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BIOPOLYMER ASSISTED GREEN SYNTHESIS OF FUNCTIONAL COBALT OXIDE NANOPARTICLES

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Master's Thesis

Supervisor
Assoc. Prof. Dr. Hakan KAYGUSUZ

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The thesis titled "BIOPOLYMER ASSISTED GREEN SYNTHESIS OF FUNCTIONAL COBALT OXIDE NANOPARTICLES," prepared by TITILAYOMI ROSELINE ADETORO and submitted on 22/08/2022 has been **accepted unanimously** for the degree of Master of Science in Biomedical Sciences.

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Titilayomi Roseline ADETORO

Signature

DEDICATION

I dedicate this thesis to my lovely family for their support morally, financially, spiritually and emotionally all through my thesis process.

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ABSTRACT

BIOPOLYMER ASSISTED GREEN SYNTHESIS OF FUNCTIONAL COBALT OXIDE NANOPARTICLES

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Cobalt oxide nanoparticles were synthesized by thermal decomposition of cobalt alginate biopolymer gel at 350 ^{o}C and 450 ^{o}C. Because of its attributes like gel responsiveness, non toxic, ion crosslinking and low cost, alginate was used to produce Cobalt oxide nanoparticles. The gel beads were prepared and the results were characterized. The confirmation of the cobalt oxide, graine size distribution and also the crystallite size was carried out using XRD analysis, TEM analysis was done to determine the particle size. The results shows the size of the cobalt oxide nanoparticles to be 32nm, GSD was also calculated using th full width at 1/5 and 4/5 of maximum of the XRD peaks. EDS coupled with SEM analysis shows the elements present in the CoNPs with their percentage.

Keywords: Cobalt oxides, Nanoparticles, Alginate, Thermal decomposition.

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ABBREVIATIONS

Co : Cobalt Oxide

CoNPs : Cobalt Oxide Nanoparticles

IVD : In – Vitro Diagnostics

LFS : Liquid Flame Spray

GQDs : Graphene Quantum Dots

SEM : Scanning Electron Microscopy

TGA : Thermogravimetric Analysis

XRD : X – Ray Diffraction

GSD : Grain Size Distribution

FWHM : Full Width at Half Maximum

FTIR : Fourier Transform Infrared Spectroscopy

TEM : Transmission Electron Microscopy

LIST OF SYMBOLS

β : Pure line boarding (FWHM)

Λ : Wavelength

θ : Incident angle (Bragg angle)

σ : Dispersion

Γ : Euler gamma function

1. INTRODUCTION

Focus on the outstanding characteristics of nanomaterials and nanoparticles, which can be used in a wide range of industries ranging from microelectronics to healthcare, has improved in recent years [2], [3]. Metal nanoparticles, which can be used either d irectly or as a component of a hybrid material, are among the many types of nanoparticles that can be created, along with nonmetals and polymeric compounds. Physical and chemical methods are used to produce and alter metallic nanoparticles. The production process for nanoparticles needs to be carefully investigated in order to produce particles with the proper crystal structure, surface area, and size. Post-synthetic modification is a technique for modifying nanoparticles after they have been created for a particular purpose (for example, PEG coating to improve biocompatibility).

A mammal's body has very little cobalt, hence the mineral must be consumed externally in the form of green vegetables and cereals. Vitamin B12, cobalamin, and a few enzymes that incorporate cobalt have been found to be the principal biological functions of cobalt. The importance of cobalt-based biomedical goods is rising due to the element's role in human metabolism.

Cobalt nanoparticles can be used for a number of things, such as medicine delivery systems, contrast agents, energy storage, and catalysts. Cobalt nanoparticles can be employed as drugcarriers due to their magnetic characteristics [27], [28]. Due to their physical and chemical characteristics and tiny size, cobalt nanoparticles are suitable for use as sensors for a wide range of substances [29]. Its focus is on the most popular synthesis techniques and applications for these nanoparticles, which range from catalysis to the most significant biomedical uses, such as anticancer therapy and diagnostic materials, and everything in between. This is due to the ease with which cobalt nanoparticles can be created and the wide range of applications that can be found for them.

Alginate is an edible polysaccharide biopolymer made up of the monomers such as mannuronate and guluronate. It has variety of uses, which includes controlled release and water filtration [16]. It serves an important role as a thickening, gel forming and stabilizing agent due to its properties such as,the capacity to form films, sensitive to pH changes and gel formation, be hydrophilic,biocompatible, biodegradable, non-toxic, processable, and exhibit ionic crosslinking. Ionic interaction between blocks of guluronic acid in the polymer chain and divalent or trivalent cations causes gel formation, resulting in a three-dimensional network of alginate molecules that is commonly referred to as the "egg-box model" [17].

Due to its biocompatibility and biodegradability, biopolymer-based wound dressing films have actually acquired research attention. Alginate (Alg) and carboxymethyl cellulose (CMC) were crosslinked with Ce^{2+} ions to create a film in a recent study, and its antibacterial activities were assessed. The film's chemical and physical properties, which include its ability to be UV-protective, vapor permeable, swellable, and antibacterial, look promising as potential benefits for wound dressings [1].

Also, a study carried out by Kaygusuz et al. shows the application of alginate in wound dressing as well.Alginate films were crosslinked with cerium(III) solution and chitosin added cerium(III) solution in this study, bringing together the benefits of the materials. The films' physical and antibacterial qualities were evaluated to those of standard calcium alginate films. Cerium ion-crosslinked alginate films and cerium ion - chitosan crosslinked alginate films both showed antibacterial effects against both Gram-positive and Gram-negative (Escherichia coli) bacteria [18].

2. LITERURE REVIEW

2.1 INTRODUCTION

Fourier-transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-Vis), X-ray photoelectron spectroscopy (XPS), energy-dispersive x-ray spectroscopy (EDS or EDX), X-ray diffraction spectroscopy (XRD), Raman spectroscopy, and photoluminescence spectroscopy are among the known spectroscopic techniques for the characterization of Cobalt oxide nanoparticles.

2.2 LITERATURE STUDIES

Cobalt oxide nanoparticles can be synthesized using a variety of physicochemical techniques, some of which are highlighted here. CoCl26H2O and hydroxyl cellulose were introduced as precursors during the casting procedure to produce cobalt oxide nanoparticles, which were then calcined to form particles with a size of 15 nm [29]. The precursors in the solution are placed to a suitable surface, like glass or stainless steel, and allowed to dry, as in the casting procedure [27]. 32.66 nm in diameter, spherical-shaped nanoparticles were produced, known precursor quantities were allowed to react in the solution in this chemical solution precipitation procedure, and the precipitate that resulted was then washed and dried. The advantage of the chemical solution precipitation approach is that it is advantageous for the mass production of materials, however the technology is not very quick and the particle shape is not well specified. For these reasons, the microwave technique was applied in the same experiment. The precursors are dissolved in a solution that is exposed to microwave energy in the microwave technique, which produces a purified and dried product [19].

The Co_3O_4 nanoparticles were made using a microwave approach, employing sodium hydroxide and $CoCl_2$ as precursors. The benefits of this process include speed, great reproducibility, and improved control over the quality and size of the nanoparticles produced. The size of the spherical nanoparticles was 72.43 mm [20]. Another work used microwave and calcination to create Co3O4 nanoparticles from cobalt (II) nitrate hexahydrate and aqueous ammonium hydroxide solution. As a result, 13 nm-sized spherical agglomerated crystalline nanoparticles were produced. Due to the benefits of being able to regulate the size, stability, and consistency of the nanoparticles, the microemulsion quenching process has also been employed to synthesize Co3O4 nanoparticles [22]. With the help of this method, which makes use of microemulsions containing advantageous precursors, a precipitate that is washed and dried to enhance the processing. All precursors produced spherical nanoparticles with a size range of 1–5 nm using the cobalt-based metallosurfactants bishexadecylamine cobalt dichloride, bishexadecyltrimethyl ammonium cobalt tetrachloride, and bisdodecylamine cobalt dichloride.

These techniques can also be used to determine if nanoparticle aggregation is present or absent. Some of these microscopes might also come with other characterisation tools, including energy-dispersive X-ray spectroscopy, to reveal the elemental makeup of the nanoparticle under investigation. Such details are crucial for evaluating the antibacterial effects of nanoparticles or nanocomposites and determining the causes of such actions. For instance, a nanoparticle's antibacterial capability depends on the elements including its size, shape, and specific surface area [2].

2.3 SYNTHESIS METHODSOF COBALT OXIDE ANOPARTICLE

The development of alternative methods for producing cobalt nanoparticles is of great interest. Cobalt nanoparticles must fulfill a number of prerequisites in order for the created technology to be particularly effective: For instance, the capacity to produce a large quantity of nanoparticles with a particular size, shape, or crystallinity. Environmentally friendly methods are the fourth. The four main categories of cobalt nanoparticle development are chemical, physicochemical, biological, and physical. Depending on the case issue, several methods should be applied when synthesizing.

2.3.1 Synthesis of Cobalt oxide Nanoparticles using Solution Method

This approach is used to manufacture solution nanoparticles. A variety of factors influence the production of nanoparticles in the liquid phase (solution). A stabilizing agent must make non-covalent interactions with nanoparticles in order to stabilize them. The basic functions of the capping agent are to stabilize nanoparticles and prevent their agglomeration. Cobalt nanoparticles can be created using a variety of stabilizers.

Since the early 2000s, Oleic acid has been used to stabilize cobalt nanoparticles [22]- [23]. Barbara Farkas et al. used ab initio modeling to investigate a cluster of cobalt nanoparticles. A carboxylic acid's interaction with NPs was studied with the aid of Valeric Acid. The monodentant connection produced by a carboxylic acid on the surface of CoNPs is no longer hydrogen-bonded after dissociation. During simulation, the second oxygen atom and cobalt were shown to be chelated together, making bidirectional linkages impossible to build. Sodium borohydride was used to chemically reduce cobalt nanoparticles. The glass flask was filled with the three chemicals, and the mixture was agitated for a number of minutes at room temperature. The sodium borohydride solution was then added to the mixture after that. The nanoparticles were then filtrated from the aqueous solution and rinsed with distilled water and acetone about 15 minutes to produce particles that were 80–100 nm in size. The EDX spectroscopy showed that the nanosized cobalt seemed to have an oxidized layer on the surface because oxygen and cobalt all were present [6].

This is the simplest approach for producing nanoparticles because no specialized equipment or unique circumstances are required to carry out reactions and produce nanoparticles [24], [12]. When an agent called a capping agent is present, organic cobalt salts that are thermally degrading could produce cobalt nanoparticles [25], [30]. Cobalt nanoparticles are generated as a result of the breakdown of octacarbonyl dicobalt. The mixture was heated to 180 °C with the addition of 1,2-dimethylbenzene (DMB), oleic acid (OA), and nitrogen. The nanoparticles were precipitated with ethanol after the dicobalt octacarbonyl was dissolved in 1,2-dichlorobenzene and heated for an additional 15 minutes to 180 °C. Centrifugation was used to split cobalt nanoparticles into 7–8 nm spherical particles [24]. However, the crystal structure of the NPs was unknown. This approach is capable of manufacturing nanoparticles with a limited size range. On the other side, implementation can be difficult. Because of its high toxicity, octacarbonyl should be avoided in this dicobalt-making technique [12], [13]. Masoud Salavati-Niasari and colleagues created cobalt nanoparticles without the usage of potentially harmful chemicals. Bis (salicylaldiminato) cobalt was first made by combining 0.6 g Cobalt with 2 ml of oleylamine were placed inside a three-neck distillation flask, and the mixture was heated about 90 minutes at 100 ^{o}C [25]. The flask was purged with high-purity argon gas throughout the procedure. A 220 °C solution of metal complex was treated with triphenylphosphine to produce cobalt nanoparticles. The solution was heated to 210 °C for 45 minutes before being cooled. Excess ethanol precipitated over-precipitated nanoparticles, resulting in 25-35 nm spheres of cobalt nanoparticles [22]. There was no sign of cobalt oxide in the data from newly produced nanoparticles. The X-ray diffraction pattern contained CoO and Co_3O_4, but there was no indication of Co(0).

This approach has benefits since it enables you to control the particle size by changing the precursor and stabilizing agent ratios throughout the formulation, due to the fact that it creates nanoparticles with a wide dispersion.

2.3.2. Hydrothermal Method of CoNPs Synthesis

S.M. Ansari et al. used the hydrothermal method to create cobalt nanoparticles [27]. KOH mixture was prepared after cobalt chloride had been dissolved into deionized water, and stirring continued for at least 15 minutes. After stirring the resulting mixture for two hours to completely dissolve the solid reagents, it was deposited into a Teflon-coated autoclave and put into an electric oven, where the temperature of the mixture was maintained at 160 ^{o}C for 24 hours. Next, hydrazine monohydrate as well as oleic acid solution was then added until the overall amount of the mixture was 2/3 of the total amount of the autoclave. The autoclave was left to naturally cool to ambient temperature after 24 hours. Finally, the final solution was centrifuged, the liquid phase was decanted, and the resulting black residue was dried in order to separate the CoNPs from the liquid phase. KOH is used in a 100 °C oven after cobalt chloride has been dissolved in deionized water [14]. The produced NPs had an average size of 192 nm, and the XRD data showed that they contained Co(0) and had a hexagonal as well as cubic crystal structure.

The current system seems to be more scalable and user-friendly. Additionally, it enables the production of spherical particles with a restricted size distribution, which has potential benefits for a variety of medical uses. In order to minimize contact with air, G. Seong et al. [28] used formic acid decomposition and supercritical hydrothermal reduction to generate CoNPs (at temperatures close to 420 ^{o}C and pressure of 22 MPa). The precursors were delivered into to the autoclave through the use of an insulator in an airtight environment. An autoclave containing an aqueous cobalt acetate with formic acid solution was heated over 10 minutes at 430 ^{o}C in an electronic oven. After 10 minutes, the autoclave then cooled in a boiling water at 25 ^{o}C until 5 minutes to prevent particle formation. The cooled autoclave got unsealed and shut to let the produced gases out. Nanoparticles were extracted with methanol, centrifuged, and then washed with methanol. The resulting particles were spherical and had a size range of 20–400 nm. The system underwent a thermodynamic study, and the results revealed that the observational data and the data estimated by the PSRK EOS match [33]. The system involves metallic cobalt and faint peaks of cobalt oxide, according to XRD examinations. Supercritical water is an environmentally safe, non-flammable solution that is used all over the world. The synthesis parameters can be altered since water's volume and dielectric constant change radically at its critical point. Although it should be emphasized that using supercritical conditions requires specialized equipment and greater energy consumption, this synthesis is environmentally beneficial.

2.3.3 Procedures, Advantages and Disadvantages of Hydrothermal Method of CoNPs Synthesis.

By modifying the temperature, pressure, reaction time, and the usage of nano templates, nanoparticle characteristics can be altered without the need of high temperatures or complex processing technologies. Aside from its high yield and superior stoichiometry, the hydrothermal process is appealing due to its smaller particle size and narrower particle size dispersion, as well as its controlled form at high reaction rates. [29] Describes a hydrothermal approach for producing magnetic nanosized $CoFe_2O_4$. Research on the size and shape of $CoFe_2O_4$nanoparticles is under underway. CTAB was used as a surfactant in the hydrothermal process for the production of $CoFe_2O_4$ nanorods. Making one-dimensional $CoFe_2O_4$ nanostructures using anodic aluminum oxide as a template is achievable, but the technique is expensive and yields are low. The size of $CoFe_2O_4$ crystals can be lowered by lowering the pH of the reaction fluid. No amount of reaction time or temperature could yield pure $CoFe_2O_4$ [28] at pH 10. The $FeCl_3$ hydrothermal technique, cobalt dodecyl sulfate, and aqueous NaOH solution were also used to create $CoFe_2O_4$ nanoplatelets. A two-hour supercritical hydrothermal method was used to create this $CoFe_2O_4$ nanoparticle. $NiFe_2O_4$ nanocrystals were created by hydrolyzing $FeCl_36H_2O$ and $NiCl_26H_2O$ with NH_3 and NaOH. $ZnFe_2O_4$ was produced in ammonia solutions utilizing Zn sheet and $FeCl_2$. Aloe vera extracts and metal acetylacetonate were utilized in the production ofMFe2O4 hydrothermally (M = Mn, Co, Zn and Ni), resulting in a high-yield, well-crystalline structure at high temperatures.

2.3.4 The Solvo-thermal Method of Cobalt Nanoparticles Synthesis

Both hydrothermal and solvo-thermal techniques use autoclaves at high temperatures and pressures, however the solvothermal approach employs organic solvents rather than water. M. Alagiri et al [22] employed this approach to create CoNPs. To begin, ethanol was quickly agitated for two hours to form a purple-purple homogenous cobalt chloride solution. Hydrozine monohydrate was added to the mixture after an hour of stirring at 50 °C. For the next two hours, triethanolamine was added to the mixture, which was vigorously stirred. The mixed solution was placed in an autoclave made of stainless steel and left for about 8 hours at 120 °C. The autoclave then was let to cool to ambient temperature (120 ^{o}C). The sample was then thoroughly cleaned by immersing it in several solvents, including acetone. It was then vacuum-dried for four hours at 60 °C. Spherical 2 nm-sized particles were generated via a metallic cobalt Co(0) structure with no additional phases (according to XRD data). An oxide layer could be prevented by utilizing this procedure to produce particles of a specific size.

2.3.5 Procedures, Advantages and Disadvantages of Solvo-thermal Method of Cobalt Nanoparticles Synthesis

Large surface area, electromagnetic saturation, and high dispersion magnetic microspheres can be made via solvo-thermal methods in liquid media official interpretation [23]. The non-aqueous solvo-thermal preparation of Co(III) acetylacetonate with Fe(III) acetylacetonate into acetophenone resulted in $CoFe_2O_4$ magnetic Nanoparticles with a size category of 2–15 nm is accompanied with a 22-hour solvothermal treatment in a Parr Acid Digestion Bomb autoclave at 120 – 200 ^{o}C. $CoFe_2O_4$ was synthesized at around 200 ^{o}C using sodium or ammonium acetates, polyethyleneglicols, ammonium urea, oleylamine, and urea. Small $NiFe_2O_4$ nanoparticles were created by varying the experimental parameters (such as reaction time, initial reactant concentrations, amount of protective agents, and acetate type) and electrostatically stabilizing them with sodium acetate as the solvent [11]. For superior signal with dispersion in liquid environments, the method produces magnetic NPs having smooth surfaces, narrow size distributions, and large surface areas. As an outcome, powerful performance is advantageous for biological applications.

2.3.6 Micro emulsion Method of Cobalt oxide Nanoparticles Synthesis

Using a micro emulsion technique, it is possible to improve the size, shape, particle-size distribution, as well as chemical composition of nanoparticles. Oil-in-water and water-in-oil emulsions are just two examples of the heterogeneous systems in which this method may be used to produce nanoparticles. Series of investigations carried out on micro emulsion approach for producing nanoparticles have been conducted. Because of the wide range of parameters that can be controlled, micro emulsion technologies are becoming increasingly popular. The variables that determine the fundamental properties of nanoparticles must still be thoroughly investigated.

Metal nanoparticles include Zn [19] and a variety of other metals such as Sn (26), Cu (67), Ti (68), Fe (69), and Ag (20). When a precursor containing Co ions, such as $Co(NO_3)_2$, is combined with a surfactant, such as Cetyltrimethylammonium bromide (CTAB), it is a phase of oil containing hydrocarbon (such as Isooctane) or alcohol (such as butanol), also a liquid phase containing alkali (another agent of reduction), micro emulsion methods can be used to create CoNPs and cobalt-containing materials. Cobalt nanoparticles can also be made via the micro emulsion technique with cobalt acetate tetra hydrate and ethylene glycol. Before adding the cobalt solution, an empty beaker was filled with ethylene glycol, and the two solutions were constantly swirled while the cobalt solution was added at a rate of 2 milliliters per minute. The end result of this technique is a pink emulsion. To improve the stability of these systems, starch and polyvinylpyrrolidone (PVP) might be added. This device can be warmed up to speed up reaction. Because ethylene glycol is used as the procedure for the response might be done at temperatures as high as 160 ^{o}C. When compared to water systems, this allows the reaction to proceed faster. Using this method, CoNPs with magnetic characteristics and a size of 35 nm (as measured by XRD and SAXS) can be created. This permits CoNPs to be used in magnetic carriers [26].

For example, it made it possible to create CoF_2 nanoparticles. A magnetic stirrer was used to stir together 5.0 g CTAB, 30.0 g 2-octanol, and 4.0 g H2O in two Teflon beakers for one hour. To synthesize $Co(NO_3)_2.6H_2O$ and NH_4F, two solutions were used: one containing 0.58 g (2.0 mmol) and the other containing 0.18 g. (5.0 mmol). Following that, the two microemulsions were combined and agitated for an additional hour. Pink precipitates formed after 30 minutes of filtrating the residue at 4000 rpm. The powder was then rinsed with ethanol and air dried for a full 24 hours before usage. Because of their high thermal stability and homogenous composition, CoNPs could be employed as cathode components in lithium-ion batteries and energy storage systems. According to microemulsion XRD data, micro emulsions can be created by combining a gasoline solution of sodium bis (2-Ethylhexosuccinate) with 0.1 M of $CoCl_2$ in deionised water. Shaking finished metal-ion reduction and nanoparticle synthesis to produce an emulsion. In a 5 mL volume, the $NaBH_4$ solution was dropped inside the metal ion. All of the NPs was washed, centrifuged, and then deposited in a burner at 80 °C about 12 hours after being agitated for two hours at room temperature [28].

2.4. GREEN METHODS OF CoNPs SYNTHESIS

Scientists are increasingly interested in developing ecologically friendly methods for synthesizing materials, particularly nanoparticles. Synthetic processes can be made safer and more environmentally friendly by employing these principles. Furthermore, nanoparticles derived from biological systems may have different structural and physicochemical properties. The capping agent's compatibility with living things (both microorganisms and humans) is a crucial aspect in the creation of new nanoparticle applications. One green chemistry technique for producing nanoparticles is to reduce cobalt precursors using plant extracts. Using aqueous or organic plant extracts, it is feasible to reduce and cap the created cobalt nanoparticles. These nanomaterials have different forms and are more biocompatible than synthetically created nanoparticles due to a collection of extractable chemicals [22]. Melvin S. Samuel and colleagues [23] employed extracts from the rotund folia vine as a green solvent for creating cobalt nanoparticles from a solution of cobalt chloride. A precipitate were filtered, processed, and dried in oven for later use once the system was alkalinized. The size of the produced nanoparticles varied. Co(0) NPs' polycrystalline cubic structure, which was also confirmed by XRD, could be related to a number of other substances in the extract. Red algae extracts can be transformed into cobalt nanoparticles by adding cobalt nitrate drop - wise to the algal extract, which is prepared by boiling dried algae for four hours at 70 °C in an aqueous medium. The solution should change color between pale pink to dark brown during the course of the night. Plant extracts, according to Ismat Bibi et al. [12], can be used to create nanoparticles. P. granatum peel extract and a cobalt precursor were mixed for 90 minutes at 70 degrees Celsius. Following that, the precipitate was separated and dried. Researchers observed that a cobalt oxide face-centered cubic crystalline phase may break down organic dyes with an efficiency of roughly 80 nm (based on XRD data).

Microorganisms, such as bacterial cultures, can also be used to create nanoparticles. Microorganism enzymes aid in the creation of CoNPs by reducing metal ions in the solution. Using microbiological systems, vast volumes of nanoparticles with high colloidal and sedimentation stability can be produced. For example, Eunjin Jang [26] discovered a process for coating bacteria with rod -shaped CoNPs. To separate and purify Bacillus subtilis, a suspension is incubated with cobalt chloride before being centrifuged and washed. With this technology, nanobiocatalysts may be manufactured at room temperature using a simple procedure, and nanoparticles have been demonstrated to be quite beneficial in this process.

According to a study by Vijayanandan A.S. with Balakrishnan R.M. [27], NPs was generated utilizing some fungus called Aspergillus-nidulans and bacterial cultures. To remove the fungal mycelium, the solution was placed in a spinning shaker at room temperature for five days before being rinsed and filtered to remove the mycelium's components. Centrifugation was used to separate the nanoparticles from the rest of the solution. The above 20 nm-diameter nanoparticles were retained throughout the development process by proteins generated from Aspergillus nidulans that contain sulfur. In a study, the International Center for Diffraction Data discovered cobalt oxide nanoparticles in their spinel phase.

According to B.A. Omran et al., Aspergillus brasiliensis ATCC 16404 cell-free filtrate can also be used to produce Co3O4 NPs. CoSO47H4O was grown for 72 hours at pH 11 on a stirrer in a dark atmosphere with 5 percent extract of A. brasiliensis mycelium. During the synthesis, the color of the solution changed from yellow to brown. The mycosynthesized CoNPs seemed to have a diameter of 20 – 26 nm and were spherical in form. They were discovered to have the ability to kill a variety of microbes as well as antimicrobial, magnetic, and antibacterial activities.

2.5. PHYSICAL METHODOF COBALT NANOPARTICLES SYNTHESIS

Mechanical, optical, and electrical manipulations of the compound are essential to physical techniques of generating CoNPs [29]. Crushing and grinding bulk metal, flame spray pyrolysis, the vapor condensation, aerosol processes, and also special mechanical processes are few of the physical processes utilized to create nanoparticles.

2.5.1. Vapor Condensation Method

Metallic nanoparticles have long been manufactured using the time-tested vapor condensation technique, which converts organic metal salts into gaseous forms under vacuum before condensing. This method results in the precipitation of a reduced metal [31], [32]. X.L. Dong et al. used chemical condensation to create cobalt nanoparticles. The apparatus chamber was heated to 60 ^{o}C for the chemical vapor condensation, and octacarbonyl dicobalt was evaporated in it before liquid nitrogen was introduced into it, as shown in. Following the completion of the treatment, the walls were cleaned of any particles. Because of their formation during the processing, cobalt oxide and string-shaped cobalt nanoparticles were present in the finished powder. Metalized Cobalt (Co (0)) was discovered via XRD analysis. Zhang H. Wang and colleagues employed carbon nanocapsules coated with a carbon film and high-purity CO2 in their experiment to synthesis dicobalt octacarbonyl [32]. Dicobalt octocarbonyl evaporation temperature was 60 degrees Celsius. In an oven, it is roasted to temperatures ranging from 400 to 1000 ^{o}C, at which time the carbon monoxide and precursor vapors are broken down and turned into nanoparticles. The carrier gas stream enters the cooling area called Chiller. Those particles were removed after chiller had cooled to a safe temperature. The amorphous carbon shell was 4-6 nanometers thick, and the nanocapsules were 20- 60 nanometers in diameter. The presence of the cobalt carbide phases Co2C and Co3C has been discovered using XRD. In a condensation chamber, pressure and/or decomposition temperature can be varied to alter the particle size range of nanoparticles. vapor condensation.

2.5.2. The Arc Plasma-Assisted Deposition Method

Supplying a high-power pulse electric currents through a thin metal wire causes the wire to explode, which is how the arc plasma-assisted deposition technique works. A significant amount of thermal energy causes the wire to melt, which is accompanied by evaporating and plasma formation. The plasma created during the process expands and cools when it comes into contact with a refrigerant, along with an inert gas phase. The nucleation process results in the formation of nanoparticles. Arc plasma evaporation, for instance, was utilized by H. Meng et al. to produce cobalt nanoparticles. A cobalt metal block was used in their experiment, which took place in a preparation room that has been well before around 0.005 Pa and filled with a hydrogen-argon mixture. The preparation chamber had an evaporating crucible that was water-cooled. After that a galvanic arc were created, the metal melted. After the creation of plasma, argon gas and metal ions inside this plasma interacted to create nanoparticles

The air flow then took the produced particles to the separating chamber. The particles were separated based on size, with larger and heavier ones settling on the cabinet's surface before smaller and lighter ones. The particles were then collected and kept in a specific vacuum container after being cooled to room temperature. The size of the created NPs ranged between 28 to 70 nm, as well as an XRD analysis showed that they are totally made up of Co(0), without any other phases being identified [24].

2.5.3. Liquid-Phase Plasma Method

Plasma is produced by an arc discharge inside a metallic salt solution to create nanoparticles. The plasma must cool first before nanoparticles can form because nucleation takes time[30]. Plasma in the liquid phase was used to create cobalt nanoparticles by Hwan-Gi Kim et al. An electric discharge was used at room temperature to stabilize the nanoparticles using sodium laurel sulfate. A pulsed electromagnetic discharge was produced via a needle-shaped electrode. The plasma therapy takes longer as the particles get bigger and more numerous. Spherical nanoparticle with a width of 10–100 nm were produced when the plasma was treated for 10–60 minutes. The width of the resultant spherical nanoparticles rose to 50-100 nm after 30 mins of plasma treatment. plasma treatments with at least 60 mins that resulted in the formation of needle crystals. XRD analysis revealed that Co(0) metal as well as Co(0) oxides are present on nanoparticle surfaces. [30].

A plasma discharge in liquid ethanol was employed by Ruslan Sergiienko et al., who then separated, dried, and heated the graphite particles [31]. A cobalt plate, a cobalt electrode tip, and an iron electrode were used for ultrasonic homogenization of ethanol in a glass tank. After cooling in an cold bath, Teflon lid was utilized to seal the glass container. A creek of argon gas then was poured inside the jar so it could be inert fully. To keep that sonicator from overheating, a 3A maximum current limit was placed on the source at 55 volts. The plasma's rays were just in front of the plate. In this discussed case, electrode stops and Cobalt plate surface were worn away by thermal evaporation. Using gravity, the larger nanoparticles in ethanol were separated from the smaller ones. The carbonaceous granules containing liquid ethanol was kept in a glass bottle once the experiment was complete. A layer of particles with a diameter greater than or equal to 200 nm formed on top of the liquid ethanol after a few days, although smaller particles were scattered throughout. Black suspension was left in the second bottle after bigger nanoparticles sank to the bottom of the first. After washing and drying, for 24 hours the powder were scratched in a 15% HCL acid solution 30 ^{o}C in order to remove the larger nanoparticles from the ethanol. The XRD study of the nanoparticles revealed that they were spherical, less than 10 nm in diameter, and contained the CoO and Co3C phases. A smaller particle size was achieved through the use of ultrasonic irradiation with this technique.

By adjusting the length of time the arc discharge travels through the fluid, the form and size of the nanoparticles may be precisely controlled. This method has a low potential for scaling because of the large amount of energy required [31].

2.5.4. The Ultrasonic Method

Because of its numerous advantages, ultrasonic nanomaterial synthesis has the potential to revolutionize nanomaterial manufacture. Acoustic cavitation happens when ultrasonic waves speed up the process of passing through a liquid. Cavitation is the gradual expansion and contraction of vapor bubbles in a liquid. Cold liquids begin to boil as a result of the rapid rise in local temperatures and pressures generated by the collapse of these holes. High-frequency sound impulses (10–120 MHz) traveling through with a liquid mass cause cavitation.

Ultrasound can assist the Ostwald maturation process because to the many effects of cavitation like sonic airflow and turbulence. Only when ultrasonic field is powerful enough to promote chemical reactions may ultrasound cavities form. While this is true, ultrasonic irradiation at low intensities does not produce chemical reactions. A variety of factors influence nanomaterial production and properties. Pressure, temperature, and ultrasonic intensity are all factors that can influence the length of time a product is subjected to these components. Ultrasonic-assisted nanomaterial preparations outperform more traditional procedures due to their excellent stability, unique shape, and crystalline structure. In the creation of nanoparticles, emulsion and solution procedures are more often used than ultrasonic techniques [27]. To synthesis cobalt sulfurides using dihydrate and thioacetamide C2H5NS as starting materials, an hour of sonochemical sonication was required to generate a crimson solution that turned black. The black precipitate was left to air dry for 24 hours after centrifugation and washing twice with water and ethanol. Physical therapies like treatment of plasma, effects of electrochemical, and also increased pressure, in addition to ultrasonic procedures, can be utilized to better prepare nanoparticles. Son electrochemical synthesis of cobalt-iron nanoparticles was proposed by M. Dabala et al. [28]. It was wired as a potentiostat to a titanium alloy cathode with ultrasonic emitter and audio signal generator, as well as a platinum grid anode. Through galvanostatic current, the son electrode received 76 W of ultrasonic power. The following procedure was used to make Nano powders: When a 0.3 or 0.5 s current pulse is supplied to the son electrode, the titanium cathode operates just as an electrode. An ultrasonic pulse was conveyed to the son electrode as soon as the electrochemical pulse was turned off to demonstrate how a vibrating ultrasonic piezoelectric element can be used. After that, we relaxed and resumed the process where it had left off. Cobalt-iron nanoparticles with cobalt concentrations ranging from 65 to 90 percent were generated as a result of this technique.

2.6. HYBRID MATERIALS PREPARATION BASEDON CoNPs

The interaction of more than two different types of elements leads in new qualities for hybrid materials that differ from the properties of the constituent parts independently. Micro emulsion technologies is been used to create cobalt-based hybrid nanoparticles. Two micro emulsion systems, each including Triton X-100 which acts as surfactant, same as propanol which is an auxiliary surfactant, also cyclohexane works for the oil phase, and liquid solutions of H 2PtCI6 and CoCI2 as metal precursors that were mixed and generated hazy micro emulsions, were used to create hybrid materials. The emulsion was mixed with propanol to create a visible system.

When drops of a reducing solution and droplets of H_2PtCI_6 and $CoCI_2$ were mixed with drops of an oil phase, nanoparticles were formed. Metal nanoparticles were responsible for the transparent fluid turning black/gray. Pt(0)-Co(0) NPs with a diameter between 3 to 4 nm and a straight particle diameter dispersion. The nanoparticles displayed outstanding catalytic capabilities in organic chemistry (better than pure Pt nanoparticles for methanol oxidation), supporting the possible applicability of such systems. The solvothermal procedure employed to create cobalt acetate in 80 mL of pure ethyl alcohol resulted in cobalt and carbon foam, yet another hybrid material. The solution was infused with cobalt acetate and stirred for 24 hours to allow the foam to absorb it. Once the suspension was homogeneous, NaOH was then crumbled in ethyl alcohol and slowly added to agitated mixture for three hours. The mixture was then placed in an autoclave and cooked in an oven for 10 hours at 160 °C. To separate the suspension, it was centrifuged and dried. The produced NPs have the CoO/Co_3O_4 structure, as proven by X-ray phase analysis.

The mixture of porous fibres and metal nanoparticles offers unique, distinctive features in addition with carbon foamy hybrid materials made of carbon fibers and different nanoparticles. After being pre-treated for 30 minutes with strong sulfuric acid to improve their hydrophilicity, carbon nanofiber membrane were repeatedly washed with deionized water to create hybrid membranes consisting of carbon nanofibers and cobalt and nickel nanoparticle. Over the next six hours, a sample containing cobalt nitrate, nickel nitrate, and urea was heated to 80°C in an oil bath with the carbon fiber membrane. Cleaning and drying the membrane at 70 °C for 24 hours eliminated any leftover byproducts from the surface. One of the numerous industries that could profit from the use of such technology is electronics [31]. For base metal catalysts, joint systems based on a carbon nanomaterial structure may be viable options. The oxygen reduction reaction, for example, was found to be more active in a hybrid material of graphene and cobalt nanoparticles Co_3O_4 (according to XRD) than in unmodified or reduced cobalt oxides [32]. Because of their substantial surface area and capacity to give electrons flow routes inside an electro catalytic system, carbon nanotube-based items are becoming more and more well-liked. Atsushi Gabe et al. [33] describe one method for creating these materials with cobalt nanoparticles. In ethanol, $Co(NO_3)_2 6H_2O$ cobaltus nitrate hexahydrate and PVP polyvinypyrrolidone are dissolved, and carbon nanotubes are vigorously stirred into the solution. Before addition of sodium borohydride ($NaBH_4$) or ammonia (NH_4OH), the system was sonicated, mixed, and then put through an ultrasonication at 0°C in an ice bath. After two hours of agitation at 0 °C, the suspension underwent filtration, washing, and drying at 80 °C to completely reduce the Co content. Cobalt nanoparticles having the Co3O4 composition were used in this study (according to XPS data). The PVP was then taken out of the cobalt nanoparticle-containing nanotubes by calcining them for a hr at 500 °C inside a N2 atmosphere.

3. EXPERIMENTAL METHOD

3.1 MATERIALS

Alginic sodium salt (CAS 9005-38-3) obtained from Sigma Aldrich, Cobalt (II) chloride hexahydrate (CAS 7791-13-1, 99% purity) was purchased from ISOLAB chemicals supplier company. For the preparation of solution, purified water was used and the chemicals were used without further purification. All experiments were carried out at the laboratory of Altinbas University, Faculty of Engineering and Natural Sciences.

3.2 PREPARATION OF COBALT OXIDE NANOPARTICLES

Cobalt oxide nanoparticles was prepared by using alginate biopolymer method. The function of adding pure water is for hydrolysis reactions by dissolving 0.2 g of alginate in 20 mL of pure water using a magnetic stirring (350- 400 rpm and 30 ^{o}C).

The next procedure was preparation of the cobalt (II) chloride solution. 5 g of $CoCl_2$ was needed to be dissolved and the the solution available is Cobalt (II) chloride hexahydrate, therefore the removal of hydrate was carried out.

MW of $CoCl_2$ hexahydarte = 237.90 g/mol

MW of $CoCl_2$ without H_20 = 129.90 g/mol

To get the amount of $CoCl_2$ hexahydrate needed:

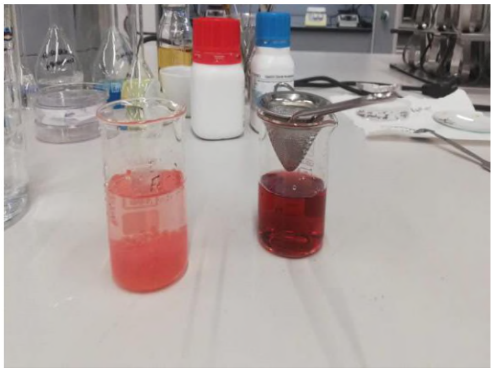
237.90 g/mol 129.90 g/mol

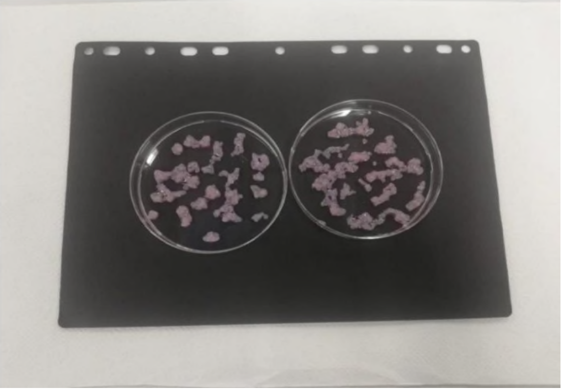
X g 5 g

= 9.157 g in 100 mL of water

But 50 mL of water was needed, therefore we have 9.157/2 = 4.58 g of $CoCl_2$ hexahydrate was dissolved in 50 mL of water and the solution was prepared.

After all the chemical materials has dissolved, a vigorous stirring process was performed to prevent agglomeration during the dropping of alginate in cobalt (II) chloride solution with the use of syringe. The solutions was kept on the magnetic stirrer for 30 minutes for complete crosslinking of the beads. The beads were then washed with pure water and filtered.





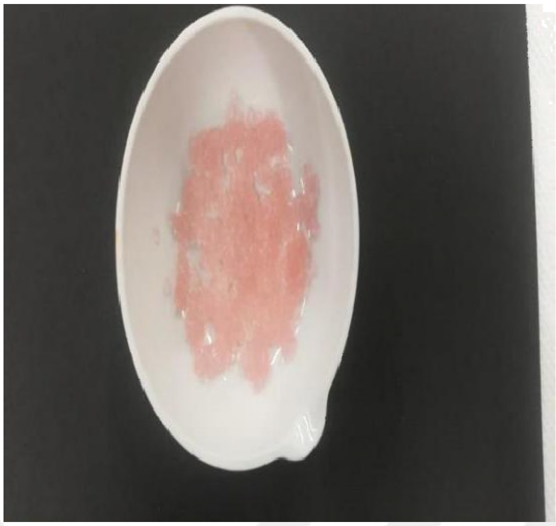


Figure 3.1. Experimental procedures for bead preparation

Then, the gel beads were placed in a porcelain crucible and immediately heated to at 350 °C for 30 minutes in a laboratory furnace. The cobalt oxide nanoparticles were then removed from the furnace at the end of this process and left at room temperature where all beads turned a dark black powder, and kept in a desiccator. Beads preparation was mainly carried out by the method proposed by Kaygusuz et al [16], [17].

Figure 3.2 CoNPs after heating.

3.3. CHARACTERIZATION

The sample powders were characterized by X-ray diffraction with the use of Advance Series powder diffractometer (Bruker D8). The X-ray diffraction (XRD) analysis was carried out to confirm $CoCl_2$ crystalline size and its phase and the results were recorded using Cu Kα radiation.

4. RESULTS AND DISCUSSIONS

The result and discussion will be displayed here. The calculations will be carried out as well.

4.1. OPTICAL STUDIES AND DISPERSIBILITY

The XRD $CoCl_2$ crystallite size samples were calculated from the peak width using the Scherrer equation.

$$D = \frac{K\lambda}{\beta cos\theta}$$

Where;

K is the shape factor (0.89)

λ is the wavelength of X-ray Cu Kα radiation (1.54 A)

β is the pure line boardening (FWHM)

θ is the Bragg angle (peak position)

As shown in Figure 4.1, the XRD pattern of $CoCl_2$ specimen synthesized with the use of alginate method. Major diffraction peak (36^{O}) was recorded and the crystallite size was calculated using Scherrer equation and found as 32 nm. Pielaszek method was also applied to data. The mean size and dispersion are found as 15.54 nm and 10 nm respectively.

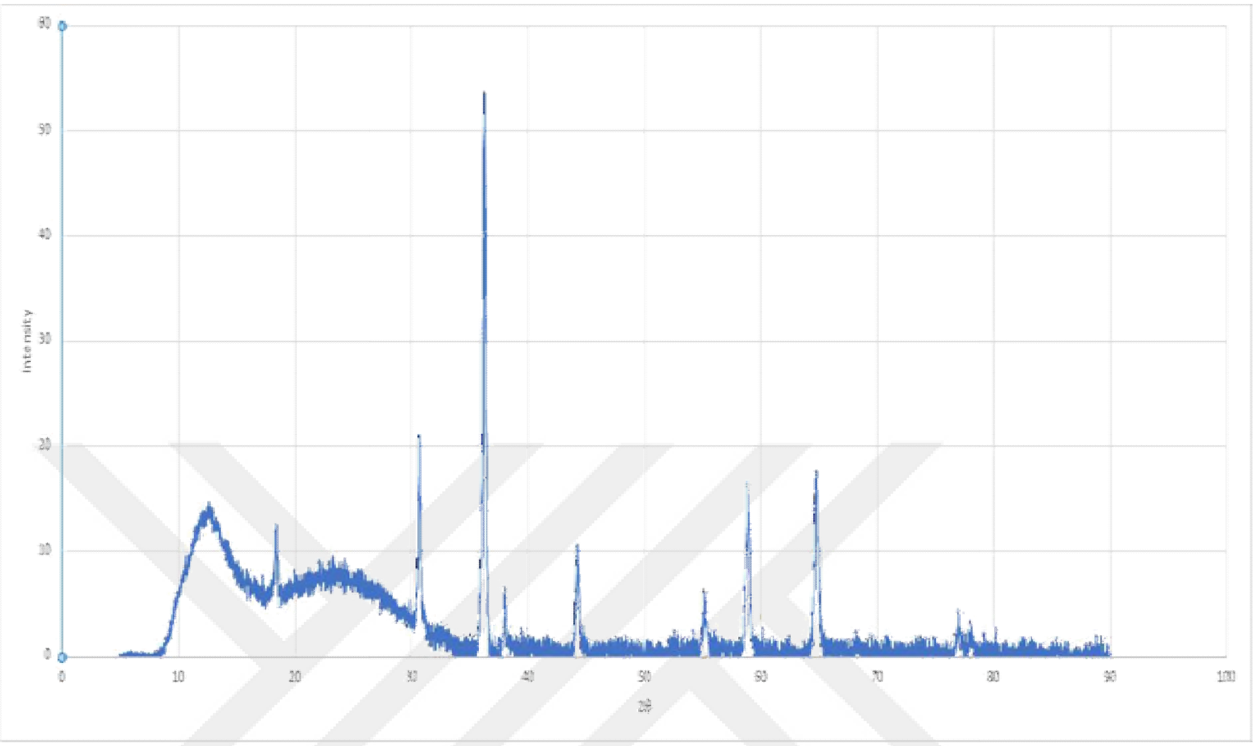


Figure 4.1 The XRD results of the $CoCl_2$ samples.

The grain size of the $CoCl_2$ beads was measured by using Pielaszek method (an extension to Scherrer formula). The full width (FWHM) of XRD peaks was taken to be 1/5 and 4/5 by the Pielaszek method and suppose that the crystallite size distribution concerning to function of

Euler gamma (hakan) as shown below:

$$< R >= \frac{2BC}{FW_{\frac{4}{5}M}}$$

Where $< R >$ is the grain size.

After calculating the full width at 4/5 of the peak maximum, A, B and C are calculated below:

$$A = \left(277069 - 105723\,\frac{FW\frac{1}{5}M}{FW\frac{4}{5}M}\right)$$

$$B = 0.001555 + 0.00884\; x \cot \cot(0.002237)$$

$$C = -0.6515 - 463695\; x\; A$$

At $FW\frac{1}{5}M$ and $\frac{4}{5}M$, the dispersion of grain size distribution can be obtained from the formula below:

$$\sigma = \frac{2B\sqrt{C}}{FW\frac{4}{5}M}$$

Also by measuring $FW\frac{1}{5}M$ and $FW\frac{4}{5}M$, a gamma distribution can be applied to obtain grain size distribution (GSD) as shown below:

$$GSD(R; R_0 m) = \frac{R_0^{-m-1}}{\Gamma(m+1)} R^m e \frac{-R}{R_0}$$

Where Γ is the Euler gamma function and R_0 and m are expressed as below:

$$R_0 = \frac{\sigma^2}{\langle R \rangle},$$

$$m = \frac{\sigma^2}{\langle R \rangle^2} - 1.$$

Results of the Pielaszek method shows that the mean size is 2.6nm.

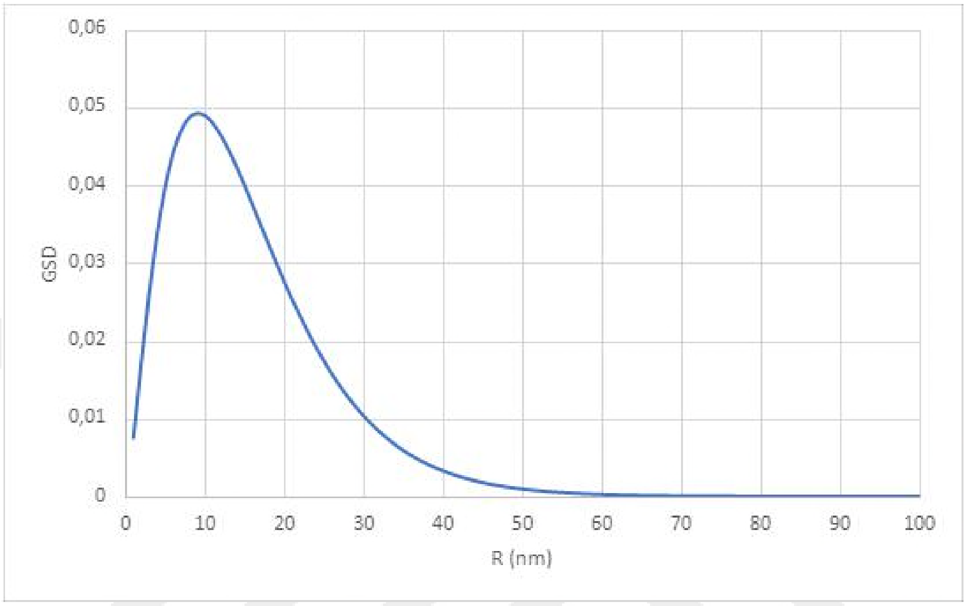


Figure 4.2 Grain size distribution of cobalt oxide nanoparticles.

The FTIR measurement of the CoO (cobalt oxide) samples shows the peaks obtained as seen in Figure 4.3. below. The X-axis indicates the infrared spectrum while Y-axis is the frequency or absorbance. The peak obtained at 1680 cm^{-1} shows the presence of CO – O stretch of the carbonate group (from alginate). The peaks obtained at 652 cm^{-1} and 580 cm^{-1} indicates the Co – O (presence of Co_3O_4). The peaks except Co – O are from the organic matter (alginate).

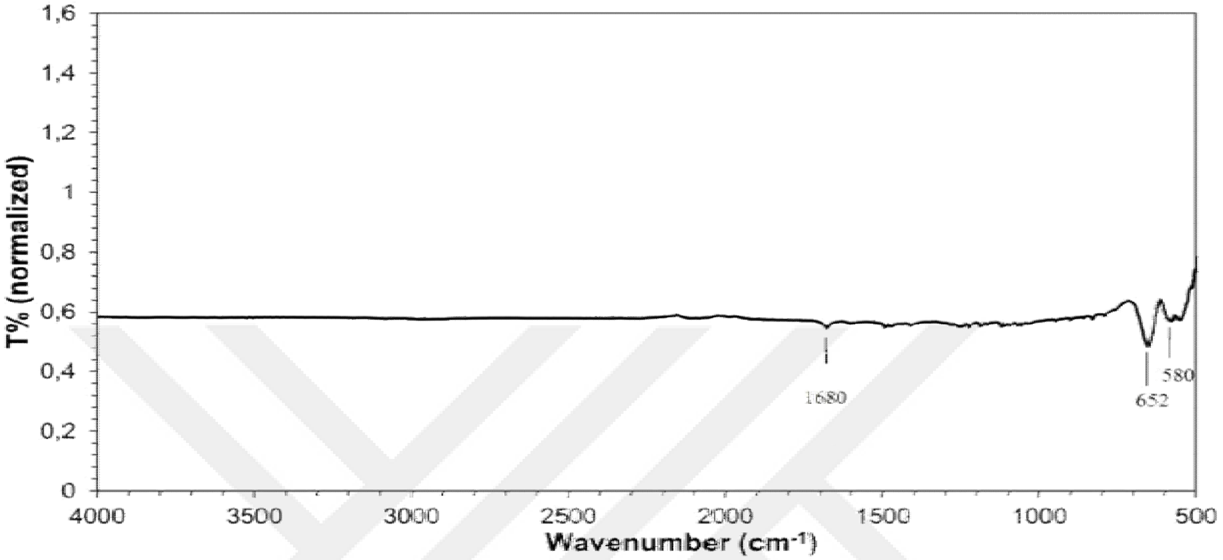


Fig 4.3: FT-IR spectrum was recorded for cobalt oxide nanoparticles after calcination at 350°C for 4 hours.

Figure 4.4 shows the results of the TGA analysis carried out on $CoCl_2$ beads, where the black line is the loss of mass against temperature and the blue line is its derivative. From temperature 0^{o}C – 200 ^{o}C is loss of water, from temperature 500 ^{o}C- 600 ^{o}C formation of cobalt oxide (Co_3O_4) took place in one phase since only one curve (peak) is present on the graph.

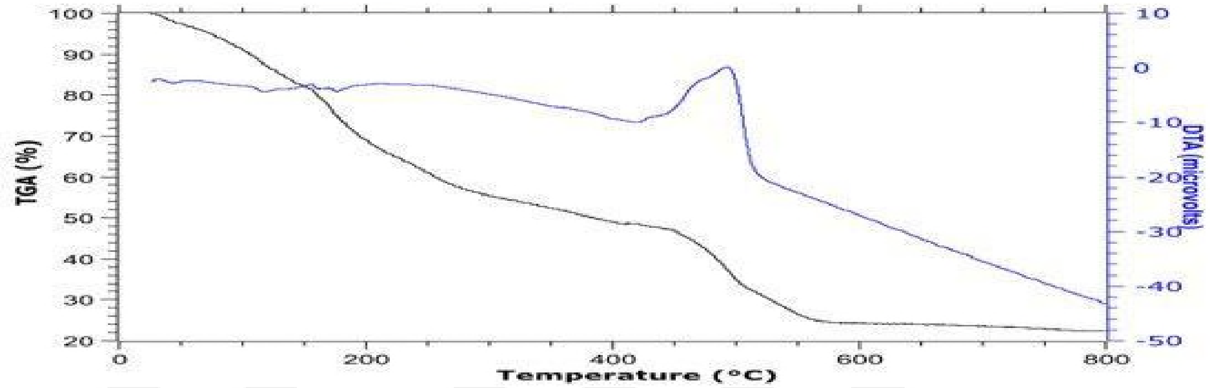
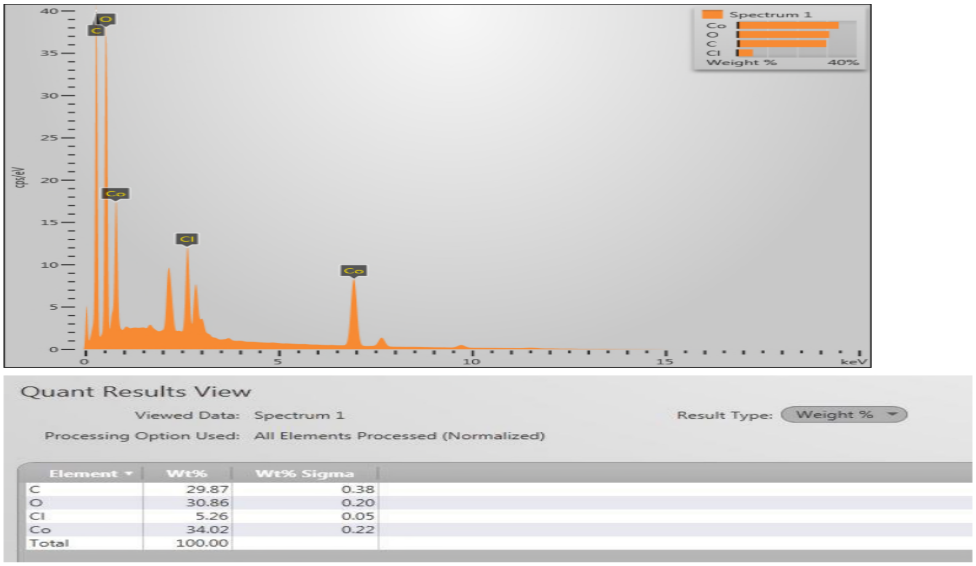


Figure 4.4 TGA analysis of $CoCl_2$ samples.

Energy dispersed spectroscopy (EDS) coupled with SEM was carried out to allows the amount of main elements present to be quantified. Figure 4.5 shows the elements present and their weight percentage respectively, which shows the sample are closely pure.



Quant Results View

Viewed Data: Spectrum 1

Result Type: Weight %

Processing Option Used: All Elements Processed (Normalized)

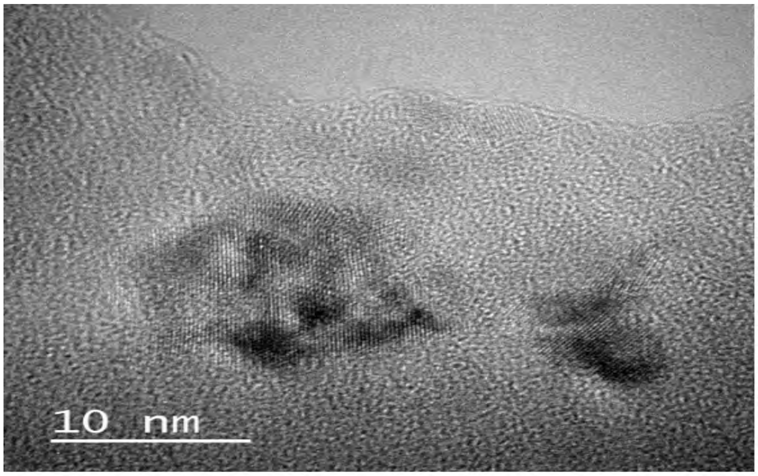
Element	Wt%	Wt% Sigma
C	29.87	0.38
O	30.86	0.20
Cl	5.26	0.05
Co	34.02	0.22
Total	100.00	

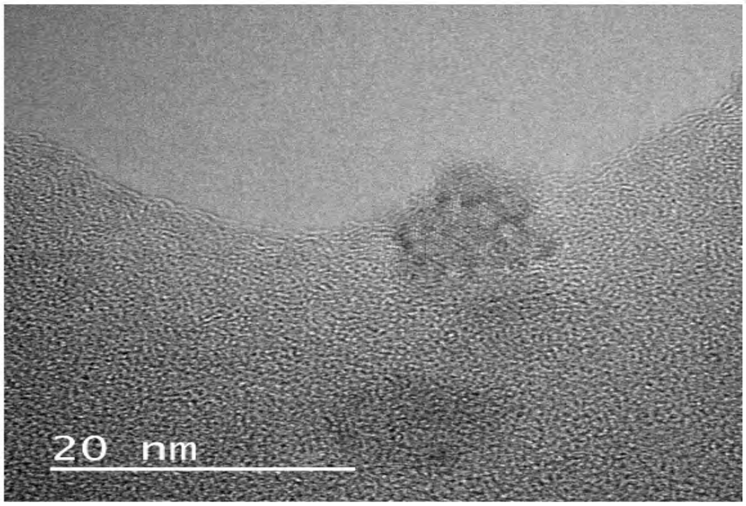
Figure 4.5 EDS of CoNPs showing the elements precent with their weight.

The crystallite and particle size analysis were conducted by TEM Figure 4.6 shows different magnifications of results of $CoCl_2$ samples ranging from 10nm – 200nm, spherical $CoCl_2$

samples are seen in the TEM images as dark shadows, which are more visible at 200 nm. The TEM images reveal that there is no agglomeration in the particles of the nanocrystal.

Also, the last two images (10 nm and 200 nm) show the comparison of each beam of light that passes through the specimen.





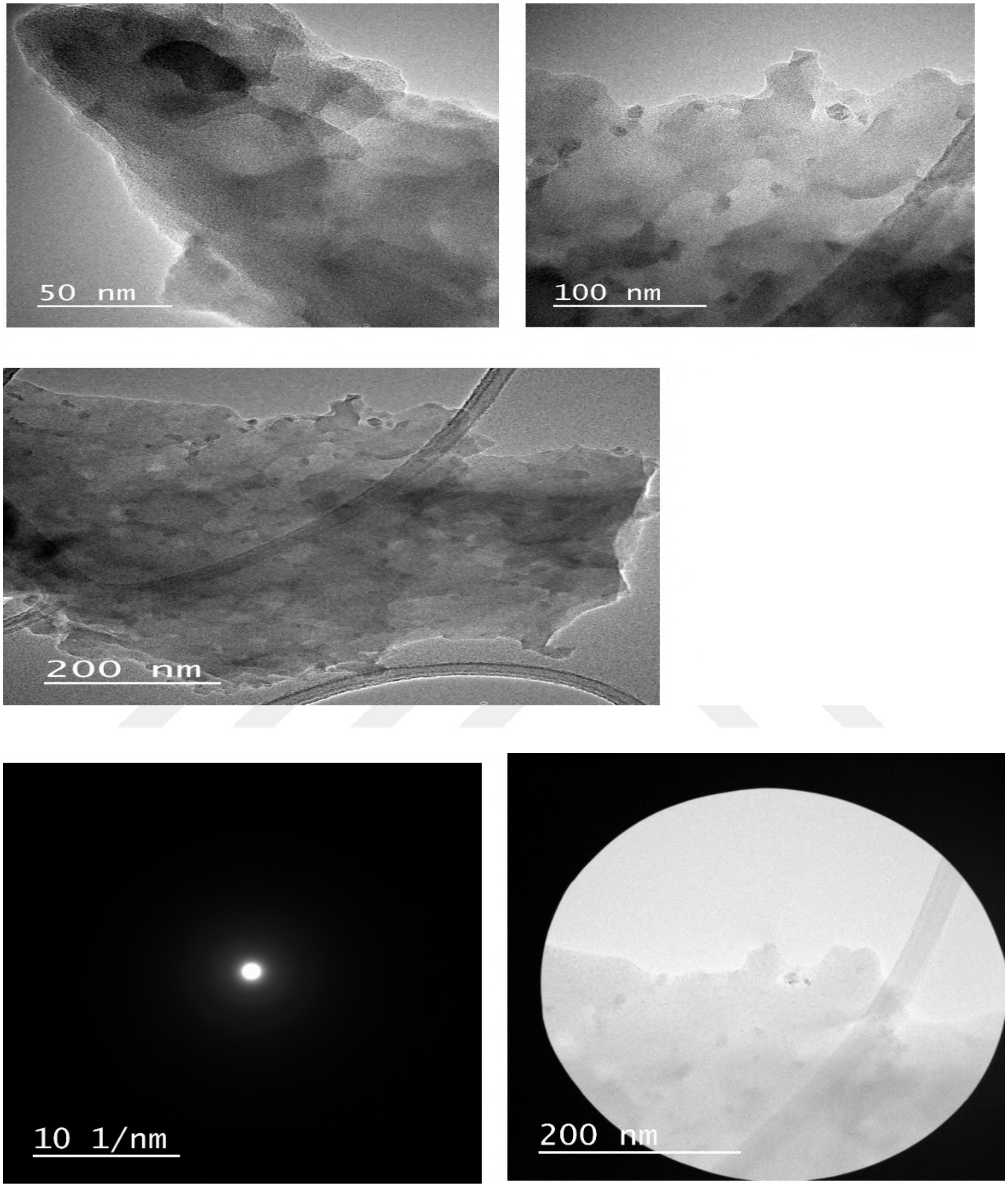


Figure 4.6 TEM analysis of CoNPs from 10nm – 200nm.

5. CONCLUSIONS

CoNP synthesis has been the subject of numerous studies. It's crucial for scientists to create a straightforward and efficient process for creating cobalt nanoparticle and to explore the critical variables that have an impact on the physio-chemical characteristics of the finished nanoparticles. In recent years, green chemical techniques have gained more traction, improving the process' safety and environmental friendliness. Solution approaches can be used to increase their interaction with other ions. This study focused on the most recent developments in the use of CoNPs across a variety of fields. The review focuses on the characteristics of CoNPs, covering their chemical composition and structure, as well as the analysis approaches.

The synthesis to produce cobalt oxide nanoparticles was approved using alginate thermal decomposition. The XRD result shows the crystallite size (32nm) which is good,TEM shows the pictures of different magnificient of results ranging from 10nm to 200nm. TGA analysis were also carried out on the beads which shows the loss of mass against temperature and its derivatives. The FTIR measurements were carried on the samples which shows the presence of O – H stretch and also the presence of Co3O4.

The product of cobalt oxide nanoparticles which is prepared by using alginate synthesis has a good grain size distribution by using the Pielaszek method.

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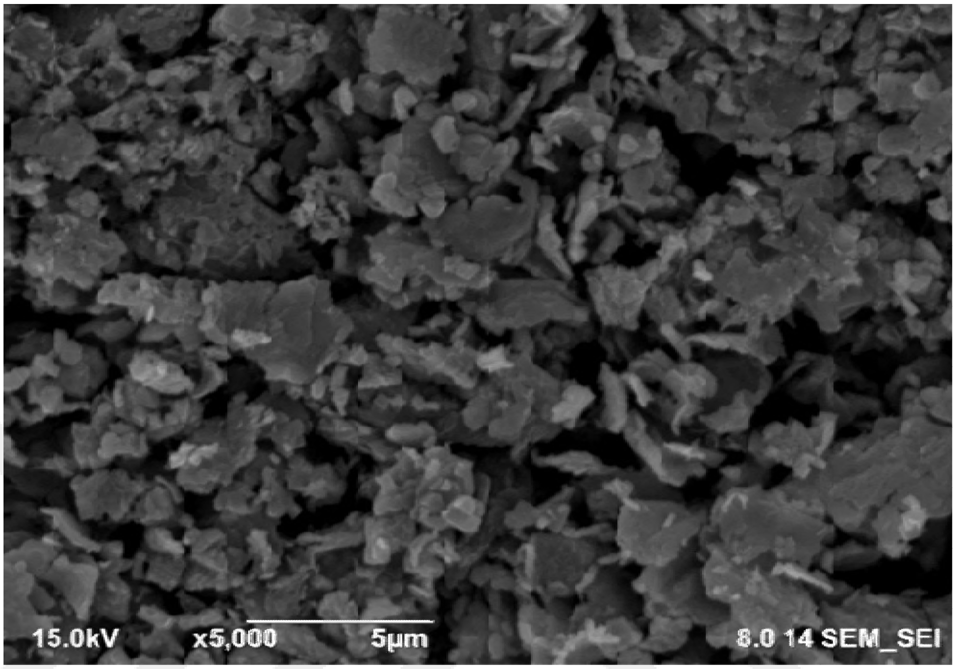
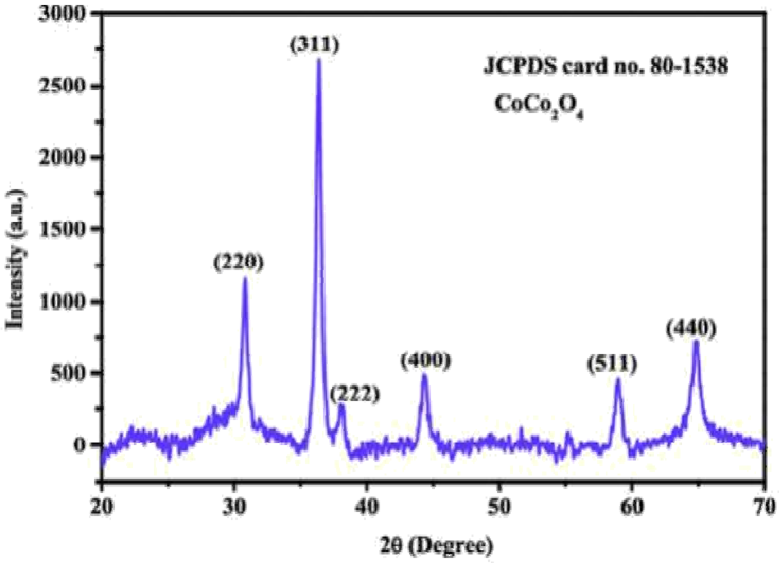
APPENDIX



Appendix 1: SEM image of CoNPs sample



Appendix 2: XRD graph image of CoNPs sample showing their major peak.