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SWELLING PROPERTIES OF CALCIUM ALGINATE-CERIUM OXIDE NANOCOMPOSITES

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ABSTRACT

SWELLING PROPERTIES OF CALCIUM ALGINATE-CERIUM OXIDE NANOCOMPOSITES

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Biopolymer-nanoparticle composites are one of the emerging materials in the interdisciplinary applications for biomedical science, mechanical engineering and chemistry. This kind of materials exhibit very useful properties such as biocompatibility, high surface area, and drug entrapment. Especially for biological applications, swelling properties of the materials are one of the very important parameters. Sustained release and diffusion parameters of the biochemical agents and drugs are related to the absorption of the liquid which the nanocomposite matrix is in contact with. In this experimental study, the swelling parameters of cerium oxide-calcium alginate nanocomposites in three different liquid medium, namely pure water, isotonic sodium chloride solution, and simulated gastric fluid is investigated. Here, nanoparticles of cerium oxide are synthesized by cerium-alginate biopolymer route and then dispersed in sodium alginate solution in order to achieve a homogeneous dispersion. Due to the origin of the nanoparticles, to the best of our knowledge, this kind of study is also reported for the first time in the literature.

Keywords: cerium oxide, alginate, nanocomposite, swelling.

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ABBREVIATIONS

NNI	:	National Nanotechnology Initiative
ISO	:	International Organization for Standardization
ASTM	:	American Society for Testing and Materials
BAuA	:	Bundesanstalt für Arbeitsschutz und Arbeitsmedizin
		(Federal Institute for Occupational Safety and Health)
BSI	:	British Standards Institution
CMNC	:	Ceramic-matrix nanocomposites
CVD	:	Chemical Vapour Deposition
EDS	:	Energy-Dispersive Spectroscopy
ISO	:	International Organization for Standardization
MMNC	:	Metal-matrix nanocomposites
NIOSH	:	National Institute of Occupational Safety and Health
PMNC	:	Polymer-matrix nanocomposites
PM	:	Powder Metallurgy
SCCP	:	Scientific Committee on Consumer Products
SEM	:	Scanning Electron Microscopy
STM	:	Scanning Tunneling Microscopy
TEM	:	Transmission Electron Microscopy
XRD	:	X-Ray Diffraction
XPS	:	X-ray photoelectron spectroscopy
XANES	:	X-ray absorption near-edge spectroscopy

HREM	:	High-Resolution Electron Microscope
TG-DTA	:	Thermo-Gravimetric Differential Thermal Analysis
EXAFS	:	Extended X-ray Absorption Fine Structure
XANES	:	X-Ray Absorption Near Edge structure
TMAOH	:	Tetramethylammonium hydroxide
CAN	:	Cerium Ammonium Nitrate
TGA	:	Thermo-Gravimetric Analysis
DTA	:	Differential Thermal Analysis
BET	:	Brunauer–Emmet–Teller
PL	:	Photo-Luminescence
UV-vis	:	Ultraviolet-Visible Absorption
FTIR	:	Fourier Transforms Infrared Spectroscopy
COD	:	Chemical Oxygen Demand
PVA	:	Poly-Vinyl Alcohol
MAH	:	Microwave-Assisted Hydrothermal
EDX	:	Energy Dispersive X-ray
SDS	:	Sodium Dodecyl Sulfate
CTAB	:	Cetyl Trimethyl Ammonium Bromide
DSC	:	Differential Scanning Calorimetry
ALD	:	Atomic Layer Deposition

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1. INTRODUCTION

1.1 General Background

Nano science is concerned with the synthesis, characterization, discovery and utilization of nanostructured materials. These materials, which are distinguished by a minimum of one dimension within the millimicron, differ. The process, structure, and properties of grain-sized materials in the tens to many millimicrons range from area-by-area research areas of right smart interest over the past few years. A revolution in materials science and engineering is taking place as researchers find ways to pattern and characterize materials at the nanometer length scale [1]. In data technology, engineering science, energy and environmental applications, new materials with extremely high electrical , optical, magnetic and mechanical properties have been developed apace device. On the nanoscale, certain physical and chemical compounds can vary greatly from those of the most organized materials of the same composition. The word “nanotechnology” was first introduced within the late nineteen seventies. Whereas several for technology exist, most teams use the National Nanotechnology Initiative (NNI) definition. The National Nanotechnology Initiative calls one thing “nanotechnology” providing it involves all of the following:

- At atomic, molecular stages, at a length of approximately 1-100 millimetres, the study and technical advancement differ.
- Creating and using structures,devices,and systems that, because of their small and/or intermediate scale, have novel properties and functions.
- Potential of atomic scale control or manipulation. [1] [2].

The interdisciplinary science of nanotechnology is therefore includes:

1. Chemistry (solar, quantum and nano colloid)
2. Nanophysics, nanophysics (quantum mechanics, spintronics).
3. Research in nanomaterials (nanopowder, nanoceramics, nanotribology and other nanotechnology) nano-nano-powdering processes
4. Nanoelectronics and nano engineering, optoelectronics
5. Nanobionics can be used to build novel bio-machine complexes such as nano-biochips, nano-biobots, and more.
6. Building nanometrology and nano-manufacturing.

While an analysis of materials on the nanometer scale may have been carried out over centuries, Moore's law of 1965 has accompanied the steady decline of the system size. The pattern is that, since 1950, the transistor volume has fallen two times every 18 months. [1]

The application of technology is used to build longer-lasting, cheaper, lighter and smaller, higher quality products. These established products are characterized by lower material and energy demand, lower prices and fast transport, a lot of convenience and a fast use. Nano-materials are currently being employed for the event of the many merchandises that we tend to use in our standard of living. athletics materials fabricated from nanofibers waterproof and short-game balls produced by victimizing clay-based chemical compounds. These commodities are technologically established, are comparatively a lot of sturdy, longer-lasting, and lighter.[3]

The enhanced field & quantum impact are two of the most important features that distinguish nanoparticles from alternatives. The atomic measurement on the interface is 5% for a particle of 30 nm, while this proportion of momentum is equal to 20% for a 10 nm scale. Nanostructures thus have a stronger comparison of surface/volume to large particles. This example makes nanostructures reactive in form of reactions, resistance, stiffness, and electrical characteristics even more than massive particles. Moreover, as materials' size in the nanoscale decreases, the quantum effects affect the optical, electrical and magnetical characteristics of the component and change it.

As the features of nanoparticles are disclosed, major advances in the field of victimization in processing and materials have emerged.. Nanostructures are particularly being wide utilized in physics and data technologies, medical applications, energy, atmosphere and applied science, textile and applied science, food trade. [4]

Table 1. 1 Nanoparticles definitions in Different organisations [5]

Organization	The definition of Nanoparticles
ISO	Particles with a diameter of 1-100 nm.
ASTM	An ultrafine particle with a length of 1-100 nm in 2 or 3 locations.
NIOSH	A particle with a diameter of 1-100 nm or a fiber ranging of 1-100 nm.
SCCP	There is at least one dimension in the nanoscale range.
BSI	All measurements or diameters are within the nanoscale spectrum.
BAuA	All measurements or diameters are within the nanoscale spectrum.

The greatest advancements in technology are in biology and medicine, especially cancer, because of the possibilities of offering creative solutions to overcome the restrictions of old medicine and radiation therapy. A number of nanomaterials of different properties have been recently developed in purgative, chemical and material sciences, that are believed to improve the therapy of many tumors which mostly prove themselves in the context of current treatment [3].

1.2 Nanoparticles

A nanoparticle is the most essential a part of the fabrication of a nanostructure. It is much smaller than several objects we tend to observe in our existence that is ruled by Newton's Motion Laws however larger than atoms or molecules subjected to the laws of quantum physics [5].

Pare classified in step with their diameter into coarse, fine (between 2500 to 100 nm), and ultrafine particles (between 100 to 1 nm) [6].

1.2.1 Metal Oxide Nanoparticles

In several fields of physics, chemistry, mechanics and materials science, metal nanoparticles play an significant role. The metal parts are prepared to produce an obsolete variety of chemical compounds. They can use a wide range of structural geometries that can have a bimetallic, microelectronics or material characteristic electronic properties. Oxides for the production of electrical equipment, sensors, electricity systems, fuel cells, passivation coatings and as catalysts are used in technical applications. The aim of the increasing field of appliqué science is to create special property nanotubes or nanoarraies that, along with their limited size as well as the high density of corners or edge surface sites, demonstrate distinctive physical and chemical characteristics for bulk or single-particle chemical compound nanotubes. Even then, it is important to take into account the rising value of surface energy and pressure with a decreasing grain size. A nanocrystals must have asurface free energy to demonstrate kinetic or structural stability. As a result of this demand, the -stable phases in bulk materials in nanomaterials become extremely stable. This discovery was found in TiO_2, Al_2O_3 or MO_x , These are functional developments [7].

The significant advantage of metal compound nanoparticles are:

- Structural changes that enable the fixing of lattice symmetry and cell parameters
- A modification in chemical science characteristics thanks to the quantum confinement effect
- Modification in surface properties resulting in a forceful increase within the bandgap that influences the conduction and also the chemical activity of the nanoparticles [8].

Potential application of nanotechnology in metal composites play a significant role in enticing scientists with a strong interest in science, medicine , agriculture, into technology, bioengineering, optics and moral science, electrochemistry, the atmosphere, electricity, senses. Adjustments in crystallite size are observed because of structural alterations in scale in nanotubes CuO, Al_2O_3, MgO, TiO_2, etc. as the size of nanostructures reduces, the related degree is generating a growing variation of surface or interfaces ions and adjacent structural disturbances. Magnetic, conductor, physical, and electrical structures can alter the specific size of the nanostructure. [9].

1.2.2 Nanomaterials common metal oxide and their uses

1. **Aluminum oxides (Al_2O_3):** The use nowadays of new nanosized alumina is to help productive modes in the chemical change region, or to provide materials with robust, deformation tolerance in moderate tempeatures or toughness greater than thirty GPA with different materials, like yag or micro-Ni/-W. There are 7 polymeric materials, but in most trade processes only four, called α, μ, da and μ, are typically affected. atomic number 13

oxides also are employed in part craft wing leading edges, Packaging materials, cutting tools, high purity vessel, winding shaft, and chamber tubes.

2. **MgO:** MgO is used extensively as air product industrial waste gasses (CO_2, SOx) washer and organic synthesis catalytic in the industry.
3. **ZrO_2:** is incredibly attention-grabbing from a technical read-only function as the solid solution, the gas sensing element and as a catalyst will be utilized as structured ceramic. Reducing the measurements of zirconia-based objects to nanosized levels results in substantial changes in physical and chemical characteristics through functional or electronic adjustments.
4. **CeO_2:** is an associate chemical compound in vital uses in chemical change, chemistry, chemistry, and science of materials. Volume CeO_2 endorses the Fm3m-style crystalline structure with its most stable portion, during which 8 gas atoms are rounded up per metal ion.
5. **TiO_2:** Ti-O seems to have an increased valence characteristic associated with the oxide gas content that increases the departure from formal oxidation from +2 to +4. Titanium oxide (TiO_2) is one of the most excellent metal oxides for the use as the white pigment in painted goods.
6. **Different oxides**: The nanoparticles of CuO are also used as catalysts for oxidation in many oxidation processes in the visible light irradiation system. ZnO is used in sun protection face creams with decreased industrial use as an Ultra violet inhibitor [7] [9].

1.3 Cerium oxides

CeO_2 (nanoceria) is a crucial material for many uses, for example solar panels, catalysts, oxygen sensors, oxygen permeation membranes, ultraviolet absorbent, and corrosion protection [10]. CeO_2 Nanoparticle systems provide anti - inflammatory effects which can be used in tissue repair formulae as an ingredient or as cerium ions formulae [11].

1.3.1 Cerium oxide (CeO_2): material properties

1.3.1.1 Electronic systems

CeO_2 is a stable oxide. The second part and the most active part of the group is the cerium. Being positive in essence, it can be found in Ce^{3+} and Ce^{4+} twin reaction modes. The amount for Ce^{4+}

oxidation is generally known to be more stable than 3, because the Ce(IV) electronic structure [Xe] $4f^0$ is more stable than the Ce^{3+} [Xe] $4f^1$. Cerium has two types of oxides, the first is cerium oxide and the second is sesquioxide (Ce_2O_3), while CeO_2 is used as primary compound because it is more advantegous than Ce_2O_3 in a much broader sense [12].

1.3.1.2 Crystalline structure

Cerium oxide (nanotubes) has a fluorite arrangement (FCC) with an area cluster and a simple boxing element sublattice that includes the Ce ions which occupy opposite cube centres.

1.3.1.3 The Micro-structure

Based on the conditions of the substratum, deposition process, deposition criteria and structure content the micro - structure of CeO_2 thin films could be of different shapes. Film growth can therefore, on the one hand, lead to the production of epitoxial films or polycrystalline films of varying grain sizes from a few nanometres. Polycrystalline films contain a number of particles that are crucial for the electrical conduction procedure in thin films by forming depletion layers similar to Schottky barrier barriers in metal-insulating interconnections with low thermal conductivity [12].

Table 1.2 Cerium Oxide Nanoparticles / Nanopowder Properties [13]

Compound Formula	CeO_2
Molecular Weight	172.12
Appearance	Brown to yellow
Melting Point	2340 °C
Boiling Point	3500 °C
Density	7.6 g/cm3
Solubility in H_2O	Insoluble
Electrical Resistivity	4 10x Ω-m
Specific Heat Expansion	390 J/kg-K
Thermal	11 µm/m-K
Young's Modulus	180 GPa
Exact Mass	171.895\t\t g/mol

Cerium oxide is synthesized by many methods, including conventional ones. [11]

- Chemical technique: Researchers for nanocerosis synthesis have documented several chemical methods. Various methods of planning such as co-precipitation have proven the creation of nanoceria [14] and deposition of chemical [15], hydrothermal [16], microwave, sonochemical, the microwave / hydrothermal process reversed precipitation [17], thermal decomposition of carbonates, sol-gel method, and others [11].

- Green method (from plant extracts): The use of green methods also could synthesize Nanoceria. The inexperienced nanoceria synthesis of the use of *Gloriosa superba L* was claimed by several authors. Another look at the synthesis of nanoceride in the use of Curvularia lunata's way of life. [17]. Other methods include nutrient-mediated like olea leaf extract green synthesized nano particles [18] and *Hibiscus sabdariffa* floral extract based green synthesis [19]. Some of the important methods for synthesizing cerium oxide nanoparticles are previously discussed in a review [20].

The highest widely-used methods have repetitively demonstrated a significant quantity of trivial cerium on the substrate of nanocerium to measure the importance of cerium ions on the surface of ceria, X-ray PHE (XPS) and X-ray fairly close-part absorption (XANES). The precursors and synthesis scenarios can be modified to create ceria nanoparticles of various stoichiometer (solvents, pH, existence of oxidizing agents or stabilizers, oxygen partial pressure, etc.) [21].

1.4 Surface area and quantum effect

The physical rules of matter function differently in two essential ways on the atomic scale: large surface to volume and quantum effects [22]. When the materials form units or particles get smaller, the surface area rises exponentially in large magnitudes, while the total volume is constant. This vast increase in the surface area will influence and improve many properties such as the material's physical, chemical and mechanical characteristics [23]**.**

The second important feature of the nanoscale is the quantum effect. In nature, all matter has electromagnetic properties. At the nanometer size range, the electromagnetic properties of particles turn for the large size change. As the particle size decreases, its wavelength decreases getting to higher gamma-ray end properties. The motional behavior of nanoparticles is not described properly because the quantum theory is still being investigated. [24]

2. LITERATURE REVIEW

This chapter discusses recent development in nanostructured ceria materials preparation, characterization techniques. The production of nanosized ceria materials is advancing significantly. For research scholars, there are exciting new possibilities and challenges. Though its synthesis of ceria nanostructures in recent years has attracted significant attention, studies nowadays should concentrate more on knowing how synthetic techniques, structure, size and shape affect the characteristics of the nanomaterials especially cerium oxide nanoparticles. through the past few years, it was found that many researchers have focused primarily on transition metal oxides like ZnO, TiO_2, CuO, Fe_3O_4, etc. Cerium oxide (CeO_2) is of great importance among the transition metal oxides for its unique properties in the nanoscale range.

2.1 Synthetic approaches of nanostructures

A variety of nanomaterial synthesis techniques have been improved and used, but for scientific research, wet chemical methods like chemical drop, precipitation, sol-gel, hydrothermal method, and sono-chemical synthesis had more attention and use. Sol-gel gained importance among other wet chemical methods as the most flexible and economical method.

Synthesis and nanofabrication techniques have experienced rapid advancement in the past decade. Different synthetic approaches were applied to produce nanomaterials and nanodevices from a wide variety of precursor substances such as solid, liquid or gaseous form. The challenge in any synthetic method in the control of particle form and size distribution during the process. Two aspects dominate all approaches; which are control of manufacture conditions, and control of environmental conditions [22].

In general, nanoparticles synthetic approaches are divided into two major approaches:

- Top-down approach: wWerein the synthesis manner starts off evolved with a bulk that breaks down to the nanoscale. This includes solid-phase techniques, like milling, etching, sputtering, lithography and aerosol-based techniques, and liquid-phase techniques. By ball milling, the production of nanostructures building blocks by controlled mechanical depletion of most of the initial material, is another top down technique. Those nano-blocks are formed into an advanced bulk material sooner or later [25].

- Bottom-up Approach: It aims to produce nanomaterials from atomic or molecular precursors using self-assembly or chemical reactions, this approach involves all the V-phase techniques, such as deposition methods (e.g. thermally CVD, and plasma-enhanced CVD), chemical vapor condensation, wet chemical techniques (e.g. sol-gel, chemical reduction, solvothermal and Sonochemical methods), self-assembly techniques (e.g.electrostatic self-assembly) [25] [26].

Top-down methods are:

- Starting with a sample generated on a bigger scale, then decreased to the nanoscale.
- Are not reasonably-priced and brief to fabricate manufacture.
- Slow and now no longer appropriate for big-scale production.

Bottom-up methods:

- Begin with atoms or molecules and increase to nanostructures.
- Fabrication is an awful lot much less expensive [27].

2.2 Synthesis of Ceria

The investigation of new properties of nanostructures and their applications was just achievable with sufficient scale, structure and chemical structure synthesized materials [27] Today, a wide variety of techniques are available for the production of nanoparticles. The solution-based processing of nanomaterials is a very important synthesis route and has been used in many materials to achieve a variety of fabrication goals [28].

Important progress has been made in fabrication techniques in recent decades and characterization techniques of nanomaterials. Numerous methods have been adopted to prepare pure nanoceria and ceria based nanocomposites, based on both top-down and bottom-up methods, including laser processing and milling [29], chemical vapour deposition [30], coprecipitation [31] [14], sol-gel methods [29], spray pyrolysis [32], microemulsion methods [33], hydrothermal synthesis [34] [16] , thermal hydrolysis [35], solvothermal method [36], sonochemical method [37], reverse micellar synthesis [38], precipitation [15] [39], thermal decomposition [40],oxidant precipitation [39], electrodeposition [41], microwave technique [40], combustion synthesis [42], electrochemical method [43], low temperature decomposition method [44], and freeze-drying [45].

Although some hopeful results were accomplished, it is still impressive and important to enhance the properties and many uses of easy and cost-effective artificial and manufacturing processes in CeO2 based nanoprocessing [47].

(Zhang, et al., 2001) [48] Cerium oxide nanoparticles were produced as an air-annealing temperature by the micro-emulsion technique. The advancement of the micro-emulsion technique provides a good way to achieve the monocrystals with a smooth surface. The CeO_2-x ($0 < x < 2$) nanoparticle was derived from rotary evaporation from microemulsion, then treated for 2 hours with heat at 473, 623, 773 and 873 K. Powders synthesized with cerium oxide were X-ray (XRD) (HRTEM) and EXAFS (XANE) diffractors.

Two models of the XRD show that the sample annealed at 623 K is amorphous, with CeO_2 monochristal forming above 773 K, together with the thermal gravimetric differential (TG-dta) thermal analysis. In the phase of nanocrystallization the local structural and morphological characteristics are studied with the Ce L_3 edge X-ray absorption spectra (XAS). The phase structure has been changed from triclinical to cubic CeO_2 and the electronic chain.

(Zhang, et al., 2002) [49] have prepared CeO_2 with a slight range of length with an ammonium reagent (0.5 mol/L hexamethylenetetretramine) at room tempature, by using 0.0375 mol/L cerium nitrate solution $Ce(NO_3)_3$. The grid factor is up to 0.45% when the particle size in XRD is down to 6 nm. Raman spectra also support the effect of particle length and subsequent grid expansion, which can be clarified by higher concentrations of point defects with decreasing particle microscope suggest that more than 99 percent of synthetic debris is crystalline, TEM and the emission of photons are used for particulate matter.

(Sharma, Gokhale, Dayal, & Lal, 2002) [50] have the use of spray drying technology synthesized ceria powders. For its partial length distribution and the singular floor space, powders have been characterized. With 12 mol percent CeO_2, the samples are gained high fracture robustness and flexural strength for sintering. The flexural strength and durability of the fractures based on concentration of CeO_2, length of crystallite, and sintered bodies' composition.

(Kamruddin, et al., 2006) [51] The use of chemical solvent and precipitante was synthesized by a non-hydrolytic strategy.

(Hwang, Huang, Tsai, Lin, & Peng, 2006) [52] The use of types of starting substances urea $[(NH_2)_2CO]$ and cerycammonium nitrate $[Ce(NH_4)_2(NO_3)_6]$, each of which appears as an ionic cerium and an oxidizing agent, has studied and synthesized ceria (CeO_2) powder using a combustion process. The surface and primary crystallized particle sizes of ceria powder were ±50 m^2 / g and ~25 nm.

(Tok, Du, Boey, & Chong, 2007) [53] Doped ceria (CeO_2) and the rare earth-doped ceria (RE= Pr, Gd, and Sm) with various concentrations of doping of 10, 20, and 30 mol percent using hydrothermal synthesis strategy of nano-particles.

(Zawadzki, 2008) [54] reported the use of diethylene glycol response containing nitrate and hexamine as a precipitating agent efficiently organized nanocrystalline ceria using a microwave-assisted process.

(Lair, Ringuede, Vermaut, & Griveau, 2008) [44] reported ceria based mostly on entirely electro-chemical substances had been synthesized. Ceria coatings have been obtained with an indirect process of electrodeposition.

(Zhang, Yang, & Ding, 2009) [55] Cerium oxide nanoparticles have been synthesized with hexagonal fluorite structures using the precipitation process using raw material cerium nitrate and precipitation agent ammonium acid carbonate. The average crystalline size could have been obtained approximately 90 nm.

(Sharma, Bhattacharya, Das, & Das) 2010 [56] reported the synthesis of nanocrystalline CeO_2 powder through any excessive ball friction and liquid processing direction.

(Walton, 2011) [57] Several hydrothermal & solvothermal techniques used in the preparing of cerium oxides have been tested. It is also known that the process of hydrothermal treatment has a role to play when new and unique cerium oxides are reported.

(Huang, Cai, Qiao, & Liu, 2011) [58] have synthesized CeO_2 nanomaterials with distinct morphologies with the aid of using adjusting the pH value. TEM analysis reveals that tightly packed granular particles (5–10 nm in diameter) are observed when CeO_2 is synthesized at pH = 5. If the pH demand is higher to 8, all spherical nanocrystals with an average of 60-70 nm are shown in this study. By increasing the pH value to 11 more, rocklike nanocrystals are fabricated with an average diameter of approximately 40 nm and a length of up to 300 nm or more.

(Jahagirdar, Ahmed, Donappa, Nagabhushana, & Nagabhushana)2012 [59] The chemical deposition method used for the development of cerium nitrate and citric acid as fuel. Crystallines were of 20 nm in average size.

(Sharma & Sanjay Kumar, 2012) [60] have synthesized a singular CeO-ZnO nanocomposite with the aid of using the sol/gel technique primarily base totally on a polymer (PVA).

(Yang, et al., 2013) [61] have fabricated the use of cerium-nitrate hexahydrate synthesis (CeO_2) powders.

(Deus, et al., 2013) [62] reported CeO_2 nanoparticles by microwave assisted hydrothermal method.

(Kannan & Sundrarajan, 2014) [63] *Acalypha Indica* leaf extract was used in green synthesis of 25 to 30 nm cerium oxide nanoparticles.

(Sabari Arul, Mangalaraj, & Han, 2015) [64] the use of an easy hydrothermal technique has been compiled by cerium oxide (CeO_2) nanomaterials. The existence of CeO_2 nanostructures is confirmed by X-ray (XRD) diffraction and transmitted-electron microscopy analyzes.

(Dutta, et al., 2016) [65] have synthesized a new and simple method for the synthesis of cerium oxide of 2-3 nm in size with the aid of an atmospheric temperature, cerium nitrate in the form of an immoderate pre-cursor aloe vera leaf extract for each oxidation and stability.

(Reshma & Ashwini, 2017) [66] reported cerium oxide nanoparticles with 20 - 100 nm diameter. Different surfactants which includes sodium sulfates (SDS) and (CTAB) own the cap potential to manipulate the form and length of the prepare of cerium oxide with the aid of using the usage of cerium nitrate hexahydrate. Additionally, the nanoceria debris exhibited inhibition for the gram-negative bacteria.

(Pujar, Hunagund, Desai, Patil, & Sidarai, 2018) [67] used coprecipitation process for fabricatnig cerium nanocomposite membranes with sodium hydroxide and with cerium(III) nitrate hexahydroxide at ambient temperature.

(Sukumar, M. Muralidhara Rao, & A. Gopala Krishna, 2019) [69] reported the co-precipitation technique for cerium-oxide nanoparticles.

(Kaygusuz & Erim, 2020) [11] reported nanoparticle synthesis with cerium alginate gel at 450 °C by thermal degradation, in which alginate acts as the precursor. The synthesis is a green, facile and one-step. It is also reported that the nanoparticles have functional groups on the surface, and, can be used for further applications.

3. EXPERIMENTAL WORK

3.1 Materials and methods

Alginic sodium salt (CAS-9005-38-3), cerium(III) nitrate hexa-hydrate (CAS-10294-41-4), purity 99.9%), Calcium chloride dihydrate, and cerium(IV) oxide nano-powder (< 25 nm, CAS 1306-38-3) have been purchased from Sigma–Aldrich (St. Louis, USA). Solution will be prepared in pure water and chemicals are used without any further purification.

3.2 Preparation of Cerium oxide Nanoparticles

Alginate powder has been dissolved in deionized water until complete powder dissolution was achieved, for the preparation of 1% (*w*/*v*) solution. Cerium(III) alginate-gel beads were formed by adding alginate solution in droplets into an already prepared aqueous solution of Cerium(III) nitrate with the concentration of 0.05 mol/L. The beads then stirred for more than 1 hour and stored for about 8 hours to achieve complete crosslinking. Formed beads are presented in Figure 3.1. The gel beads have been filtered and washed using pure water and placed in Petri-dishes. It is important to note that wet beads have been used without drying in the heat treatment. Beads were then placed in heat resistant porcelain crucibles and heated at 450 °C. After heating all the beads have been converted into somewhat yellow-white powder, and then the crucibles have been removed from the furnace and stored in a desiccator.

Figure 3.1. Synthesized cerium(III) alginate gel-beads.

3.3 Preparation of Ca-alginate gel beads

Alginate solution of 1% (*w/v*) ratio is shown in figure 3.2 was formed by completely dissolving 0.4 g of alginate powder in 40 mL of deionized water (pure water) with the aid of a stirring device and magnetic stirrer. Cerium oxide was added to the alginate solution to a ratio of 0.1% (*w/v*) dispersion. To achieve this ratio of concentration, 0.043 g of cerium(IV) oxide was added into 40 ml of the alginate solution.

To achieve bead formation a 3% (*w/v*) ratio $CaCl_2$ solution had prepared by mixing 4 g of calcium chloride dihydrate in 100 mL of pure water until the calcium chloride was completely dissolved.

The alginate – cerium oxide dispersion was crosslinked with the $CaCl_2$ solution with the aid of a syringe in order to achieve bead formation. Upon the formation of the beads, they were stirred for about an hour to achieve complete crosslinking. After crosslinking had been achieved the beads were filtered and washed with pure water and presented in Figure 3.3. The beads were left in a petri dish for 48 hours to achieve complete dryness (Figure 3.4 and 3.5) Swellings tests were then performed.

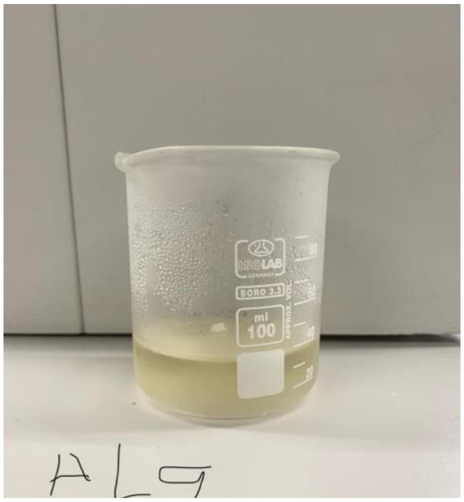

Figure 3.2. Alginate solution.

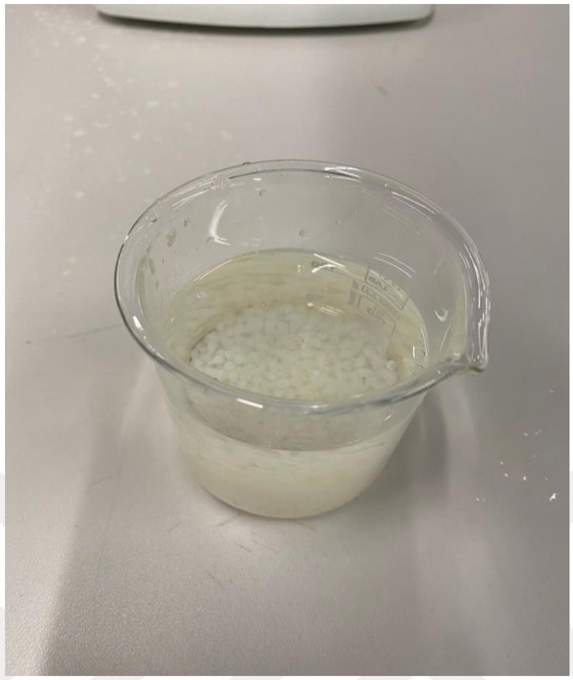

Figure 3.3. Bead formation.

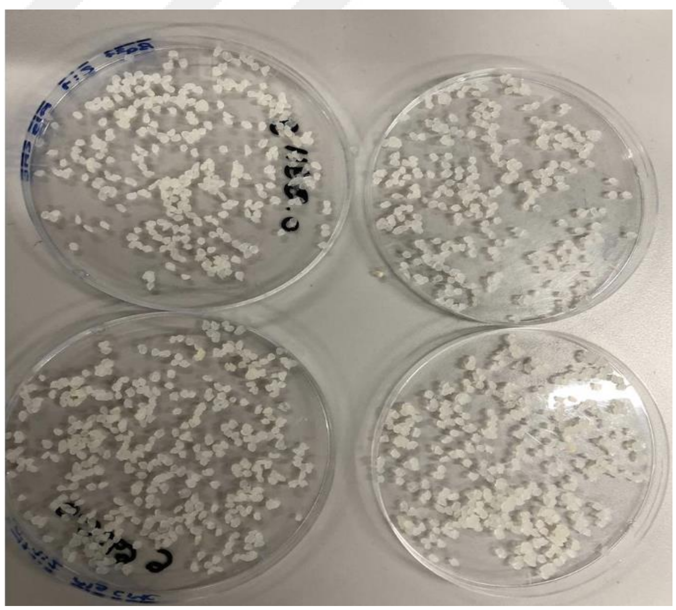

Figure 3.4. Synthesized calcium alginate/cerium oxide gel beads (wet state).

Figure 3.5. Synthesized calcium alginate/cerium oxide gel beads (dried state).

3.4 Swelling test procedure

After finishing the preparation of calcium alginate beads, the swelling tests were performed. 0.1 g of dry calcium alginate beads were placed in pure water, isotonic sodium chloride solution and simulated gastric fluid separately (10 mL each) and placed in the shaking water bath (Nüve ST 30, Ankara, Turkey) as shown in Figure 3.6 for definite time intervals (15, 30, 45, 60, 90, 120, 150 and 180 minutes). Each time the beads were filtered carefully and the mass was recorded.

$$Swelling\ ratio(\%) = \frac{m_2 - m_1}{m_1} x100$$

Where m_1 and m_2 are the masses of the beads before and after swelling, respectively.

Figure 3.6. Shaking water bath with nanocomposite formulations

4. RESULTS AND DISCUSSION

Swelling ratio of the beads in each formulation were given in Tables 4.1, 4.2 and 4.3 whhere the results are also visualized in Figures 4.1, 4.2 and 4.3. As shown in the results, beads are swelling more in isotonic sodium chloride solution and and among the three formulations, simulated gastric fluid is found to be the least one. This is expected since acidic medium can result in shrinking of the alginate beads since alginate has a pKa at acidic region, which can result in conversion of alginate into alginic acid counterpart. On the other hand, the swelling behavior in distilled water shows a stepwise increase around 50 minutes. This may be due to the change in diffusion behavior, e.g. extending of the hydrogel network which can result in a change in diffusion parameter.

Table 4.1. Swelling ratio (SR) and standard deviations for the measurements in distilled water.

	Distilled water	
Time (min)	SR (%)	± STD
0	0	0
15	15.9	6.3
30	16.4	6.1
45	16.6	9.6
60	24.9	5.4
90	26.5	9.3
120	25.5	5.1
150	23.9	7.0
180	22.7	4.8

Table 4.2. Swelling ratio (SR) and standard deviations for the measurements in isotonic NaCl solution..

	Isotonic NaCl solution	
Time (min)	SR (%)	± STD
0	0	0
15	3.2	1.2
30	17.7	1.6
45	22.7	2.6
60	24.5	3.7
90	24.2	4.1
120	23.6	3.8
150	25.1	2.4
180	26.3	4.2

Table 4.3. Swelling ratio (SR) and standard deviations for the measurements in simulated gastric fluid.

	Simulated gastric fluid	
Time (min)	SR (%)	± STD
0	0	0
15	19.7	3.8
30	20.9	7.5
45	27.2	2.3
60	26.4	5.4
90	23.6	5.1
120	18.0	2.0
150	18.7	3.3
180	18.1	0.9

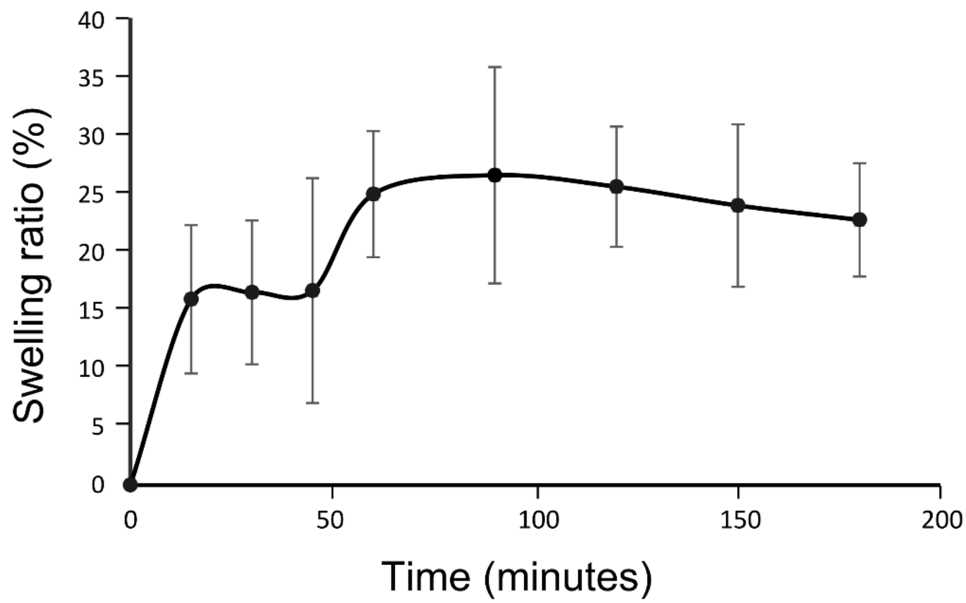

Figure 4.1. Swelling ratio percentage graph for pure water.

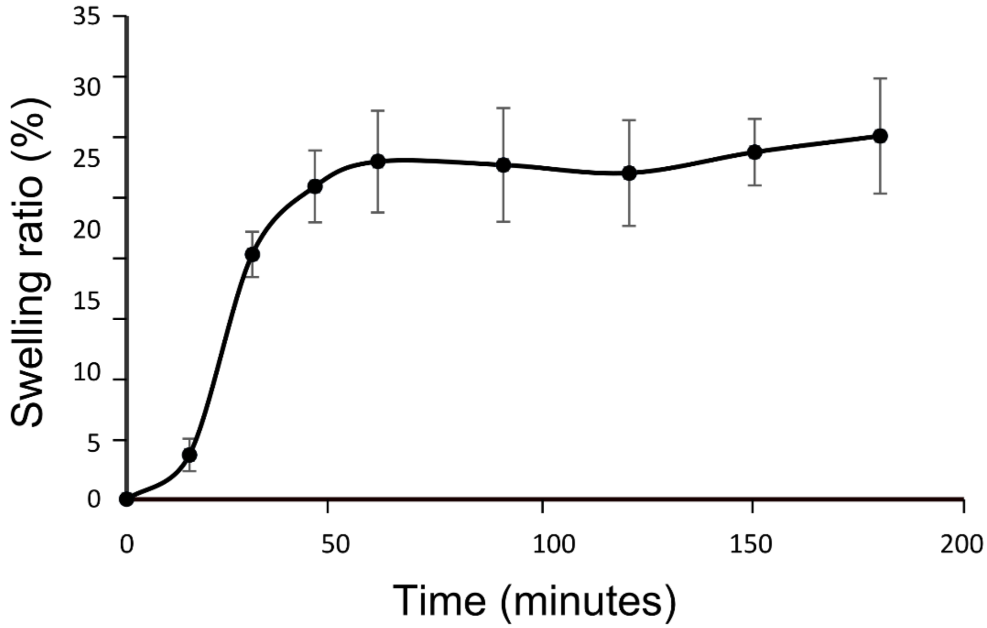

Figure 4.2. Swelling ratio percentage graph for isotonic sodium chloride solution.

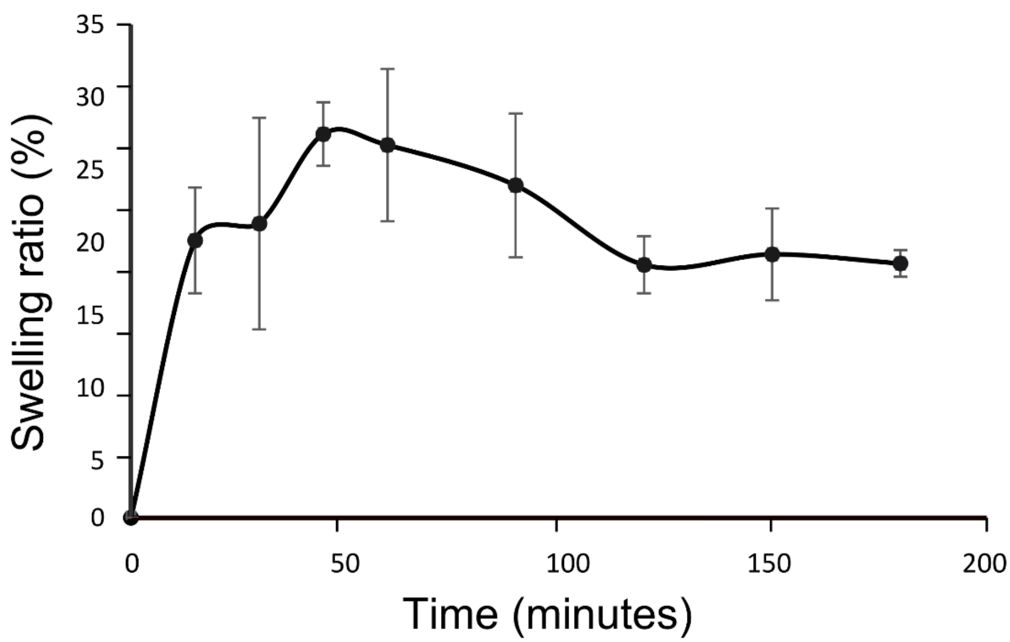

Figure 4.3. Swelling ratio percentage graph for simulated gastric fluid.

In their study, Kaygusuz and Erim reported the preparation and physical properties of alginate/bovine serum albumin/montmorillonite clay composites for controlled release experiments [70]. This formulation was not classified directly as a nanocomposite, but more than that, a structure with intercalated clay layers of nanometer width. It should be noted that in that case an intercalation refers to a nanocomposite [71]. In the report of Kaygusuz and Erim about the alginate/protein/clay composite, the swelling behavior of the beads were investigated in simulated gastric fluids and simulated intestinal fluids, where the ratios were found around 80% and 5000%, respectively. Basic medium of the simulated gastric fluid (NaH_2PO_4 - NaOH buffer solution at pH = 7.2) leads to the ionization of the carboxylic groups in alginic acid polyelectrolyte, which results in a significant increase [70]. In this thesis study, simulated intenstinal fluid was not studied, however due to the presence of alginate one can easily expect a similar increase in the swelling.

On the other hand, when compared to this formulation, the swelling in SGF is close (~30%) but lower for alginate-cerium oxide nanocomposites than alginate/protein/clay composites. In another study by Kaygusuz et al. [72] a controlled release formulation based on montmorillonite doped calcium alginate and barium alginate beads were investigated. Among the vairous physical and chemical characterization, swelling was studied in SGF and SIF. For calcium alginate-montmorillonite clay the swelling was found around 40% for SGF and 6000% for SIF, and for barium alginate 30% for SGF and 2000% for SIF. Again, similar results were obtained for calcium- and barium alginate montmorillonite composites.

Another recent study by Kurdtabar and Bardajee [73] reports magnetic iron oxide doped hydrogels based on polyacrylic acid grafted alginate and their drug release (Doxorubicin and tetracycline) and swelling properties. The swelling capacity in pure water was between 200 to 400 g/g of water, showing a much higher efficiency.

However, it should be noted that in their report [73] the gravimetric method was different, the authors placed the samples in a teabag and immersed the teabag in the liquid, and in definite time intervals the tebag was taken out and hung up for five minutes in order to remove excess liquid. In this study, the experiment employs a step of nanoparticle filtration, similar to some previous studies [70, 71, 74].

Considering the obtained values for the swelling percentage, the reported alginate-cerium oxide composite can be theoretically useful in drug delivery systems based on the findings. Further studies will be useful such as encapsulating a model drug in the formulation and considering the drug release behavior. It should be noted that this sample, to the best of our knowledge, is being reported for the first time in the literature.

5. CONCLUSION

This study reports the cerium oxide-calcium alginate nanoparticles, where the cerium oxide was prepared by the cerium alginate route. Therefore, the material which is being reported here is prepared for the first time. The results of experiments show that typical swelling behavior of alginate beads, a rapid increase for the first 10 minutes which is followed by a second and slower neck. The curves obtained here can be modeled For different applications, such as the delivery of a drug. The interesting result here is the decrease in the swelling in acidic medium. The decrease just starts after 90 minutes, which is not observed at neutral solutions. This is mainly due to the dissolution of cerium oxide nanoparticles in strongly acidic medium, where cerium oxide particles are being converted into cerium(III) and/or cerium(IV) ions. The loss of the mass can be attributed to this chemical change, which indicates a useful route for specific and targeted delivery of cerium ions, instead of a burst release mechanism. Further experiments on the swelling/deswelling cycles and mechanical parameters might be useful for understanding the pattern of hydrogel network extension and physical properties such as elasticity.

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