. Zero-valued nano-iron particles were synthesized by reduction method with calm average distribution around 45 nm to provide bacterial permeability. Yoghurt bacteria Lactobacillus Bulgaricus and Streptococcus thermophilus isolates were grown in solid medium in order to calculate the effect rate of nanoparticles on the development. As a result of the study, it was observed that the maximum value was reached at the end of the incubation period and the growth rate of the control group samples. It is seen that 5 ppm amount is the fastest development among the other groups in which nanoparticle is added. However, it was determined that the media ratio above 5ppm prevents bacterial growth.

Keywords: Biomaterials, Nanoirons, Nanomaterials, Nanotechnologys.

ÖZET

APPLICATION OF ZERO VALENT NANO IRON ON BACTERIAL GROWTH

MOHAMMED, Farooq Omar
Yüksek Lisans Tezi, Makine Mühendisliği Anabilim Dalı
Tez Danışmanı: Dr. Öğrt. Üyesi Halil İbrahim YAVUZ
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Bu tez çalışmasında çalışmada nanopartikül halinde sıfır değerlikli demir (Fe)’in bakteriler üzerine gelişimlerinin etkilerinin pozitif-negatif etkilerinin belirlenmesi amaçlanmıştır. sifir degerlikli nano demir parcaciklari bakteri gecirgenligini saglamak amacli olarak 45 nm civarinda sakin ortalama dagilim ile indirgenme yontemi ile sentezlenmistir. yogurt bakterileri Lactobacillus Bulgaricus ve Streptococcus thermophilus izolatlarının gelişimlerine nanopartiküllerin etki oranının hesaplanabilmesi amacıyla katı besiyerinde ekimleriyapilmiştır. Çalışma sonucunda kontrol grubu örnekleri hem gelişim hızı hem de inkübasyon süresi sonunda maksimum değerine ulaşıldığı görülmüştür. Nanopartikül eklemesi yapılan diğer gruplar içerisinde en hızlı gelişimin 5 ppm miktarı olduğu görülmektedir. Ancak besiyeri oranının 5ppm ustunde olmasının bakteriyel gelişimi engellediği tespit edilmiştir.

Anahtar kelimeler: Biyomalzeme, Nanodemir, Nanomalzeme, Nanoteknoloji.

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To begin with I would like to thank “Allah” (Praise be to him) for implanting the soul of endurance and faith in myself to complete this study and showing me the way to through.

My deepest gratitude and sincere thanks to my supervisors Assoc. Prof. Dr. Halil Ibrahim YAVUZ for his guidance and support throughout the research. I highly appreciate his high scientific supervision and infinite patience in following up the research.

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Farooq Omar MOHAMMED

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SYMBOLS AND ABBREVIATIONS

Some symbols and abbreviations used in this study are presented below, along with descriptions.

Symbols	**Description**
µm	Micrometer
n	Refractive index
kg	Kilogram
G	Gram
L	Liter
S	Sulfur
Pb	Lead
S_8	Octal-sulfur

Abbreviation	**Description**
XRD	Crystal Structure
SEM	crystal shape and size
VSM	Magnetic properties
EDDHA	Sodium Ferric EDDHA
Co	Cobalt
B	Sodium Borohydride
IRON (II)	Sulfate Heptahydrate
IRON (III)	Chloride Hexahydrate
NPs	Nanoparticles
NCs	Nanoclusters

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1. INTRODUCTION

Conventional Fe–Co alloys are important soft magnetic materials that have been widely and commercially used in industry. Nanostructured (NS) materials exhibit superior magnetic properties, such as higher permeability and lower coercivity compared with their polycrystalline counterparts due to a single domain configuration (Lesile, 1996). NS materials are fabricated through various kinds of method including vapor quenching, inert gas condensation, electro-deposition, mechanical alloying etc. Among these methods, mechanical alloying (MA) is the method of choice in terms of ease of operation and its ability to produce large amounts of NS powders in a short time (Fecht, 1995). With serious energy consumption, the development of a new energy system is becoming the focus of extensive studies. Hydrogen as a new energy carrier is believed to be an ideal energy source, because its combustion only produces water. The past decades have witnessed numerous efforts in developing hydrogen energy to meet growing global energy demands (Dharmarathne, 2012). Accordingly, renewed interest in hydrogen generation from chemical hydrides is an important component of multifaceted strategy (Zhou, 2012). The most distinctive feature of nanoscale materials is the size dependence often displayed by these properties. Size dependence is usually quantitative: the optical response, the catalytic reactivity, or the magnetic moment exhibit variations that vary with the nanoparticle size, smoothly at first in the so-called scalable regime, then nonmonotonically when the particle becomes small enough. Under some circumstances, the dependence is more qualitative and can arise from some changes in chemical bonding. Besides its size, the shape of a nanoparticle can also affect its property, opening interesting avenues of research, e.g. in the design of photoelectronic devices such as nanoantennas(Florent, 2013).

Mixing several metals together provides another opportunity for tuning a physical or chemical property at the nanoscale. This ambition is rooted in the achievements of early metallurgists from the Bronze age who found several millennia ago that the strength and durability of their materials could be enhanced by mixing different metals. Metal alloys at the nanoscale are a prime example of nanoalloys in which the relative composition is a new variable to be varied, expectantly having a profound influence on the desired property along with size itself. However, it should be made clear here that nanoalloys do not only refer to mixed, nanoscale alloys. For sake of a general definition (and perhaps by lack of a more rigorous term), nanoalloys are currently understood as multimetallic nanoparticles, with no assumption about the chemical order within them. Fully phase-separated particles, such as core/shell compounds, represent an important class of nanoalloys, among other possible arrangements (Yang, 2014). Adding the dimension of composition to the existing roles of size and structure entails a significant complexity, which could only be addressed after research on pure metal nanoparticles had reached some level of maturity. Tackling this complexity by experimental or theoretical means requires dedicated tools that build upon methods available for monometallic systems, as well as methods more specific to the presence of several metals. One first objective of the present book is to provide a broad introduction to such methods, either for synthesis purposes or for fundamental investigations. Beyond fundamentals, and although a relatively young discipline, nanoalloys have also started to receive a considerable attention for their potential interest in several applied fields, for energy production, magnetic storage, or biomedicine. These topics are closely related to specific chemical or physical issues but deserved dissertations of their own(Florent, 2013).

The last decade has seen a booming development of nanosciences, which now stand as their own field across physics, material sciences, chemistry and medicine. Nanoscale objects include organic particles such as fullerenes, carbon nanotubes or even graphene, semiconducting devices such as quantum dots for electronic or photonic applications, and even hydrogen-bonded compounds like water droplets for their relevance as nucleation seeds in atmospheric processes. The interplay between atomic and electronic structures makes metal nanoparticles highly versatile, already with many uses as catalysts, magnetic devices or optical probes. Although dating back to the mid nineteenth century and their discovery by Faraday, nanoparticles have become a major scientific topic when researchers gained the ability to synthesize them and, more importantly, to observe and understand their fascinating properties(Aiken, 1999).

Nanotechnology is hailed as having the potential to increase the efficiency of energy consumption, help clean the environment, and solve major health problems. It is said to be able to massively increase manufacturing production at significantly reduced costs. Products of nanotechnology will be smaller, cheaper, lighter yet more functional and require less energy and fewer raw materials to manufacture, claim nanotech advocates (Yang, 2014).

2. LITERATURE REVIEW

2.1. Introduction

Nanotechnology is science, engineering, and technology conducted at the nanoscale, which is about 1 to 100 nanometers. Nanoscience and nanotechnology are the study and application of extremely small things and can be used across all the other science fields, such as chemistry, biology, physics, materials science, and engineering. Nanotechnology is not just a new field of science and engineering, but a new way of looking at and studying (Feynman, 1961). Nanotechnology is hailed as having the potential to increase the efficiency of energy consumption, help clean the environment, and solve major health problems. It is said to be able to massively increase manufacturing production at significantly reduced costs. Products of nanotechnology will be smaller, cheaper, lighter yet more functional and require less energy and fewer raw materials to manufacture, claim nanotech advocates (Burda, 2005).

2.2. History Nanotechnology and Nano Alloys

The ideas and concepts behind nanoscience and nanotechnology started with a talk entitled “*There’s Plenty of Room at the Bottom” by* physicist Richard Feynman at an American Physical Society meeting at the California Institute of Technology (CalTech) on December 29, 1959, long before the term nanotechnology was used. In his talk, Feynman described a process in which scientists would be able to manipulate and control individual atoms and molecules. Over a decade later, in his explorations of ultra-precision machining, Professor Norio Taniguchi coined the term nanotechnology. It wasn't until 1981, with the development of the scanning tunneling microscope that could "see" individual atoms, that modern nanotechnology began (Tsung, 2009).

In June 1999, Richard Smalley, Nobel laureate in chemistry, addressed the US House Committee on Science on the benefits of nanotechnology. "The impact of nanotechnology on the health, wealth, and lives of people," he said, "will be at least the equivalent of the combined influences of microelectronics, medical imaging, computeraided engineering and man-made polymers developed in this century" (Feldheim, 2002).

2.3. Fundamental Concepts in Nanoscience and Nanotechnology

It’s hard to imagine just how small nanotechnology is. One nanometer is a billionth of a meter, or 10^{-9} of a meter. Here are a few illustrative examples: There are 25,400,000 nanometers in an inch, A sheet of newspaper is about 100,000 nanometers thick, On a comparative scale, if a marble were a nanometer, then one meter would be the size of the Earth Nanoscience and nanotechnology involve the ability to see and to control individual atoms and molecules. Everything on Earth is made up of atoms the food we eat, the clothes we wear, the buildings and houses we live in, and our own bodies.

But something as small as an atom is impossible to see with the naked eye. In fact, it’s impossible to see with the microscopes typically used in a high school science classes. The microscopes needed to see things at the nanoscale were invented relatively recently about 30 years ago. Once scientists had the right tools, such as the scanning tunneling microscope (STM) and the atomic force microscope (AFM), the age of nanotechnology was born. Although modern nanoscience and nanotechnology are quite new, nanoscale materials were used for centuries. Alternate-sized gold and silver particles created colors in the stained glass windows of medieval churches hundreds of years ago. The artists back then just didn’t know that the process they used to create these beautiful works of art actually led to changes in the composition of the materials they were working with.

Today's scientists and engineers are finding a wide variety of ways to deliberately make materials at the nanoscale to take advantage of their enhanced properties such as higher strength, lighter weight, increased control of light spectrum, and greater chemical reactivity than their larger-scale counterparts (Feynman, 1961).

2.4. Colloidal Transition Metal Nanoclusters

Transition metal nanoclusters are isolable particles in size about 1–10 nm (10–100 Å) (Aiken, 1996). They have generated intense interest over the past decade due to their unique properties, derived in part from the fact that these particles and their properties lie somewhere between those of bulk and single-particle species (Pool, 1990). A particle should have the following criteria to be defined as a nanocluster (Feldheim, 2002) the size of the particle is to be smaller than 10 nm with a narrow size distribution, σ≤15%; b) its synthesis should be reproducible; c) it has to be compositionally welldefined, isolable, and redissolvable.

The main reason to make metal nanoclusters scientifically so interesting is their unique properties which do not follow the classical physical laws as all bulk materials do (Schmid, 1994). This phenomenon can be simply as seen in Figure (2.1.) depending on the fact that the number of surface atoms becomes larger as the particle size decreases. Additionally, the surface atoms in metal nanoclusters do not necessarily order themselves in the same way that those in the bulk do (Pool, 1990). Furthermore, owing to the quantum size effect, confinement of electrons to small regions of space in one, two, or three dimensions, the electrons in nanoclusters are confined to spaces that can be as small as a few atom-widths across (Schmid, 1999).

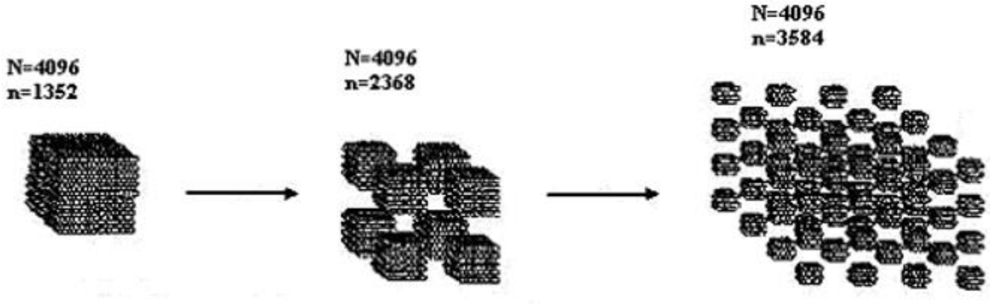

Figure 2.1. The effect of particle size on the ratio of the number of surface atoms to the total number of atoms. N= the total number atoms; n= the number of surface atoms.

When a metal particle with bulk properties is reduced to the nanometer size scale, the density of states in the valence and the conduction band decreases to such an extent that the quasi-continuous density of states is replaced by a discrete energy level structure and the electronic properties change dramatically as shown in Figure (1.2.)

Such a dramatic change in the electronic properties of a metal in nanometer size results in many different physical and chemical properties which can be exemplified by gold case. If bulk gold is reduced to ca. 50 nm in solution, the yellow color spontaneously disappears and turns to blue, further reduction results in purple and finally red color. Additionally, the bulk gold is catalytically inactive but there are many studies on gold nanoparticle catalyzed reactions (Campbell, 2004).

However, transition metal nanoclusters are only kinetically stable and thermodynamically unstable in solution to agglomerate into bulk metal. Therefore, special precautions have to be taken to avoid their aggregation or precipitation during the preparation of such nanoclusters in solution (Aiken, 1996). Consequently, considerable effort has been focused on the stabilization of transition metal nanoclusters in solution which is crucial if practical applications of metal nanoclusters are to be realized. Therefore, general and critical aspects on the stabilization of transition metal nanoclusters should be mentioned before beginning a description of synthetic methods for the preparation of them.

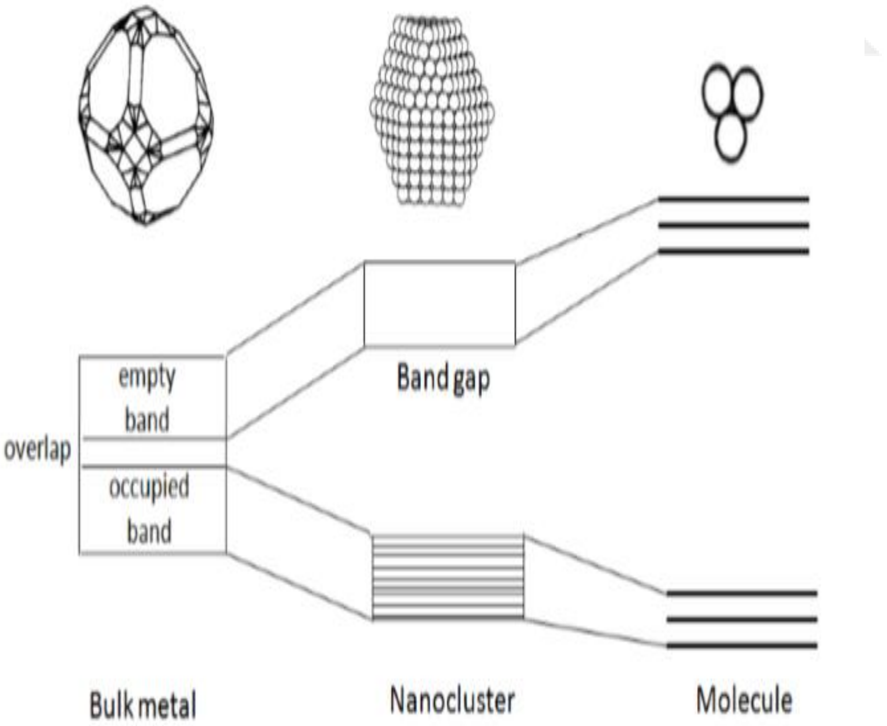

Figure 2.1. Formation of discrete electronic energy levels on the way from bulk to molecule (Corain, 2008).

2.5. Stabilization of Transition Metal Nanoclusters

At short interparticle distances, two particles would be attracted to each other by Van der Waals forces and in the absence of repulsive forces two counteract this attraction an unprotected sol would coagulate (Ninham, 1999). In the literature of colloidal stability and in Derjaguin-Landau-Verway-Overbeek (DLVO) theory (Verwey, 1999), colloidal stabilization is well established to involve both: (i) electrostatic stabilization and (ii) steric stabilization; (*i*) Electrostatic stabilization; the adsorption of negatively or positively charged ions to the coordinatively unsaturated surface of the nanoparticles results in a coulombic repulsion between the particles. The coulombic repulsion opposes Van Der Waals attractions and the net result is shown schematically in Figure (2.3). The coulombic repulsion between the particles decays approximately exponentially with the particle distance. The weak minimum in potential energy defines a stable situation. Thus, if the electric potential resulting from the double layers is high enough, electrostatic repulsion prevents aggregation (Klabunde, 2001).

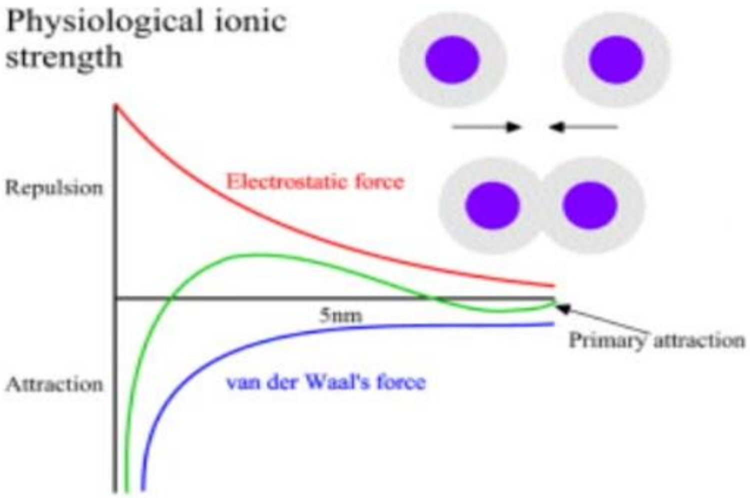

Figure 2.2. Schematic representation of the electrostatic stabilization of transition metal nanoclusters.

(ii) Steric stabilization: it is achieved by the absorption of molecules such as polymers, surfactants or long chain ligands at the surface of the nanoclusters, thus providing a protective layer (Ott, 2006). These large adsorbates provide a steric barrier which prevents close contact of metal nanoclusters to each other as demonstrated in Figure (2.4).

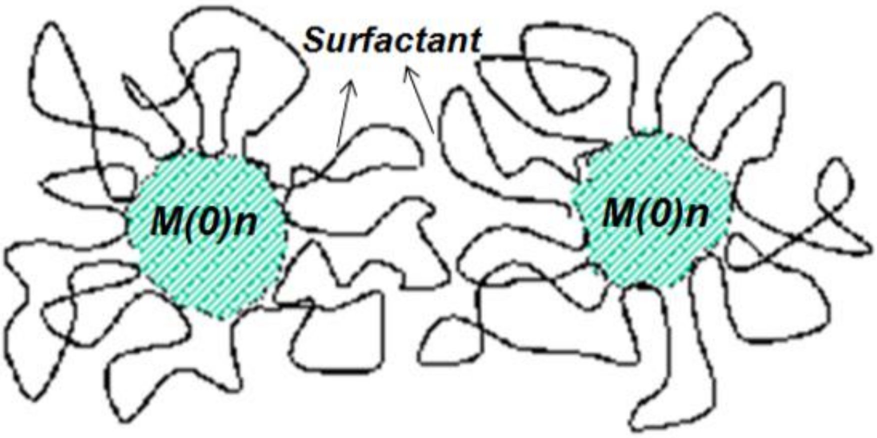

Figure 2.3. The schematic representation of the steric stabilization of transition metal nanoclusters.

Steric Stabilization by polymers: polymers are widely used, and it is obvious that the protectant, in order to function effectively, must not only coordinate to the particle surface, but must also be adequately solvated by the dispersing fluid such polymers are termed amphiphilic. The structure of polymer stabilized metal nanoclusters can be illustrated in Figure (2.5.), where the polymers were thought to adsorp physically on the surface of metal nanoclusters (Hirai, 1986). Detailed characterization studies of the adsorbed polymer have demonstrated that the polymers can coordinate to the metal forming rather strong chemical bonds. The polymer molecule can coordinate to the metal particle at multiple sites.

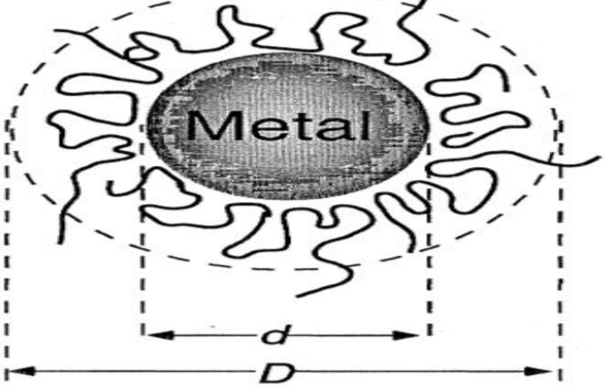

Figure 2.4. Structure model of polymer-stabilized metal nanoclusters (Toshima, 2000).

Two models are suggested for the stabilization of the metal nanocluster by a polymer as shown in Figure 2.6; (a) the stabilization of each nanoclusters by one polymer chain (the widely accepted one, Figure 2.6a) (b) the stabilization of many nanoclusters by one polymer chain (Figure 2.6b). As clearly seen for the both models, there still exists a large catalytically active exposed surface which is crucial for heterogeneous catalytic applications. The choice of polymer as a stabilizer is determined by consideration of the solubility of the metal colloid precursor, the solvent of choice, and the ability of the polymer to stabilize the reduced metal particles in the colloidal state [Schmidm, 1994). For this reason, it is important to investigate a broad variety of protective polymers for their ability to stabilize metal nanoclusters. The use of polymeric matrix as stabilizer improves some properties of the nanoclusters such as the solubility, thermal stability and catalytic activity (Hirai, 1986).

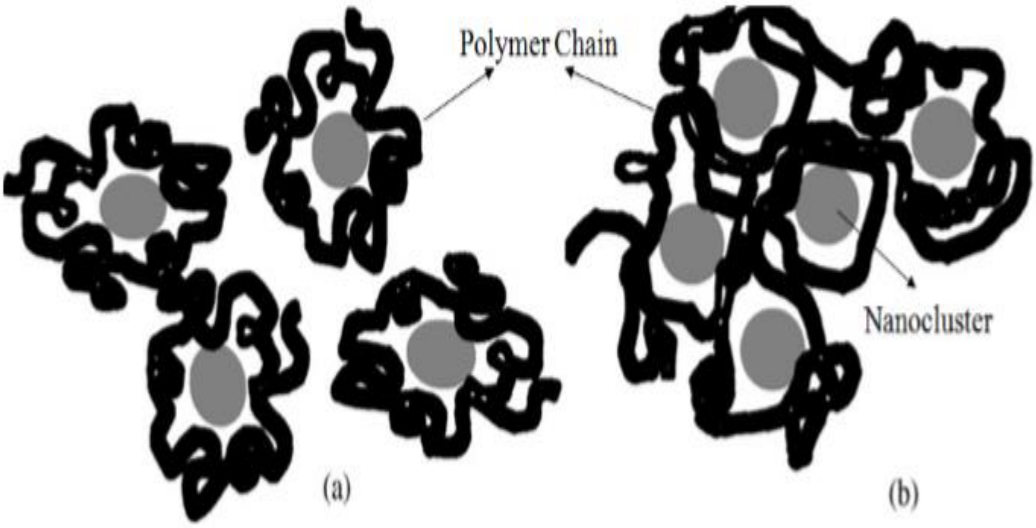

Figure 2.5. Two models suggested for the stabilization of the metal nanocluster by a polymer; (a) the stabilization of each nanocluster by one polymer chain (the widely accepted one); (b) the stabilization of many nanoclusters by one polymer chain.

Steric stabilization by polymers has several distinct advantages over electrostatic stabilization (Sato, 1980) relative insensitivity to the presence of electrolytes; for instance, for 1:1 electrolytes (I = z.2c), a charge-stabilized dispersion will not be stable and coagulate when the concentration of electrolytes exceeds the 10-1 M limit. The dimensions of polymer chains display no such dramatic sensitivity and sterically stabilized dispersions are relatively insensitive to the presence of electrolyte. ¾ Equal efficacy in both aqueous and nonaqueous dispersion media; charge stabilization is less effective in nonaqueous dispersion media than it is in aqueous media. This is primarily due to the low relative dielectric constant (<10) of most nonaqueous media. In contrast, steric stabilization is effective in both nonaqueous media and aqueous media. Equal efficacy at both high and low solids content; in charge stabilization in nonaqueous media, the thickness of the double layers can be so large, (due to the low dielectric constant of the dispersion medium), that the mere preparation of high solids dispersions forces the particles too close together which then leads to coagulation. In aqueous dispersion media, the preparation of charge-stabilized particles at high solids dispersions is often difficult because of the gel formation induced by the interactions between the double layers surrounding each particle. Reversibility of flocculation; the coagulation of charge-stabilized particles (induced by the addition of electrolyte) is usually irreversible by subsequent dilution. In contrast, flocculation of sterically stabilized dispersions (induced by the addition of a nonsolvent for the stabilizing moieties) can usually be reversed spontaneously by mere dilution of the nonsolvent concentration to a suitably low value. This difference is due to the fact that sterically stabilized dispersions may be thermodynamically stable while charge stabilized dispersions are only thermodynamically metastable. As a consequence, for charge stabilized dispersions, the coagulated state represents a lower energy state and the coagulation can be reversed only after input of work into the system. Another crucial consequence of the thermodynamic stability of sterically stabilized dispersions is that they can which is very important for catalytic applications.

Another source of colloidal stabilization, electrosteric stabilization, is the combination of electrostatic and steric stabilization like as in the use of long-chain alkyl ammonium cations and surfactants (Zahmakiran, 2009). This kind of stabilization is generally provided by means of ionic surfactants. These compounds bear a polar head group able to generate an electrical double layer and a lypophilic side chain able to provide steric repulsion (Figure 2.7.). The electrosteric stabilization can be also obtained from polyoxoanions such as the couple ammonium (Bu4N+)/polyoxoanion (P2W15Nb3O629-).

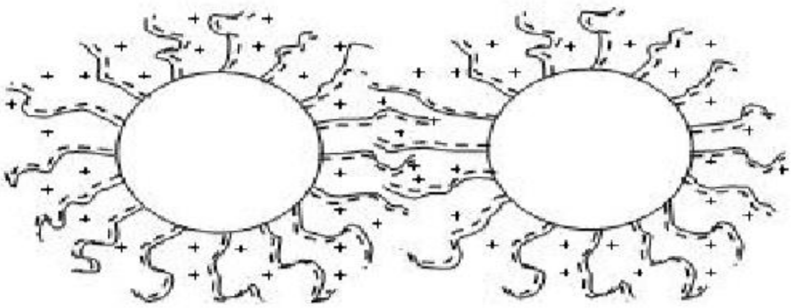

Figure 2.6. The schematic representation of the electosteric stabilization of transition metal nanoclusters.

2.6. Preparation of Transition Metal Nanoclusters

Semiconductors are sensitive infrared detector which can produce an electrical energy from optical energy by the internal photo electronic effect (Emmons, 1975). Radiation is absorbed within the semiconductor material by interaction with electrons. The observed electrical output signal results from the changed electronic energy distribution. The photon-detectors exhibit the selective wavelength dependence of the response per unit incident radiation power. They show both a very fast response and perfect signal-to-noise performance, but for obtain this, the photon-detectors require cryogenic cooling (Rogalski, 2003). Cooling requirements are the main obstacle to the more widespread use of IR systems based on semiconductor photo detectors making them heavy, expensive, bulky and inconvenient to use. Can be classify the photon-detector to the another types like extrinsic detectors, intrinsic detectors, quantum well detectors and photo-emissive detectors (Rogalski, 2002).

Transition metal nanoclusters can be obtained via so called ‘top down methods or physical route’ e.g., by the mechanical grinding of bulk metals and subsequent stabilization of the resulting Nanosized particles by the addition of colloidal protecting agents (Gaffet, 1996). However, the top-down approach yields poor dispersions where the particle size distribution is very broad typically larger (>10 nm) and not reproducibly prepared giving irreproducible catalytic activity (Willner, 1989). The most widely used approach is the so called ‘bottom-up methods or chemical route’. In the bottom up methods, the nanoclusters are prepared via wet chemical techniques, through which the nucleation and growth of metallic atoms take place. The bottom-up approach provides more convenient ways to control the size of the particles than top down methods and it includes following synthetic methods: (i) chemical reduction of transition metal complexes (Wang, 2002) including electrochemical pathways, (ii) thermolysis (Esumi, 1990) including photolytic and sonochemical pathways (Tano, 1989), (iii) Ligand reduction and ligand displacement from organometallics (Duteil, 1993). (*i*) Chemical reduction of transition metal complexes: the reduction of transition metal salts in solution is the most widely accomplished method for the generation of colloidal metal nanoparticles. All chemical based synthetic routes to nanosized metal particles start with the reduction of positively charged metal atoms, either as simple ions or as centers of complexes in solution (Schmid, 1994). Solvents can vary from water to very nonpolar media depending on the nature of the metal salt or the complex used. In aqueous systems, the reducing agent must be added or generated in situ, but in non-aqueous systems the solvent and reducing agent can be one and the same (Corain, 2008). The kind of reducing agent is determined on the nature of metal compound. A wide range of reducing agents have been used to obtain colloidal materials, gas such as hydrogen or carbon monoxide, hydrides or salts such as sodium borohydride or sodium citrate, or even oxidizable solvents such as alcohols (Duteil, 1993). (*ii*) Thermolysis: this technique is based on the thermal decomposition of many organometallic compounds of transition metals to their respective metals under relatively mild conditions, these compounds provide a rich source of nanoparticle precursors. The method is widely applicable. The thermolysis of carbonyl-containing complexes of rhodium, iridium, ruthenium, osmium, palladium, and platinum in polymer solutions has been used to prepare polymer-stabilized collodial metals with particle sizes in the range 1-10 nm, possibly by decomposition of polymer-bound organometallic intermediates (Smith, 1981). (iii) Ligand reduction and ligand displacement from organometallics: reduction of metal can be carried out prior to colloid preparation, giving a zerovalent metal complex as the immediate colloid precursor. The synthesis of metal carbonyls and their subsequent thermolysis in nanoparticles synthesis is an example of this approach. The zero-valent palladium and platinum complexes with dibenzylideneacetone Pd(dba)2 and M2(dba)3 (M = Pd, Pt) have been known since

1970 to react under mild conditions with either hydrogen or carbon monoxide with the formation of metal (Takahashi, 1970).

Among the preparation methods mentioned above, the chemical reduction of transition metal salts is the most convenient route to prepare the transition metal nanoclusters in the laboratory conditions as it provides reproducible syntheses of the nanoclusters in size of 1-10 nm with a well-defined surface composition and size control (Corain, 2008).

2.7. Characterization of Transition Metal (0) Nanoclusters

The characterization of metallic nanoclusters is a complex task since many aspects have to be considered as the structures of metal nanocluster depend on many parameters such as: composition, preparation method, heat treatments, environmental variables, supports and so on. The properties of colloidal metal nanoclusters that are of interest include size, structure and composition. In order to entirely understand the physico-chemical behaviour of metal nanoclusters and their properties, many complementary techniques have to be used to figure out the many parameters involved (Cheysaac, 1994). The most widely used and essential technique for the characterization of nanoparticles is transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) which provide direct visual information of the size, dispersity, structure and morphology of nanoparticles. In this technique, a high voltage electron beam passes through a very thin sample, and the sample areas that do not allow the passage of electrons form an image to be presented. Thanks to the advancements in electronics, computers and cameras, the image of heavy atoms in nanoparticle sizes and shapes are easily imaged with modern high voltage instruments having resolution up to 0.08-0.05 nm. Other commonly used methods for the characterization of metal nanoparticles can be summarized as follows: (i) UVVisible spectroscopy; the reduction of metal precursors and the formation of the metal nanoclusters in the presence of a stabilizer can be followed nicely (Metin, 2007). Such observations done by UV-Vis spectroscopy depend on the disappearing of an absorpstion of the metal precursor and growing of a new absorption feature for the nanoclusters (Creighton, 1991). (ii) X-ray photoelectron spectroscopy (XPS); is a semiquantitative technique used for the determination of the surface chemical properties of the materials. The oxidation state of the metal atom on the surface of metal nanoclusters can be determined via XPS which is very important issue in heterogeneous catalysis (Niemantsverdriet, 2000). (iii) X-ray diffraction; probes the average crystallographic structure in samples and allow, through an accurate analysis of diffraction line shape, the extraction of relevant information relating to crystallite size, crystallographic defects as well as compositional and chemical inhomogeneties (Wechuysen, 2004). To a less extent the following methods are used for the characterization of metal nanoparticles: scanning electron microscopy (SEM), infrared spectroscopy (IR), elemental analysis (ICP-OES), energy dispersive spectroscopy (EDS), nuclear magnetic resonance spectroscopy (NMR), extended X-ray absorption fine structure (EXAFS), scanning tunneling microscopy (STM), atomic force microscopy (AFM). An overall picture of the methods most commonly used in the characterization of metal nanoparticles are given in Figure (Aiken, 1999).

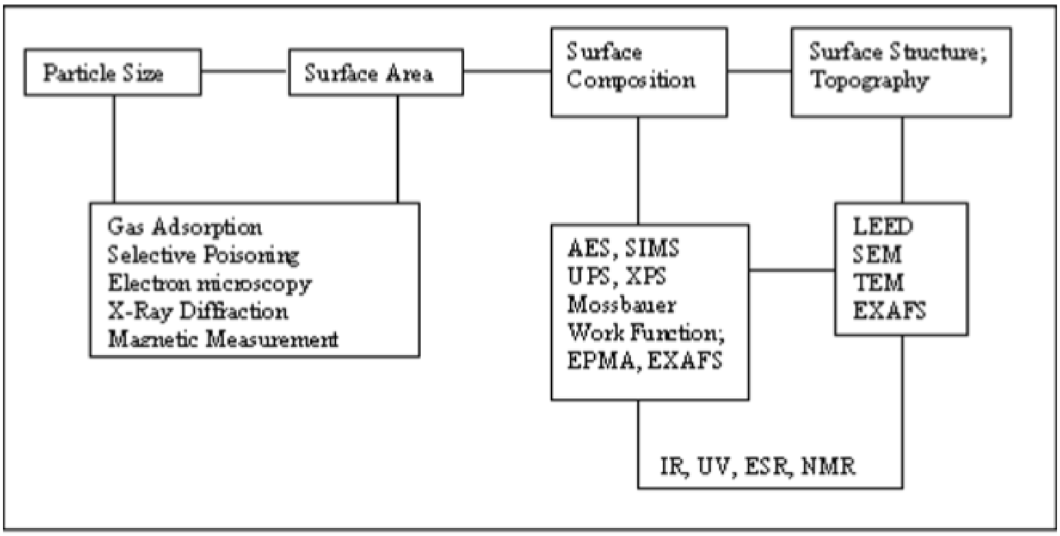

Figure 2.7. The methods most commonly used in the characterization of metal nanoparticles.

2.8.Applications of Transition Metal Nanoclusters

Transition metal nanoclusters are of considerable current interest, both fundamentally and for their possible applications in catalysis, in nanobased chemical sensor, as light emitting diodes, in ‘quantum computers’ or other molecular electronic devices. There are also additional possible applications of nanoclsuters: as ferrofluids for cell seperations or in optical, electronic, or magnetic devices constructed via a building block ‘bottoms-up’ approach. However, our main interest has been focused on the synthesis, characterization of transition metal (0) nanoclusters and their applications in catalysis (Metin, 2008). For this reason, the following chapter of this dissertation will give brief information about the general principles of catalysis and the use of transition metal nanoclusters as catalyst.

2.9.Catalysıs

2.9.1. General principles of catalysis

A catalyst is a substance that makes a reaction go faster, without being stoichiometrically consumed in the process. The phenomenon occurring when a catalyst acts is termed catalysis. Because the catalyst is not consumed in the process, each catalyst molecule can take part in many repeated cycles, so we need only a small amount of catalyst relative to substrate. There are many types of catalyst ranging from the proton, through the lewis acids, organometallic complexes, organic or inorganic polymers, enzymes and so on. However, to simplify things, the catalysis can be divided into three main categories; (i) heterogeneous catalysis, (ii) homogeneous catalysis, and (iii) biocatalysis as shown in Figure (2.9.).

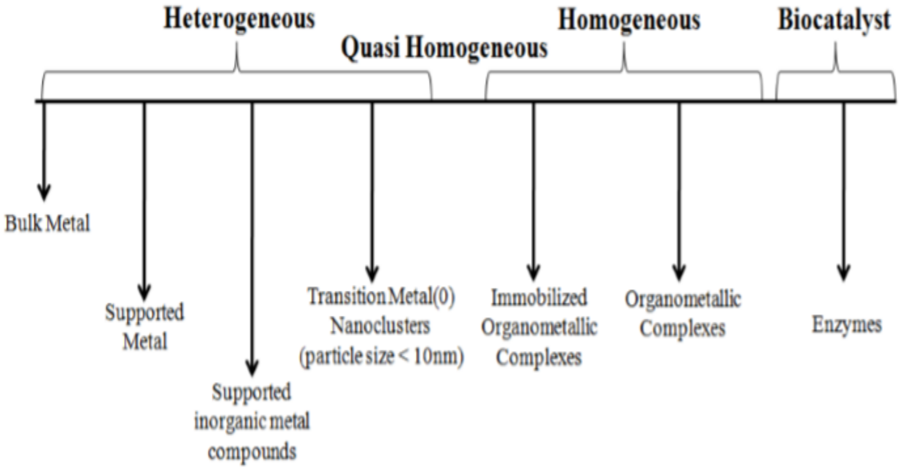

Figure 2.8. The classification of catalysts (Rothenberg, 2008).

The classification of homogeneous and heterogeneous catalysis depends on existence of catalyst in the same phase as the substrate or not. In homogeneous catalysis, the catalyst is in the same phase as the reactants and products. Many homogeneous catalysts are transition metal atom which is stabilized by a ligand. The ligands are usually organic molecules that attach to the metal atom. The properties of such a homogeneous catalyst can be altered by changing the type of ligand. In heterogeneous catalysts are those that act in different phase than substrates. In heterogeneous catalysis, the reactants diffuse to the catalyst surface (generally metal surface) and adsorb onto it, via the formation of chemical bonds. After reaction, the products desorb from the surface and diffuse away. For solid heterogeneous catalysts, the surface area of the catalyst is critical since it determines the availability of catalytic sites. Heterogeneous catalysis is of paramount importance in many areas of the chemical and energy industries. Most catalytic processes are heterogeneous in nature, typically involving a solid catalyst and gas- or liquid-phase reactants. Today, the majority of the industrial processes involve heterogeneous catalysis (Gates, 1992), because of their advantages such as easy separation of reaction products, reusability, stability, low-cost and low-toxicity (Thomas, 1997). Heterogeneous catalysis has attracted Nobel prizes for Fritz Haber and Carl Bosch in 1918, Irving Langmuir in 1932, and Gerhard Ertl in 2007 and other e.g. Ziegler-Natta etc. However, heterogeneous catalysts often tend to require high temperatures and pressures and they have low selectivity compared to homogeneous catalysts. The biocatalysis is rather special case, somewhere between homogeneous and heterogeneous catalysis. The biocatalyst is generally an enzyme- a complex protein that catalyzes the reactions in living cells (Anthonsen, 1999). They are not only the highly efficient catalyst that they can catalyze the 1000 catalytic cycles in one second but also very selective catalysts.

Catalysts increase the rate of reaction by providing an alternative mechanism involving a different transition state and lower activation energy that is called as transition-state theory. In the transition-state theory, the entropy of activation in a catalyzed reaction will usually be less than in corresponding uncatalyzed reaction because the transition state is immobilized on the catalyst surface with consequent loss of translational freedom. There must therefore be a corresponding decrease in the enthalpy of activation to compensate for this, or to overcompensate for efficient catalysis. Thus, according to the theory the activation energy for a catalyzed reaction ought to be less than for the same uncatalyzed reaction (Figure 2.10.). Consequently, more molecular collisions have the energy needed to reach the transition state. Hence, catalysts can enable reactions that would otherwise be blocked or slowed by a kinetic barrier. However, the apparent activation energy (Eaapparent) term is generally used for the activation energy of a catalytic reaction go on many steps because there are many ways to product side in this type of reactions and so there are many rate constants (kapp) affect by temperature. The Eaapparent is the combination of these rate constants. Catalysts do not change the extent of a reaction: they have no effect on the chemical equilibrium of a reaction because the rate of both the forward and the reverse reaction are both affected. If a catalyst does change the equilibrium, then it must be consumed as the reaction proceeds, and thus it is also a reactant. The activity of a catalyst can also be described by the turnover number (or TON) and the catalytic efficiency by the turnover frequency (TOF).

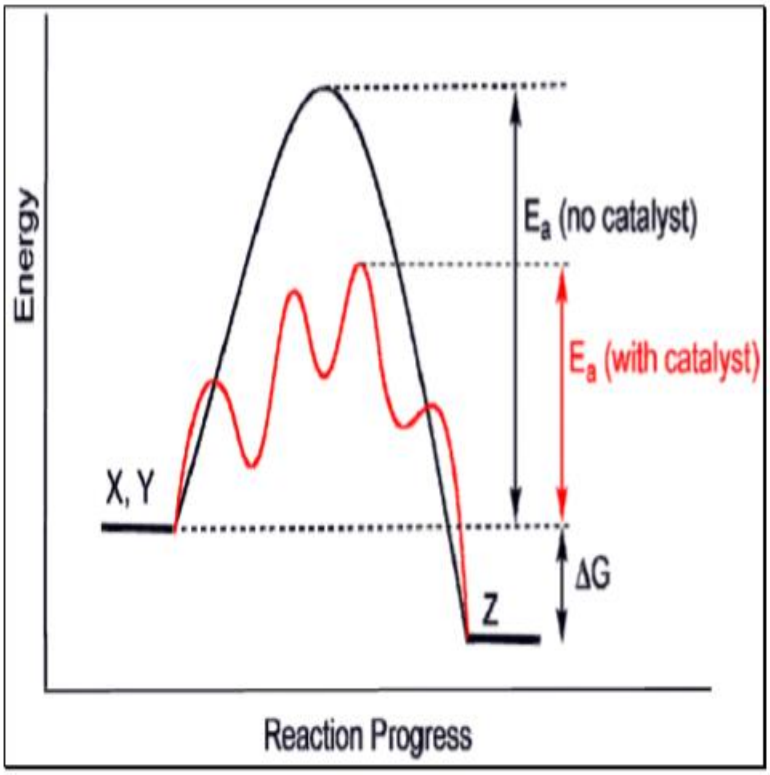

Figure 2.9. Generic potential energy diagram showing the effect of a catalyst in a hypothetical exothermic chemical reaction X + Y to give Z. The presence of the catalyst opens a different reaction pathway (shown in red) with a lower activation energy. The final.

2.9.2. Key definitions in catalysis

The catalytic lifetime of a catalyst is usually expressed as total turnover number (TTON) which equals to the number of moles of product per mole of catalyst Eq. (2.1); this number indicates the number of total catalytic cycles before deactivation of the active catalyst in a given process.

$$\text{TTON} = \frac{\text{mole of product}}{\text{mole of catalyst}} \tag{2.1}$$

The turnover frequency, N, is often used to express the efficiency of a catalyst. For the conversion of A to B catalyzed by Q and with a rate ν, Eq. (2.2);

$$A \xrightarrow{Q} B \qquad v = \frac{d[B]}{dt} \tag{2.2}$$

The turnover frequency is given by the Eq. (2.3), (|Q| is mole of the catalyst).

$$N = \frac{v}{|Q|} \tag{2.3}$$

Selectivity; is another important parameter that should be considered in the evaluation of the performance of any catalyst. A selective catalyst yields a high proportion of the desired product with minimum amount of the side products. High selectivity plays a key role in industry to reduce waste, to reduce the work-up equipment of a plant, and to ensure a more effective use of the feedstocks.

2.9.3. Enhancement of catalytic activity by decreasing the particle size in heterogeneus catalysis

As mentioned earlier part of the dissertation, from macroscale to nanoscale there exists a considerable change in the intrinsic properties of materials. One of the best example for these changes is the increasing activity of the heterogeneous catalyst by the reduction of particle size as the activity of heterogeneous catalysts is directly related to surface area (Özkar, 2009). Of particular interest, metal nanoclusters exhibit unusual surface morphologies and possess more reactive surfaces, hereby open a new perspective in the surface chemistry. For these reasons, they opened a great potential in catalysis because of their large surface area. The resultant huge surface areas of them dictate that many of the atoms lie on the surface, thus allowing a good ‘atom economy’ in surface-gas, surface-liquid, or even surface-solid reactions (Richards, 2006). Transition metal nanoclusters have a high percentage of surface atoms and they do not necessarily order themselves in the same way that those in bulk do. As an illustrative example Klabunde and co-workers calculated the percentage of surface iron atoms on spherical iron (0) nanoclusters depending on their size (Figure 2.11).

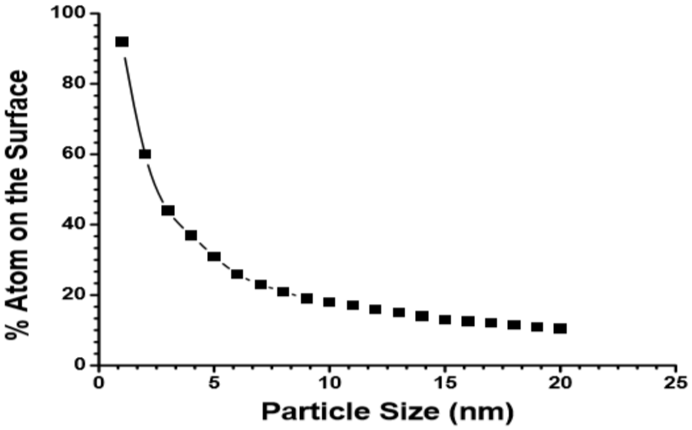

Figure 2.10. The change in percentage of surface iron atoms depending on the size of iron (0) nanoclusters (Klabunde, 1996).

The increasing proportion of surface atoms with decreasing particle size, compared with bulk metals, makes metal nanoclusters more active catalysts than their bulk counterparts, as surface atoms are the active centers for catalytic elementary processes. Among the surface atoms, those sitting on the edges and corners are more active than those in planes. Metal clusters which have a complete, regular outer geometry are designated full-shell, or ‘magic number’, clusters. Many nanocluster distributions center around one of these full-shell geometries. Each metal atom has the maximum number of nearest neighbors, which imparts some degree of extra stability to full-shell clusters. Note that as the number of atoms increases, the percentage of surface atoms decreases as illustrated in Figure (2.12.).

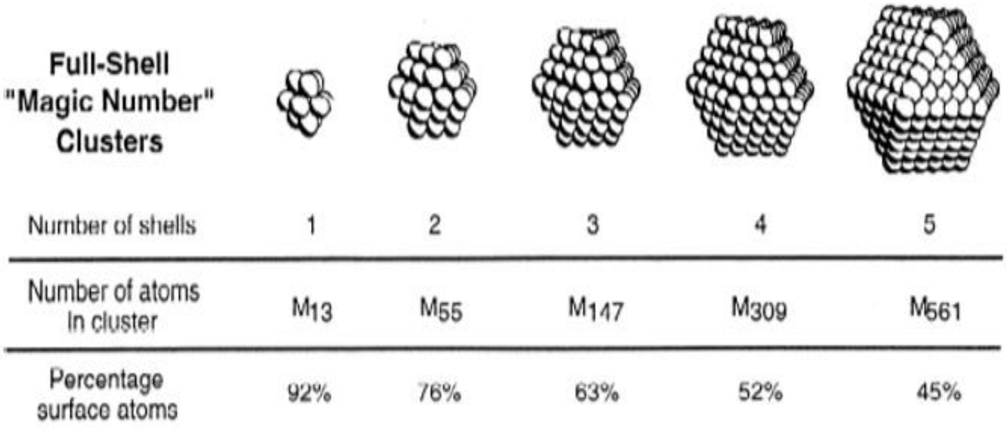

Figure 2.11. The relation between the total number of atoms in full shell clusters and the percentage of surface atoms (Schmid, 1990).

Among the chemical properties of transition metal nanoclusters discussed above, catalysis is of great interest because of their high surface to volume ratio and a unique combination of reactivity, stability, and selectivity.

2.10. Hydrogen Economy

2.10.1. Hydrogen as an energy carrier

Currently more than 80 % of the world energy supply comes from fossil fuels. Besides the exhaustion of reserves and resources, air pollution and modification of the atmospheric composition, with their impacts on climate and on human health, are now of primary importance. Greenhouse gas emissions, especially CO_2 produced by the combustion of fossil fuels, are in the centre of the environmental concerns. Moreover, fuel supply security is a serious concern, particularly for the transportation sector. A variety of efficient end-use technologies and alternative energy sources such as solar, wind, hydropower energy have been proposed to help address future energy-related environmental and/or supply security challenges in fuel use. However, besides their relatively high cost, energy production from renewable sources has the problem of discontinuity; for example, solar or wind energy is not always available. The obvious solution to this predicament is the energy storage. In this context, hydrogen appears to be the best energy carrier as it has an abundant and secure source, clean, renewable, and widely available from diverse sources. Hydrogen is the simplest and lightest of all chemical elements and the most spread in the universe. It is not a primary source of energy as it occurs only in nature in combination with other elements, primarily with oxygen in water and with carbon, nitrogen and oxygen in living materials and fossil fuels. However when split from these other elements to form molecular hydrogen, it becomes an environmentally attractive fuel. It can be burned or combined with oxygen in a fuel cell without generating CO_2, producing only water. Hydrogen can be made from widely available primary energy sources including natural gas, coal, biomass, wastes, solar, wind, hydro, geothermal or nuclear power, enabling a more diverse primary supply for fuels. Hydrogen can be used in fuel cells and internal combustion engines with high conversion efficiency and essentially zero tailpipe emissions of green house gases and air pollutants. If hydrogen is made from renewables, nuclear energy, or fossil sources with capture and sequestration of carbon, it would be possible to produce and use fuels on a global scale with nearly zero full fuel cycle emissions of green house gases and greatly reduced emissions of air pollutants. Technologies for hydrogen production, storage and distribution exist, but need to be adapted for use in an energy system. Building a new hydrogen energy infrastructure would be expensive and involves logistical problems in matching supply and demand during a transition. Hydrogen technologies such as fuel cells, and zero-emission hydrogen production systems are making rapid progress, but technical and cost issues remain before they can become economically competitive with today's vehicle and fuel technologies.

2.10.2. Hydrogen storagea big challenge in hydrogen economy

Storage of hydrogen is clearly one of the key challenges to the transition of the world into hydrogen economy because high-pressure and cryogenic hydrogen storage systems are impractical for mobile applications due to safety concerns and volumetric constraints (Schlapbach, 2001). In this regard, various kinds of solid materials for hydrogen storage such as metal hydrides (Sandrock, 1992), metal organic frameworks nanostructures and chemical compounds have been investigated. Among the solid state hydrogen storage materials, chemical hydrogen storage materials, due to their high hydrogen contents, are one of the best promising hydrogen sources for fuel cells applications at ambient conditions (Figure 2.13.), (Züttel, 2003).

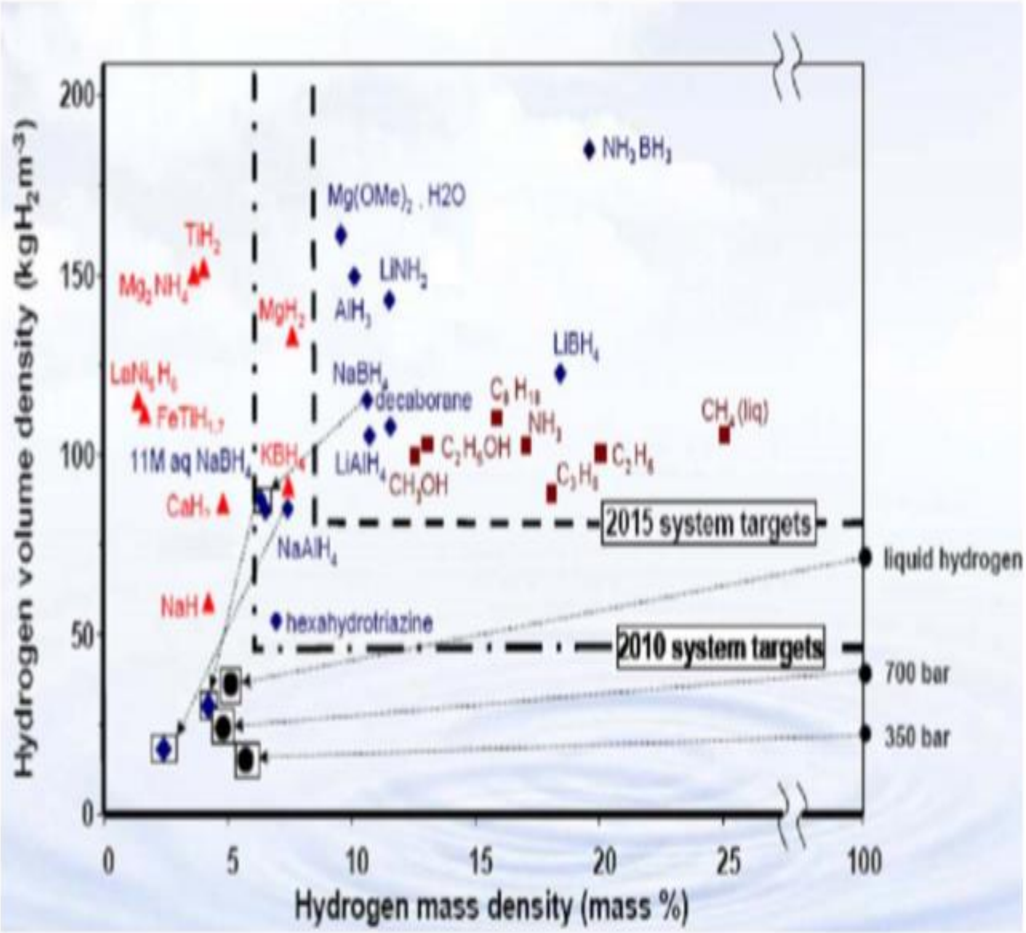

Figure 2.12. Hydrogen mass density versus hydrogen volume density of many compounds considered to be a chemical hydrogen storage material (Züttel, 2003).

Recently, much attention has been paid to hydrogen generation from the hydrolysis of sodium borohydride ($NaBH_4$) that can theoretically release very high hydrogen content of 10.3 wt % (Liu, 2009) at room temperature, respectively. $NaBH_4$ is stable in alkaline solution; however, hydrolysis in the presence of a suitable catalyst generates hydrogen gas in the amount twice its hydrogen content and also watersoluble sodium metaborate, $NaBO_2$, at moderate temperature (Amendola, 2000) Eq. (2.4). By this way hydrogen can be generated safely for the fuel cells.

$$NaBH_4 + 2H_2O \xrightarrow{\text{catalyst}} NaBO_2 + 4H_2 \tag{2.4}$$

Catalytic hydrogen gas generation from $NaBH_4$ solutions has many advantages: $NaBH_4$ solutions are nonflammable, the reaction products are environmentally benign, rate of H_2 generation is easily controlled, the reaction product $NaBO_2$ can be recycled, H_2 can be generated even at low temperatures. Such a hydrolysis of $NaBH_4$ can be accelerated by catalysts (60), by acid (James,1970), or under elevated temperature (Aicllo, 1999). This reaction occurs to some extent even without a catalyst if the solution $pH < 9$. However to increase the shelf life of $NaBH_4$ solutions (and to prevent H_2 gas from being slowly produced upon standing), $NaBH_4$ solutions are typically maintained as a strongly alkaline solution by adding NaOH. The key feature of using a catalyzed reaction to produce H_2 is that H_2 generation in alkaline ($pH > 14$) $NaBH_4$ solutions occurs only when these solutions contact selected heterogeneous catalysts. Without a catalyst, strongly alkaline $NaBH_4$ solutions do not produce appreciable H_2. This reaction is extremely efficient on a weight basis, since out of the 4 moles of H_2 that is produced, half comes from $NaBH_4$, and the other half from H_2O. The reaction is exothermic, so no energy input is needed to generate H_2.

The only other product of reaction, sodium metaborate (in solutions with $pH > 11$ the predominant solution product is sodium tetrahydoxyborate $NaB(OH)_4$), is water soluble and environmentally innocuous. Since the hydrolysis of $NaBH_4$ is completely inorganic reaction and does not contain sulfur, it produces virtually no fuel poisons such as sulfur compounds, carbon monoxide, soot, or aromatics. Therefore this reaction is considerably safer, more efficient, and more easily controllable than producing H_2 by other chemical methods (Lee, 2002). The heat generated by the reaction 75 kJ/mole H_2 formed is considerably less than typical > 125 kJ/mole H_2, produced by reacting other chemical hydrides with water (Davis, 1949). This promises a safer and more controllable reaction.

More recently, ammonia borane (AB, H_3NBH_3) complex, which is formed through a dative bond in which the lone pair of the NH_3 interacts with empty pz orbital of boron in BH3, is identified as one of the leading candidates as a solid state hydrogen reservoir owing to its high hydrogen content (19.6 wt%), high stability under ordinary fuel cell reaction conditions and nontoxicity (Marder, 2007). AB is isoelectronic to ethane; however, the physical properties are very different. AB is synthesized by facile methods for laboratory-scale preparation. The combination of ammonium salts with borohydrides (salt metathesis) gives AB in a high yield (Ramachadran, 2007). AB is a tetragonal white crystal at room temperature with a melting point of > 110 oC, having a staggered conformation with a B–N bond distance of 1.564(6) A°, B–H bond distance of 0.96(3)–1.18(3)A°, and N–H bond distance of 0.96(3)–1.14(2)A°(Klooster, 1999). The solid state structure exhibits short BH/HN intermolecular contacts; the hydridic hydrogen atoms on boron are 2.02 A° away from the protic hydrogen atoms on nitrogen of an adjacent molecule, a distance less than the Van der Waals distance of 2.4 A°, implying an interaction constituting a dihydrogen bond (Richardson, 1995). The stability conferred by the dihydrogen bonding (ca. 90.4 kJ mol-1) contributes to the existence of AB as a solid under standard conditions.

Hydrogen stored in the AB complex can be released through either pyrolysis or solvolysis route. Experimental results have revealed that hydrogen release of only 6.5 wt % of the initial mass was obtained upon thermal decomposition of AB at 385 K and the release of more hydrogen from AB requires much higher temperatures (> 500 oC) (68). In contrast, the rapid hydrogen generation rate can be obtained via catalytic hydrolysis of AB (Chandra, 2006). The hydrolysis of AB in the presence of a suitable catalyst provides 3 moles of hydrogen per mole of AB at room temperature Eq. (2.5).

$$H_3NBH_3(aq) + 2H_2O\,(l) \xrightarrow{\text{catalyst}} (NH_4)BO_2(aq) + 3H_2(g) \tag{2.5}$$

In this dissertation, water soluble polymer stabilized transition metal(0) (metal : Ni, Co and Ru) nanoclusters were developed as catalyst in hydrogen generation from the hydrolysis of $NaBH_4$ and AB. The kinetics of hydrogen generation from both catalytic hydrolysis reactions were studied depending on catalyst concentration, substrate concentration and temperature as well as the activation parameters (Arrhenius activation energy (Ea), activation enthalpy (ΔH≠) and activation entropy (ΔS≠) of both catalytic hydrolysis calculated from the kinetic data.

2.10.3. The motivation of the dissertation

As mentioned in the previous sections, the stabilization of transition metal(0) nanoclusters in solution is of great importance to obtain stable nanocluster with controllable size to their potential applications in many fields, including catalysis. In my MS thesis (Metin, 2006), we reported the ‘Synthesis and characterization of hydrogenphosphate stabilized nickel(0) nanoclusters as catalyst for the hydrolysis of sodium borohydride’. However, hydrogenphosphate stabilized nickel(0) nanoclusters showed low catalytic lifetime as determined by measuring the total turnover number (TTON = 1450) for the hydrolysis of sodium borohydride which can be attributed to the weak electrostatic stabilization of nanoclusters. The electrostatic interactions become weaker at high pH which is a requirement for the hydrolysis of sodium borohydride for application of safe hydrogen generation in fuel cells (Zhang, 2007). Therefore, a stronger stabilizer such as polymer is needed to prevent agglomeration of nickel(0) nanoclusters in aqueous solution at high pH medium, acting as catalyst in the hydrolysis of sodium borohydride. The use of polymeric matrix as stabilizer improves some properties of the nanoclusters such as the solubility, thermal stability and catalytic activity (Schmid, 2004). A variety of preparative methods is available for obtaining polymer-stabilized metal nanoclusters (Mayer, 2001). The most widely used synthetic method involves the reduction of the metal ions in solution to its colloidal metal in zerovalent state within the polymer medium, followed by coalescence of the polymer onto the nanoclusters (Mark, 2004). Polymers possessing a hydrophobic backbone and hydrophilic side groups, such as vinyl addition homopolymers, are frequently employed as a stabilizer for the metal nanoclusters in polar solvents. By considering the advantages of polymer stabilization, we developed a facile method for the preparation of PVP stabilized metal(0) (Ni, Co and Ru) nanoclusters from the reduction of metal chlorides by sodium borohydride in methanol solution at reflux conditions (Metin, 2008). Compared to the hydrogenphosphate-stabilized nickel(0) nanoclusters (Metin, 2006), PVP stabilized nickel(0) nanoclusters were much more stable, and catalytically more active providing 8700 total turnovers in the hydrolysis of NaBH4 over 27 hours at ambient temperatures. PVP stabilized cobalt(0) and ruthenium(0) nanoclusters were also showed very high activity and stability in hydrogen generation from the hydrolysis of $NaBH_4$. After obtaining such good results with PVP stabilized nickel(0), cobalt(0) and ruthenium(0) nanoclusters in the hydrolysis of $NaBH_4$, their catalytic applications were extended to hydrolysis of AB which is recently considered as the best candidate for chemical hydrogen storage. In the second part of the dissertation, we aimed to prepare polymer stabilized transition metal(0) nanoclusters in the catalytic reaction medium by considering the difficulties in the separation processes of a catalyst that generally results in a significant loss of catalyst. In this regard, for the first time, poly(4-styrene sulfonic acid-co-maleic acid), PSSA-co-MA, stabilized nickel(0), cobalt(0) and ruthenium(0) nanoclusters were in situ generated during the hydrolysis of AB. The PSSA-co-MA stabilized nickel(0), cobalt(0) and ruthenium(0) nanoclusters showed much better activity than PVP stabilized ones and most of the catalyst system tested in the hydrolysis of AB. As a summary, in this dissertation, we present our detailed study on the synthesis and characterization of water soluble polymer stabilized nickel(0), cobalt(0) and ruthenium(0) nanoclusters as catalyst in hydrogen generation from the hydrolysis of $NaBH_4$ and AB.

3. MATERIAL AND METHODS

3.1. Material

The study was conducted in Van Yüzüncü Yıl University, Van Yüzüncü Yıl University, Biotechnology Application and Research Center Laboratory. L. used in the study Garvieae isolates were used from bacteria that were kept in culture. Zero used in workgroups The valuable nano-iron was obtained in the laboratory of the Center for Biotechnology Application and Research.

3.2. Method

3.2.1. Microbiological identification

The biological test of material of Nano Iron counducted with Streptococcus thermophilus (ST) and Lactobacillus Bulgaricus (LB) After 24 hours incubation at 21 ° C in TSA medium, 1 drop of 0.6% FTS was added onto the slide for Gram staining. Then, 1 min crystal viole, 1 min ligole, 15 sec alcohol and 1 min safranin treatment was completed with staining. The preparations which were allowed to dry were first examined at 4X and then at 10X, 40X and 100X magnifications on a binocular microscope (Leica ICC50 HD). After Gram staining blue-purple color isolates were Gr (+), red-pink color isolates were evaluated as Gr (-) (Bilgehan, 1995). Bactident Oxidase commercial kit was used for oxidase testing. After 24 hours incubation period at 21 ° C in TSA medium, some amount was taken from the colonies with sterile extract and applied to sterile filter papers moistened with oxidase kit. The color changes on the paper surface were examined within 30 seconds. While the formation of blue color oxidase was evaluated as positive, the absence of any color was evaluated as negative result (Çağırgan, 2007). For the catalase test, 1-2 drops of 3% hydrogen peroxide were dropped onto the slide and placed on TSA medium at 21 ° C. After an incubation period of 24-48 hours, it was mixed with sterile loop from the breeding colonies. Depending on the release of oxygen on the slide gas-producing isolates catalase positive, no gas formation was observed in the isolates were evaluated as catalase negative (Austin and Austin, 1999). Biochemical properties of colonies evaluated litatature from the API reading table in accordance with the manufacturer's instructions (Önalan, 2016).

4. DISCUSSIONS AND CONCLUSION

4.1. SEM Analysis

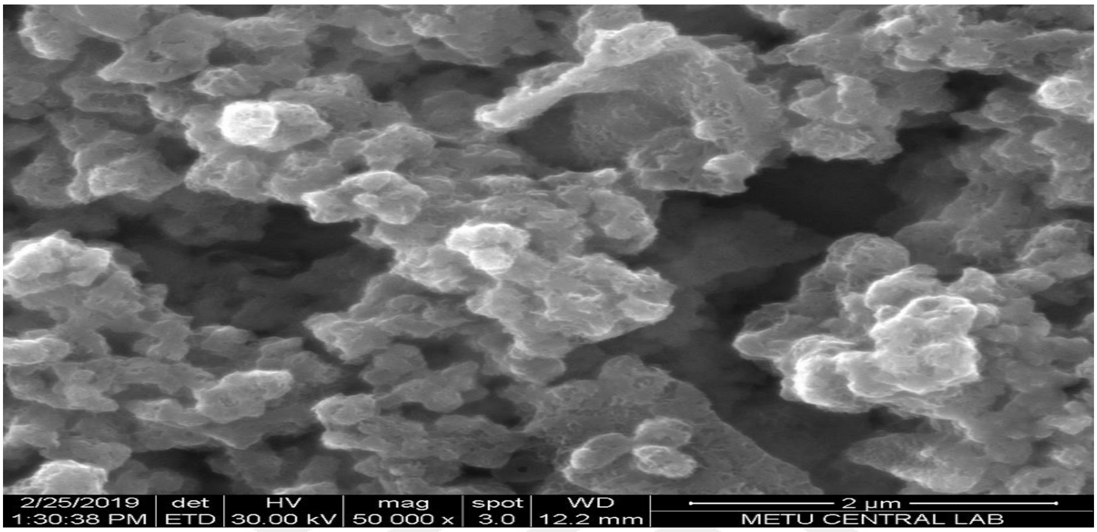

Figure 4.13. SEM images of zero valent iron nanoparticles of 50K magnafication.

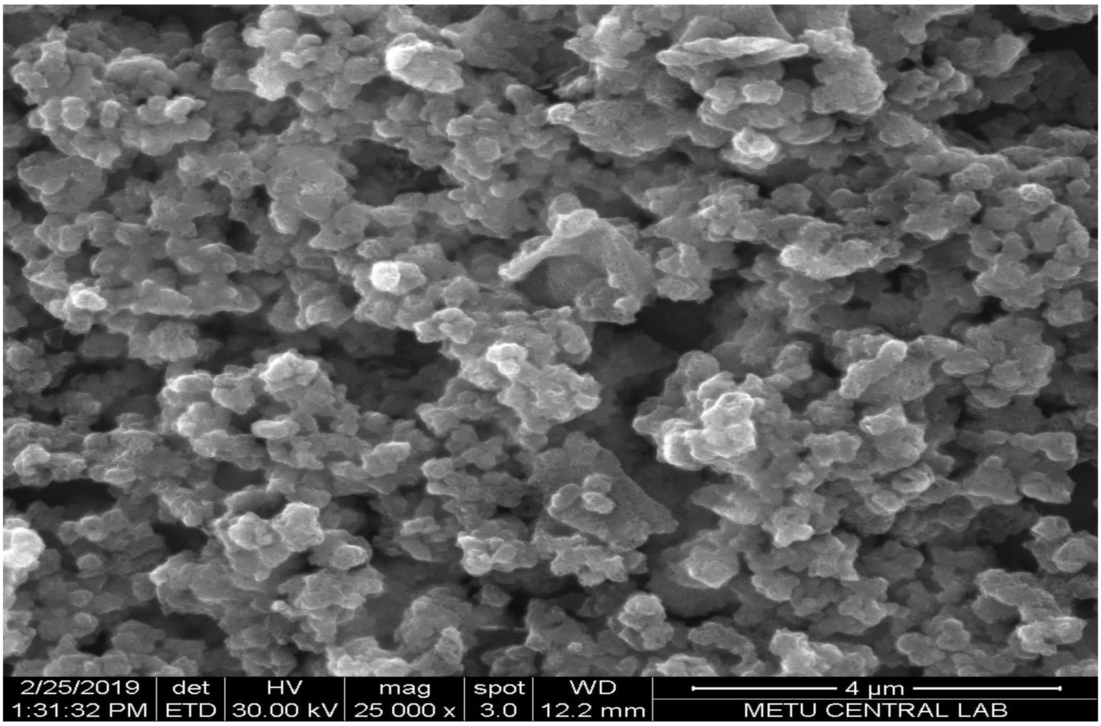

Figure 4.14. SEM images of zero valent iron nanoparticles of 25K magnafication.

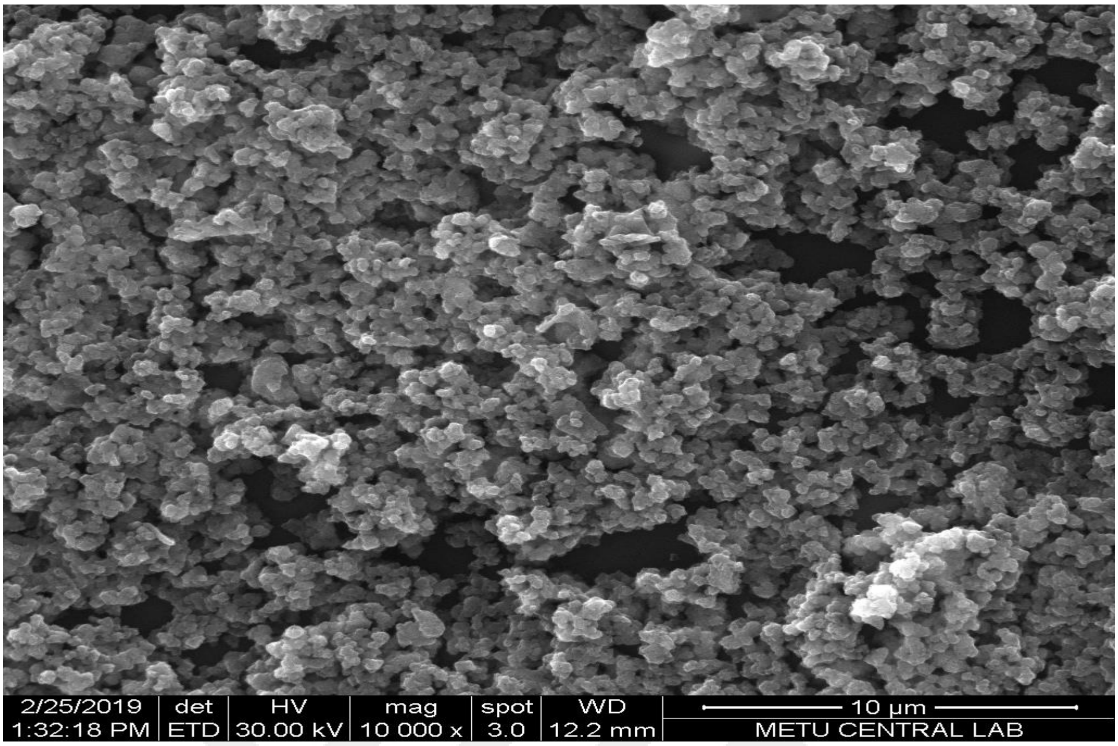

Figure 4.15. SEM images of zero valent iron nanoparticles of 10K magnafication.

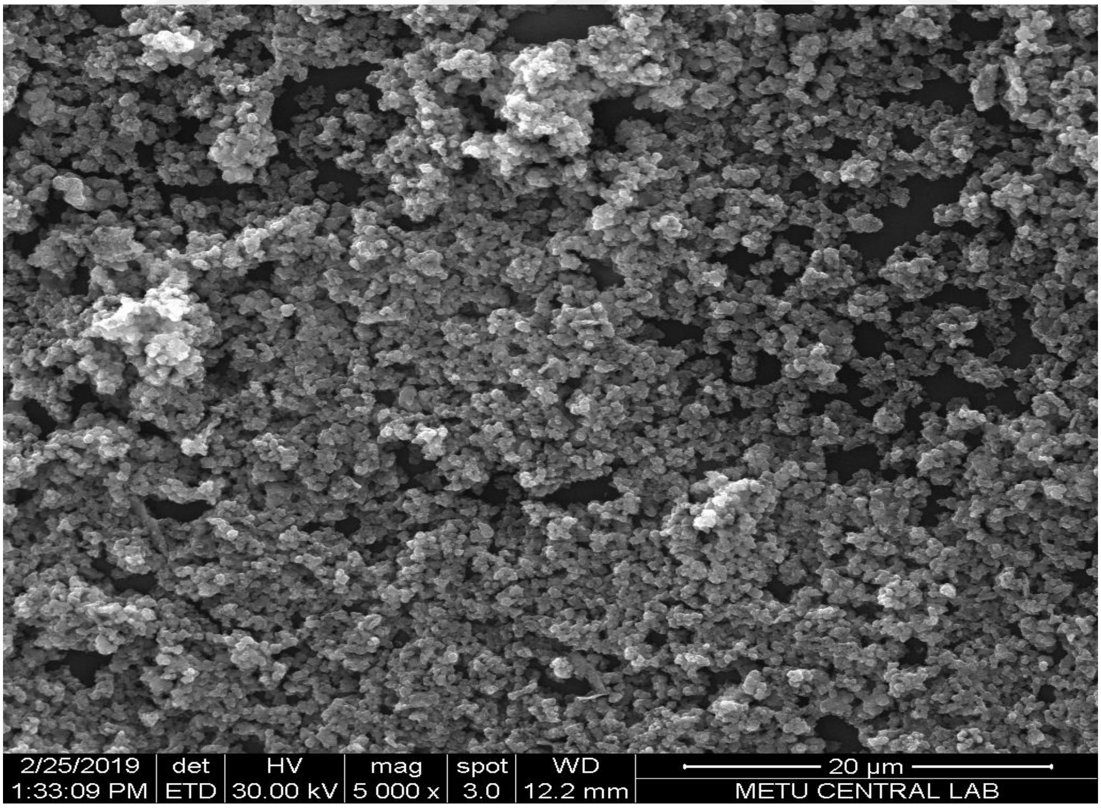

Figure 4.16. SEM images of zero valent iron nanoparticles of 5K magnafication.

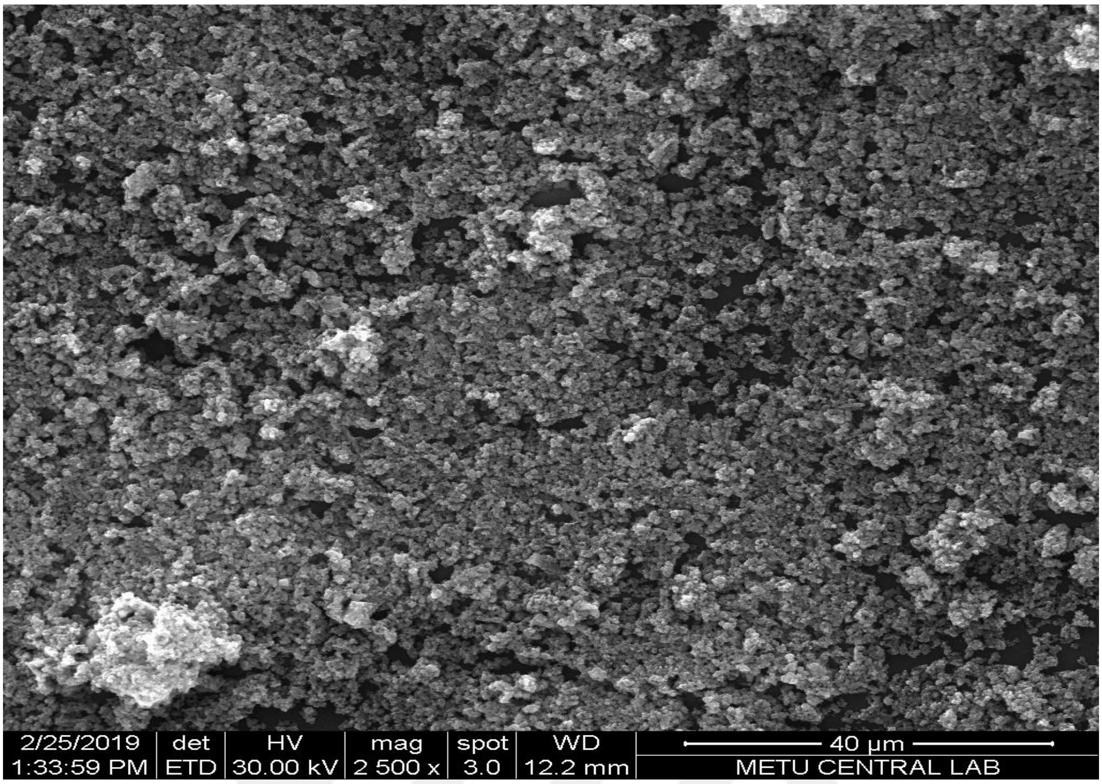

Figure 4.17. SEM images of zero valent iron nanoparticles of 2.5K magnafication.

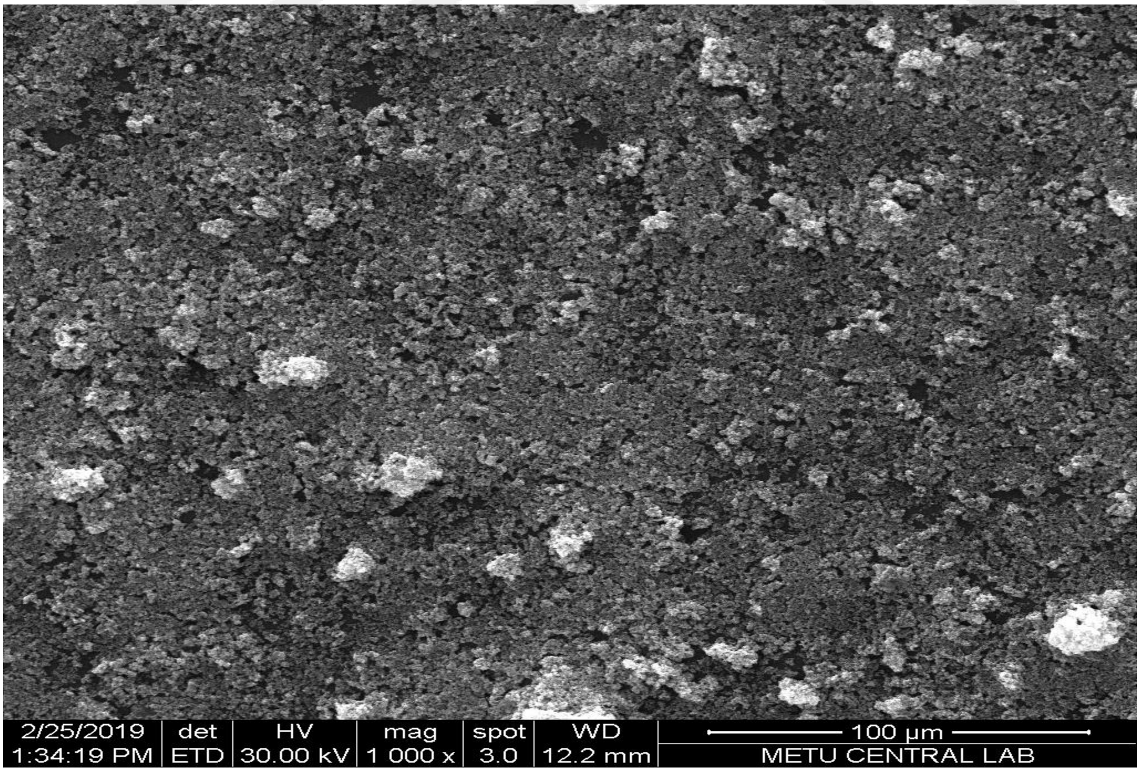

Figure 4.18. SEM images of zero valent iron nanoparticles of 1K magnafication.

As can be seen from the SEM images of the nanoparticles, the particles are uniform and nearly equal in their distribution. According to sem analysis, the average particles are around 45nm. The data obtained in BET analysis is approximately 40 nm. this shows that particles having surface catalytic properties are obtained. however, no oxidation but adherent particles were obtained in water.

4.2. Bacterial Analysis

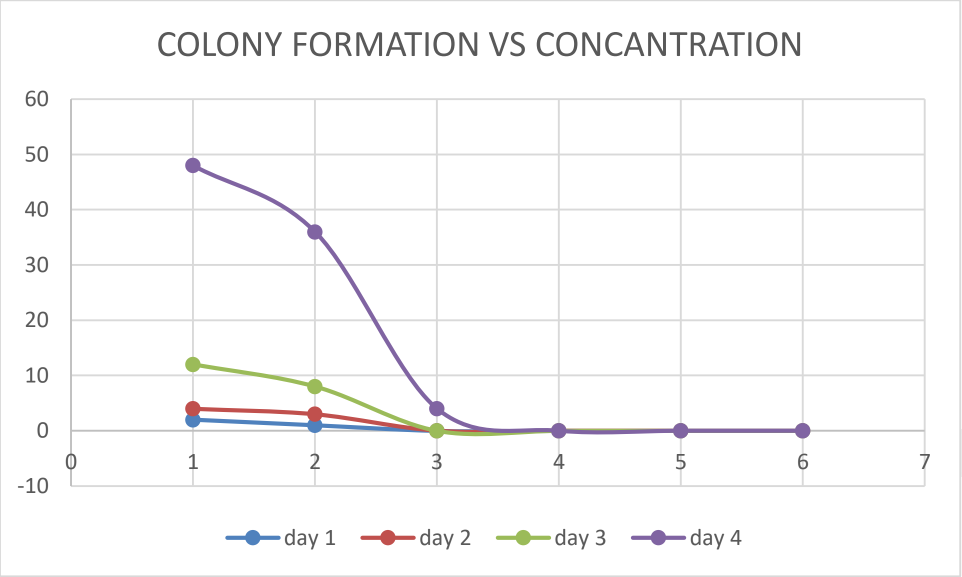

Figure 4.19. Production analyzes of bacteria.

New colony formation on medium was examined with the help of microscope. Witnesses in the sample (o ppm) were observed from the first day, production stopped at 5 ppm and no higher concentrations were observed. This shows that nano iron has a negative effect on yeast and fermentation against yogurt bacteria.

5. RESULTS

The study was conducted in Van Yüzüncü Yıl University, Van Yüzüncü Yıl University, Biotechnology Application and Research Center Laboratory. L. used in the study Garvieae isolates were used from bacteria that were kept in culture. Zero used in workgroups The valuable nano-iron was obtained in the laboratory of the Center for Biotechnology Application and Research. this shows that particles having surface catalytic properties are obtained. however, no oxidation but adherent particles were obtained in water. New colony formation on medium was examined with the help of microscope. Witnesses in the sample (o ppm) were observed from the first day, production stopped at 5 ppm and no higher concentrations were observed. This shows that nano iron has a negative effect on yeast and fermentation against yogurt bacteria.

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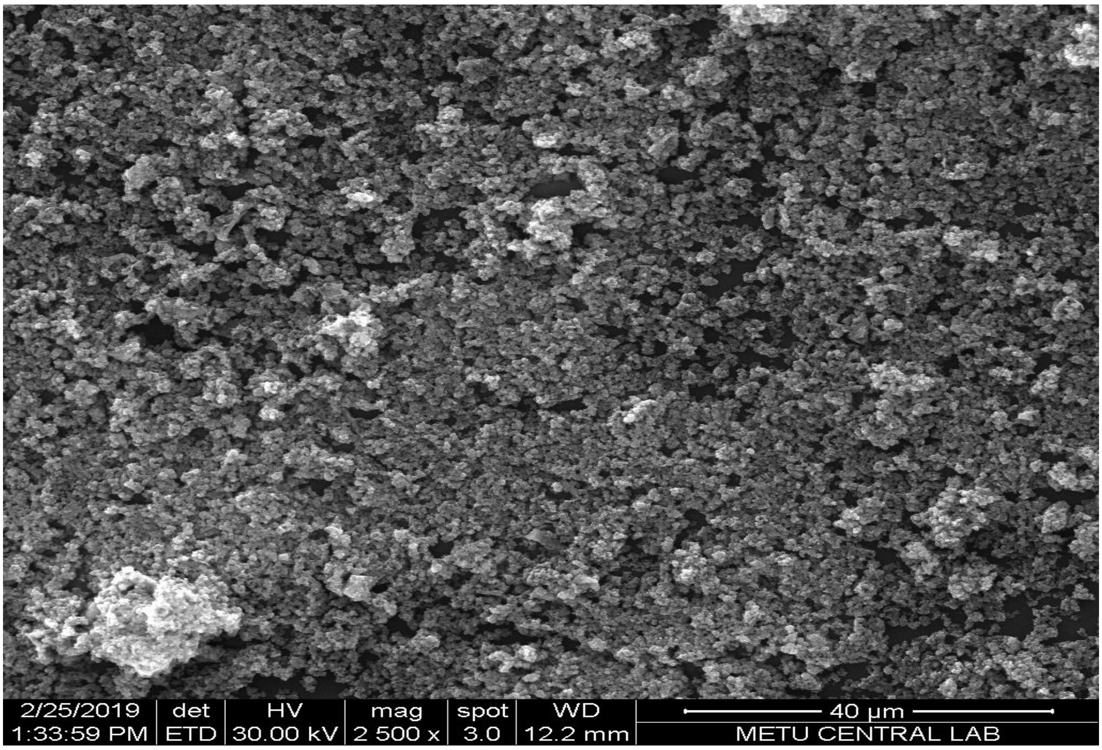
APPENDIX

EXTENDED TURKISH SUMMARY

(GENİŞLETİLMİŞ TÜRKÇE ÖZET)

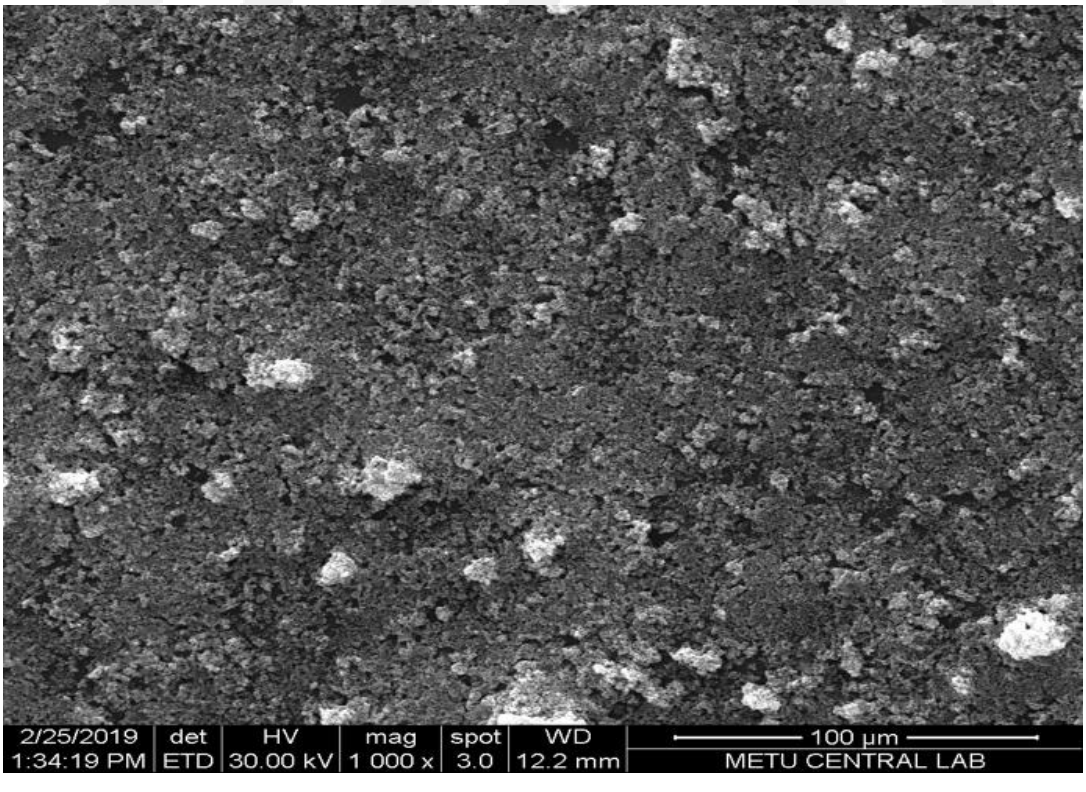
TEZİN AMACI VE ÖNEMİ

Bu tez çalışmasında çalışmada nanopartikül halinde sıfır değerlikli demir (Fe)'in bakteriler üzerine gelişimlerinin etkilerinin pozitif negatif etkilerinin belirlenmesi amaçlanmıştır. Sıfır değerlikli nano demir parçacıkları bakteri geçirgenligini sağlamak amaçlı olarak 45 nm civarında sakin ortalama dagılım ile indirgenme yöntemi ile sentezlenmistir. Yoğurt bakterileri Lactobacillus Bulgaricus ve Streptococcus thermophilus izolatlarının gelişimlerine nanopartiküllerin etki oranının hesaplanabilmesi amacıyla katı besiyerinde ekimleri yapılmıştır. Çalışma sonucunda kontrol grubu örnekleri hem gelişim hızı hem de inkübasyon süresi sonunda maksimum değerine ulaşıldığı görülmüştür. Nanopartikül eklemesi yapılan diğer gruplar içerisinde en hızlı gelişimin 5 ppm miktarı olduğu görülmektedir. Ancak besiyeri oranının 5 ppm üstünde olmasının bakteriyel gelişimi engellediği tespit edilmiştir.



Şekil 1.1. Sıfır valent demir nano parçacıklarının 10K büyütülmüş SEM görüntüleri.

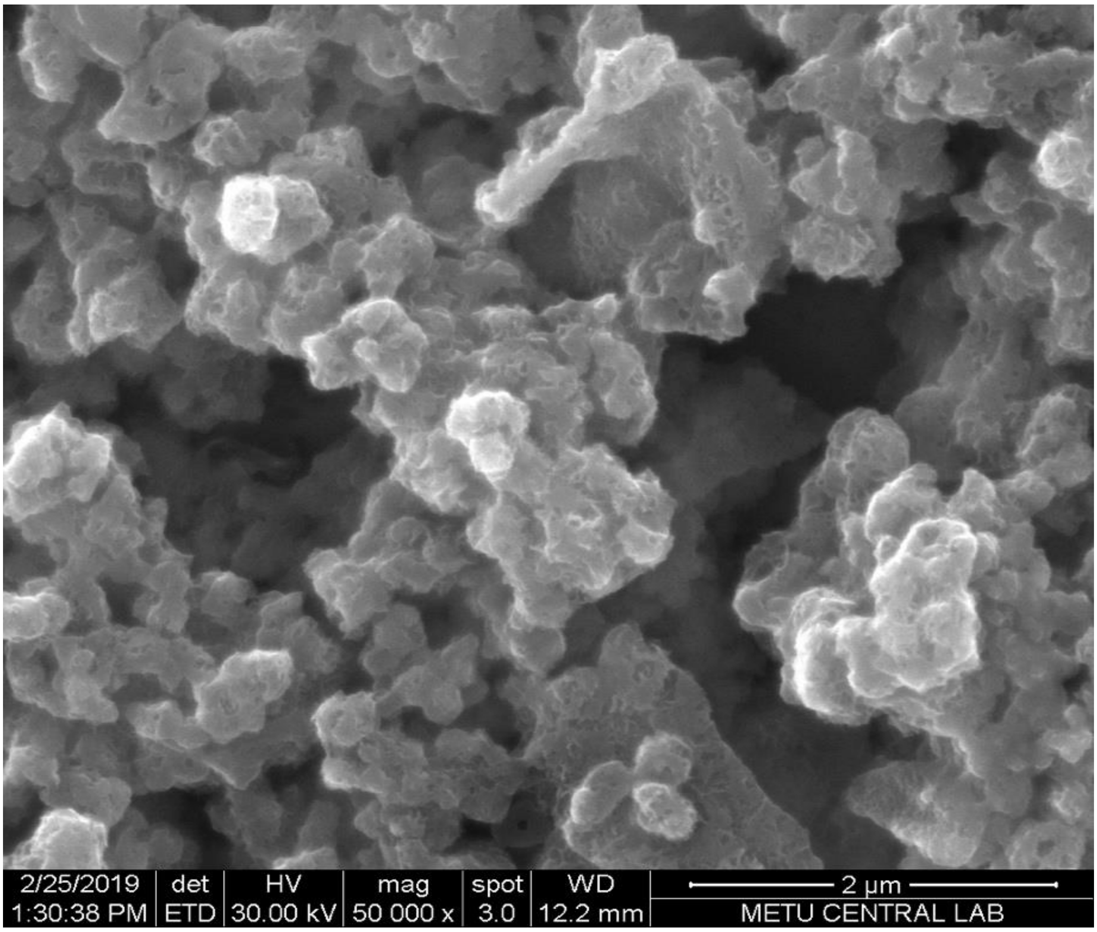
Nano teknoloji, nano metre boyutlarındaki (1 nm=10^{-9} m) sistemler ve malzemeler ile ilgili olup, yaklaşık olarak son 50 yıldır üzerinde yoğun bir şekilde çalışıldığı bilinmektedir. Ünlü fizikçi Feynman'ın "aşağıda daha çok yer var" başlıklı konuşmasından sonra bu alandaki çalışmalarda büyük bir hız kazanmıştır. Günümüzde kullanmış olduğumuz bilgisayar, akıllı telefonlar ve diğer pek çok teknolojik ürün nano teknolojinin gelişmesiyle eş zamanı olarak hayatımızda daha fazla yer almaya başlamıştır. Tabi ki bu gelişmeler sadece elektronik ürünlerle sınırlı kalmamıştır. Bugün nano teknolojinin, savunma sanayi, tıp, enerji, otomotiv, çevre, gıda ve tarımda uygulamaları bulunmakta olup bütün bu alanlarda büyük kolaylıklar sağladığı görülmektedir. Sıfır değerlikli nano demir sentezi, daha önce farklı uygulamalar için kullanılmış olup (çevre temizleme, arıtma vb. gibi), bizim çalışmamızda da bitkiler için demir gübresi olarak kullanılması düşünülmüştür. Demir gübresi olarak kullanmak istenmesinin sebebi, bitkilerde oluşan demir eksikliğinin önüne geçilmesinin hedeflenmesidir. Bitkilerde oluşan demir eksikliği bu bitki ile beslenen diğer canlılarda da eksikliğini göstermekte olup tüm besin zincirini olumsuz olarak etkilediği düşünülmektedir.



Şekil 1.2. Sıfır valent demir nano parçacıklarının 1K büyütülmüş SEM görüntüleri.

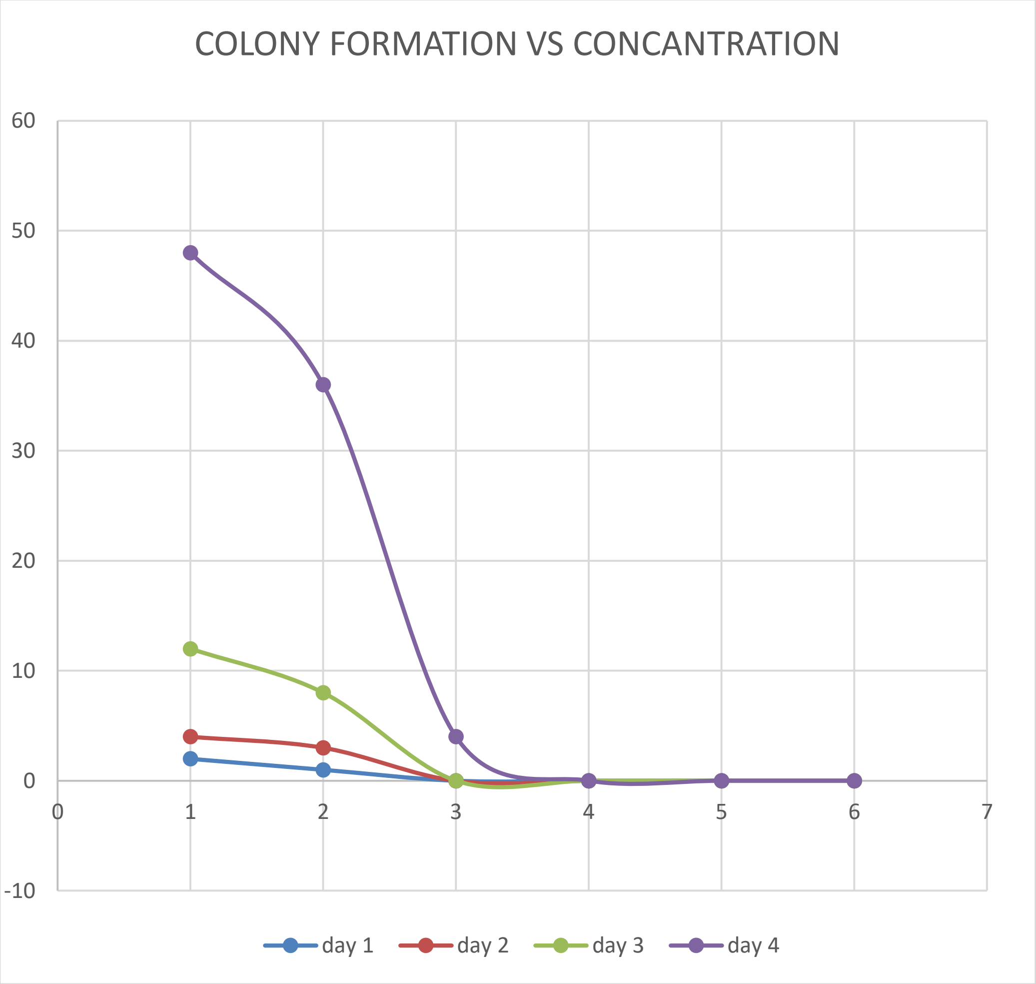
Ülkemizde de insanlarda en çok eksikliği görülen mineral olan demirin, vücudumuz için pek çok hayati önem taşıyan fonksiyonu olduğu bilinmektedir. Bu sebeple, çalışmamızın amacı, hem bitkilerde demir eksikliğinin önüne geçilmesi hem de başta insanlar olmak üzere bu bitki ile beslenen tüm canlıların demir minerali yönünden problem yaşamamasıdır.

Bu tezin amacı bakterilerin demir eksiklerini gidermek için nano teknolojinin kullanılmasını sağlamak ve bakterilerin vücutlarında bulunan demir miktarının artırılarak ikincil zincirdeki bitkideki demir miktarını %2 artırabilmektedir. Eğer bitki üzerindeki demir miktarı %2 artırılabilirse dünyada açlık oranı %1'lerin altına düşeceği öngörülmektedir. Son yıllarda, demir nano partikülleri üretmek, nano parçacık yüzey özelliklerini değiştirmek, bu alandaki saha çalışmalarının verimliliğini arttırabilmek için çeşitli sentetik yöntemler geliştirilmiştir.



Şekil 1.3. Sıfır valent demir nano parçacıklarının 50K büyütülmüş SEM görüntüleri.

Bu tez ile kimyasal çöktürme yöntemi ile nano demir başarı ile sentezlenmiştir. Sentezlenen demir partikülleri XRD analizleri ile saf demir formunda olduğu SEM analizleri ile ise yaklaşık partikül boyutlarının 4 nm civarında olduğu saptanmıştır. Bununla birlikte sentezlenen demir parçacıkları içeren bakteriyel besi ortamlarında ekimler yapılmış diğer besiyerlerle ile aynı şartlarda karşılaştırılmıştır. Bakteriyel büyüme analizleri içeren sonuçlara göre, Nano Fe'nin diğer gruplar içerisinde en hızlı gelişimin 5 ppm miktarı olduğu görülmektedir. Ancak besiyeri oranının 5 ppm üstünde olmasının bakteriyel gelişimi engellediği tespit edilmiştir bunun nedeni ise demir miktarının daha önce söylendiği gibi bioaktivitelerinden kaynaklanabileceği, bunun araştırmasının bu çalışmanın daha sonraki çalışmalarla aydınlatılabileceği düşünülmektedir. Şekilde elde edilen demir parçacıkları ve elde edilen büyüme sonuçları görülmektedir.



Şekil 1.4. Bakteri üretim analizi.

Çalışma grubunda kullanılan sıfır değerli nano demir Biyoteknoloji Uygulama ve Araştırma Merkezi laboratuvarında elde edildi. Bu yüzey katalitik özelliklere sahip parçacıkların elde edildiğini göstermektedir. Bununla birlikte, oksidasyon yoktur, fakat su içinde yapışkan partiküller elde edilmiştir. Ortamda yeni koloni oluşumu mikroskop yardımıyla incelenmiştir. Numunedeki gelişimler (o ppm) ilk günden itibaren gözlemlenmiş, üretim 5 ppm'de durmuş ve daha yüksek konsantrasyonlar gözlenmemiştir. Bu nano demirin maya ve yoğurt bakterilerine karşı fermantasyon üzerinde olumsuz bir etkisi olduğunu göstermektedir.

Sonuçlar şu şekilde sıralanabilir nano demir başarı ile sentezlenmiştir, nano demirlerin ortalama çaplari 45 nm gibi bulunmuştur, litaratürde ilk defa yoğurt mayası üzerine nano malzemelerin etkileri araştırılmıştır, Biyo malzeme konsantrasyonlarının biyolojik yapı ile uyumu incelenmiş ve değişik konsantrasyonların değişik guruplar üzerindeki etkileri görülmüştür. Ortamda yeni koloni oluşumu mikroskop yardımıyla incelenmiştir. Numunedeki gelişmeler (o ppm) ilk günden itibaren gözlemlenmiştir, üretim 5 ppm'de durmuş ve daha yüksek konsantrasyonlar gözlenmemiştir. Bu, nano demirin maya ve yoğurt bakterilerine karşı fermantasyon üzerinde olumsuz bir etkisi olduğunu göstermektedir. Bu sonuçlar ışığında çökelme yöntemi ile sentezlenen nano demir parçacıklarının demir eksiklikleri ve demir ihtiyaçları konusunda bir alternatif olarak kullanılabileceği ispatlanmış olmaktadır.

CURRICULUM VITAE

My name is Farooq Omar Mohammed, my surname is ALABDI, my nationality is Kurdish, I am from north of Iraq, I was born 20-4-1988 in zakho, I am married. My phone number is +9647504171857, E-mail address is (farooqomar1020@gmail.com). I finished primary school and secondary or high school in zakho city. I finished B. Sc – Mechanical engineering (production and metallurgy department) -faculty of engineering- Sulaimani Polytechnic University, Iraq (2007-2011). I started master degree in 2016 at Van Yuzuncu Yil University- Faculty of Engineering- Mechanical Engineering.

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