



Faculty of Resource Science and Technology

**Synthesis of Cerium Oxide Nanoparticles and its Behavior under
Aqueous Environmental Factors**

Syazani Azaim bin Eddie Halim

**Master of Science
2024**

Synthesis of Cerium Oxide Nanoparticles and its Behavior under Aqueous Environmental Factors

Syazani Azaim bin Eddie Halim

A thesis submitted

In fulfillment of the requirements for the degree of Master of Science

(Environmental Chemistry)

Faculty of Resource Science and Technology

UNIVERSITI MALAYSIA SARAWAK

2024

DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.



.....

Signature

Name: Syazani Azaim bin Eddie Halim

Matric No.: 22020029

Faculty of Resource Science and Technology

Universiti Malaysia Sarawak

Date: 12th February 2024

ACKNOWLEDGEMENT

First and foremost, Alhamdulillah for his blessing throughout my study and for giving me the strength to complete my thesis writing even during difficult times.

Special thanks to my beloved parents, Eddie Halim bin Sabri and Nori Othman and my family for their unconditional love, motivation and financial support during my study. The motivation to continue my study even during the difficult times has always been because of their non-stop prayers. Another special thanks to my fiancée, Nur Syuhada binti Marjane @ Bujang for her continues motivation and advices especially when I need them the most to complete my study.

I would like to express my sincere gratitude to my supervisor, Dr. Wee Boon Siong for his guidance and advice in completing every step of my project. I would also like to thank all the Chemistry Department staffs at Faculty of Resource Science and Technology for helping me in doing the analyses and their guidance especially Mr. Tomy Bakeh, Mr. Wahab bin Marni, Mr. Shafri bin Semawi and Mdm. Ting Woei as well as Mr. Airul Azhar bin Jitai from Faculty of Engineering and Dr. Thye Foo Choo from Malaysian Nuclear Agency. Another big thanks to Mdm. Leida anak Anthony and Mdm. Dayang Fatimawati binti Awang Alli for their help and advices especially about the safety in doing lab works.

Huge acknowledgement also to my lab mates and friends especially Muhd Firdaus bin Maligan and Then Sze Ing for their support and knowledge both in doing my lab work and writing my thesis.

Finally, thank you Zamalah Graduate Scholarship UNIMAS for providing financial support throughout my study.

ABSTRACT

Cerium oxide, CeO₂ nanoparticles (NPs) are metal oxide NPs used in various applications such as in fuel oxidation catalysis, solar-driven energy production and as fuel additives. However, CeO₂ NPs have been reported to behave differently when released to the environment due to the difference in pH, ionic strength (IS) and concentration of natural organic matter (NOM). In this study, CeO₂ NPs were synthesized using the hydrothermal method at 70 °C using cerium nitrate hexahydrate, Ce(NO₃)₃ • 6 H₂O and sodium hydroxide, NaOH as the precursors while deionized water was used as the solvent. The synthesized CeO₂ NPs were characterized using field emission scanning electron microscope (FESEM), transmission electron microscope (TEM), energy dispersive X-ray (EDX), ultraviolet visible (UV-Vis) spectrometer, Fourier transform infrared (FTIR) spectroscopy, X-Ray Diffraction (XRD) and Brunauer -Emmett-Teller (BET) method. High specific surface area of 185 m²/g, average particle size of (TEM: 3.5 nm, BET: 4.5 nm) and crystallite size of 3.05 nm was determined through the characterization process. The absorption peak at 305 nm and 447.20 cm⁻¹ for UV-Vis and FTIR analyses respectively confirmed the presence of CeO₂ NPs. The absence of impurities from EDX and XRD diffraction pattern proved that the synthesized CeO₂ NPs was of high purity. The adsorption of HA on CeO₂ NPs was performed using UV-Vis to measure the amount of HA adsorbed at the absorbance of 254 nm. Higher adsorption was observed at acidic pH compared to the alkaline pH and the adsorption was following the Pseudo-second order and Langmuir isotherm. The dissolution of CeO₂ NPs was studied by measuring the dissolved Ce⁴⁺ using inductively coupled plasma-optical emission spectroscopy (ICP-OES). Increased in ionic concentration and pH was found to decrease the dissolution of CeO₂ NPs while increased in HA concentration and pH resulted into a greater stability of CeO₂ NPs.

Keywords: Cerium oxide nanoparticles, hydrothermal, humic acid, dissolution, adsorption.

Sintesis Nanopartikel Serium Oksida dan Kelakuannya di bawah Faktor Persekitaran Akueus

ABSTRAK

Nanopartikel (NP) serium oksida, CeO₂ ialah NP oksida logam yang digunakan dalam pelbagai aplikasi seperti dalam pemangkinan pengoksidaan bahan api, pengeluaran tenaga dipacu suria dan sebagai bahan tambahan dalam bahan api. Bagaimanapun, NP CeO₂ telah dilaporkan bertindak balas dengan cara berlainan apabila dilepaskan ke persekitaran kerana kelainan pH, kekuatan ion (IS) dan kepekatan bahan organik semula jadi (NOM) Dalam kajian ini, NP CeO₂ telah disintesis menggunakan kaedah hidroterma pada suhu 70 °C menggunakan serium nitrat hexahidrat, Ce(NO₃)₃ • 6 H₂O dan natrium hidroksida, NaOH sebagai precursor, manakala air deionized digunakan sebagai pelarut. NP CeO₂ yang disediakan telah dicirikan dengan menggunakan mikroskop medan pengimbas electron (FESEM), mikroskop elektron transmisi (TEM), penyebaran tenaga X-Ray (EDX), spektroskopi ultraviolet kelihatan (UV-Vis), Fourier transform inframerah (FTIR), pembelauan X-Ray (XRD) and metode Brunauer-Emmett-Teller (BET). Luas permukaan spesifik yang tinggi iaitu 185 m²/g, saiz purata partikel (TEM: 3.5 nm BET: 4.5 nm) dan saiz kristal (XRD: 3.05 nm) telah diperolehi melalui proses pencirian. Puncak penyerapan di 305 nm dan 447.20 cm⁻¹ bagi analisis UV-Vis dan FTIR masing-masing mengesahkan kehadiran NP CeO₂. Ketiadaan bendasing daripada analisis EDX dan XRD membuktikan bahawa NP CeO₂ yang disediakan mempunyai ketulenan yang tinggi. Penjerapan asid humic (HA) pada CeO₂ NPs dilakukan menggunakan UV-Vis untuk mengukur jumlah HA yang diserap di wavelength 254 nm. Proses penjerapan didapati lebih tinggi di pH asid berbanding dengan pH alkali dan mengikuti kinetik tertib kedua Pseudo dan isotherm Langmuir. Penyebaran NP CeO₂ pula dikaji dengan mengukur Ce terlarut menggunakan

spektroskopi pelepasan optik-plasma yang digabungkan secara induktif (ICP-OES). Peningkatan kekuatan ionik dan pH didapati mengurangi kelarutan NP CeO₂ manakala peningkatan kepekatan HA dan pH menyebabkan NP CeO₂ yang lebih stabil.

Kata kunci: *Nanopartikel serium oksida, hidroterma, asid humic, penyebaran, penyerapan.*

TABLE OF CONTENTS

	Page
DECLARATION	i
ACKNOWLEDGEMENT	ii
ABSTRACT	iv
ABSTRAK	vi
TABLE OF CONTENTS	viii
LIST OF TABLES	xii
CHAPTER 1 INTRODUCTION	1
1.1 Background of the Study	1
1.2 Problem Statement	2
1.3 Objectives	4
CHAPTER 2 LITERATURE REVIEW	5
2.1 Nanoparticles	5
2.1.1 Properties of Nanoparticles	5
2.1.2 Application of Nanoparticles in Nanotechnology	6
2.2 Cerium Oxide Nanoparticles	8
2.2.1 Characteristics of Cerium Oxide Nanoparticles	8
2.2.2 Cerium Oxide Nanoparticles in the Environment	11

2.3	Synthesis of Cerium Oxide Nanoparticles	14
2.3.1	Chemical Synthesis Method	15
2.3.2	Green Synthesis Method	20
2.3.3	Nutrient Synthesis Method	22
2.4	Characterization of Cerium Oxide Nanoparticles	23
2.4.1	Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM)	23
2.4.2	Energy-Dispersive X-Ray (EDX)	27
2.4.3	X-Ray Diffraction (XRD)	28
2.4.4	Brunauer-Emmett-Teller (BET) Method	29
2.4.5	Fourier Transform Infrared Spectroscopy	31
2.4.6	Ultraviolet Visible – Spectroscopy (UV-Vis)	32
2.5	Influence of Environmental Conditions to the Behavior of Cerium Oxide Nanoparticles	33
2.5.1	Humic Acid	33
2.5.2	Ionic Strength	40
2.5.3	Effects of pH on Cerium Oxide Nanoparticles	41
	CHAPTER 3 METHODOLOGY	44
3.1	Materials	44
3.2	Synthesis of Cerium Oxide Nanoparticles	44
3.3	Characterization of Cerium Oxide Nanoparticles	47

3.3.1	Field Emission Scanning Electron Microscopy (FESEM) Analysis	47
3.3.2	Transmission Electron Microscope (TEM) Analysis	47
3.3.3	Energy-Dispersive X-Ray Spectroscopy (EDX) Analysis	47
3.3.4	UV-Visible Spectroscopy (UV-Vis) Analysis	48
3.3.5	Fourier Transform Infrared Spectroscopy (FTIR) Analysis	48
3.3.6	X-Ray Diffraction (XRD) Analysis	49
3.3.7	Brunauer-Emmett-Teller (BET) Method	49
3.4	Preparation of Humic Acid Stock Solution	49
3.5	Preparation of Cerium Oxide Nanoparticles Stock Solution and Dispersion	50
3.6	Adsorption of Humic Acid on Cerium Oxide Nanoparticles	50
3.6.1	Characterization of Humic Acid	50
3.6.2	Standard Calibration Curve of Humic Acid	51
3.6.3	Adsorption Study	51
3.6.4	Characterization of HA-CeO ₂ NPs After Adsorption	51
3.7	Dissolution Measurement of Cerium Oxide Nanoparticles	52
CHAPTER 4 RESULTS AND DISCUSSION		54
4.1	Characterization of Cerium Oxide Nanoparticles	54
4.1.1	Field Emission Scanning Electron Microscope (FESEM)	54
4.1.2	Transmission Electron Microscope (TEM)	55
4.1.3	Energy-Dispersive X-Ray Spectroscopy (EDX)	57

4.1.4	UV-Visible Spectroscopy (UV-Vis) Analysis	58
4.1.5	Fourier Transform Infrared Spectroscopy (FTIR) Analysis	59
4.1.6	X-Ray Diffraction (XRD) Analysis	60
4.1.7	Brunauer-Emmett-Teller (BET) Method	63
4.2	Adsorption of Humic Acid on Cerium Oxide Nanoparticles	65
4.2.1	Characterization of Humic Acid	65
4.2.2	Adsorption Kinetics	69
4.2.3	Adsorption Isotherms	73
4.2.4	Adsorption mechanism of humic acid on CeO ₂ NPs	79
4.2.5	FESEM of HA-CeO ₂	81
4.3	Dissolution of Cerium Oxide Nanoparticles under Different Aqueous Environmental Factors	82
4.3.1	Effects of Different Ionic Concentrations and pH	82
4.3.2	Effects of Humic Acid and pH on CeO ₂ NPs	84
4.3.3	Dissolution of CeO ₂ NPs in the Environment	88
	CHAPTER 5 CONCLUSION AND RECOMMENDATIONS	90
	REFERENCES	92
	APPENDICES	113

LIST OF TABLES

	Page
Table 2.1 Specific surface area and pore structure of CeO ₂ NPs prepared through solvothermal method using methoxyethanol and different bases (Hosokawa, 2016).	18
Table 2.2 Morphologies of CeO ₂ NPs according to their synthesis method (Dhall & Self, 2018)	23
Table 2.3 Particle size and surface area of CeO ₂ NPs in previous studies	31
Table 4.1 EDX results of CeO ₂ NPs synthesized through hydrothermal method	58
Table 4.2 Crystallite size of CeO ₂ NPs synthesized through hydrothermal method	62
Table 4.3 Specific surface areas of CeO ₂ NPs in previous studies compared with this study	64
Table 4.4 Average particle size of CeO ₂ NPs in different analyses	65
Table 4.5 Pseudo-first order and pseudo second order parameters for the 5 mg/L HA adsorption on CeO ₂ NPs at pH5, pH6, pH7, pH9	72
Table 4.6 Pseudo-first order and pseudo second order parameters for the 10 mg/L HA adsorption on CeO ₂ NPs at pH5, pH6, pH7, pH9	73
Table 4.7 Langmuir, Freundlich and Temkin isotherms parameters for the HA adsorption on CeO ₂ NPs at (a) pH5, (b) pH6, (c) pH7, (d) pH9.	78

LIST OF FIGURES

	Page
Figure 2.1 Role of nanotechnology during the pandemic of COVID-19 (Rasmi et al., 2021).	7
Figure 2.2 Nanotechnology in food industries (Nile et al., 2020)	8
Figure 2.3 Face-centred cubic fluorite lattice structure of CeO ₂ NPs where yellow circle represents cerium atoms and green circle represents oxygen atoms (Singh et al., 2020).	9
Figure 2.4 Dismutation mechanism of superoxide radical by CeO ₂ NPs (Celardo et al., 2011; Singh et al., 2020)	10
Figure 2.5 Life cycle and sources of ENPs released into the environment (Bathi et al., 2021; Caballero-Guzman & Nowack, 2016).	12
Figure 2.6 Top-down and bottom-up approaches to synthesize NPs (Ju-Nam & Lead, 2008).	15
Figure 2.7 Phases of hydrothermal synthesis (Ali, 2021)	19
Figure 2.8 Schematic diagram for the synthesis of CeO ₂ NPs using <i>Rheum turkestanicum</i> plant extract through sol-gel method (Sabouri et al., 2020).	21

Figure 2.9	Schematic diagram for the synthesis of CeO ₂ NPs using <i>Moringa oleifera</i> leaf extract through precipitation method (Eka Putri et al., 2021).	22
Figure 2.10	SEM image of CeO ₂ NPs after 18 hours of solvothermal treatment (Pang et al., 2019)	25
Figure 2.11	TEM images of CeO ₂ NPs (a) before solvothermal treatment, (b) after 10 hours of solvothermal treatment and (c) after 18 hours of solvothermal treatment (Pang et al., 2019)	25
Figure 2.12	HRTEM image of CeO ₂ NPs synthesized through solvothermal method by (Muduli et al., 2014)	26
Figure 2.13	CeO ₂ NPs synthesized through precipitation method under (a) TEM and (b) HRTEM (Pop et al., 2020)	27
Figure 2.14	XRD patterns of CeO ₂ NPs synthesized through solvothermal method in different duration of time and after calcination (Pang et al., 2019)	29
Figure 2.15	N ₂ adsorption-desorption isotherms of CeO ₂ NPs (Khan et al., 2020)	30
Figure 2.16	FTIR spectrum of CeO ₂ NPs (Farahmandjou & Zarinkamar, 2016)	32
Figure 2.17	Optical absorption spectrum of CeO ₂ (Valsaraj & Divyarthana, 2019)	33
Figure 2.18	Most abundant functional groups presence in HA at different pK _a values (Jayalath et al., 2018).	35

Figure 2.19	Zeta potential and PZC of CeO ₂ NPs synthesized by efficient combustion (green line) and hydroxide mediated (blue line) methods (Mahato & Gupta, 2021)	37
Figure 2.20	Morphology of CeO ₂ NPs at different pH under TEM where (a) acidic solution, (b) neutral solution and (c) basic solution (Yan et al., 2007)	43
Figure 3.1	Purple colloid formed after hydrothermal treatment at 70 ± 2 °C	45
Figure 3.2	Schematic diagram of hydrothermal synthesis of CeO ₂ NPs	46
Figure 4.1	FESEM image of CeO ₂ NPs synthesized through hydrothermal method	55
Figure 4.2	TEM image of CeO ₂ NPs synthesized through hydrothermal method	56
Figure 4.3	Size distribution of CeO ₂ NPs synthesized through hydrothermal method.	57
Figure 4.4	EDX pattern of CeO ₂ NPs synthesized through hydrothermal method	58
Figure 4.5	UV-Vis spectrum of CeO ₂ NPs synthesized through hydrothermal method	59
Figure 4.6	FTIR spectrum of CeO ₂ NPs synthesized through hydrothermal method	60
Figure 4.7	XRD diffractogram of CeO ₂ NPs synthesized through hydrothermal method	61

Figure 4.8	Williamson-Hall plot of CeO ₂ NPs synthesized through hydrothermal method	63
Figure 4.9	N ₂ adsorption-desorption isotherm of CeO ₂ NPs synthesized through hydrothermal method	64
Figure 4.10	FESEM image of humic acid	66
Figure 4.11	UV-Vis spectrum of humic acid	67
Figure 4.12	FTIR spectrum of humic acid	68
Figure 4.13	Pseudo-first and pseudo-second order kinetic models of 5 mg/L HA adsorption on CeO ₂ NPs at (a) pH5, (b) pH 6, (c) pH 7 and (d) pH 9	70
Figure 4.14	Pseudo-first and pseudo-second order kinetic models of 10 mg/L HA adsorption on CeO ₂ NPs at (a) pH5, (b) pH 6, (c) pH 7 and (d) pH 9	71
Figure 4.15	Langmuir, Freundlich and Temkin isotherms of HA adsorption on CeO ₂ NPs at (a) pH5, (b) pH6, (c) pH7, (d) pH9	76
Figure 4.16	Protonation and deprotonation of surface sites of CeO ₂ NPs	80
Figure 4.17	FESEM image of HA-CeO ₂ NPs at (a) pH 5, (b) pH 6, (c) pH 7 and (d) pH 9	82
Figure 4.18	Dissolved Ce ⁴⁺ under the influence of different pH and IS of (a) 0 mM NaCl and (b) 3 mM NaCl	84
Figure 4.19	Dissolved Ce ⁴⁺ under the influence of different pH and HA concentrations of (a) 5 mg/L and (b) 10 mg/L	87

LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
NP	Nanoparticle
3-D	Three-dimensional
$\text{Ce}(\text{NO}_3)_3$	Cerium nitrate
$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	Cerium (III) nitrate hexahydrate
CeO_2	Cerium oxide
COVID-19	Coronavirus Disease
DI	Deionized
DLS	Dynamic light scattering
DTA-TG	Thermal Analysis Method
EDX	Energy dispersive X-Ray
FTIR	Fourier transform infrared
HA	Humic acid
HR-TEM	High-resolution transmission electron microscopy
ICP-OES	Inductively coupled plasma – optical emission spectroscopy
LOD	Limit of detection
LOQ	Limit of quantitation
N_2	Nitrogen
NOM	Natural Organic Matter
PPE	Personal protective equipment
PZC	Point of zero charge
ROS	Reactive oxygen species

FESEM	Field emission scanning electron microscope
SD	Standard deviation
TEM	Transmission electron microscope
UV-Vis	Ultraviolet-Visible
XPS	X-ray photoelectron spectroscopy
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Nanoparticles (NPs) particles with the size scale of 1 to 100 nm and are composed of either carbon, silicon and metals (Wu, 2005). In recent decades, nanotechnology has been studied extensively and used in various fields including medicine and catalysis (Sharma et al., 2022). The central processing units in smartphones used in our daily life is also a part of nanotechnology that has been created by electrical engineers (Bayda et al., 2020). The potential of this technology in many different areas is exciting and will be used in our daily activities especially in the future which will lead to mass production of NPs. Consequently, engineered NPs will constantly be released to the environment and therefore, the impacts of NPs towards the environment are important to be studied.

The behavior of these engineered NPs in the environment have raised concerns especially in the aquatic environment. NPs are released to the environment through various sources which include forest fires, volcanic eruptions, automobiles, commercial products and naturally from living organisms (Belkacem et al., 2022). When released to the environment, these NPs are altered by environmental parameters such as temperature, pH and ionic strength which then affect the dissolution, aggregation and agglomeration of the NPs. Changes in their behavior could give significant impacts on the pathway and degree of these NPs when released to the environment (Maurer-Jones et al., 2013).

Cerium oxide, CeO₂, NPs are used in many industries including solar cells, fuel oxidation catalysis and as chemical mechanical polarization (Dhall & Self, 2018). CeO₂ NPs has also been found effective as antioxidants to protect cells against impairment by free radicals and reactive oxygen species (ROS) due to the ability of these NPs to store oxygen (Nyoka et al., 2020). Since 1980s, the catalytic behavior of CeO₂ NPs has been employed in vehicle engines because these NPs have the ability to reduce hydrocarbons and the release of nitrous oxide into the atmosphere (Scirè & Palmisano, 2020). Despite multiple studies reporting the ability of CeO₂ NPs as an antioxidant, some studies have concluded that CeO₂ NPs can also induced the formation of ROS. These NPs have been reported to damage the liver of rats and also human tissues. However, these negative effects might be caused by the differences in morphology of these NPs and its redox ability (Dahle & Arai, 2015; Nalabotu et al., 2011; Park et al., 2008). Therefore, further studies about the behavior of CeO₂ NPs while considering their morphology is crucial to understand the impacts of these NPs towards the environment.

1.2 Problem Statement

Hydrothermal synthesis is one of the most used methods to synthesize CeO₂ NPs. This is mainly due to its environmental friendliness and economical procedures (Ali, 2021). However, the synthesis process of NPs is difficult in terms of complexity and the cost needed for the process is very high when high temperatures are involved (Kumar et al., 2021). Most of the hydrothermal method performed in previous studies were at high temperatures ranging from 200 °C and up to 450 °C with expensive precursors needed to prepare desired size and shape of NPs (Darr et al., 2017). Thus, this study focuses on the hydrothermal synthesis of CeO₂ NPs with high efficiency in terms of synthesis conditions, simplicity and cost needed.

The wide applications of CeO₂ NPs commercially have led to mass production of this metal oxide NPs. Although the impacts of CeO₂ NPs towards the human health have been the focus in recent years, the interpretation about the behavior of these NPs in the ecosystem is still lacking. Environmental parameters such as pH, ionic strength, natural organic matter (NOM) and temperature give significant impacts towards the behavior of CeO₂ NPs (Liu et al., 2018). Behavioral changes such as aggregation, agglomeration and sedimentation of CeO₂ NPs in the aqueous environment were studied extensively in the recent decades. However, few studies were done about the dissolution of CeO₂ NPs. Researches have also concentrated on the dissolution of CeO₂ NPs in plant growth medias but limited studies were conducted on the dissolution of these NPs under the aqueous environmental factors. The dissolution of CeO₂ NPs is vital to be studied because dissolved Ce³⁺ or Ce⁴⁺ ions react differently compared to undissolved Ce. Dissolved Ce³⁺ or Ce⁴⁺ ions have been reported to induce cell death while the undissolved Ce has been found to increase the generation of reactive oxygen species (ROS) and contaminated the aquatic environment (Mittal & Pandey, 2014). Therefore, this study focuses on the hydrothermal synthesis of CeO₂ NPs and the influence of aqueous environmental factors which are pH, HA and ionic strength on the dissolution of CeO₂ NPs. Hence, the modified hydrothermal method used in this study is expected to synthesize CeO₂ NPs in a shorter reaction time and lower reaction temperature while the environmental factors studied are expected to alter the dissolution of CeO₂ NPs in the aqueous environment which may cause significant negative impacts towards living organisms.

1.3 Objectives

The objectives of this study were as follows:

- i. To synthesize CeO_2 NPs by a modified hydrothermal method and characterize the synthesized CeO_2 NPs.
- ii. To determine the effects of aqueous environmental factors which are pH, ionic strength and HA concentrations on the dissolution of CeO_2 NPs.
- iii. To study the adsorption kinetics and adsorption isotherms of humic acid on the synthesized CeO_2 NPs at different pH.

CHAPTER 2

LITERATURE REVIEW

2.1 Nanoparticles

2.1.1 Properties of Nanoparticles

Nanotechnology is one of the most exciting and propitious technology in recent decades. This technology involves the preparation and application of NPs in the scale of 1 to 100 nm in many different fields (Bayda et al., 2020). NPs exist in both amorphous and crystals. These particles possess a high specific surface area and are very reactive because of the very small size of the NPs (Buzea et al., 2007). The unique properties of NPs are the reasons why nanotechnology is commonly used in various fields which include medicine, energy, industrial, environmental and commercial (Ju-Nam & Lead, 2008).

NPs are divided into many different categories such as carbon-based NPs, metal NPs, metal oxide NPs and semiconductor NPs (Khan et al. 2019). These carbon-based NPs include fullerenes, carbon nanotubes and graphene. Fullerenes are popularly used in organic solar cells due to their high electron affinity and the ability to accept electric charge. On the other hand, the high stability of carbon nanotubes to withstand high temperatures and their high conductivity have made them ideal as sensor and biosensors in many different applications such as in electronic devices and medicine (Siqueira & Oliveira, 2017).

Titanium oxide, TiO_2 NPs, zinc oxide, ZnO NPs, iron oxide, Fe_2O_3 and cerium oxide, CeO_2 NPs are metal oxide NPs that have shown various uses such as in catalysis,

photovoltaic cell and biomedicine. One of the uniqueness of metal oxide NPs is their ability to be synthesized using many different techniques including co-precipitation method and hydrothermal method (Alhalili, 2023). These NPs are also unique compared to the other type of NPs due to their high density and narrow size of corners and edges on the surface of the NPs (Chavali & Nikolova, 2019).

2.1.2 Application of Nanoparticles in Nanotechnology

Prevention and treatment of viruses such as influenza virus, Ebola virus and the recent pandemic of COVID-19 (coronavirus disease) have been studied in nanoscales because nanotechnology has been found to be effective in reducing the infection cycles (Ruiz-Hitzky et al., 2020). The COVID-19 pandemic has also proved that nanotechnology is vital as prevention, diagnosis and treatment of this disease as shown in Figure 2.1. Facemasks, gloves and personal protective equipment (PPE) designed at nanoscales have been heavily involved around the world in order to significantly reduce the spread of COVID-19 (Tharayil et al., 2021). To filter respiratory droplets efficiently, NP-based facemasks are composed of nanofibers and nanofiber webs which are highly permeable and small size. Moreover, nanofibers are known to minimize intake of pathogens through respiration due to their ability to deactivate the viruses (Akduman & Akcakoca Kumbasar, 2018; Rasmi et al., 2021).

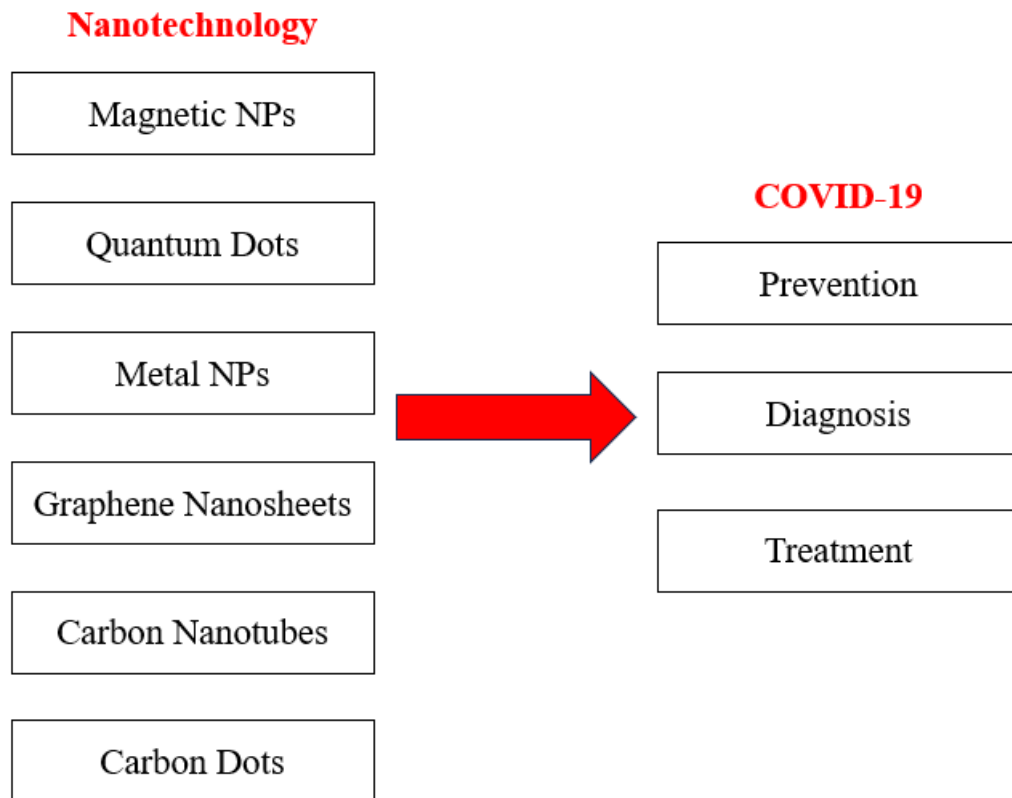


Figure 2.1: Role of nanotechnology during the pandemic of COVID-19 (Rasmi et al., 2021)

NPs are also widely used in the food industries. They are used in materials collection, food processing, product manufacturing and food safety as shown in Figure 2.2. Antibacterial nano coatings have been used to pack foods such as meats and fruits to increase their shelf life by acting as a moisture barrier. Meanwhile, nanoscale filters have also been used in the production of milk. These filters allow manufacturers to remove lactose from milk and replace it with other disaccharides which suits the lactose-intolerant patients (Nile et al., 2020). The use of nanosensors and nanotracers in the food industries have also significantly improve the safety of foods produced. The ability of nanosensors to detect very low levels of microorganisms or toxins allow the manufacturers to produce a higher quality and safer food products (Duncan, 2011).

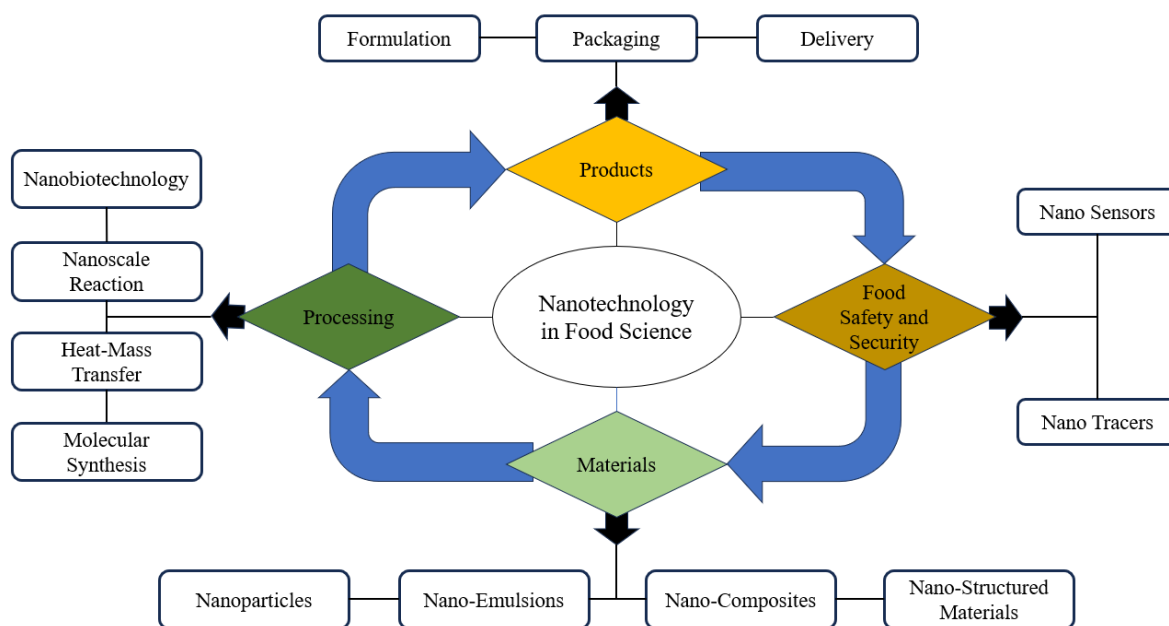


Figure 2.2: Nanotechnology in food industries (Nile et al., 2020)

2.2 Cerium Oxide Nanoparticles

2.2.1 Characteristics of Cerium Oxide Nanoparticles

Cerium, Ce is one of the lanthanides that are rarely found in the Earth's crust. It consists of 4 stable isotopes which are ^{136}Ce , ^{138}Ce , ^{140}Ce and ^{142}Ce with the ^{140}Ce being the most abundant (88.5%) (Dahle & Arai, 2015). This soft and ductile metal exists in the trivalent state (Ce^{3+}) and the tetravalent state (Ce^{4+}) while forming oxides of cerium dioxide (CeO_2) and cerium sesquioxide (Ce_2O_3) through redox reactions with the cubic fluorite structure as shown in Figure 2.3 (Scirè & Palmisano, 2020). The structure contains 4 cerium atoms and 8 oxygen atoms bonded in a tetrahedral position.

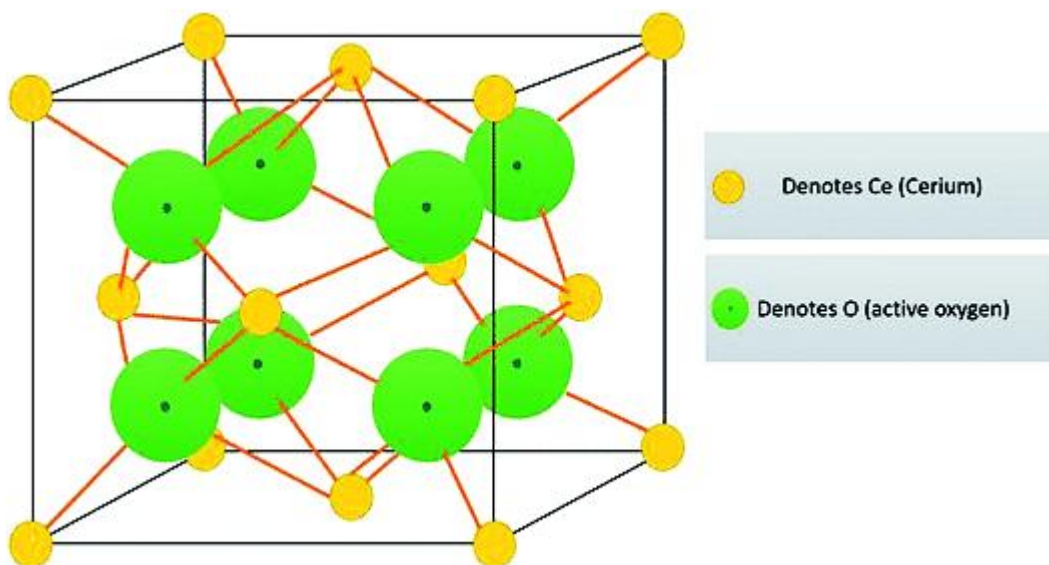


Figure 2.3: Face-centred cubic fluorite lattice structure of CeO₂ NPs where yellow circle represents cerium atoms and green circle represents oxygen atoms (Singh et al., 2020)

One of the most vital characteristics which differs the CeO₂ NPs with the bulk CeO₂ is the large surface area of the NPs. Larger surface area provides NPs with more active sites which causes the NPs to become more reactive compared to bulk NPs (Singh et al., 2020). Furthermore, the higher ratio of Ce³⁺/Ce⁴⁺ in CeO₂ NPs compared to the bulk CeO₂ also causes the NPs to be more reactive and have a higher rate of redox reactions (Handy et al., 2008; Ma et al., 2016). Therefore, CeO₂ NPs have a higher tendency of switching between Ce³⁺ and Ce⁴⁺. This unique ability has been studied to be useful for CeO₂ NPs to scavenge free radicals. CeO₂ NPs were found to have the ability to mimic the function of biological enzymes found in all living organisms, superoxide dismutase (SOD), which scavenges ROS specifically the superoxide radical and protects the organisms from diseases due to the excess amount of superoxide radicals (Walkey et al., 2015; Younus, 2018). Xu and Qu (2014) proposed the mechanism of dismutation of superoxide radicals by CeO₂ NPs as shown below.



The mechanisms above showed that the Ce^{3+} or Ce^{4+} reacts with superoxide radical and neutralize it to form oxygen or hydrogen peroxide (Singh et al., 2020). Further representation of the dismutation mechanism is shown in Figure 2.4. The superoxide radical binds to the vacant Ce^{3+} at (4) until they formed H_2O_2 and Ce^{4+} at (6). By removing H_2O_2 molecules, superoxide radical then binds with the vacant Ce^{4+} in stage (7) and (1) and the same process was repeated again (Celardo et al., 2011; Singh et al., 2020).

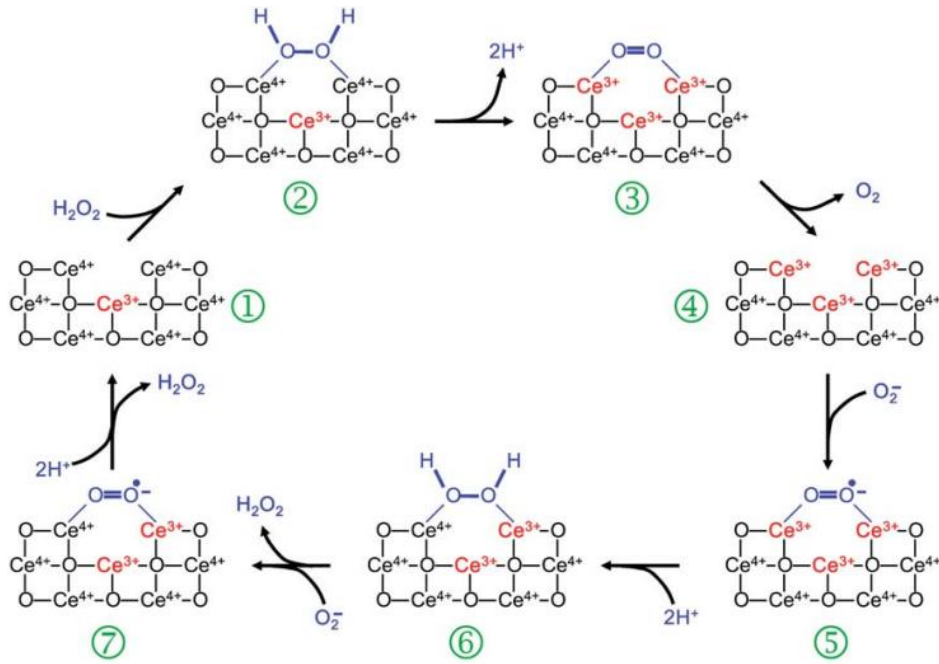


Figure 2.4: Dismutation mechanism of superoxide radical by CeO_2 NPs (Celardo et al., 2011; Singh et al., 2020)

2.2.2 Cerium Oxide Nanoparticles in the Environment

2.2.2.1 Fate and Transport of Cerium Oxide Nanoparticles

Engineered Nanoparticles (ENPs) are released to the environment through various sources. Figure 2.5 shows the life cycle and its sources that leads to the released of ENPs into the aquatic environment. Factories manufacturing products with the use of NPs are one of the major sources of NP-polluted aquatic environment. Despite treatment, the wastewater from these factories could not prevent some fractions of the NPs to be released to the environment (Dahle & Arai, 2015). Factories manufactured and handled ENPs until the products are used for commercial. The handling of such products however possessed a risk of contaminating natural surface water with NPs even after the wastewater treatment process was performed (Bathi et al., 2021; Caballero-Guzman & Nowack, 2016). However, the usage and disposal of the ENPs' products are the ones that contribute to the highest release of NPs to the aquatic environment due to the high amount of usage in daily activities (Boxall et al. 2007; Bathi et al., 2021).

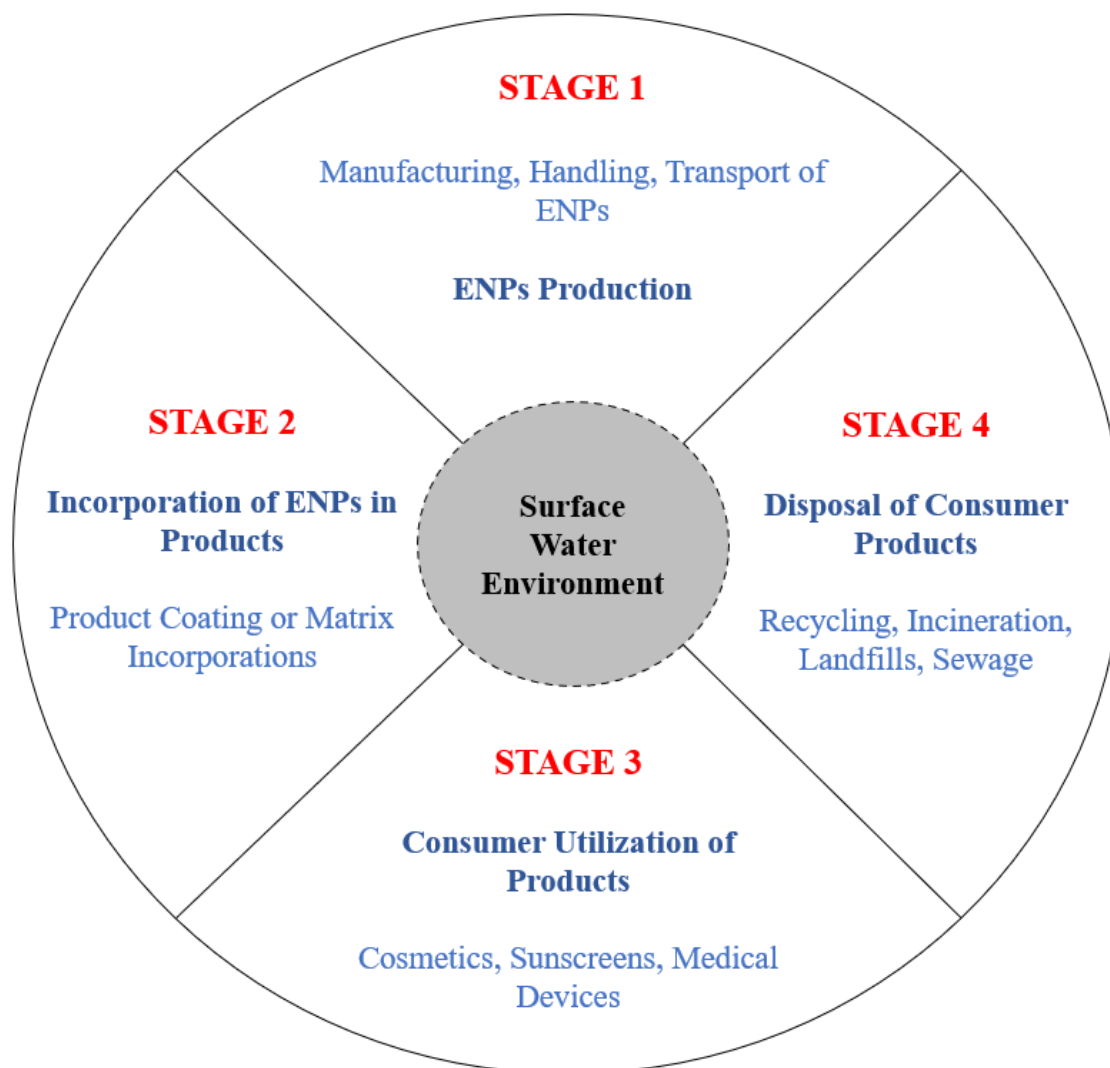


Figure 2.5: Life cycle and sources of ENPs released into the environment (Bathi et al., 2021; Caballero-Guzman & Nowack, 2016)

The released of CeO₂ NPs in the environment may also come from treated water as NPs are difficult to be filtered due to their very small size. The amount of CeO₂ NPs released to the environment through treated wastewater treatment plants to the aquatic environment was expected to be between 0.003 to 1.17 µg L⁻¹ (Collin et al. 2014). However, the amount of CeO₂ NPs released is also expected to increase rapidly due to the higher usage of NPs in various fields.

When released and exposed to the environmental parameters such as pH, IS, temperature and the presence of natural organic matters (NOM), CeO₂ NPs have been studied to behave differently in terms of aggregation, agglomeration and dissolution due to the ability of CeO₂ NPs to convert between their redox states rapidly (You et al., 2020).

The dissolution of CeO₂ NPs in the environment has been a part of major concerns towards the aquatic environment and the human health in recent decades. Dissolved Ce³⁺ and Ce⁴⁺ have been reported to cause different toxicity towards living organism compared to the undissolved Ce. Despite the poor solubility properties of CeO₂ NPs in water, CeO₂ NPs were found to dissolve partially in acidic pH which was mostly reported in high microbial activity zones such as water bodies near the discharge of sewage and anthropogenic pollutants (Yap et al., 2011). Dissolved Ce³⁺ and Ce⁴⁺ have been reported to cause cell deaths in living organisms while the undissolved Ce has been more likely to cause contamination to the water bodies due to their higher mobility in water (Mittal & Pandey, 2014).

2.2.2.2 Toxicity of Cerium Oxide Nanoparticles

NPs in the aquatic environment are usually in coated form due to the reactions between the NPs and naturally occurring materials such as NOM and ionic compounds (Yang et al., 2009). Due to this reason, studies have been focusing on the adsorption of NOM and ionic compounds on NPs and the effects of the complexes formed towards the environment rather than the bare NPs.

The small size of CeO₂ NPs compared to the bulk CeO₂ is one of the major factors leading to its toxicity in the biological systems. This is due to its bigger surface area which allows the NPs to be more reactive. CeO₂ NPs has been known to be toxic because of its ability to release free radicals, reaction products and its photocatalytic behavior (Dahle & Arai, 2015). The presence of free radicals may cause oxidative degradation which is harmful to the biological cells (Thomas & Aust, 1986). Moreover, other physicochemical properties such as agglomeration and surface charge also affected the toxicity of CeO₂ NPs. Different properties of CeO₂ NPs behave differently in the aquatic environment. A decrease in size of the NPs leads to an increase in agglomeration which results into a lower toxicity of CeO₂ NPs towards living organisms in the aquatic environment. The lower toxicity is due to the interaction of the NPs with NOM that increases the stability of CeO₂ NPs by adsorption while preventing the NPs from interacting with bacteria. Furthermore, high agglomeration of CeO₂ NPs has also been found to lower its dissolution rate. Thus, changing the exposure route to another location (You et al., 2021).

2.3 Synthesis of Cerium Oxide Nanoparticles

Different synthesis method may produce different physicochemical properties of CeO₂ NPs. According to Rajeshkumar and Naik (2018), there were three different synthesis methods used to produce CeO₂ NPs which were the chemical synthesis, green synthesis and nutrient synthesis.

2.3.1 Chemical Synthesis Method

Previous researches have synthesized CeO₂ NPs through many different chemical methods. According to Nikam et al. (2018), the synthesis of metal oxide NPs can be performed by the top-down and bottom-up approach as shown in Figure 2.6. The top-down approach is performed using large starting materials which then undergo processes to produce NPs. Meanwhile, the bottom-up approach is performed using atomic or molecular species to form the NPs desired. Wet chemical route is one of the bottom-up approach used to synthesize metal oxide NPs. This route includes methods that are commonly used such as hydrothermal method, thermal decomposition, precipitation method and sol-gel method.

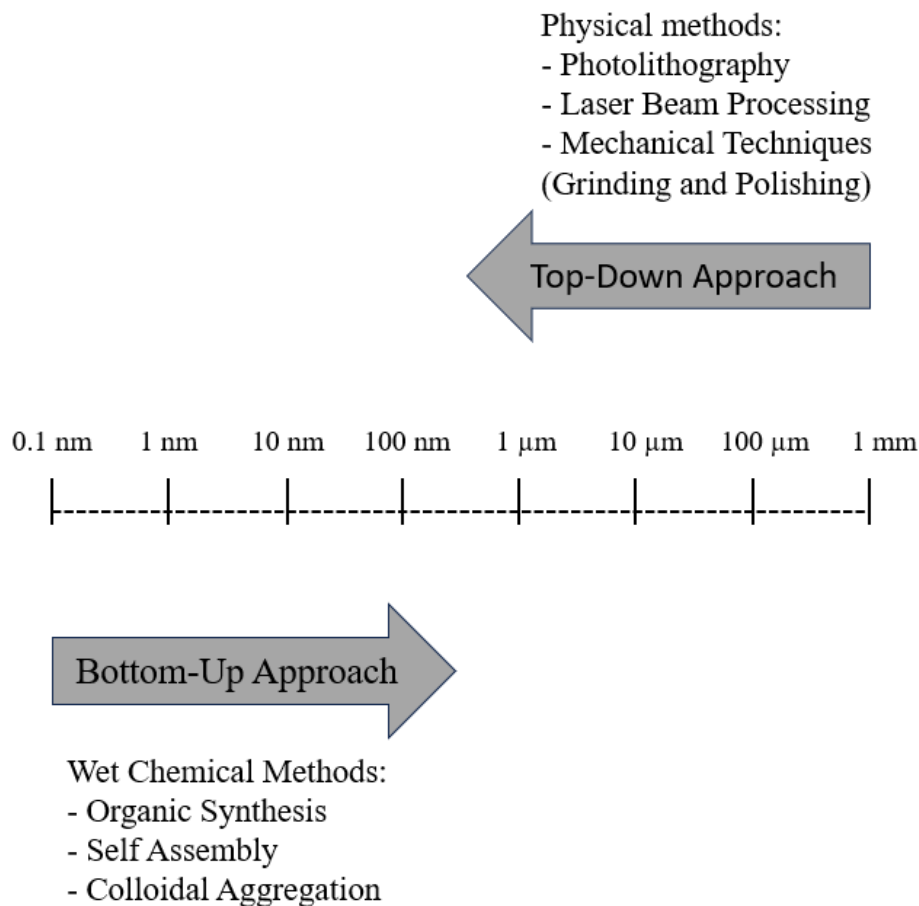


Figure 2.6: Top-down and bottom-up approaches to synthesize NPs (Ju-Nam & Lead, 2008)

2.3.1.1 CO-Precipitation Method

CO-precipitation is the method used to synthesize NPs through the formation of oxides intermediates with the presence of precipitating agents (Bajaj & Joshi, 2021).

Farahmandjou and Zarinkamar (2016) synthesized CeO_2 NPs through CO-precipitation method by using cerium nitrate hexahydrate, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and potassium carbonate, K_2CO_3 as the precursors. This method produced an intermediate species of cerium (III) carbonate, $\text{Ce}_2(\text{CO}_3)_3$. After drying at 65°C for 2 hours and 220°C for 2.5 hours, the powder obtained undergo calcination at 600°C for 3 hours before characterization process. Results showed that this method successfully synthesized spherical CeO_2 NPs with the size range of 40 to 80 nm.

2.3.1.2 Precipitation Method

The precipitation method requires at least one precipitating agent which is alkaline and has been proven by previous studies to be efficient in producing NPs with large surface areas (Li et al., 2018).

Putri et al. (2019) synthesized CeO_2 NPs through precipitation method. The starting materials used were cerium (III) nitrate hexahydrate, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and ammonium hydroxide, NH_4OH with isopropanol as the solvent. The precipitate formed after the starting materials were mixed was then dried at 60°C for 2 hours and calcinated at 300°C for 4

hours. Results showed that this method was able to synthesize CeO₂ NPs with the size range of 7 to 10 nm from the TEM analysis while 11 to 99 nm from the XRD analysis.

Pop et al. (2020) also synthesized CeO₂ NPs using precipitation method using cerium nitrate as the precursor and oxalic acid solution as the solvent. This method was performed at pH 7 while adding tetraethylammonium hydroxide as the precipitating agent. The product formed after precipitation was filtered and dried. It was then air dried at 400 °C for 1 hour, washed, centrifuged and dried again to obtain the NPs. The size and shape of the CeO₂ NPs synthesized using this method were between 5 to 20 nm and pseudo-spherical shape respectively.

2.3.1.3 Solvothermal Method

Solvothermal is a method used to synthesize NPs under the temperature closed to or above the boiling point of the solvent which is used to create high pressures between the solution (Choudhury et al., 2022). Walton (2011) summarized the solvothermal synthesis of CeO₂ NPs of previous studies. Recent studies have shown that this type of synthesis was mostly performed under mild conditions ($T < 250^{\circ}\text{C}$) because of the high melting point of CeO₂ NPs. In this condition, researches were also able to control the size of this nanoparticle. Different cerium salts were used as the starting material of this method. According to the summarization, majority of previous studies used ethanol as a solvent while some used 2-methoxyethanol, carbon tetrachloride, benzyl alcohol and ammonia solution. Sodium hydroxide, NaOH was used as additives and the reaction condition was between 100 to 180°C.

Hosokawa (2016) studied the solvothermal synthesis of CeO₂ NPs using methoxyethanol at 250°C and calcination at 300 °C. This method successfully synthesized CeO₂ NPs with specific surface areas of 61 to 122 m²/g using different bases as shown in Table 2.1 and using ammonia solution as an additive.

Table 2.1: Specific surface area and pore structure of CeO₂ NPs prepared through solvothermal method using methoxyethanol and different bases (Hosokawa, 2016)

Types of bases used	Specific surface area (m ² /g)	Pore structure
Na ₂ CO ₃	61	microporous
NaHCO ₃	75	macroporous
NaOH	122	mesoporous

Muduli et al. (2014) also synthesized CeO₂ NPs through solvothermal method. However, the precursor used was ceric ammonium nitrate with ethylene glycol and isopropanol as the solvents and were heated at 130°C. TEM analysis revealed that the synthesized CeO₂ NPs were of size between 50 to 70 nm and were spherical shape.

2.3.1.4 Hydrothermal Method

Hydrothermal technique meanwhile is similar to the solvothermal method but water is used as the solvent which is heated below its supercritical temperature (Choudhury et al., 2022). According to Ali (2021), the synthesis of CeO₂ NPs through hydrothermal technique is performed in two phases as shown in Figure 2.7. The first phase is the nucleation phase where the cerium ions (Ce³⁺/Ce⁴⁺) aggregated together and the product formed are then dried to undergo dehydration to further the nucleation process. The second phase is the ripening of the nuclei formed which outcomes into the production of pale-yellow powder, CeO₂ NPs.

In a study by Wang et al. (2008), cerium (III) nitrate hexahydrate, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was used as the cerium salt and deionized water (DI) as the solvent. The solution was then added with NaOH at pH between 13 and 14. The product formed was heated in an autoclave at 180 °C for 24 hours to produce CeO_2 NPs powder. Through TEM imaging, the morphology of the synthesized CeO_2 NPs revealed that the size was 4 to 5 nm while having quasi zero-dimensional shape particles. BET method performed also confirmed that the NPs synthesized possessed a high surface area of 125 m^2/g .

Sankar and Kumar (2021) also synthesized CeO_2 NPs using hydrothermal technique. However, precursors used were $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and urea solution. The precursors were heated at 180°C for 8 hours and then 600°C in a furnace for 4 hours. According to the SEM imaging performed, the NPs have a flower-like shape while the XRD analysis confirmed that the crystallite size were between 15 to 24 nm.

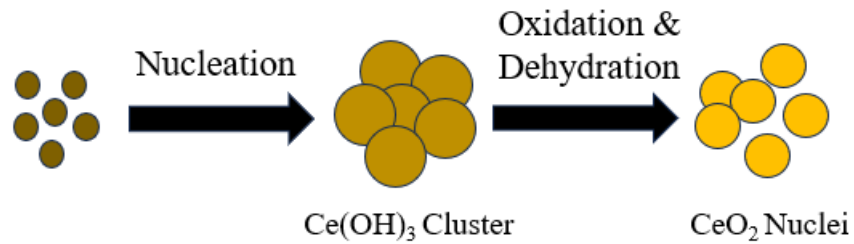


Figure 2.7: Phases of hydrothermal synthesis (Ali, 2021)

2.3.2 Green Synthesis Method

Green synthesis uses plant extracts to synthesize CeO₂ NPs. Sabouri et al. (2020) synthesized CeO₂ NPs using *Rheum turkestanicum* plant extract through a sol-gel method to study the photocatalytic activity and toxicity of CeO₂ NPs. A cerium nitrate, Ce(NO₃)₃ solution was used as a cerium precursor while the plant extract was used as a stabilizing agent. The gels obtained then undergo calcination at high temperatures (400-600 °C) before obtaining the CeO₂ powder. Figure 2.8 shows the simplified steps used in the study to synthesize CeO₂ NPs.

Altaf et al. (2021) used *Acorus calamus* extract to synthesize CeO₂ NPs. Cerium nitrate, Ce(NO₃)₃ solution was added with the plant extract until precipitate was formed. The mixture was centrifuged, dried and powdered before powder was formed. The powder was calcinated and ground to obtain the CeO₂ NPs.

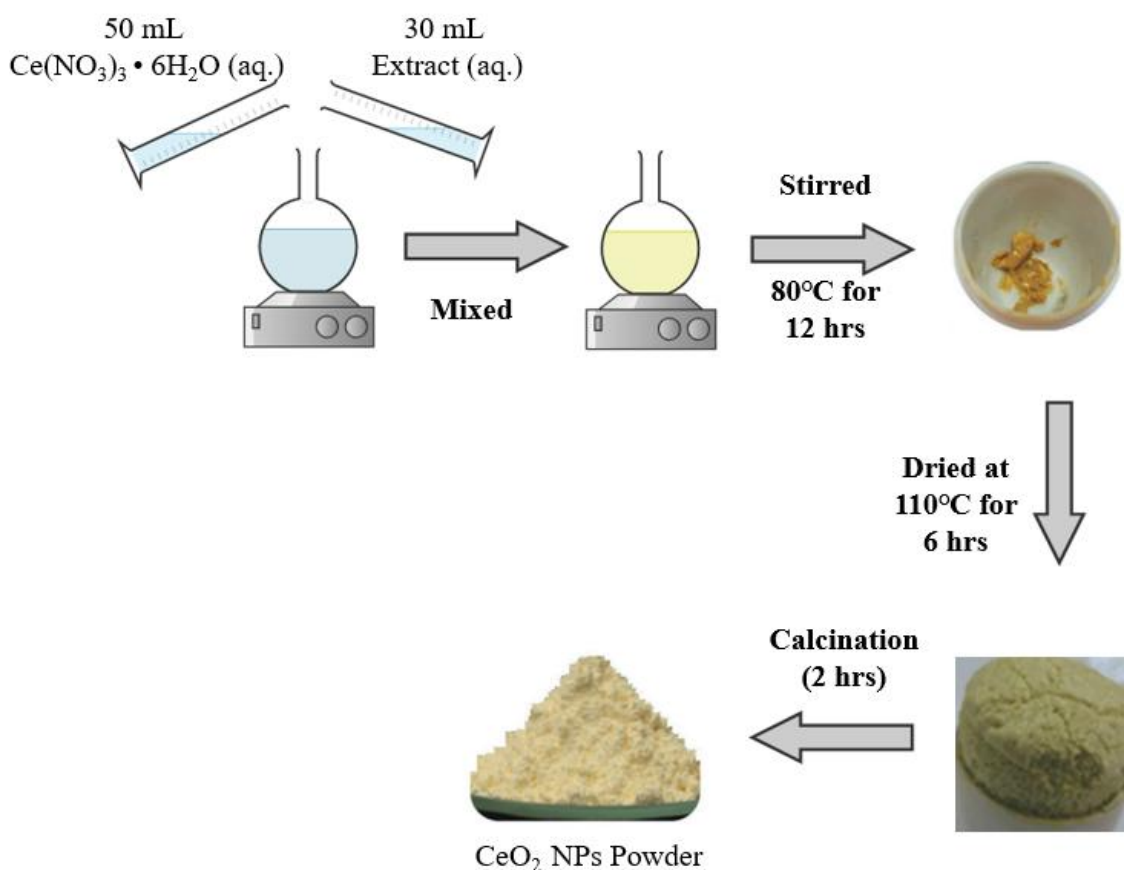


Figure 2.8: Schematic diagram for the synthesis of CeO₂ NPs using *Rheum turkestanicum* plant extract through sol-gel method (Sabouri et al., 2020)

Eka Putri et al. (2021) synthesized CeO₂ NPs using *Moringa oleifera* leaf extract as the solvent and cerium (III) nitrate hexahydrate, Ce(NO₃)₃ • 6H₂O as the cerium salt. The mixture was stirred at 80 °C for 2 hours before calcination at 600 °C for another 2 hours. Figure 2.9 below shows the simplified steps of the synthesis method used. Results showed that this synthesis method were able to produce spherical CeO₂ NPs and an average size of 17 nm.

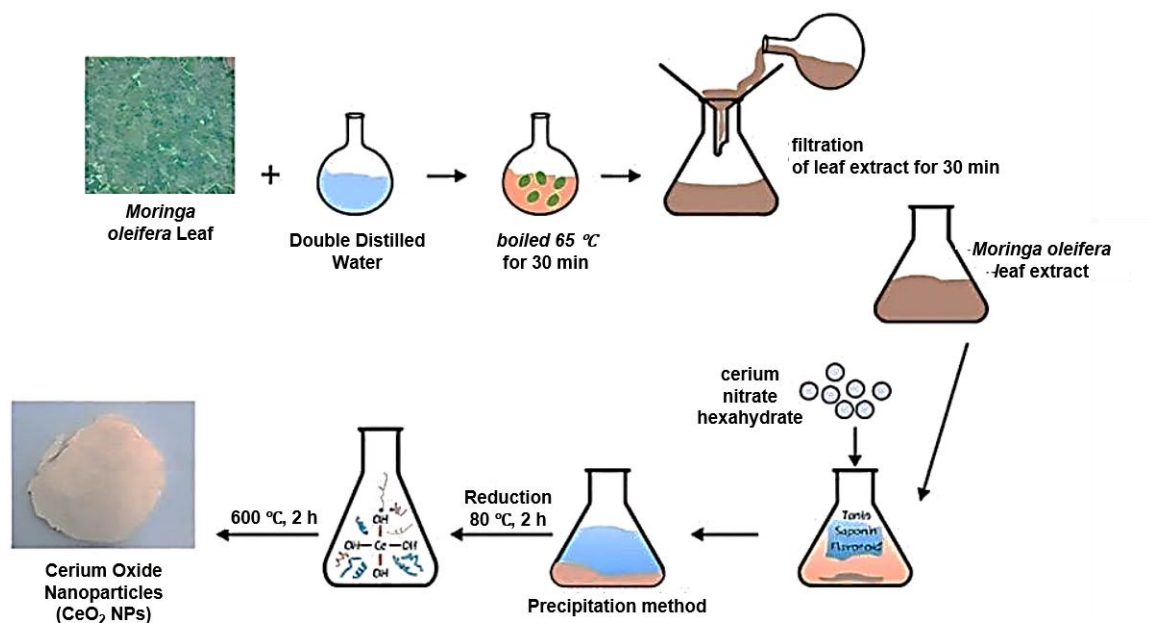


Figure 2.9: Schematic diagram for the synthesis of CeO₂ NPs using *Moringa oleifera* leaf extract through precipitation method (Eka Putri et al., 2021)

2.3.3 Nutrient Synthesis Method

The nutrient synthesis is another method used in previous studies to obtain CeO₂ NPs. Kumar et al. (2021) studied the synthesis of CeO₂ NPs using egg white. The egg white was first mixed with DI water. Ce(NO₃)₃ • 6H₂O was then added to the solution where egg white played an important role to trap the cerium ions which caused them to form gels. The mixture was dried and ground, forming fine powders. This powder was then dried again at high temperature to form spherical CeO₂ NPs and with the size of 6.8 nm from the TEM analysis.

2.4 Characterization of Cerium Oxide Nanoparticles

The physicochemical properties of NPs are affected by many different factors. Previous studies reported that different types of synthesis method and solvents used produced different morphological properties of NPs as shown in Table 2.2 (Dhall & Self, 2018). The characteristics of NPs can also be affected when they are released to the environment. The particle size, particle charge, particle number, particle shape, mass concentration and elemental composition are vital characteristics that affect the behavior of NPs in the environment (Farré et al., 2009). A large surface area provides CeO₂ NPs the ability as a free radical scavenger. Therefore, the smaller the size of CeO₂ NPs, the larger the space to store oxygen which allows it to undergo redox reactions rapidly (Nyoka et al., 2020). Hence, the characterization of CeO₂ NPs is important to study how the different properties of CeO₂ NPs determine their novel activities.

Table 2.2: Morphologies of CeO₂ NPs according to their synthesis method (Dhall & Self, 2018)

Synthesis Method	Particle Size (nm)	Morphology
Solvothermal	~8	Polyhedral
Precipitation	15	Spherical
Spray Pyrolysis	~17	Cubic
Hydrothermal	5	Octahedral

2.4.1 Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM)

TEM and high resolution-transmission electron microscope (HRTEM) were used in previous studies to determine the morphology, agglomeration and aggregation of CeO₂ NPs.

Rogers et al. (2015) studied the size and shape of CeO₂ NPs using TEM and measured that the NPs were of 10 to 30 nm in size and were spherical.

In another study by Pang et al. (2019), the effects of solvothermal treatment time on the size and shape of the synthesized CeO₂ NPs were studied using SEM and TEM. SEM imaging was performed to determine the shape and agglomeration of the CeO₂ NPs. The SEM image as shown in Figure 2.10 revealed that after 18 hours of solvothermal treatment, the NPs were of spheroidal shaped and were weakly agglomerated. The TEM images as shown in Figure 2.11 showed that as the solvothermal treatment time increased, the size of the NPs increased too while the morphology also showed gradual changes. Figure 2.11(a) showed the CeO₂ NPs before solvothermal treatment. The size of the CeO₂ NPs was 4.8 nm and the shape was hexagonal. After 10 hours of solvothermal treatment as shown in Figure 2.11(b), the NPs were seen to be increasing in size at an average of 7.1 nm while few of the NPs changed shape to spheroidal. The size of the CeO₂ NPs became bigger in the range of 7.8 and 10.0 nm when the solvothermal treatment time was 18 hours while the shape changed to spherical as shown in Figure 2.11(b).

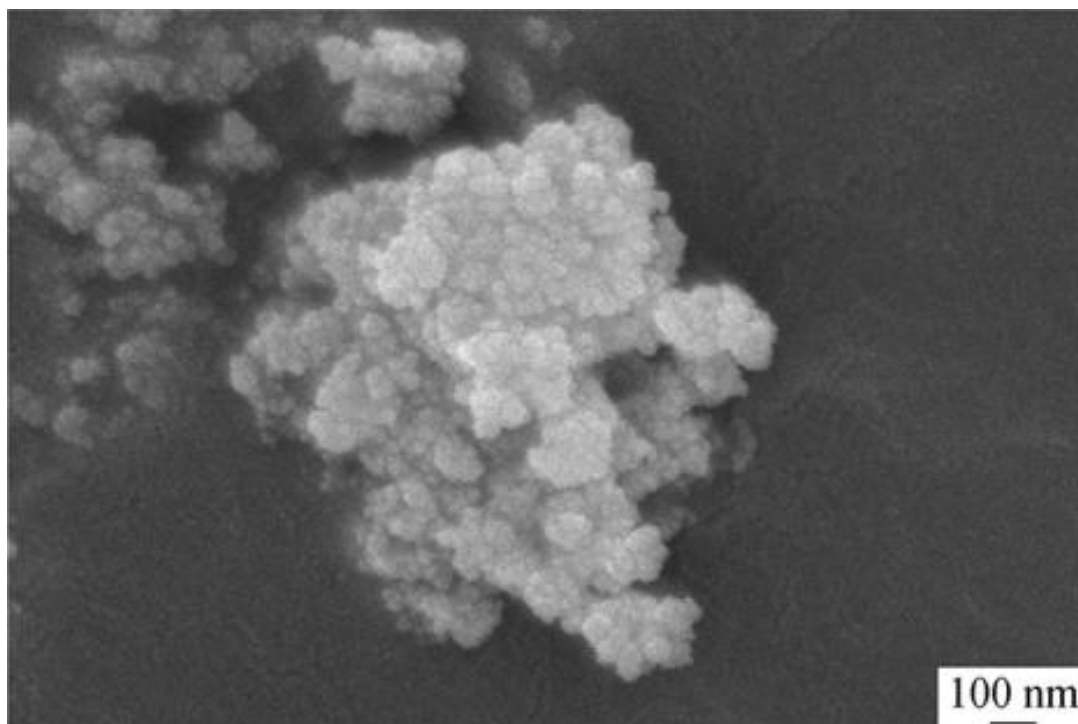


Figure 2.10: SEM image of CeO₂ NPs after 18 hours of solvothermal treatment (Pang et al., 2019)

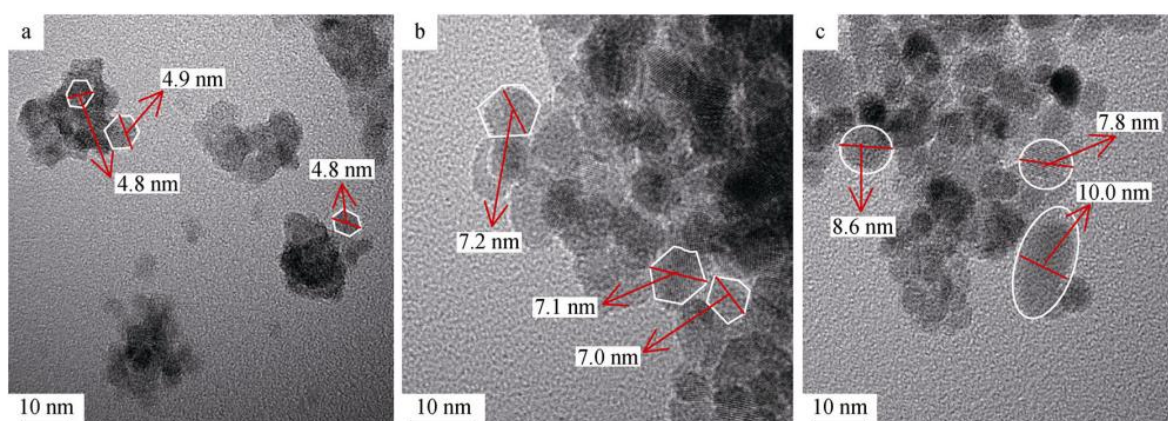


Figure 2.11: TEM images of CeO₂ NPs (a) before solvothermal treatment, (b) after 10 hours of solvothermal treatment and (c) after 18 hours of solvothermal treatment (Pang et al., 2019)

Muduli et al. (2014) studied the morphology of CeO₂ NPs using both TEM and HR-TEM. The image from TEM revealed that the size of CeO₂ NPs synthesized through solvothermal method was in the range of 50 to 70 nm and the shape was spherical. To study deeper about the crystalline domains of CeO₂ NPs, HR-TEM was used due to its ability to obtain a higher magnification which allows researchers to obtain a better image of nanoscale samples compared to TEM (Davis, 2021). HR-TEM image obtained as in Figure 2.12 allowed this study to measure the size of the crystalline domains which were 4 to 5 nm.

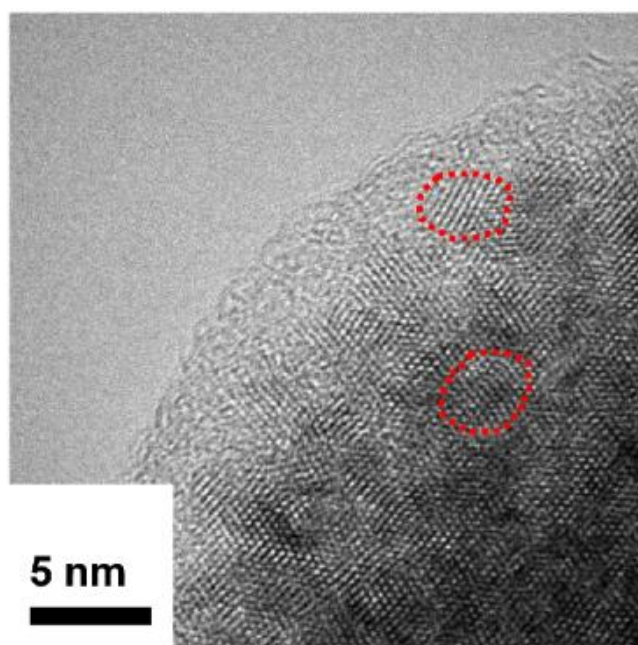


Figure 2.12: HRTEM image of CeO₂ NPs synthesized through solvothermal method by (Muduli et al., 2014)

Meanwhile, Bohinc et al. (2021) used HR-TEM to obtain a higher resolution image of the CeO₂ NPs synthesized through hydrolysis method. The CeO₂ NPs were observed to have an average size of 4 nm while the shape was spherical.

Pop et al. (2020) performed TEM and HRTEM analysis as shown in Figure 2.13. The TEM and HRTEM images showed that the size of CeO_2 NPs synthesized through precipitation method were between 5 to 20 nm and were oval-shaped. These instruments also allow this study to reveal that the synthesized CeO_2 NPs were highly agglomerated and aggregated which was suggested to occur because of the presence of cerium oxalate which was treated at high temperature during the synthesis process.

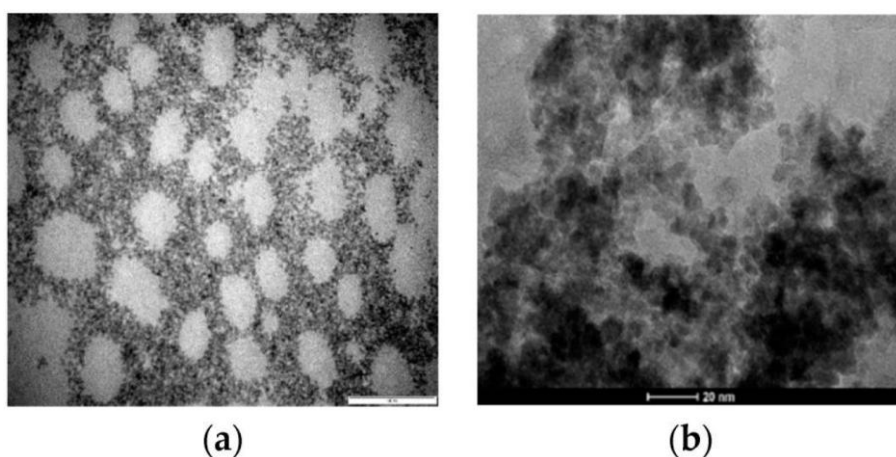


Figure 2.13: CeO_2 NPs synthesized through precipitation method under (a) TEM and (b) HRTEM (Pop et al., 2020)

2.4.2 Energy-Dispersive X-Ray (EDX)

EDX was performed to characterize CeO_2 NPs to determine the composition of atoms in the NPs. Rogers et al. (2015) used the EDX to confirm that cerium (97%) and oxygen (2%) atoms were present in the CeO_2 NPs which proved that the CeO_2 NPs were pure. Another study by Valsaraj & Divyarthana (2019) also confirmed the purity of the synthesized CeO_2 NPs through EDX analysis by determining the percentage of present atoms in the sample.

2.4.3 X-Ray Diffraction (XRD)

Another technique used to characterize CeO₂ NPs include XRD which is utilized to substantiate its chemical configuration and study the crystallographic data of the CeO₂ NPs. Bohinc et al., (2021) used the XRD to confirm that the particles analyzed were composed of pure CeO₂ NPs.

Pang et al. (2019) used XRD to obtain the crystallographic data of CeO₂ NPs. Based on the result obtained in Figure 2.14, obvious increased in the cubic fluorite of CeO₂ NPs peak was observed when the solvothermal treatment time increased. The peaks at (111), (220) and (311) became intense for the pattern of CeO₂ NPs that was treated for 2 hours compared to the pattern of the precursor used, Ce(NO₃)₃ • 6H₂O. After 6 hours, of solvothermal treatment, there were no significant changes towards the peaks. However, the peaks showed stronger intensity and new peaks of (222), (400) and (331) were produced on the diffraction pattern when the treatment time increased to 10 hours. As the solvothermal treatment time was increased to 18 hours, these peaks showed much stronger intensity. The crystallinity of CeO₂ NPs was dramatically improved due to the high 2θ angle of 69.40° and 76.68° at the peaks of (400) and (331). The diffraction pattern also did not produce any new peaks compared to the diffraction patterns obtained after reaction time of 2, 6 and 10 hours. This result showed that the solvothermal synthesis produced a high purity CeO₂ NPs. After 20 hours of solvothermal treatment, the peaks also showed no significant changes anymore which indicated that 18 hours of solvothermal reaction was the most favorable time to prepare CeO₂ NPs.

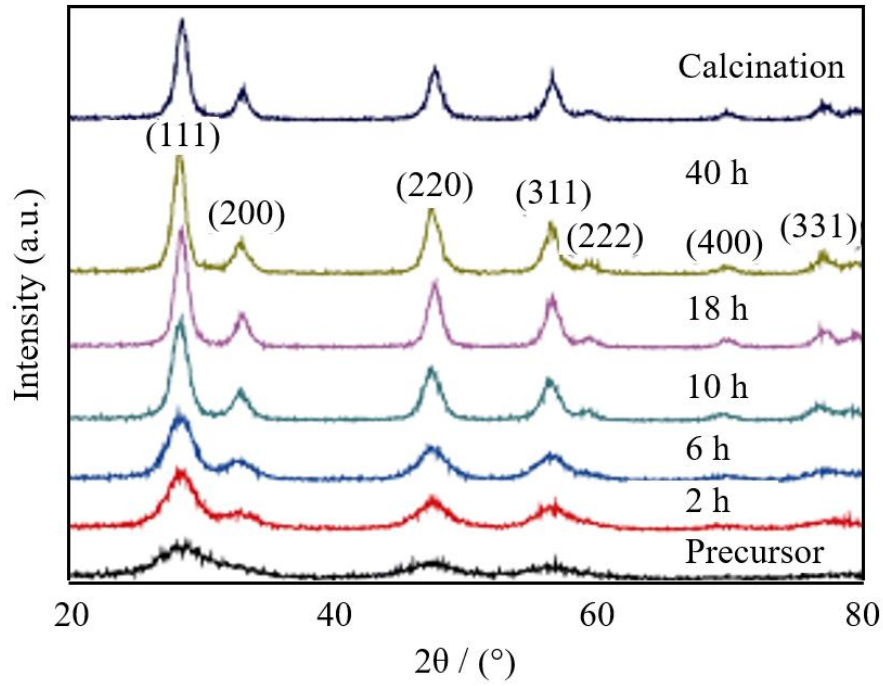


Figure 2.14: XRD patterns of CeO₂ NPs synthesized through solvothermal method in different duration of time and after calcination (Pang et al., 2019)

Muduli et al. (2014) also characterized CeO₂ NPs using XRD by studying the crystalline domains of the CeO₂ NPs. The crystalline domain size was determined as 4.8 nm which was calculated using the Debye-Scherrer's equation as shown below:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad \text{Equation 2.3}$$

2.4.4 Brunauer-Emmett-Teller (BET) Method

BET method was performed to study the specific surface area of CeO₂ NPs based on the N₂ adsorption-desorption isotherm data as shown in Figure 2.15. Previous studies have reported different particle size and surface areas of CeO₂ NPs relative to their synthesis

method and solvents used. Some of the reported surface areas are summarized in Table 2.3 below.

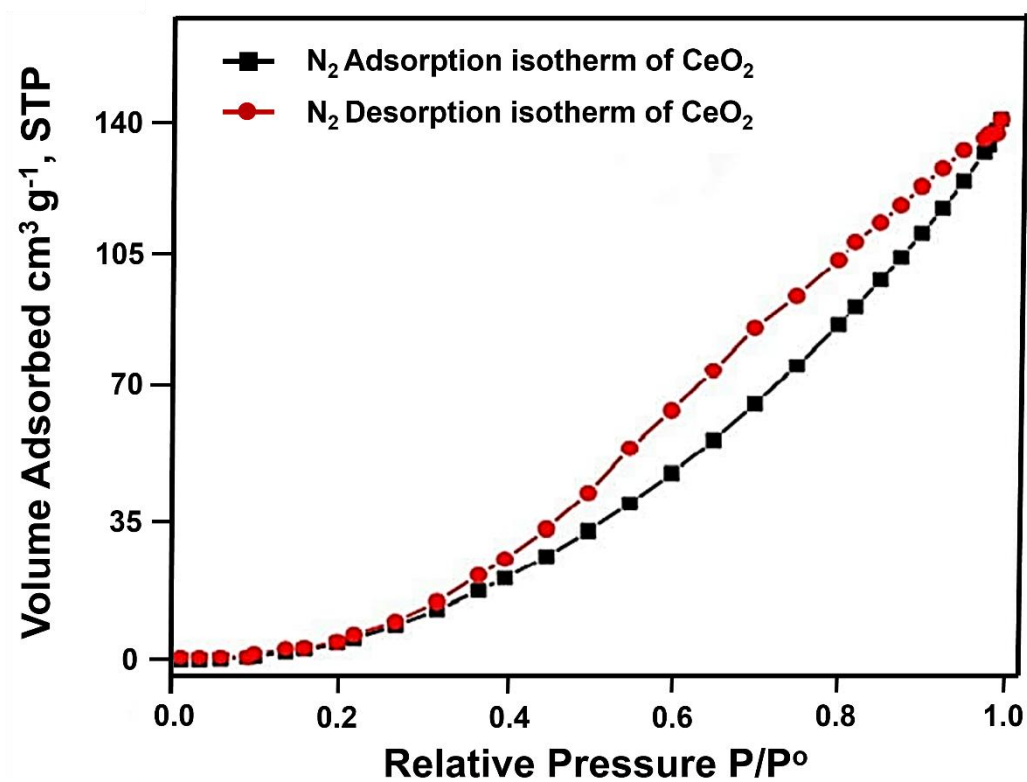


Figure 2.15: N₂ adsorption-desorption isotherms of CeO₂ NPs (Khan et al., 2020)

Table 2.3: Particle size and surface area of CeO₂ NPs in previous studies

Synthesis Method	Particle Size (nm)	Surface Area (m ² /g)	Reference
Precipitation	10.0	236.8	(Saikia et al., 2017)
Solution Combustion	8.0	88.0	(Kang et al., 2018)
Hydrothermal	5.9	226.0	(Kurajica et al., 2016)
Hydrolysis	2.6	119.0	(Yurova et al., 2020)
Precipitation and Hydrothermal	106.5	165.0	(Khan et al., 2020)

2.4.5 Fourier Transform Infrared Spectroscopy

FTIR spectroscopy is used to identify the presence of different functional groups and chemical bonds in CeO₂ NPs. According to a study by Prabakaran et al. (2016), weak absorptions were found at 2380 cm⁻¹ and 1430 cm⁻¹ which were due to C-H bending vibration. The absorption at 1634 cm⁻¹ was due to the bending vibration of H-O-H while the absorption at 450-550 cm⁻¹ was due to the O-Ce-O stretching.

Farahmandjou and Zarinkamar (2016) also characterized CeO₂ NPs using FTIR in the range of 400-4000 cm⁻¹. According to result obtained as shown in Figure 2.16, the absorption band at 3465 cm⁻¹ was due to the stretching of O-H while the strongest peak at 1464 cm⁻¹ was due to the bending vibration of C-H. The stretching of Ce-O as shown from the absorption band at 500 cm⁻¹ was the indication of the presence of CeO₂ NPs in the studied sample.

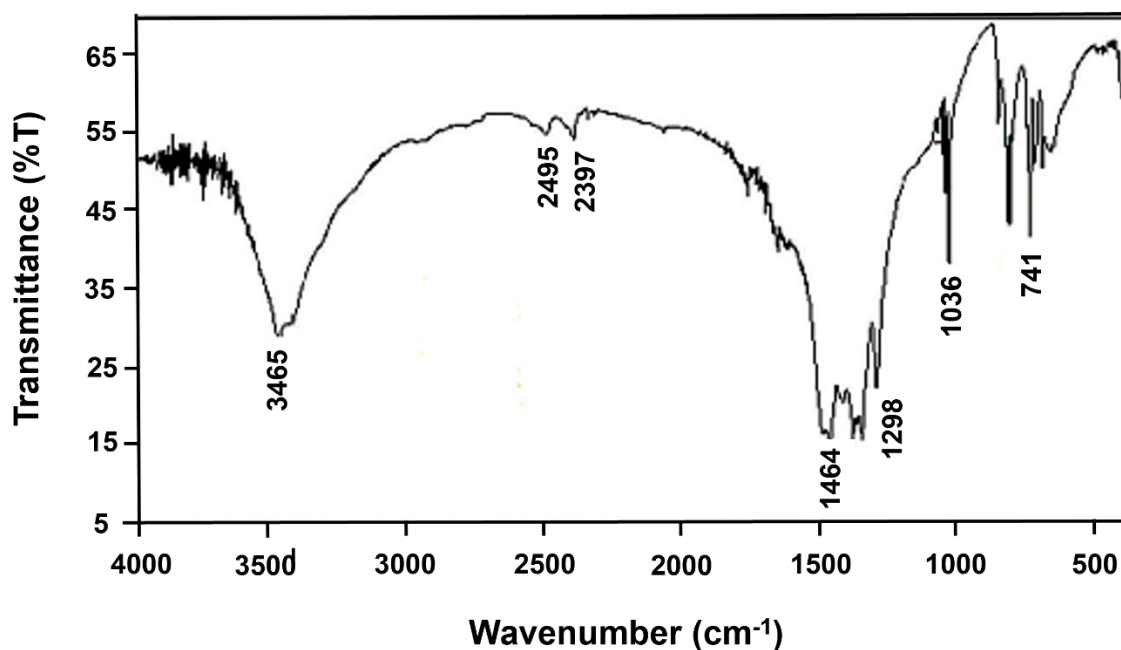


Figure 2.16: FTIR spectrum of CeO₂ NPs (Farahmandjou & Zarinkamar, 2016)

2.4.6 Ultraviolet Visible – Spectroscopy (UV-Vis)

UV-Vis spectroscopy is another technique applied to characterize CeO₂ NPs in previous studies to study the optical absorption of the NPs. Valsaraj and Divyarthana (2019) used UV-Vis to obtain the absorption bands as shown in Figure 2.17. Broad absorption bands were found at 250 nm and 340 nm indicating the redox reaction between Ce³⁺ and Ce⁴⁺ which proved the presence of CeO₂ NPs in the synthesized compound.

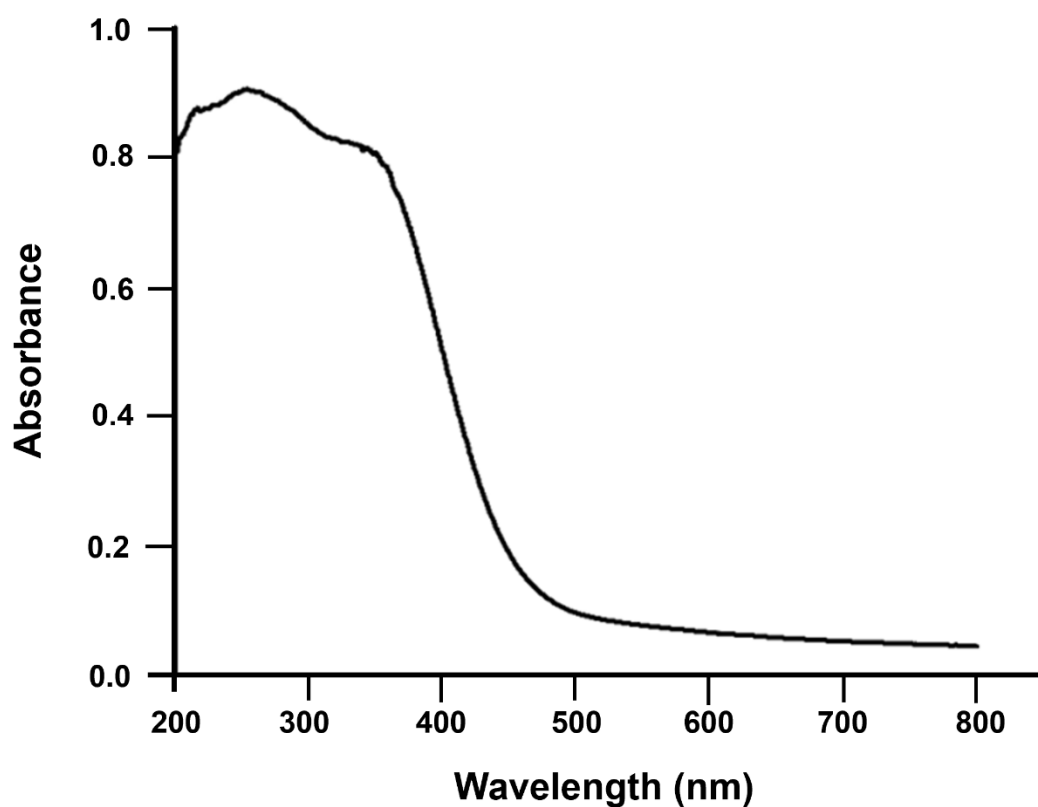


Figure 2.17: Optical absorption spectrum of CeO₂ (Valsaraj & Divyarthana, 2019)

2.5 Influence of Environmental Conditions to the Behavior of Cerium Oxide Nanoparticles

The morphology of CeO₂ NPs affects the behavior of this NP. However, environmental factors like the NOM, pH and ionic strength also lead to behavioral changes of CeO₂ NPs (Keller et al., 2010).

2.5.1 Humic Acid

HA is one of the NOM formed from the decomposition of plants and animals in the environment and exists in the surface water at the concentration between 0.1 to 20 mg/L

(Basumallick & Santra, 2017). HA are composed of many compounds including lignins and tannins (Ampong et al., 2022). Despite being naturally present in the environment, this NOM may cause changes in the behavior of heavy metals including nanomaterials which eventually become a threat to the aquatic environment (Zhu et al., 2023).

2.5.1.1 Effects of Humic Acid on Cerium Oxide Nanoparticles

HA is a major component of NOM that are mostly consist of carboxylic (-COOH) and phenolic (-OH) functional groups. These functional groups cause the adsorption of HA to make significant changes towards the surface characteristics of NPs, thus, affecting their stability and transport patterns in the aquatic environment (Zhang et al., 2020).

Lv et al. (2014) studied the effects of humic acid on the retention and transport of CeO₂ NPs in a saturated porous media. Without the use of HA, CeO₂ NPs was found to be instable compared to when HA was used. The concentration of CeO₂ NPs was found to remain at least 83% of its initial concentration after 2 hours when HA was present. This result indicated that the presence of HA resulted into a greater stability of CeO₂ NPs. Due to this stability, the CeO₂ NPs coated with HA was highly mobile in saturated sand columns while only little mobility was observed when no HA was used. From the results obtained, it was proven that HA promoted the retention and transport of CeO₂ NPs in saturated porous media because of its ability to increase the electrostatic and steric repulsions between these particles.

HA are composed of many different functional groups. However, the most abundant functional group was also found to be different at different pK_a as shown in Figure 2.18. The presence of these functional groups allows HA to bind with the positively-charged ions (Jayalath et al., 2018). Van Hoecke et al. (2011) studied the effects of pH in the range of pH 6 to 9 and the presence of NOM on the CeO_2 NPs. Increasing pH retarded the adsorption process between HA and CeO_2 NPs. At $pH > 7$, the charged molecules of NOM undergo adsorption on the surface of the NPs which prevented the excess uncharged NOM molecules from binding to the surface of the NPs. However, higher adsorption was observed at $pH < 7$ due to the negatively-charged NOM having a strong electrostatic attraction with the positively-charged surface of CeO_2 NPs.

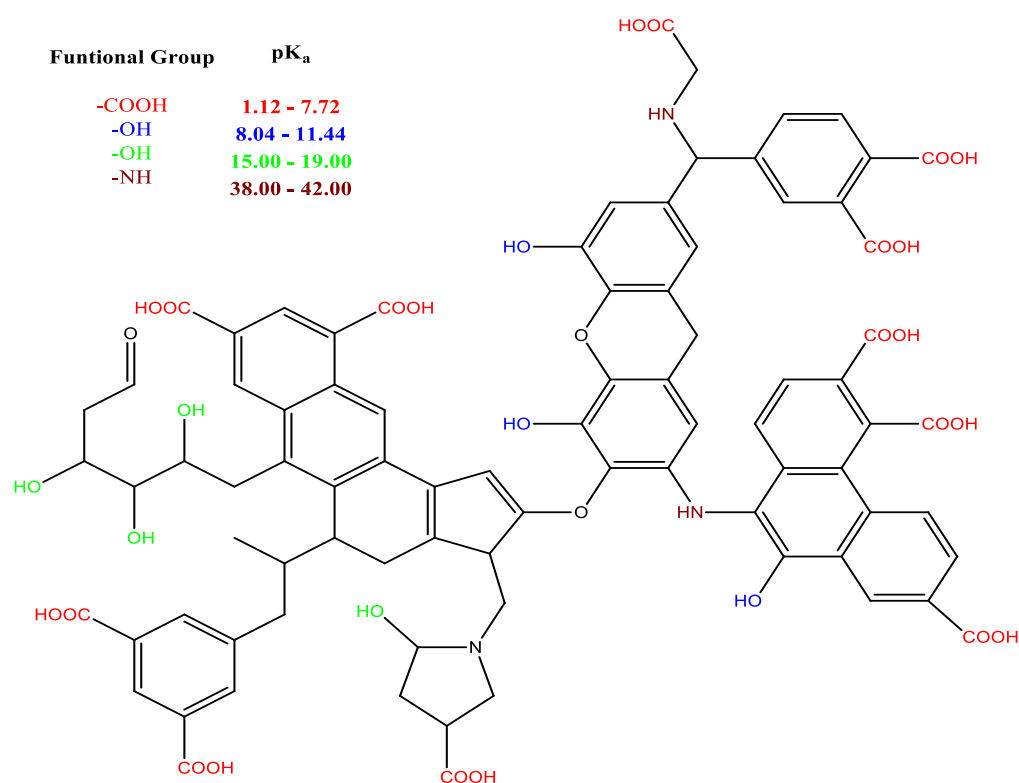


Figure 2.18: Most abundant functional groups presence in HA at different pK_a values (Jayalath et al., 2018)

Another study by Mahato and Gupta (2021) also obtained a similar result for the adsorption of HA on the surface of CeO₂ NPs which increased at pH < 7. The zeta, ζ potential and point of zero charge (PZC) of the adsorption of HA on CeO₂ NPs were studied as shown in Figure 2.19 to determine surface charge of CeO₂ NPs at certain pH. The PZC of the CeO₂ NPs studied was determined to be at pH 7 which proved that the surface charge of CeO₂ NPs at pH > 7 is negative and positive at pH < 7. This is due to the transformation of the ζ potential value from positive to negative at that pH. The positively-charged surface of CeO₂ NPs at pH < 7 allowed the negatively-charged HA particles to bind on its surface which caused a higher adsorption. On the other hand, the negatively-charged surface of the NPs at pH > 7 retarded the adsorption process because of the electrostatic repulsion of the surface of NPs and the HA molecules.

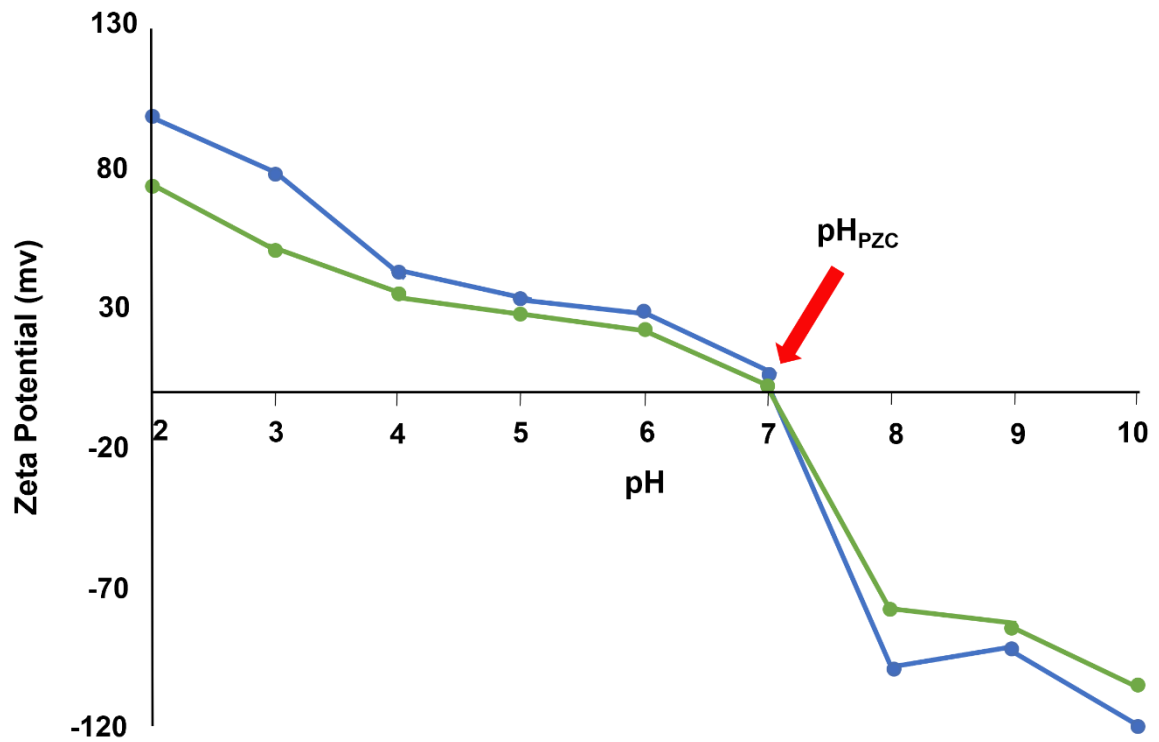


Figure 2.19: Zeta potential and PZC of CeO₂ NPs synthesized by efficient combustion (green line) and hydroxide mediated (blue line) methods (Mahato & Gupta, 2021)

2.5.1.2 Adsorption Kinetics

The adsorption kinetics of HA on the surface of NPs has been studied using adsorption kinetic models such as the pseudo-first order, pseudo-second order and intraparticle diffusion model (Gupta et al., 2020). The correlation coefficient value (R^2) will be compared between these models to determine the better fitting of the adsorption data.

The linear equation of the pseudo-first order is as shown below:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303} \right) t \quad \text{Equation 2.4}$$

Where q_e and q_t are the amount of HA adsorbed on CeO₂ NPs (mg/g) at equilibrium time and at time, t , respectively while k_1 (min⁻¹) is the pseudo-first order rate constant (Nurhasanah et al., 2020). Experimental data with a better fitting using the pseudo-first order kinetic model is assumed to undergo physisorption (Liu et al., 2019). In physisorption, the HA molecules adsorb on the surface of NPs by Van der Waals forces (Agboola & Benson, 2021).

On the other hand, the linear equation of pseudo-second order is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{Equation 2.5}$$

Where q_e and q_t are the same as in the pseudo-first order equation while k_2 (g mg⁻¹ min⁻¹) is the pseudo-second order rate constant (Liu et al., 2019). Experiment data that follows the pseudo-second order is assumed to undergo chemisorption which involves chemical reactions that form bonds between the HA molecules and NPs (Agboola & Benson, 2021).

Meanwhile, the intraparticle diffusion linear equation is as expressed below:

$$Q_t = k_d t^{\frac{1}{2}} + C \quad \text{Equation 2.6}$$

Where Q_t is the amount of HA adsorbed on CeO₂ NPs (mg/g) at equilibrium time, k_d is the rate constant for the kinetic model while C is the mass transfer resistant. The

intraparticle diffusion model assumes that the adsorption process is through a diffusion of fine particles on the surface of the adsorbent (Gupta et al., 2020).

2.5.1.3 Adsorption Isotherms

The adsorption isotherm of HA molecules on the surface of CeO₂ NPs has also been studied using the Langmuir isotherm, Freundlich isotherm and Temkin isotherm.

The Langmuir isotherm linear equation is expressed as shown below:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_l} \frac{1}{C_e} \quad \text{Equation 2.7}$$

Where q_e is the amount of humic adsorbed (mg/g), q_m is the maximum adsorption capacity, and C_e is the equilibrium concentration while K_l is the Langmuir isotherm constant. A correlation factor (R^2) that is close to unity for this isotherm suggests that the adsorption process is monolayer on the surface of the adsorbent (Akrawi et al., 2021).

On the other hand, the linear equation of Freundlich isotherm is as follows:

$$\log(q_e) = \log(K_f) + \frac{1}{n} \log(C_e) \quad \text{Equation 2.8}$$

Where K_f is the constant for the Freundlich isotherm and $1/n$ is the measure of intensity of the Freundlich isotherm. An experimental data that fit with the Freundlich

isotherm suggests the surface of the adsorbent is heterogenous which allows more adsorption compared to the monolayer adsorption (El-Sayed et al., 2013).

The third isotherm is the Temkin isotherm with the linear equation expressed as follows:

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \quad \text{Equation 2.9}$$

Where b_T and A_T are the Temkin constant (kJ mol^{-1}) and Temkin isotherm constant (L mg^{-1}) respectively. R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature (Inyinbor et al., 2016). R^2 that is closed to unity for this isotherm suggests that the adsorption process is based on a consistent distribution of binding energy (Piccin et al., 2011).

2.5.2 Ionic Strength

The aquatic environment consists of various amount of ions that interact with materials entering the aquatic matrices. According to Gutierrez et al. (2023), the ionic strength water is different in every type of water. The ionic strength of surface water is from 1 mM to 5 mM and 1 mM to 20 mM for groundwater.

2.5.2.1 Effects of Ionic Strength on Cerium Oxide Nanoparticles

Different ionic concentrations in the aquatic environment leads to behavioral changes in NPs. In high ionic concentrations, most NPs undergo aggregation and form larger particles (Rogers et al., 2015).

Bohinc et al. (2021) studied the effects of ionic concentrations on electrophilic mobility of CeO₂ NPs. In this study, two different ionic strength values were used which were 0.002, 0.011 mol dm⁻³ containing Na⁺ ions and 0.011 mol dm⁻³ containing Cs⁺ ions. The results of mobility measurement showed that hysteresis occurred for the basic to acidic titration region due to the decreased in pH value. The hysteresis occurred was also greater in the neutral region than in basic and acid pH regions because of a faster equilibration in those pH regions.

According to Plakhova et al. (2016), the dissolution of CeO₂ NPs under different ionic strength are separated into 2 regions based on pH. The first region was from pH 2 to pH 4.5 while the second region was at pH 5 to 7. In the first region, the dissolution of CeO₂ NPs varies on the concentration of H⁺ ions. However, the dissolution of CeO₂ NPs in the second region is pH dependent but a more significant dissolution was observed compared to the first region. The acidic pH was separated into 2 due to the difference in redox conditions between the two pH range.

2.5.3 Effects of pH on Cerium Oxide Nanoparticles

Yan et al. (2007) reported that different pH values influenced the morphology, aggregation and dissolution of CeO₂ NPs. The morphology of CeO₂ NPs in an acidic solution, neutral solution and basic solution were compared using TEM as shown in Figure 2.20. The shape of CeO₂ NPs was spherical when the solution was acidic, rod-like when the solution was basic and a combination of both shapes when in a neutral solution. Different pH values affect the conversion of cerium ions (Ce³⁺/ Ce⁴⁺) in the solution. In this

experiment, the reduction potential of the acid solution, E_{acid} (0.152 V) was reported to be lower than the reduction potential of basic solution, E_{basic} (0.762 V) according to the Nernst equation below:

$$E_{acid} = E^0 - \frac{RT}{F} \ln \frac{a_{Ce^{4+}}}{a_{Ce^{3+}} \cdot a_{H^+}} \quad \text{Equation 2.10}$$

$$E_{basic} = E^0 - \frac{RT}{F} \ln \frac{a_{Ce^{4+}} \cdot a_{OH^-}}{a_{Ce^{3+}}} \quad \text{Equation 2.11}$$

Where E^0 is the standard potential and R is the universal gas constant. The higher E in the basic solution indicated that the oxidation of Ce^{3+}/Ce^{4+} occurred faster than in acid and neutral solution. This caused the spherical shape of cerium hydroxide, $Ce(OH)_3$ in basic solution to form $Ce(OH)_4 [CeO_2 \cdot 2H_2O]$ complex in a shorter time than in the acidic solution. As a consequence, the spherical shape extended and become rod-like due to a faster rate of reaction.

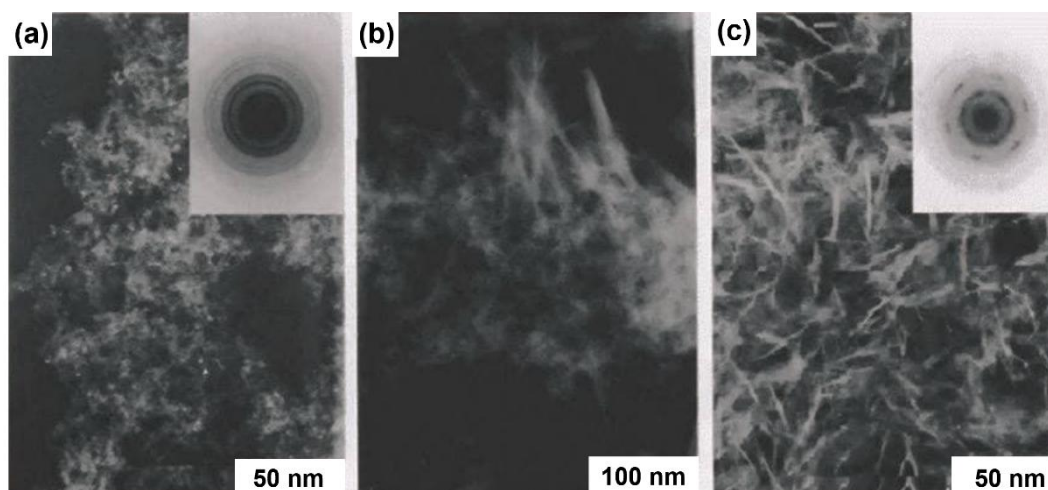


Figure 2.20: Morphology of CeO₂ NPs at different pH under TEM where (a) acidic solution, (b) neutral solution and (c) basic solution (Yan et al., 2007)

Dahle et al. (2014) studied the effects of pH on the dissolution of small and large CeO₂ NPs. At pH 1.65, highest dissolution was reported in both size of CeO₂ NPs. However, the dissolution kinetics at pH 4.45 were about just half of the dissolution at pH 1.65. Thus, this study concluded that the dissolution of CeO₂ NPs was at their highest in a strongly acidic solution due to the increased in hydrogen ions activity that greatly enhanced the dissolution of CeO₂ NPs while there was no significant dissolution at pH above neutral.

CHAPTER 3

METHODOLOGY

3.1 Materials

In this study, the hydrothermal synthesis of CeO₂ NPs was carried out by using cerium nitrate hexahydrate, Ce(NO₃)₃ • 6 H₂O (Sigma Aldrich, France) and 0.3 M sodium hydroxide, NaOH (R & M Chemicals) as the precursors while deionized (DI) water was used as the solvent. In the dissolution measurement of CeO₂ NPs, 1 M NaOH and 1 M nitric acid, HNO₃ (Fisher Chemicals) were used to adjust the pH of the solutions and it was measured using Martini Instruments (Model Mi 150) pH meter. A 1 M stock solution of sodium chloride, NaCl was used to adjust the ionic strength. HA (Sigma-Aldrich, Switzerland) was also used to study the adsorption of HA on CeO₂ NPs and the dissolution of CeO₂ NPs while 95 % ethanol (HmbG Chemicals) was used to disperse the CeO₂ NPs powder.

3.2 Synthesis of Cerium Oxide Nanoparticles

The synthesis of CeO₂ NPs was carried out using the hydrothermal method according to the procedure by Wang et al. (2008) but with some modifications. These modifications include a lower temperature, lower pH and shorter hydrothermal treatment time used in this study compared to the previous study of 180 °C, pH 13-14 and 24 hours respectively. To prepare a Ce(NO₃)₃ solution, 1.0 g of Ce(NO₃)₃ • 6 H₂O was dissolved into 30 mL of DI water under constant stirring at a temperature of 70 ± 2 °C using the electric hotplate magnetic stirrer (FAVORIT) until purple colloid was formed as shown in Figure 3.1. This solution was then slowly added into 60 mL of 0.3 M NaOH solution with vigorous stirring

at the same temperature and maintained at pH 10. The mixture was then left to cool down at room temperature for 4 hours. It was then centrifuged at 3500 rpm for 15 minutes using a centrifuge (Fleta 5, Hanil). The residue was rinsed using ethanol twice and DI water once to remove the impurities. The product formed was collected and dried in the oven at 80 °C overnight. It was then ground to form powder. Figure 3.2 shows the schematic diagram for the hydrothermal synthesis of CeO₂ NPs.



Figure 3.1: Purple colloid formed after hydrothermal treatment at 70 ± 2 °C

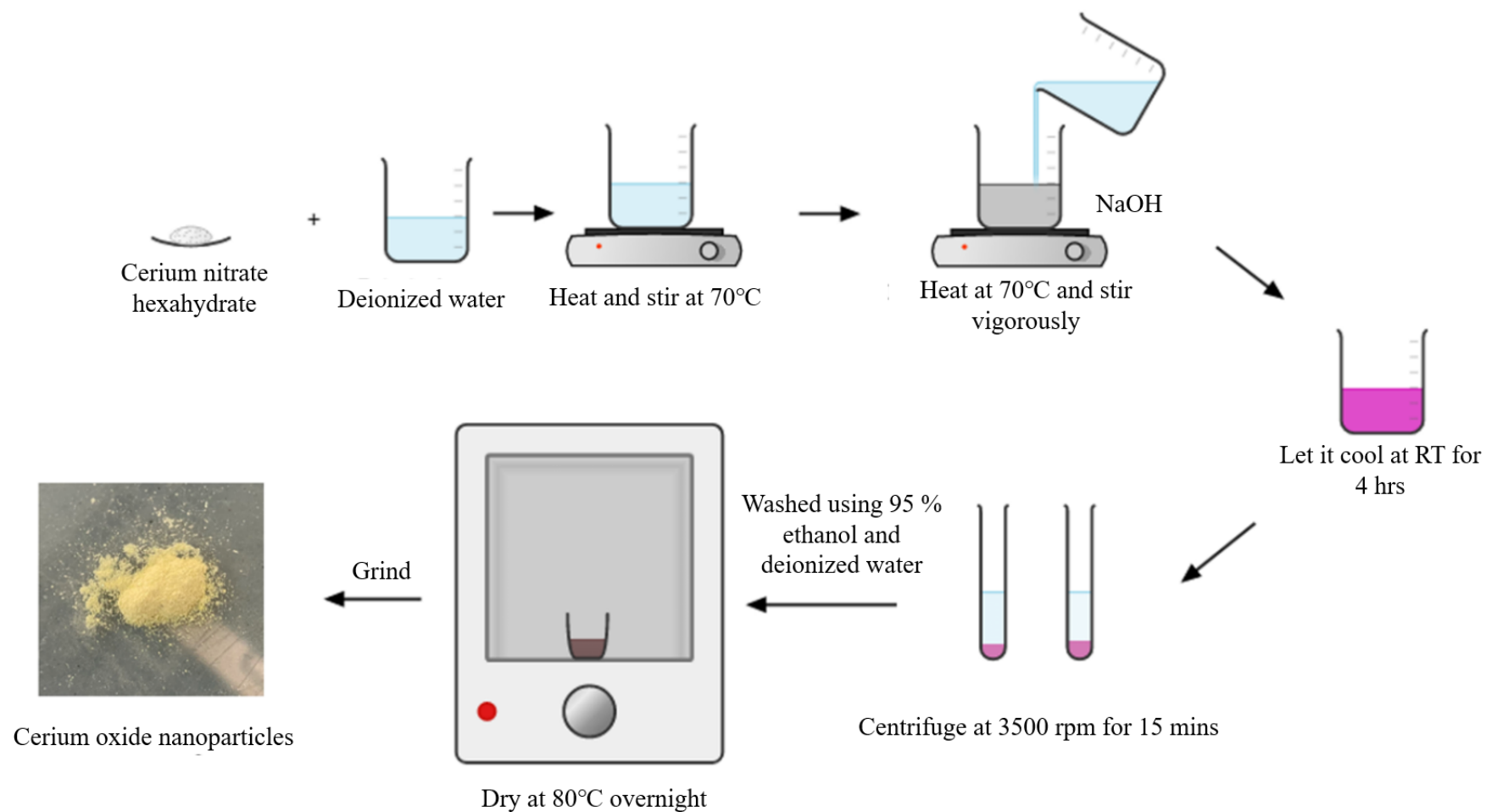


Figure 3.2: Schematic diagram of modified hydrothermal synthesis of CeO₂ NPs

3.3 Characterization of Cerium Oxide Nanoparticles

3.3.1 Field Emission Scanning Electron Microscopy (FESEM) Analysis

The shape and agglomeration of the synthesized CeO₂ NPs were determined using field emission scanning electron microscope (JEOL JSM-6390LA, Japan). Prior to analysis, 5 mg of the CeO₂ NPs powder was suspended in 10 mL of 95 % ethanol. This solution was then sonicated for 30 minutes using ultrasonic cleaner (Elma, Germany) and 10 µL of it was loaded onto an aluminium plate. It was left to dry in the desiccator for 48 hours before the analysis.

3.3.2 Transmission Electron Microscope (TEM) Analysis

The size and shape of the CeO₂ NPs were determined using transmission electron microscope (JEOL JEM-1230, Japan). 3 mg of the CeO₂ NPs powder was suspended in 10 mL of 95% absolute ethanol. This solution was then sonicated for 30 minutes using ultrasonic cleaner (Elma, Germany) and 5 µL of it was transferred onto Foamvar coated copper grid (FF300-Cu). Under room temperature, it was left to dry in the desiccator for 48 hours and then placed into the TEM.

3.3.3 Energy-Dispersive X-Ray Spectroscopy (EDX) Analysis

The purity and composition of atoms in the CeO₂ NPs was determined by using energy-dispersive X-ray spectroscopy (JEOL JSM-6390LA, Japan). Before the analysis, 5 mg of the CeO₂ NPs powder was suspended in 10 mL of 95 % ethanol. This solution was

then sonicated for 30 minutes using ultrasonic cleaner (Elma, Germany) and 10 μL of the sample was loaded onto an aluminium plate. It was left to dry in the desiccator for 48 hours before the EDX analysis.

3.3.4 UV-Visible Spectroscopy (UV-Vis) Analysis

UV-Vis (Perkin Elmer Lambda 25) was used to study the optical absorption of the CeO_2 NPs. Prior to analysis, 5 mg of the CeO_2 NPs powder was dispersed in 10 mL of 95% ethanol. The solution was then sonicated using ultrasonic cleaner (Elma, Germany) and placed into a cuvette. The cuvette was cleaned and wiped using Kim wipes before placing the sample into the spectroscopy to measure its absorbance.

3.3.5 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The surface functional groups present in the synthesized CeO_2 NPs was identified using Fourier transform infrared spectroscopy (Thermo Scientific Nicolet iS10, US). Before the analysis, 95 mg of potassium bromide, KBr was dried at 80 $^{\circ}\text{C}$ in the oven overnight. The CeO_2 NPs powder was mixed with the dried KBr in a ratio of 1:19 (Shamhari et al. 2018; Yang et al., 2009). The mixture was crushed and compressed in a metal hole until thin discs were formed. The thin discs sample was then used for the FTIR analysis in the range 400 to 4000 cm^{-1} .

3.3.6 X-Ray Diffraction (XRD) Analysis

The crystallite size and structure of the NPs was determined by X-ray diffraction (Xpert Pro MPD PW3040/60) analysis. The synthesized CeO₂ NPs powder was sent to Malaysian Nuclear Agency for XRD analysis. The XRD pattern was obtained using X-ray diffractometer with Cu-K α radiation at 45 kV and 30 mA while the step size was 0.017°. The average crystallite size of the CeO₂ NPs was calculated according to Williamson-Hall fitting.

3.3.7 Brunauer-Emmett-Teller (BET) Method

The specific surface area of the CeO₂ NPs was determined using Brunauer-Emmett-Teller (Quantachrome, US). Prior to the analysis, 500 mg of the CeO₂ NPs powder was placed in the surface area analyser tube. Under flowing liquid nitrogen, the powder was degassed at 200 °C for 1 hour (Yurova et al., 2020). The specific surface area of the NPs was then calculated according to the N₂ adsorption-desorption isotherm and the multi-point linear plot obtained as shown in Appendix B.

3.4 Preparation of Humic Acid Stock Solution

The preparation of HA stock solution was performed according to the method reported by Mahato & Gupta (2021) with few modifications. 0.1 g of HA powder and 10 mL of 0.1 M NaOH were diluted to 0.1 L using DI water to prepare a 100 mg/L HA stock solution. The solution was stirred for 24 hours. The stock solution was kept in the fridge without any light source when not in used.

3.5 Preparation of Cerium Oxide Nanoparticles Stock Solution and Dispersion

The preparation of CeO₂ NPs stock solution was done according to the method by Keller et al. (2010) with few modifications. 0.25 g of CeO₂ NPs were added into 250 mL of DI water to prepare a 1000 mg/L stock solution. This solution was then sonicated for 30 minutes using ultrasonic water bath (Elma, Germany) and stored in the fridge. Before analyses, the solution was sonicated again for 15 minutes to finely disperse the CeO₂ NPs.

3.6 Adsorption of Humic Acid on Cerium Oxide Nanoparticles

3.6.1 Characterization of Humic Acid

The characterization of HA was done to determine its physical and chemical properties. In this study, FESEM, UV-Vis and FTIR were used to characterize HA.

The physical structure of HA was studied using FESEM (JEOL JSM-6390LA, Japan). Prior to analysis, 5 mg of HA powder was suspended in 10 mL of 95% ethanol. This solution was sonicated for 30 minutes using ultrasonic cleaner (Elma, Germany) and 10 μ L of the solution was then loaded onto an aluminium plate. It was left to dry for 48 hours in the desiccator before analysis.

UV-Vis spectroscopy (Agilent) was used to determine the absorbance of HA used. Before analysis, 5 mg of the HA powder was dispersed in 10 mL of 95% ethanol. The solution was then sonicated using ultrasonic cleaner (Elma, Germany) and placed into a cuvette before being inserted into the UV-Vis spectroscopy for analysis.

The presence of functional groups in the HA was determined using FTIR spectroscopy (Thermo Scientific Nicolet iS10, US). Prior to analysis, HA powder was mixed

with KBr in the ratio of 1:19. The mixture was crushed until it forms thin disc and then placed into FTIR for analysis in the range of 400 to 4000 cm^{-1} .

3.6.2 Standard Calibration Curve of Humic Acid

The standard calibration curve of humic acid was prepared using humic acid concentrations of 0.5 mg/L, 1.0 mg/L, 3.0 mg/L, 5.0 mg/L, 8.0 mg/L and 10.0 mg/L. The standard solutions were analysed using UV-Vis (Agilent) and standard calibration curve was then plotted based on the absorbance as shown in Appendix C.

3.6.3 Adsorption Study

The adsorption study of HA on CeO_2 NPs was performed according to the method by Gupta et al. (2020). These solutions were adjusted to pH 5, pH 6, pH 7 and pH 9 using 1 M HNO_3 solution and 1 M NaOH solution. The solutions were then added with 5 mg of CeO_2 NPs powder and shaken for 1 hour using wrist shaker (Fisherbrand). The samples prepared were filtered using 0.22 μm syringe filter (HmbG) and collected for UV-Vis (Agilent) analysis at the wavelength of 254 nm for the determination of HA concentrations adsorbed onto the CeO_2 NPs (Asgari et al., 2012). The experiment was conducted at room temperature and in duplicates.

3.6.4 Characterization of HA- CeO_2 NPs After Adsorption

HA- CeO_2 NPs complex was also characterized using FESEM (JEOL JSM-6390LA, Japan) to determine their morphology after adsorption process. Before FESEM imaging, the samples prepared at pH 5, pH 6, pH 7 and pH 9 were collected and sonicated using ultrasonic

cleaner (Elma, Germany) for a better dispersion. About 10 μL of the samples were then loaded onto the aluminium plates and then left to dry in the desiccator for 48 hours prior to analysis.

3.7 Dissolution Measurement of Cerium Oxide Nanoparticles

From the 1000 mg/L CeO_2 stock solution, 100 mg/L CeO_2 solutions were prepared and used for the effects of pH, HA and ionic strength on the dissolution of CeO_2 NPs.

In this study, 5 different pH values were used to study the effects of pH on the dissolution of CeO_2 NPs. These pH values were pH 3, pH 5, pH 6, pH 7 and pH 9, where 0.1 M NaOH solution and 0.1 M HNO_3 solution were used to adjust the pH of the prepared 100 mg/L CeO_2 NPs solutions. The solutions were sonicated again for 10 minutes prior to use.

To study the behavior of CeO_2 NPs under different pH and ionic concentrations, 100 mg/L CeO_2 NPs solutions were adjusted to pH 3, pH 5, pH 6, pH 7 and pH 9. A stock solution of 100 mM NaCl was prepared to adjust the ionic strength of the 100 mg/L CeO_2 solutions to 0 mM NaCl, 3 mM NaCl and 5 mM NaCl. After 30 minutes, first aliquot of 0.5 ml was collected from the solutions and then filtered using 0.22 μm syringe filter. The subsequent aliquots were collected and filtered every 2 hours for 3 days (9.00 am to 3.00 pm). The samples collected were diluted to 10 mL and amount of dissolved Ce^{4+} was measured using ICP-OES (Perkin Elmer – Optima 8000, USA) at 413.764 nm wavelength, back pressure of 223.0 kPa and flow rate of 0.55 L/min.

The pH was also kept at pH 3, pH 5, pH 6, pH 7 and pH 9 to study the effects of HA on the dissolution of CeO₂ NPs. HA solutions with concentration of 0 mg/L, 5 mg/L and 10 mg/L were prepared from the 100 mg/L HA stock solution. The solutions were stirred for 24 hours using electric hotplate magnetic stirrer (FAVORIT). About 5 mg of CeO₂ NPs powder was then added into the 0 mg/L, 5 mg/L and 10 mg/L HA solutions before stirring for 30 minutes. The HA solutions were covered using aluminium foil to minimize sunlight exposure. The same number of aliquots were collected, filtered and diluted for ICP-OES analysis.

The quantification of dissolved Ce⁴⁺ was performed to measure the dissolution of CeO₂ NPs under the aqueous environmental parameters. The mean and standard deviation for 3 replicates of different dissolution measurements were reported. To calculate the limit of detection (LOD) and limit of quantitation (LOQ) for the analysis, 1 blank standard and 5 standard solutions of different concentrations were prepared which include 0.2 ppm, 0.5 ppm, 1.0 ppm, 3.0 ppm and 5.0 ppm. A calibration curve was plotted based on the standard solutions as shown in Appendix C.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of Cerium Oxide Nanoparticles

4.1.1 Field Emission Scanning Electron Microscope (FESEM)

The surface morphology of the synthesized CeO₂ NPs was determined using FESEM with acceleration voltage of 20.0 kV and 10.4 mm working distance. Figure 4.1 shows the FESEM image of the CeO₂ NPs synthesized through the hydrothermal method. Noticeably, the image revealed that the synthesized CeO₂ NPs have irregular shape aggregates and were highly agglomerated. Since the CeO₂ NPs itself is hydrophobic, the particles were highly agglomerated only due to the adherence of covalent and metallic bonds involved in the NPs (Gosens et al., 2010). However, these bonds were not the only factors that affect the agglomeration of the synthesized sample. A study by Ogholaja et al. (2017) revealed that particle size also affects the agglomeration of the particles. As the size of particles decrease, the particles involved have a higher tendency to agglomerate due to an increased rate of collision between the particles and increased in the surface energy between the particles, which consequently increased the surface tension of the synthesized CeO₂ NPs (Bhuiyan et al. 2015). Therefore, according to the result obtained in the FESEM imaging, CeO₂ NPs were highly agglomerated and this leads to the particles forming bigger entities.

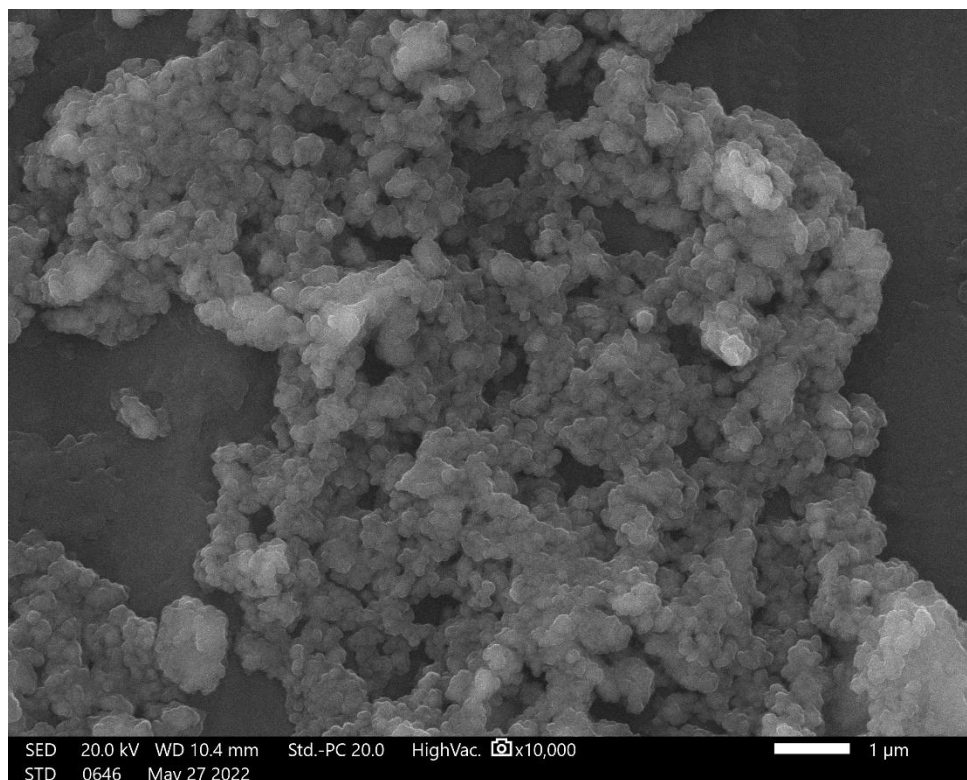


Figure 4.1: FESEM image of CeO₂ NPs synthesized through hydrothermal method

4.1.2 Transmission Electron Microscope (TEM)

TEM analysis was done to obtain a higher resolution image of the synthesized CeO₂ NPs and to determine the particle size and shape (Smith, 2015). The images revealed that the shape of the CeO₂ NPs were spherical. About 150 particles were chosen randomly and measured to calculate the average particle size of the synthesized CeO₂ NPs. Figure 4.2 and Figure 4.3 showed that the CeO₂ NPs have a narrow size distribution and the average particle size was calculated to be 3.54 ± 1.02 nm. According to result obtained, 3 and 4 nm size particles were most of the synthesized CeO₂ NPs which contributed to 32% and 34% of the 150 particles respectively. The smallest particle measured was about 2 nm (3%) while the biggest particle measured was about 7 nm (2%). Wang et al. (2008) also synthesized CeO₂ via hydrothermal method and using Ce(NO₃)₃ • 6H₂O and NaOH as precursors, but with the

reaction condition of higher temperature (180 °C) and longer reaction time (24 hours). Their method was also able to synthesize spherical shape of CeO₂ NPs with the size of about 4 to 5 nm. This study proved that spherical CeO₂ NPs with the size of below 5 nm can also be prepared through hydrothermal synthesis with lower reaction temperature (70 °C) and shorter reaction time (4 hours).

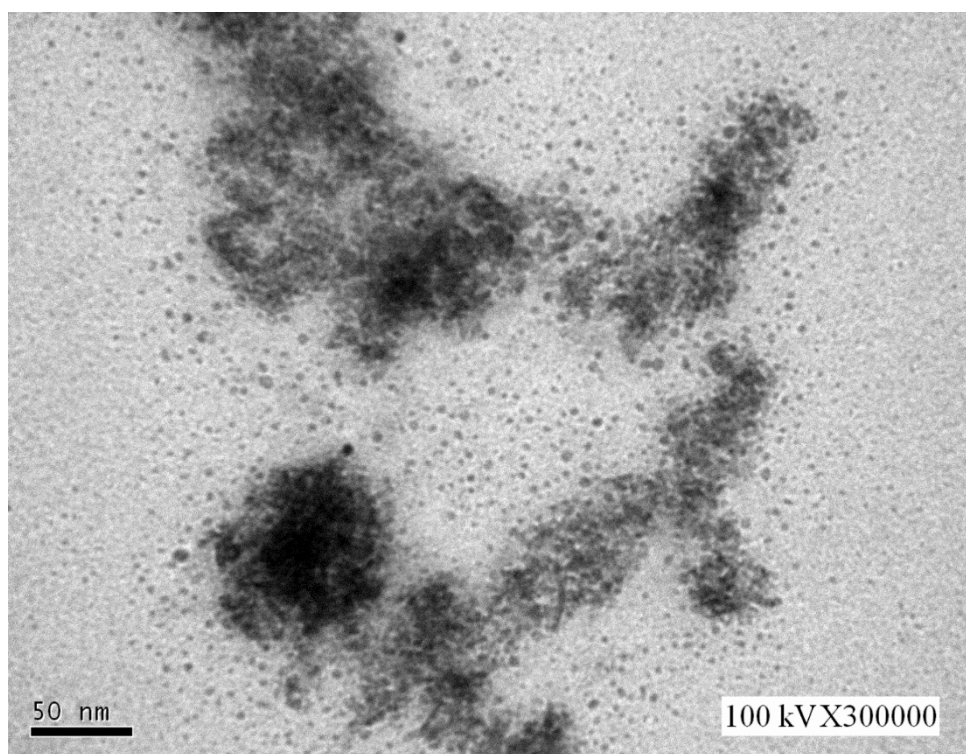


Figure 4.2: TEM image of CeO₂ NPs synthesized through hydrothermal method

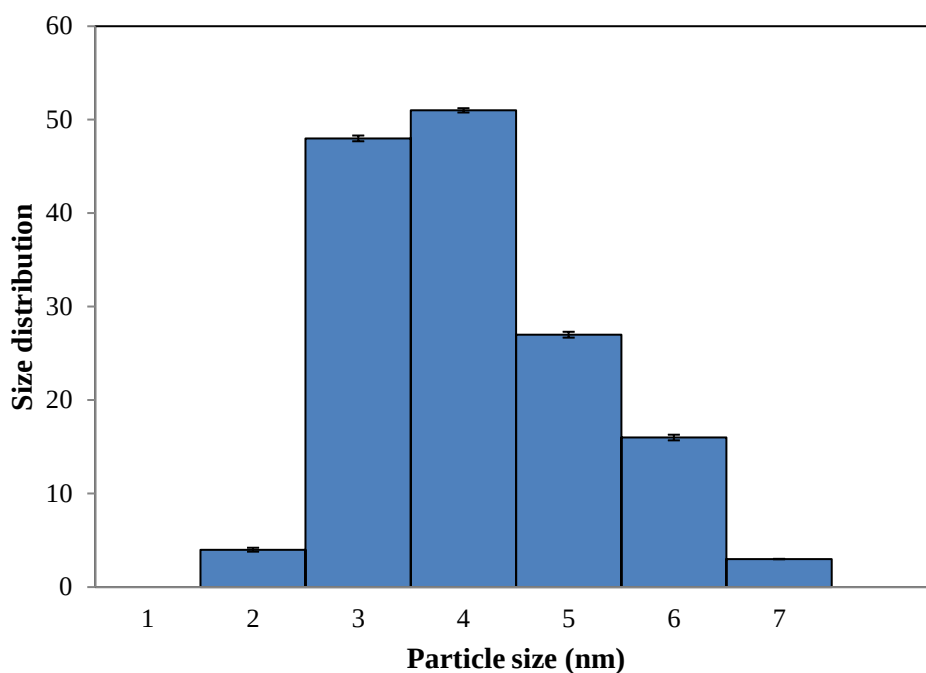


Figure 4.3: Size distribution of CeO₂ NPs synthesized through hydrothermal method

4.1.3 Energy-Dispersive X-Ray Spectroscopy (EDX)

EDX was used to determine the purity and composition of atoms in the CeO₂ NPs by generating X-rays towards the sample (Raval et al., 2018). The EDX pattern in Figure 4.4 showed that only Ce and O was present in the synthesized sample. The mass percentage of the sample in Table 4.1 were 19.64 ± 0.06 % and 80.36 ± 0.50 % for O and Ce respectively while the atomic mass percentage were 68.16 ± 0.19 % and 31.84 ± 0.20 %. The absence of impurities in the sample proved that the method used was able to synthesize CeO₂ NPs of high purity. From the EDX data, the percent yield of the hydrothermal synthesis method was calculated and determined to be ~99% which showed that the method was also capable to synthesize CeO₂ NPs in a very high yield.

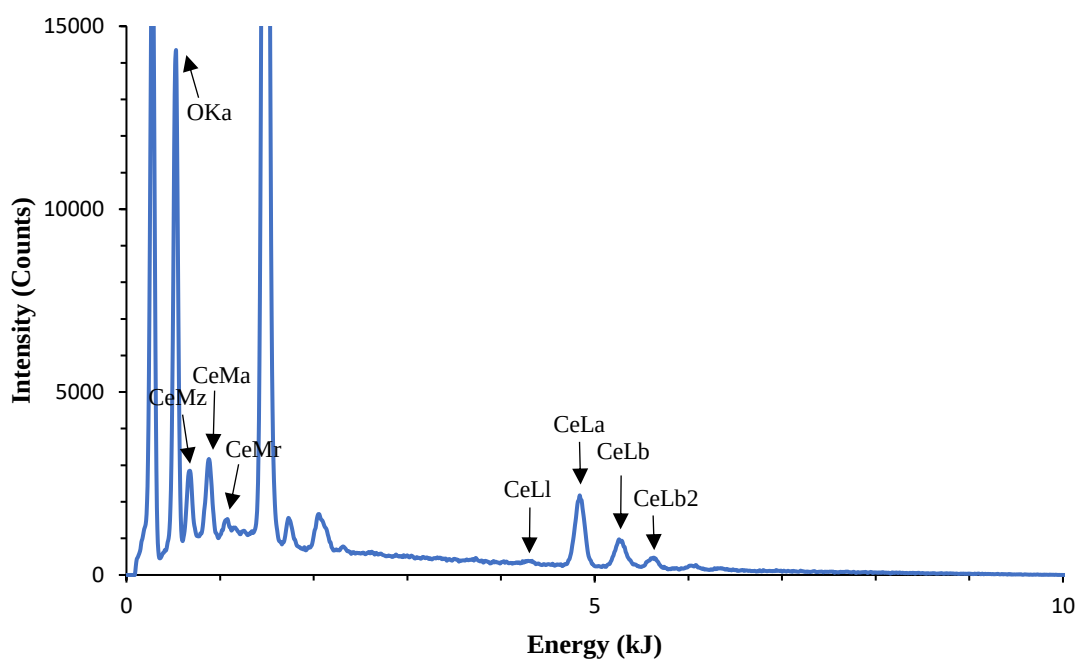


Figure 4.4: EDX pattern of CeO₂ NPs synthesized through hydrothermal method

Table 4.1: EDX results of CeO₂ NPs synthesized through hydrothermal method

Element	Line	Mass (%)	Atom (%)
O	K	19.64 ± 0.06	68.16 ± 0.19
Ce	L	80.36 ± 0.50	31.84 ± 0.20
Total		100.00	100.00
Fitting ratio: 0.7456			

4.1.4 UV-Visible Spectroscopy (UV-Vis) Analysis

UV-Vis spectroscopy was used to study the optical absorption of the CeO₂ NPs. The analysis was carried out in the wavelength range of 200 to 400 nm. Based on the result obtained in Figure 4.5, the absorption peak was observed at 305 nm. A study by Altaf et al.

(2021) also found an absorption peak at 296 nm while Chelliah et al. (2012) found the absorption peak at 325 nm which confirmed the presence of CeO₂ NPs in the synthesized sample.

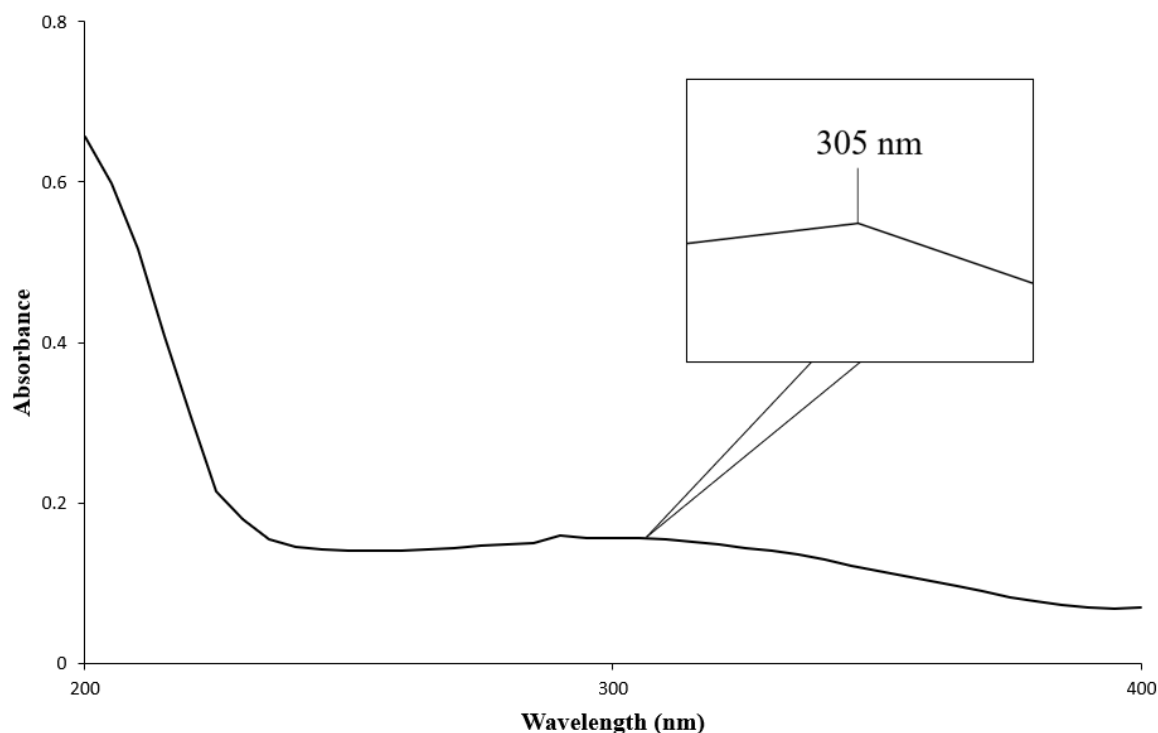


Figure 4.5: UV-Vis spectrum of CeO₂ NPs synthesized through hydrothermal method

4.1.5 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR spectrum of the synthesized CeO₂ NPs as shown in Figure 4.6 was carried out in the range of 400-4000 cm⁻¹ wavenumbers to identify the surface functional groups presence in the CeO₂ sample by transmitting infrared radiation (Khan et al., 2018). The spectrum obtained showed that there were 3 intense peaks at 3172.03 cm⁻¹, 1400.46 cm⁻¹ and 447.20 cm⁻¹. The strong broad band at 3172.03 cm⁻¹ was due to the O-H stretching vibrations from the OH⁻ groups. The sharp absorption peak at 1400.46 cm⁻¹ was due to C-H bending

vibration. The intense peak at 447.20 cm^{-1} referred to the Ce-O stretching vibration. This result showed correlation with the study by Eka Putri et al. (2021) who found the peak of Ce-O stretching at 453.00 cm^{-1} which confirmed the presence of CeO_2 NPs in the synthesized sample. Medium absorption bands at 1522.13 cm^{-1} and 1628.99 cm^{-1} referred to the O-C-O stretching vibration and H-O-H bending vibrations respectively.

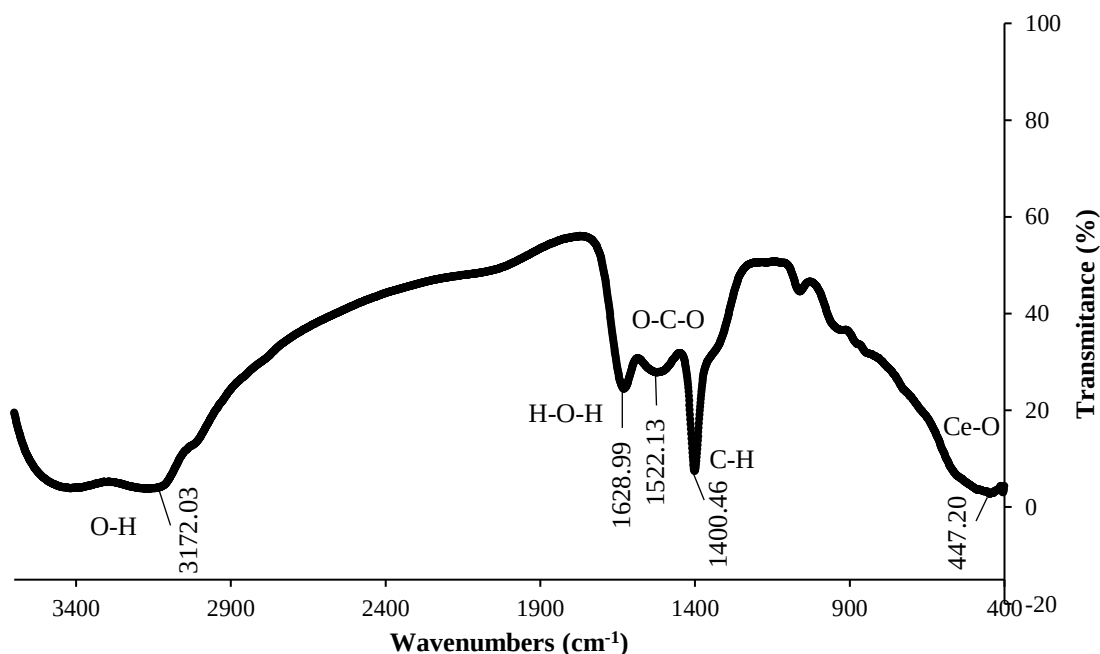


Figure 4.6: FTIR spectrum of CeO_2 NPs synthesized through hydrothermal method

4.1.6 X-Ray Diffraction (XRD) Analysis

XRD was used to study the crystallographic data of the CeO_2 NPs. The XRD diffractogram as in Figure 4.7 was obtained using X-ray diffractometer with Cu-K α radiation at 45 kV and 30 mA while the step size was 0.017° . The intense peaks obtained as shown in Table 4.2 at 2θ of 28.48° , 33.00° , 47.38° , 56.23° , 59.13° , 69.27° , 76.54° and 79.15° which correspond to (1 1 1), (2 0 0), (2 2 0), (2 2 2), (3 1 1), and (3 3 1) clearly showed that the

sample was of high purity with cubic fluorite crystalline structure (JCPDS No. 41-0013). This finding was correlated to a previous literature by Divya et al. (2021) who synthesized CeO₂ NPs through hydrothermal method.

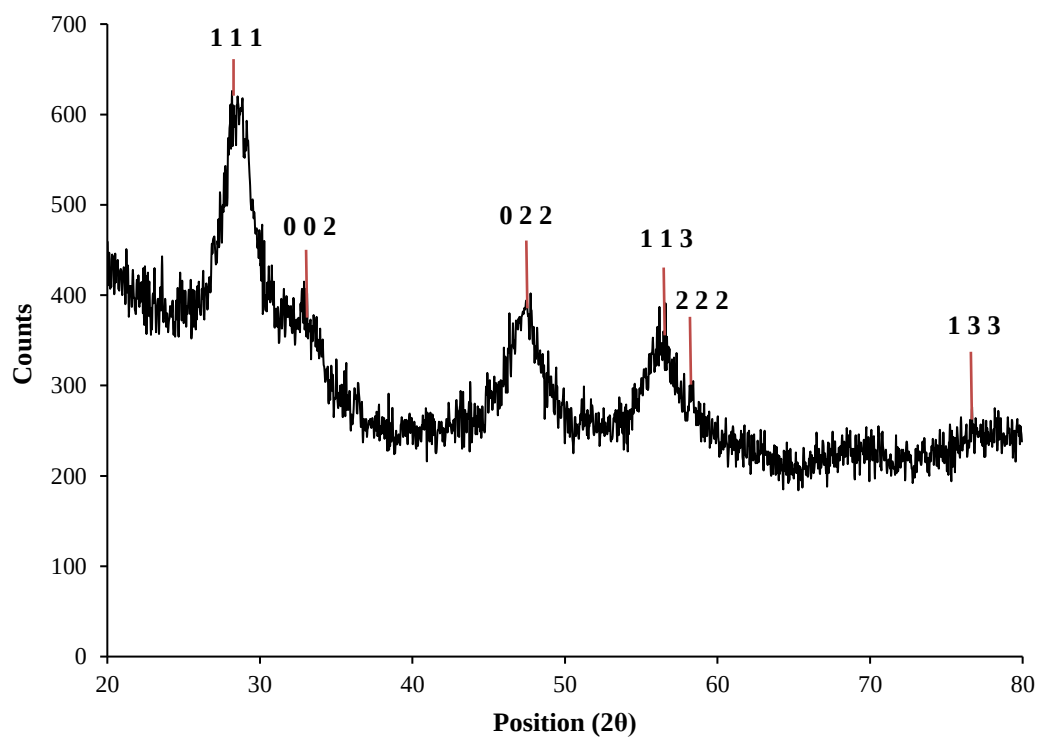


Figure 4.7: XRD diffractogram of CeO₂ NPs synthesized through hydrothermal method

Table 4.2: XRD data of CeO₂ NPs synthesized through hydrothermal method

Peak position, 2 θ	FWHM, β	hkl
28.4762	2.189	1 1 1
33.0031	1.853	0 0 2
47.3823	2.603	0 2 2
56.2256	2.341	1 1 3
69.2719	1.402	0 0 4
76.5424	2.305	1 3 3

The crystallite size of the CeO₂ NPs was calculated according to the Williamson-Hall fitting using the equation formula below:

$$\beta \cos \theta = \varepsilon(4 \sin \theta) + \frac{k\lambda}{D} \quad \text{Equation 4.1}$$

Where β is the full width half maximum (FWHM) of the peaks, ε is the lattice strain, k is a constant with the value of 0.94, λ is the wavelength of CuK α with the value of 0.154 nm, θ is the diffraction angle of the peak and D is the crystallite size. Using this equation, the Williamson-Hall fitting was able to be plotted as shown in Figure 4.8. The calculated crystallite size, D obtained was 3.05 nm.

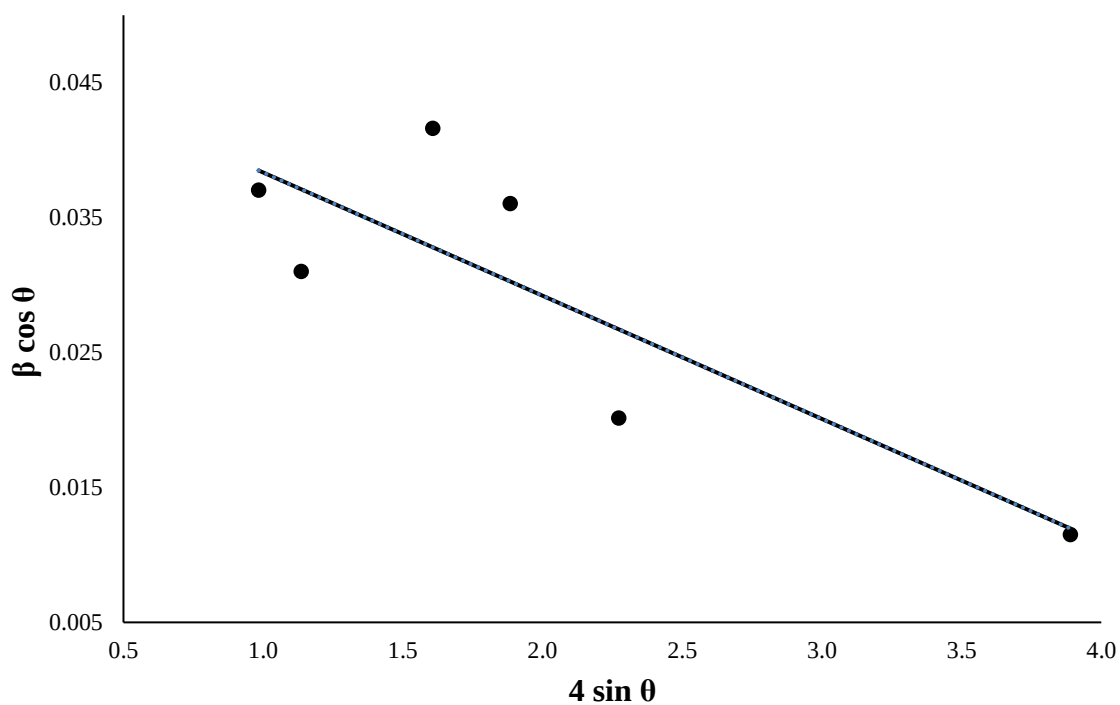


Figure 4.8: Williamson-Hall plot of CeO₂ NPs synthesized through hydrothermal method

4.1.7 Brunauer-Emmett-Teller (BET) Method

BET was performed to determine the specific surface area of the CeO₂ NPs. Figure 4.9 shows the N₂ adsorption-desorption isotherm of the synthesized CeO₂ NPs. The result obtained showed that the CeO₂ NPs have a specific surface area of 185 m²/g which proved that the synthesized CeO₂ NPs were of high specific surface area compared to most of previous studies which reported the specific surface area in the range of 125 - 226 m²/g as shown in Table 4.3.

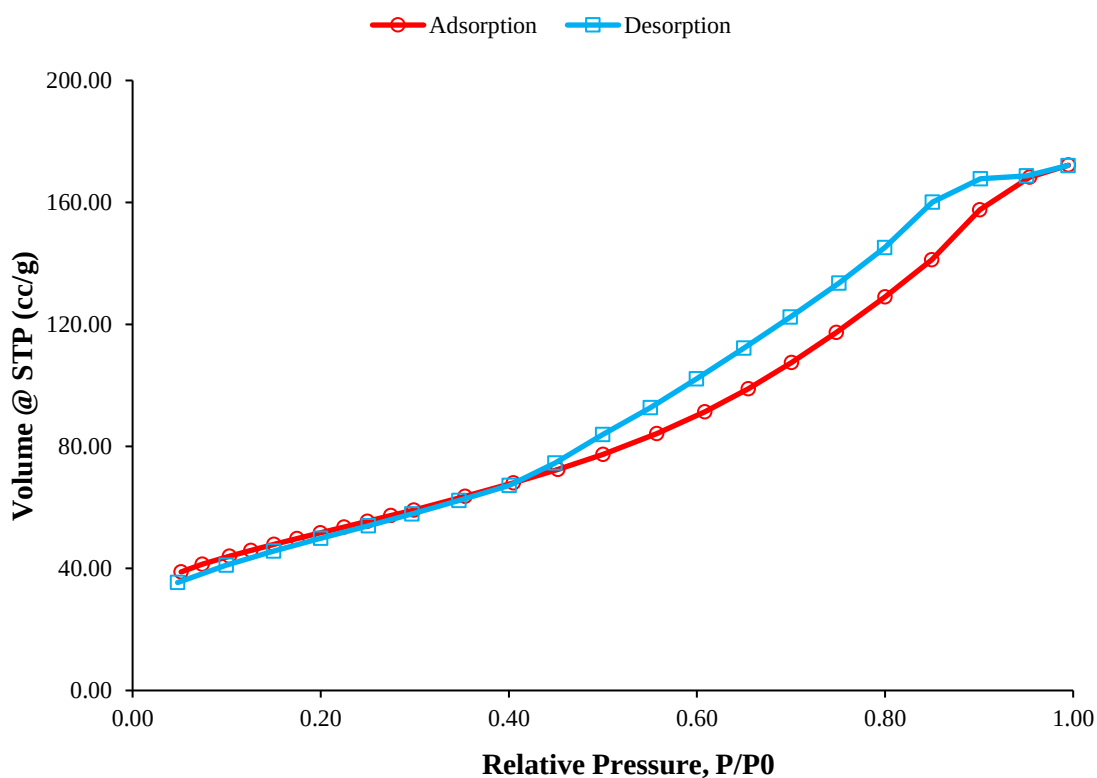


Figure 4.9: N₂ adsorption-desorption isotherm of CeO₂ NPs synthesized through hydrothermal method

Table 4.3: Specific surface areas of CeO₂ NPs in previous studies compared with this study

Synthesis Method	Particle Size (nm)	Specific Surface Area (m ² /g)	References
Hydrothermal	4.5	185	Current study
Reverse micellar	3.7	168	(Sathyamurthy et al., 2005)
Hydrothermal	4.0 – 5.0	125	(Wang et al., 2008)
Hydrothermal	5.9 – 21.4	65 - 226	(Kurajica et al., 2016)
Reverse microemulsion	4.0	150	(Iqbal et al., 2021)

CeO₂ NPs are also known for their excellent antioxidant properties. Factors leading to this ability include their ability to undergo redox reactions between Ce³⁺ and Ce⁴⁺ high specific surface area which allows the removal of ROS and has a larger oxygen storage vacancy compared to lower surface area NPs respectively (Bunghez et al., 2012; Tian et al., 2021). Moreover, Kang et al. (2018) also stated that high specific surface area of CeO₂ is vital in the catalytic properties of this NPs as higher specific surface area attributes to higher number of active sites.

The average particle size of the CeO₂ NPs was calculated according to the equation by Shamhari et al. (2018) where $D_{\text{BET}} = 6000 / p \cdot S_w$. D_{BET} is the average particle size, p is the theoretical density of CeO₂ NPs and S_w is the specific surface area. The average particle size of the CeO₂ NPs was calculated to be 4.5 nm which was correlated with the result obtained from TEM and XRD as shown in Table 4.4.

Table 4.4: Average particle size of CeO₂ NPs using different characterization techniques

	TEM	BET		XRD
Average particle size	3.54 nm	4.55 nm	Average crystallite size	3.05 nm

4.2 Adsorption of Humic Acid on Cerium Oxide Nanoparticles

4.2.1 Characterization of Humic Acid

4.2.1.1 FESEM Analysis

The physical structure of HA (Sigma Aldrich, Switzerland) was characterized using FESEM with acceleration voltage of 5.0 kV and working distance of 9.9 mm as shown in

Figure 4.10. The FESEM image revealed that the morphology of HA was highly heterogeneous and consists of irregular shapes and sizes. The HA particles were also observed to be aggregated and agglomerated.

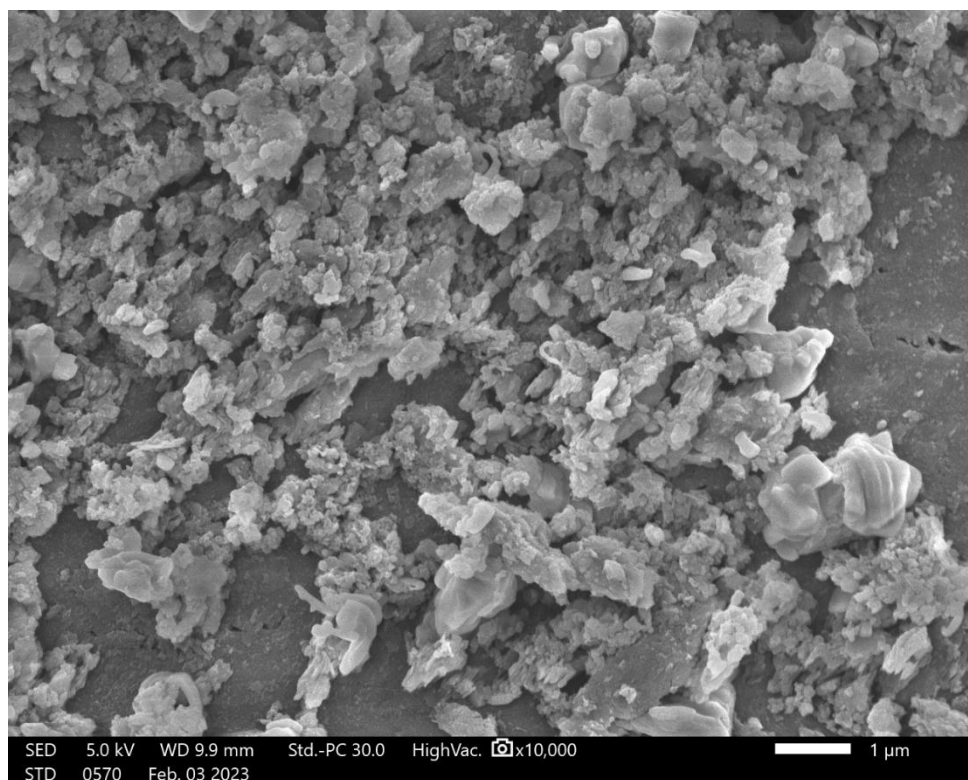


Figure 4.10: FESEM image of humic acid (Sigma Aldrich, Switzerland)

4.2.1.2 UV-Vis Analysis

Figure 4.11 shows the UV-Vis spectrum of HA (Sigma-Aldrich, Switzerland). The absorption of HA decreased when the wavelength increased from 200 to 300 nm. A small peak was observed at 270 nm which was in agreement with studies by (Mahato & Gupta, 2021; Matilainen et al., 2011) that suggested the range of 220 to 280 nm is the wavelength that indicates the presence of aromatic compounds in HA.

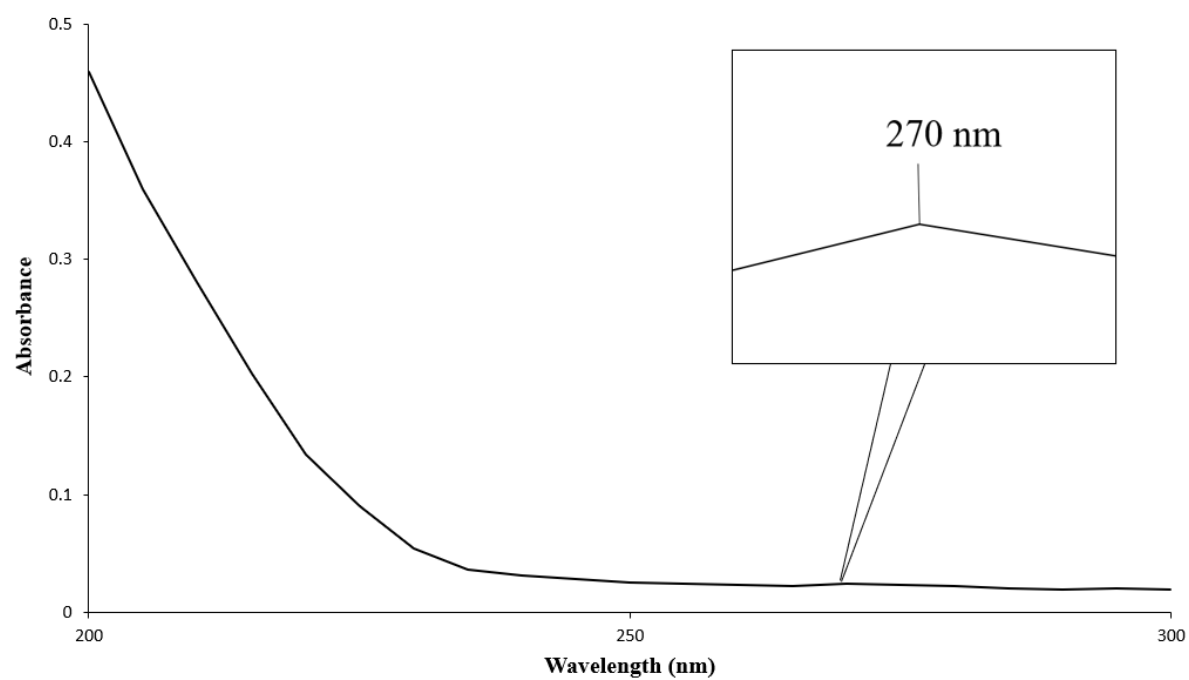


Figure 4.11: UV-Vis spectrum of humic acid (Sigma-Aldrich, Switzerland)

4.2.1.3 FTIR Analysis

The HA (Sigma-Aldrich, Switzerland) was also characterized using FTIR for the functional groups' presence. According to Figure 4.12, the broad band in the region of 3600 to 3100 cm^{-1} indicates the presence of O-H bonds of the hydroxyl groups which may form alcohols, phenols and carboxylic acids. The intense band at 1610 cm^{-1} was the stretching of C-C bonds from the aromatic rings which indicates the presence of carboxylate groups in the HA. Meanwhile, another strong absorption band at 1400 cm^{-1} was attributed to the bonds of C-H from methyl and methylene groups. Another absorption bands at 1100 cm^{-1} and 1029 cm^{-1} were observed from the FTIR spectrum indicating the presence of -COOH groups bound to metal ions and C-O bonds respectively (Da Silva et al., 2018).

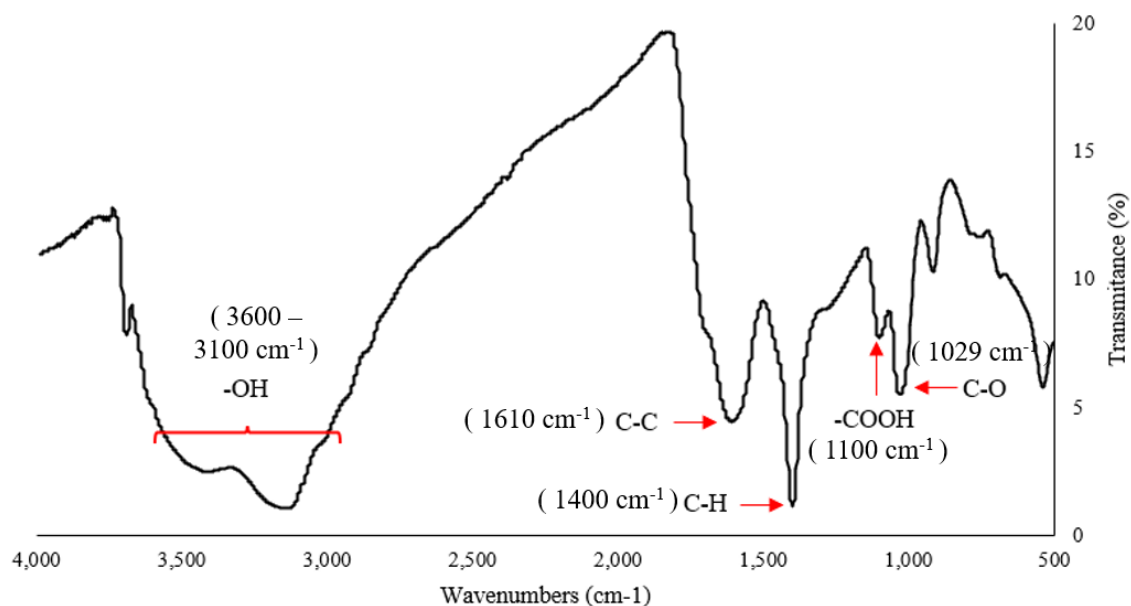


Figure 4.12: FTIR spectrum of humic acid (Sigma-Aldrich, Switzerland)

4.2.2 Adsorption Kinetics

The adsorption of HA on CeO₂ NPs at various pH was tested for its kinetics using the linear form of pseudo-first order and pseudo-second order kinetic model as follow.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \quad \text{Pseudo-First Order}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{Pseudo-Second Order}$$

Where q_e and q_t are the amount of HA adsorbed on CeO₂ NPs (mg/g) at equilibrium time and at time, t , respectively. k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the pseudo-first order rate constant and pseudo-second order rate constant respectively (Gupta et al., 2020). These kinetic models were used to determine the rate of HA adsorption on the synthesized CeO₂ NPs as shown in Figure 4.13 and Figure 4.14.

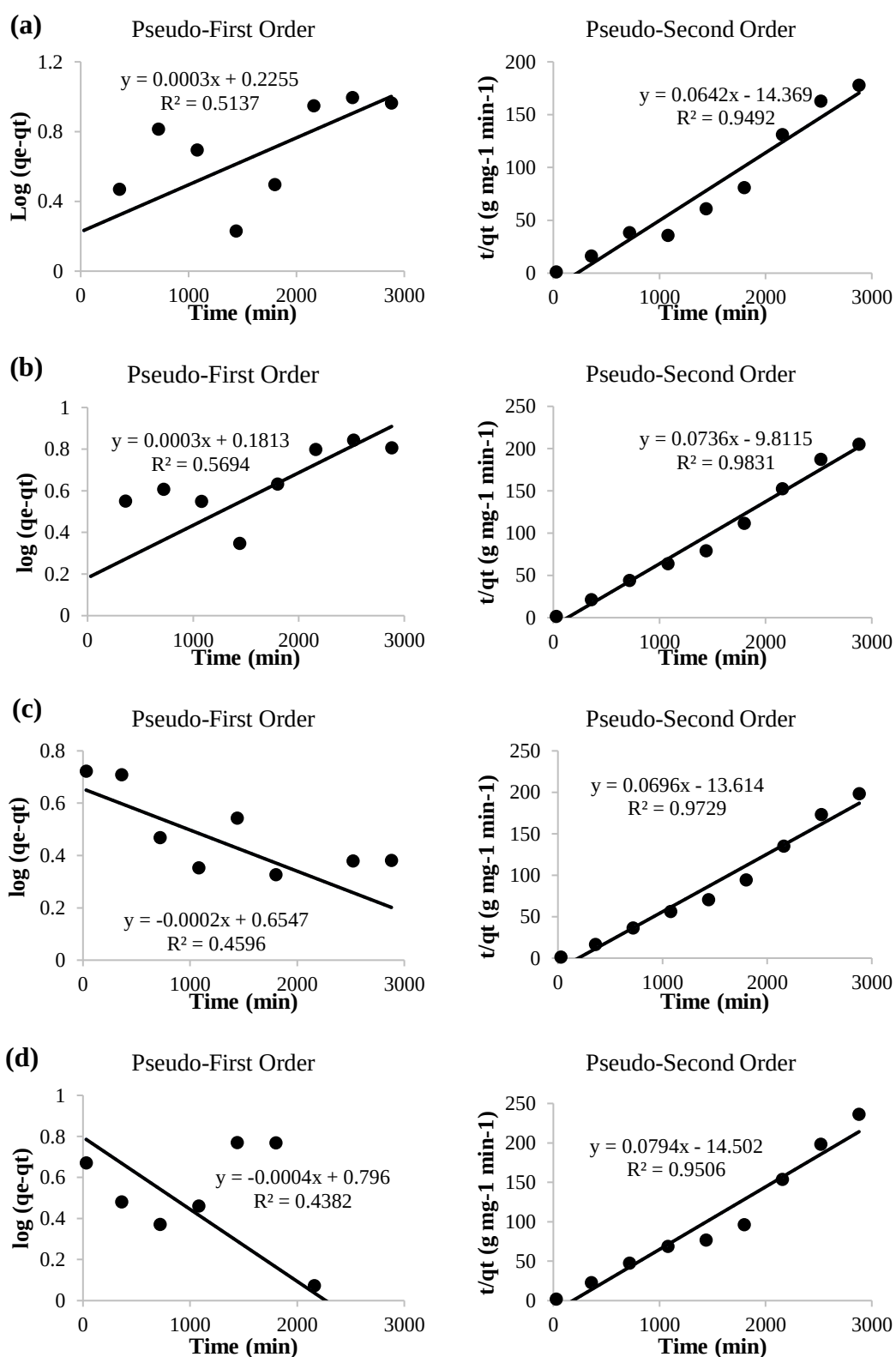


Figure 4.13: Pseudo-first and pseudo-second order kinetic models of 5 mg/L HA adsorption on CeO₂ NPs at (a) pH 5, (b) pH 6, (c) pH 7 and (d) pH 9

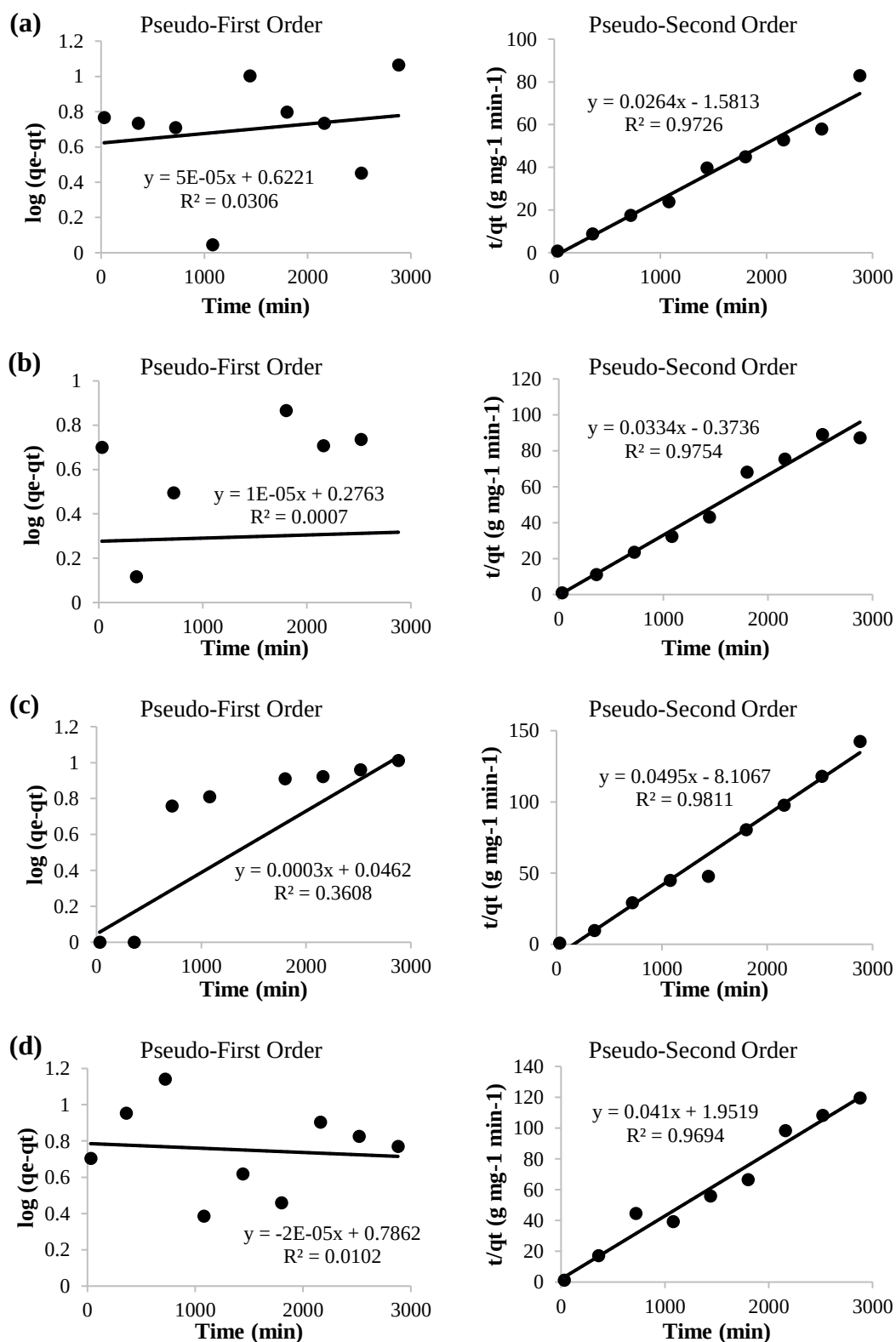


Figure 4.14: Pseudo-first and pseudo-second order kinetic models of 10 mg/L HA adsorption on CeO₂ NPs at (a) pH 5, (b) pH 6, (c) pH 7 and (d) pH 9

The fitting parameters of the kinetic models for the adsorption of 5 mg/L and 10 mg/L HA on CeO₂ NPs were summarized in Table 4.5 and Table 4.6. The results obtained show that the correlation coefficients (R^2) for pseudo-second order were higher than the pseudo-first order at all pH for both HA concentrations used. The experimental value of q_e was also closer to the theoretical value of q_e and lower relative error (χ) was determined in the pseudo-second order compared to the pseudo-first order. This finding proved that the adsorption of HA on CeO₂ NPs is following the pseudo-second order kinetics which confirms that HA adsorb on the surface of CeO₂ NPs by chemisorption (Sahoo & Prelot, 2020).

Table 4.5: Pseudo-first order and pseudo second order parameters for the 5 mg/L HA adsorption on CeO₂ NPs at pH5, pH6, pH7, pH9

Kinetic Model	Parameters	pH 5	pH 6	pH 7	pH 9
Pseudo-First Order	R^2	0.5137	0.5694	0.4596	0.4382
	k_1	6.909×10^{-4}	6.909×10^{-4}	4.606×10^{-4}	9.212×10^{-4}
	$q_e \text{ exp (mg/g)}$	25.37	20.43	16.93	12.88
	$q_e \text{ (mg/g)}$	1.68	1.52	4.52	6.25
	Δ_{qt}	23.69	18.91	12.41	6.63
	χ	14.09	12.46	2.75	1.06
Pseudo-Second Order	R^2	0.9492	0.9831	0.9729	0.9506
	k_2	16.885	18.815	15.163	10.938
	$q_e \text{ exp (mg/g)}$	25.37	20.43	16.93	12.88
	$q_e \text{ (mg/g)}$	15.58	13.59	14.37	12.59
	Δ_{qt}	9.79	6.84	2.56	0.29
	χ	0.63	0.50	0.18	0.02

Where: $q_e \text{ exp}$ is the experimental amount of HA adsorbed at equilibrium time and χ is the relative error between experimental value of q_e and theoretical value of q_e .

Table 4.6: Pseudo-first order and pseudo second order parameters for the 10 mg/L HA adsorption on CeO₂ NPs at pH5, pH6, pH7, pH9

Kinetic Model	Parameters	pH 5	pH 6	pH 7	pH 9
Pseudo-First Order	R²	0.0306	0.0007	0.3608	0.0102
	k₁	1.152×10^{-4}	2.303×10^{-5}	6.909×10^{-4}	4.606×10^{-5}
	q_e exp (mg/g)	46.35	33.76	30.50	29.99
	q_e (mg/g)	4.19	1.89	1.11	6.11
	Δ_{qt}	42.16	31.87	29.38	23.88
	χ	10.06	16.87	26.42	3.91
Pseudo-Second Order	R²	0.9726	0.9754	0.9811	0.9694
	k₂	907.356	2399.386	50.344	304.772
	q_e exp (mg/g)	46.35	33.76	30.50	29.99
	q_e (mg/g)	37.88	29.94	20.20	24.39
	Δ_{qt}	8.47	3.82	10.29	5.60
	χ	0.22	0.13	0.51	0.23

Where: q_e exp is the experimental amount of HA adsorbed at equilibrium time and χ is the relative error between experimental value of q_e and theoretical value of q_e.

4.2.3 Adsorption Isotherms

The adsorption of HA on the synthesized CeO₂ NPs at pH5, pH6, pH7 and pH9 were tested using the linear equations of Langmuir, Freundlich and Temkin isotherms as follow:

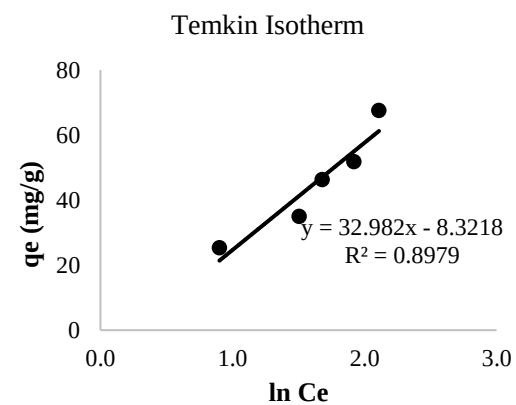
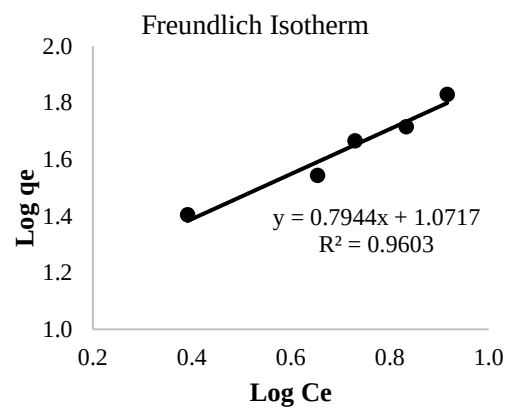
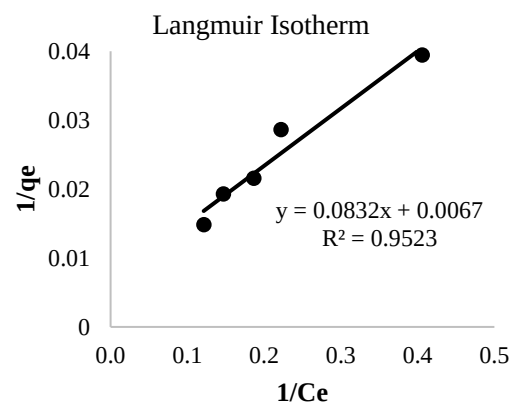
$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_l} \frac{1}{C_e} \quad \text{Langmuir Isotherm}$$

$$\log(q_e) = \log(K_f) + \frac{1}{n} \log(C_e) \quad \text{Freundlich Isotherm}$$

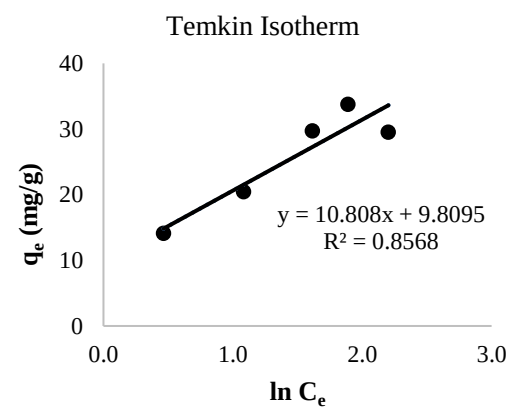
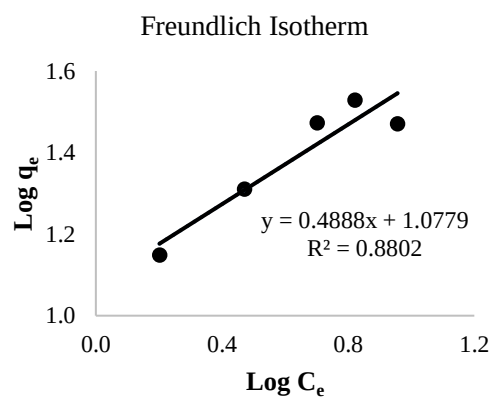
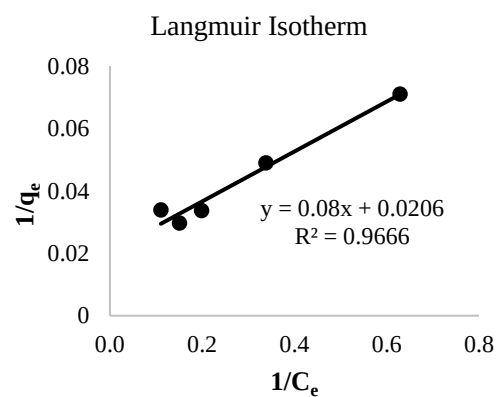
$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \quad \text{Temkin Isotherm}$$

Where q_e is the amount of humic adsorbed (mg/g), q_m is the maximum adsorption capacity, and C_e is the equilibrium concentration. K_l and K_f are the Langmuir isotherm constant and Freundlich isotherm constant respectively. For Temkin isotherm equation, b_T and A_T are the Temkin constant (kJ mol^{-1}) and Temkin isotherm constant (L mg^{-1}) respectively. Meanwhile, R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature (Inyinbor et al., 2016). The isotherms of the adsorption of HA on CeO_2 NPs were plotted as shown in Figure 4.15.

(a)



(b)



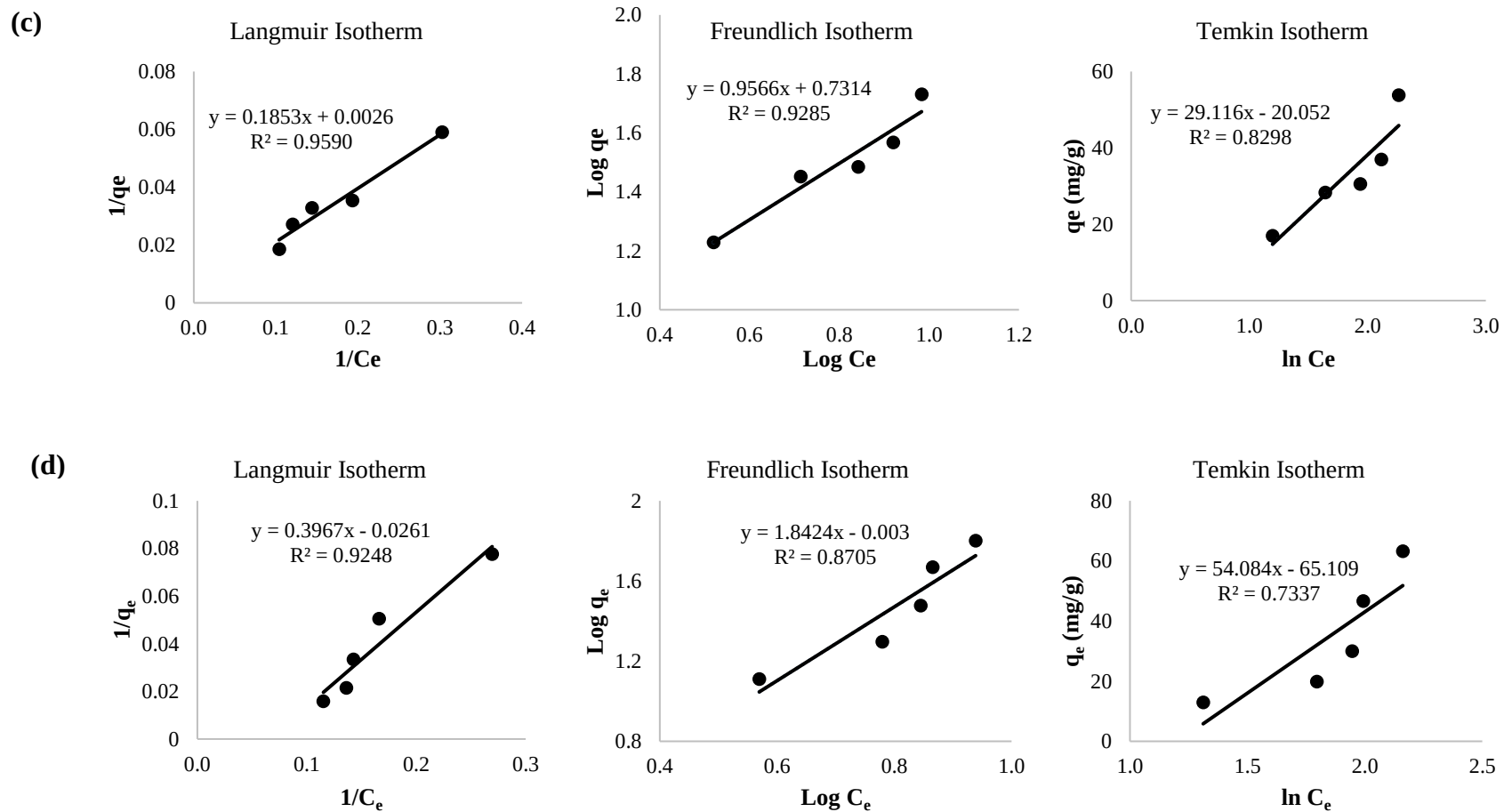


Figure 4.15: Langmuir, Freundlich and Temkin isotherms of HA adsorption on CeO₂ NPs at (a) pH5, (b) pH6, (c) pH7, (d) pH9

Fitting the data using the Langmuir, Freundlich and Temkin isotherms gave the following parameters in Table 4.7. The result obtained showed that the adsorption of HA onto CeO₂ NPs followed the Langmuir isotherm due to the higher R² at all pH except at pH 5. The presence of carboxyl groups in the HA molecules was an important factor for the differences between adsorption isotherms at acidic, neutral and alkaline conditions. At pH < 6, the carboxyl groups in HA deprotonated by releasing H⁺ ions which resulted into an increase rate of adsorption between CeO₂ NPs and HA molecules (Ahmed et al., 2017). Thus, the high adsorption rate suggested that the adsorption of HA on CeO₂ NPs at pH 5 followed both Freundlich and Langmuir isotherms where the adsorption process was both physisorption and chemisorption which further enhanced the adsorption of HA. The better fitting on Langmuir isotherm for most of the pH also suggests that the adsorption of HA on CeO₂ NPs was a monolayer type of sorption. The Langmuir isotherm also suggests that the active sites on the surface of the synthesized CeO₂ NPs was of high homogeneity and the adsorption of HA was not dependent on the surface coverage of the CeO₂ NPs (Osmari et al., 2013).

Table 4.7: Langmuir, Freundlich and Temkin isotherms parameters for the HA adsorption on CeO₂ NPs at (a) pH5, (b) pH6, (c) pH7, (d) pH9

Isotherm	Parameters	pH 5	pH 6	pH 7	pH 9
Langmuir	R²	0.9523	0.9666	0.9590	0.9248
	q_m (mg/g)	149.25	48.54	384.62	38.31
	K_L	0.00056	0.00165	0.00048	0.01035
	R_L	0.9917	0.9759	0.9742	0.8656
Freundlich	R²	0.9603	0.8802	0.9285	0.8705
	1/n	0.7944	0.4888	0.9566	1.8424
	n	1.2588	2.0458	1.0458	0.5428
	K_f	11.80	11.96	5.39	1.01
Temkin	R²	0.8979	0.8568	0.8298	0.7337
	b_T (kJ/mol)	32.98	10.81	29.12	54.08
	A_T (L/mg)	1.287	2.47	1.991	3.333

The $0 < R_L < 1$ values at all pH for the Langmuir isotherm also indicates that the adsorption of HA on CeO₂ NPs was favourable. This range of R_L value in the isotherm also assumes that the number of active sites on the surface of CeO₂ NPs for adsorption were limitless which associated well with the heterogeneous HA having various organic compounds and functional groups (Akrawi et al., 2021).

According to Singh (2016), $1/n$ in Freundlich isotherm linear equation is the measure of intensity of the adsorption isotherm. The $1/n$ value of less than 1 at all pH except pH 9 as shown in Table 4.7 indicate that the adsorption isotherm is normal while the $1/n$ value of more than 1 at pH 9 indicates a cooperative adsorption isotherm (El-Sayed et al., 2013).

In Temkin isotherm, the constant value b_T and A_T are related to the heat of HA adsorption on CeO_2 NPs and the binding energy of the adsorption at equilibrium respectively (Mohamad et al., 2014). The $b_T > 8$ values at all pH further proved that the adsorption process of HA on the surface of CeO_2 NPs was by chemisorption instead of physisorption (Nandiyanto et al., 2022).

4.2.4 Adsorption mechanism of humic acid on CeO_2 NPs

The presence of NOM increases the stability of metal oxide NPs due to their ability to adsorb NOM (Quik et al., 2010). These abilities include high specific surface area of the synthesized CeO_2 NPs ($185 \text{ m}^2/\text{g}$). However, the difference in pH also affects the adsorption of HA on CeO_2 NPs. At $\text{pH} > 7$, charged HA molecules undergo adsorption on the surface of CeO_2 NPs. However, the uncharged HA molecules could not undergo adsorption process at $\text{pH} > 7$ due to the strong lateral repulsion between charged HA molecules and the surface CeO_2 NPs which retarded the adsorption process (Van Hoecke et al., 2011).

The surface charge of CeO_2 NPs is highly pH-dependent. The pH where the surface charge of the CeO_2 NPs is equal to zero is called as the point of zero charge (PZC). In the case of CeO_2 NPs, the PZC reported from previous studies were approximately pH 7 (Mahato & Gupta, 2021). Therefore, at $\text{pH} < 7$, the surface charge of CeO_2 NPs is positive which was possibly due to the protonation of the surface sites of the NPs as expressed in the schematic diagram in Figure 4.16.

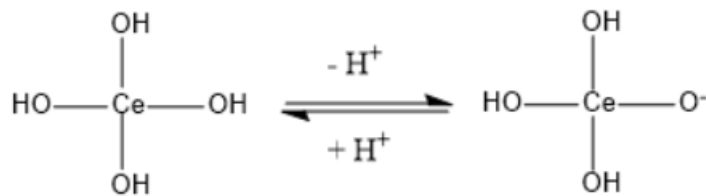


Figure 4.16: Protonation and deprotonation of surface sites of CeO₂ NPs

Thus, allowing the positively-charged surface of CeO₂ NPs to bind and form a strong electrostatic attraction with the negatively-charged HA molecules. Nevertheless, the adsorption process of HA on CeO₂ NPs became retarded at alkaline pH because the surface charge of CeO₂ NPs is negative at pH above the PZC (Mahato & Gupta, 2021). This is due to the deprotonation of the surface sites of CeO₂ NPs. Consequently, electrostatic repulsion between the negatively charged surface of CeO₂ NPs and the negatively charged HA molecules occurred and the adsorption rate decreased.

4.2.5 FESEM of HA-CeO₂

The sample of HA-CeO₂ was also characterized using FESEM to study the effects of adsorption of HA on CeO₂ NPs at different pH. According to Mahato and Gupta (2021), the adsorption of HA on CeO₂ NPs is pH-dependent. The result in Figure 4.17 shows that more aggregation occurred at higher pH leads to more particles forming bigger entities compared to the lower pH (Hoecke et al., 2021). The adsorption result showed that the adsorption of HA on CeO₂ NPs favoured acidic pH. According to Linse & Wennerstrom (2012), adsorption occurred more on surface sites of particles that were less aggregated because the adsorption of particles tends to dense and form the first layer of the surface sites and avoid multiple layers formed by aggregation of particles. This finding proved that lower aggregation of HA-CeO₂ particles was observed at lower pH compared to higher pH because of the higher adsorption at acidic pH.

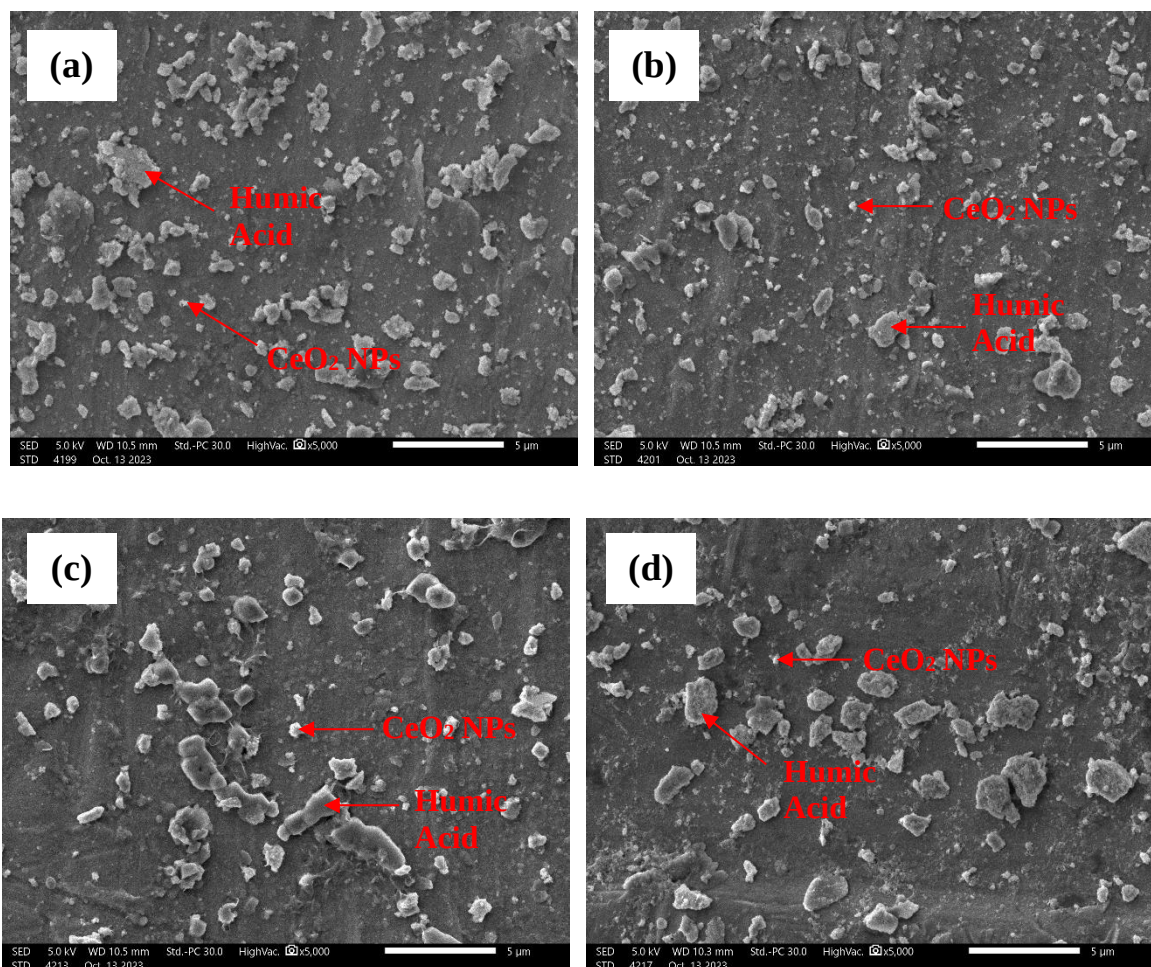


Figure 4.17: FESEM image of HA-CeO₂ NPs at (a) pH 5, (b) pH 6, (c) pH 7 and (d) pH 9

4.3 Dissolution of Cerium Oxide Nanoparticles under Different Aqueous Environmental Factors

4.3.1 Effects of Different Ionic Concentrations and pH

The dissolution of CeO₂ NPs was studied using different ionic concentrations of 0 mM NaCl, 3 mM NaCl and 5 mM NaCl at pH 3, pH 5, pH 6, pH7 and pH 9. According to the result in Figure 4.18(a), the amount of dissolved Ce⁴⁺ decreased for all pH except at pH 9 without the addition of NaCl (0 mM NaCl). This similar finding was also observed by Van Hoecke et al. (2011) where increasing pH leads to more aggregation and a decrease in dissolution. The dissolution of CeO₂ NPs at pH < 7 depends on the concentration of H⁺ and

the redox reactions of the NPs (Plakhova et al., 2016). The result obtained from ICP-OES analysis proved that lower pH and higher H^+ activity leads to a decrease in amount of dissolved Ce^{4+} ions. However, pH 5 showed a higher amount of dissolved Ce^{4+} ions compared to pH 3. This result could be due to the lower redox activity at $pH > 4.5$ which was correlated with a study by (Plakhova et al., 2016).

Under the influence of 3 mM NaCl as shown in Figure 4.18(b), the amount of dissolved Ce^{4+} decreased at every pH except at pH 3. This result was possibly due to the high proton activity at pH 3 and the higher solubility of CeO_2 NPs at low pH (Plakhova et al., 2016). On the other hand, the presence of NaCl inhibited the proton activity at pH 5 although it was in the acidic region which was possibly due to the ability of the ligands of NaCl to attach with the complex presence on the surface of the synthesized CeO_2 NPs (Dahle et al., 2015). Thus, the presence of 3 mM NaCl minimized and decreased the dissolution rate of CeO_2 NPs as observed at $pH > 5$. However, CeO_2 NPs are insoluble at $pH > 7$ which explained the non-detected amount of dissolved Ce^{4+} ions from the ICP-OES analysis.

The experiment using 5 mM NaCl however did not yield any detectable amount of dissolved Ce^{4+} ions. The result obtained suggested that higher concentration of NaCl leads to a higher frequency of collision. Therefore, the chances of forming complexes were higher which resulted into the non-detectable Ce ions.

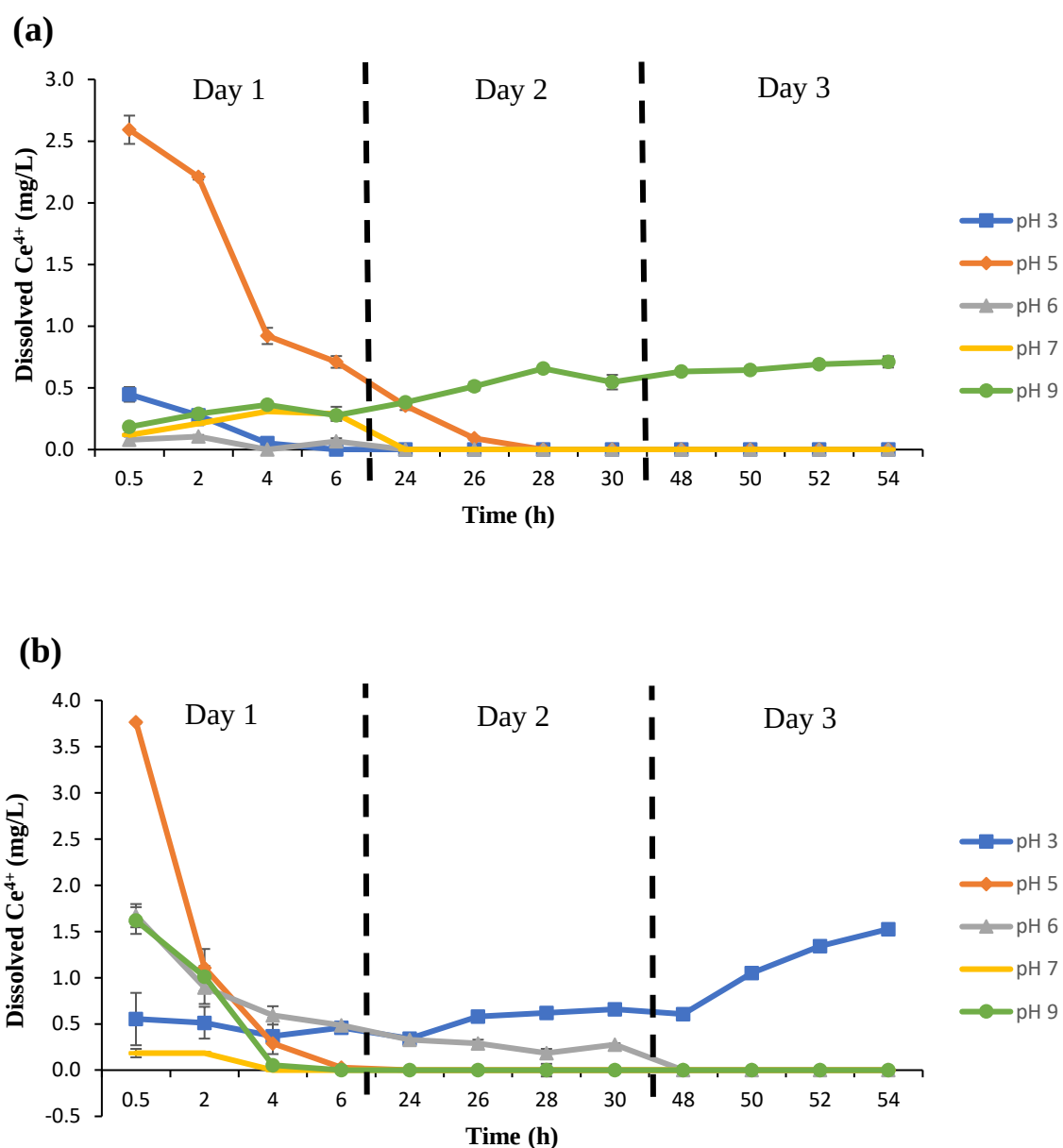


Figure 4.18: Dissolved Ce^{4+} under the influence of different pH and IS of (a) 0 mM NaCl and (b) 3 mM NaCl

4.3.2 Effects of Humic Acid and pH on CeO_2 NPs

Another dissolution study was performed on CeO_2 NPs when influenced by different HA concentrations of 5 mg/L and 10 mg/L.

At lower concentration of HA (5 mg/L), the amount of dissolved Ce^{4+} ions increased at strongly acidic pH (pH 3 and pH 5) as shown in Figure 4.19(a). However, the amount of dissolved Ce^{4+} ions at pH 6 and pH 7 were mostly below the LOD of the instrument. This result might be due to the increased stability of CeO_2 NPs at a higher pH compared to acidic pH as shown in the adsorption experiment. As the adsorption rate increased, the aggregation rate of the particles increased too. According to Liu et al. (2018), the aggregation and dissolution of NPs are negatively correlated which proved that the presence of HA could also impede the dissolution of CeO_2 NPs but in a manner of pH-dependency. Van Hoecke et al. (2011) studied the effects of NOM towards CeO_2 NPs and also found that higher pH and NOM concentrations lead to an increase in aggregation. However, small amount of dissolved Ce^{4+} ions was detected on the first day at pH 9. The amount of dissolved ions gradually decreased until it reached below the LOD. This result further proved that at the concentration of 5 mg/L HA, adsorption of HA molecules on CeO_2 NPs resulted into a greater stability of the NPs at higher pH.

Similar result was obtained when 10 mg/L HA was used at pH 6 and pH 7 as no significant dissolution was observed as shown in Figure 4.19(b). However, a lower amount of dissolved Ce^{4+} ions was detected at acidic pH (pH 3 and pH 5) compared to when using 5 mg/L HA. Higher concentration of HA leads to an increase in aggregation and adsorption on the CeO_2 NPs (Quik et al., 2010). This is due to the presence of higher number of various functional groups specifically carboxyl and phenolic groups that provide a greater steric repulsion between the electrolytes of HA and the surface of ENPs (Nanja et al., 2020). Consequently, increased in concentration of HA provides greater stability to the CeO_2 NPs.

However, the amount of dissolved Ce^{4+} ions decreased at pH 9. Despite having a higher amount of dissolved Ce^{4+} ions on the first day at pH 9, the amount of dissolved ions continued to decrease until no amount of dissolved Ce^{4+} was detected. The result obtained was possibly due to the high solubility of HA at high pH which provided a higher amount of available functional groups (Liu et al., 2018). This result proved that HA can both increase and decrease the dissolution rate of CeO_2 as also studied in previous literatures for the dissolution of metal oxide NPs (Chen et al., 2018; Loosli et al., 2015; Ghosh et al., 2008). Jiang et al. (2015) also reported a similar result using ZnO NPs and concluded that NOM could promote the dissolution of NPs by chelation of surface atoms between the HA molecules and the surface of the NPs.

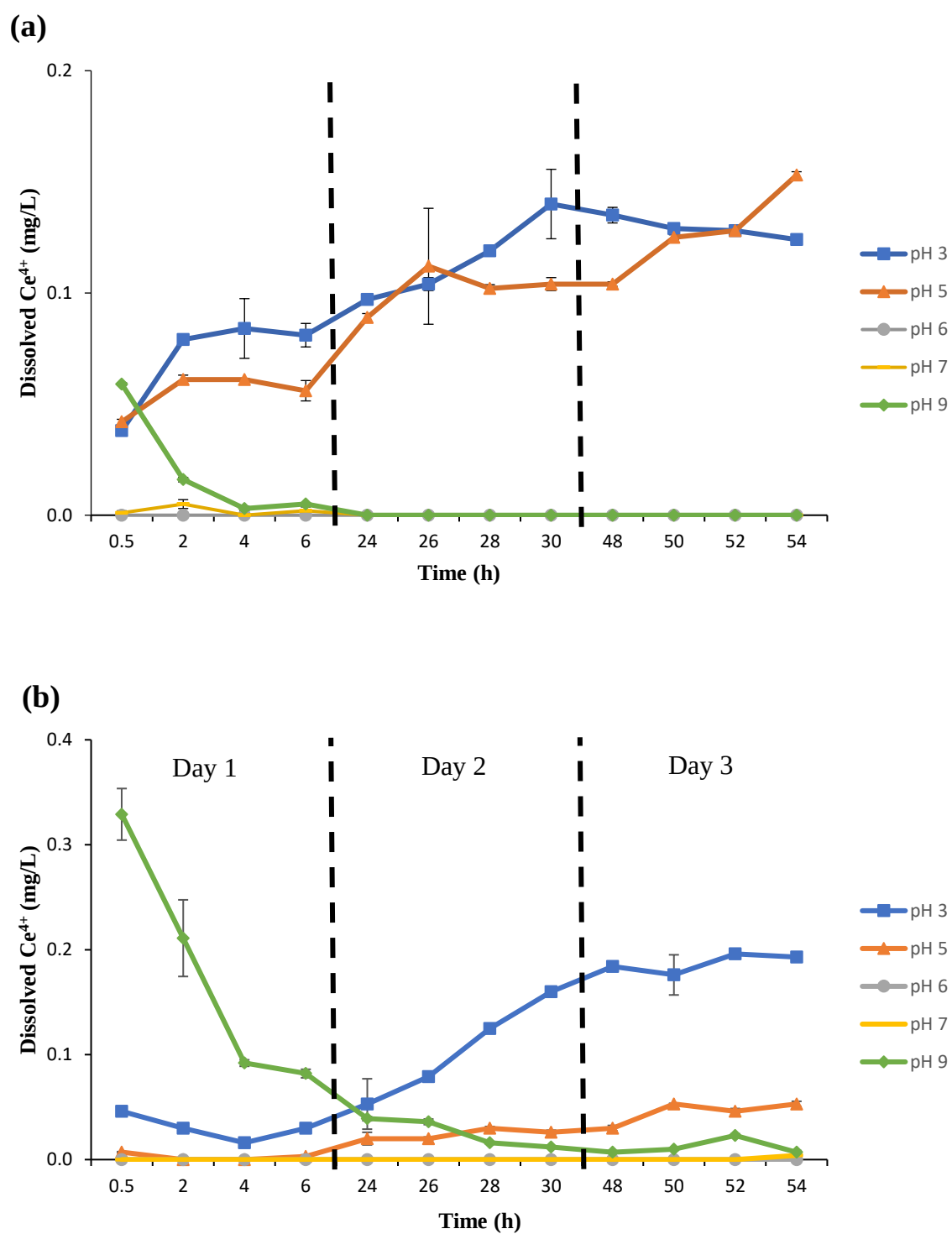


Figure 4.19: Dissolved Ce^{4+} under the influence of different pH and HA concentrations of (a) 5 mg/L and (b) 10 mg/L

4.3.3 Dissolution of CeO₂ NPs in the Environment

Environmental parameters have shown to affect the behavior of CeO₂ NPs. Difference in pH and HA/IS was determined to be significant in the dissolution of CeO₂ NPs.

According to Idrus et al. (2017), the pH of the surface seawater near Sarawak is in the range of pH 7.63 to 7.82. The amount of dissolved Ce⁴⁺ ions determined from this study at pH 7 was the closest to that pH of the surface seawater near Sarawak. With the absence of HA and IS, the amount of dissolved Ce⁴⁺ ions showed a decreasing trend in day 1 until no detectable amount of dissolved Ce⁴⁺ ions in day 2 and day 3. The result obtained showed that CeO₂ NPs became insoluble at pH 7 and it is expected that this NPs will also be insoluble in the surface seawater of Sarawak. However, the ionic strength of surface seawater is high and the dissolution of CeO₂ NPs are also expected to be insoluble as studied in the result obtained in the dissolution experiment when using 5 mM NaCl and at pH 7.

On the other hand, the range of pH in surface coastal water in south of Peninsular Malaysia is between pH 5.5 to 8.5 at various locations including fishing areas, aquaculture sites and residential zones. Low pH obtained was due to the photosynthetic activity and microbial respiration such as the discharged of sewage, anthropogenic pollutants and mangrove areas (Yap et al., 2011). Results obtained from the dissolution experiment in this study showed that CeO₂ NPs were also insoluble at this pH range with the absence of HA and IS. However, the presence of 3 mM NaCl at pH 6 resulted into a decrease in the amount of dissolved Ce⁴⁺ ions from 1.671 mg/L to 0.276 mg/L from day 1 to day 2 while no amount

of dissolved Ce^{4+} was detected on day 3. This result proved that a low amount of ionic concentration at pH 6 could also affect the solubility of CeO_2 NPs in surface waters. However, no significant dissolution was observed at pH 7 and pH 9.

The concentrations of HA studied in the dissolution experiment was also in the range of HA concentrations generally found in surface waters (Basumallick & Santra, 2017). At pH of surface waters, the presence of HA was found to greatly enhance the stability of CeO_2 NPs as no amount of dissolved Ce^{4+} ions was detected from day 1 until day 3. The greater stability is expected to affect the transportation and fate of CeO_2 NPs in aqueous environment as higher amount of CeO_2 NPs will remain in the suspension which might result into enhanced toxicity of the NPs towards the aquatic organisms (Ahmad et al., 2019; Van Hoecke et al., 2011).

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

CeO₂ NPs has been widely used in many different applications and consequently released to the aquatic environment. In this study, spherical CeO₂ NPs was successfully synthesized using the hydrothermal method under a favourably low temperature (70 °C) for 4 hours using Ce(NO₃)₃ • 6 H₂O and NaOH as the precursors while deionized water was used as the solvent. The synthesized CeO₂ NPs were characterized for their morphology and unique properties. TEM and BET method confirmed that the average particle size of the CeO₂ NPs were 3.5 nm and 4.5 nm respectively. The very small size of the NPs also contributed to its high specific surface area as confirmed through BET method (185 m²/g). The synthesized CeO₂ also was determined to be high purity from the results obtained in EDX and XRD.

The adsorption of HA on CeO₂ NPs has also been studied. Result showed that the adsorption of HA on CeO₂ NPs favoured at acidic pH due to the strong electrostatic attraction between the negatively-charged HA molecules and the positively-charged surface of CeO₂ NPs. However, lower adsorption rate was observed at pH ≥ 7 due to the negatively-charged surface of CeO₂ NPs which repulse the negatively-charged HA molecules.

The dissolution of CeO₂ NPs under different pH and ionic strength or concentration of humic acid were also studied. Higher ionic strength was found to increase the stability of CeO₂ NPs. However, the difference in pH also affects the solubility of the NPs. At a very

low pH (pH 3), the solubility of CeO₂ NPs was found to be increasing due to high proton activity which allows more Ce ions to be released. However, higher ionic concentration causes a lower dissolution of CeO₂ NPs due to the higher chances of complexes being formed.

On the other hand, the adsorption study of HA on the surface of the synthesized CeO₂ NPs is also important to be studied. HA adsorption caused significant changes towards the behavior of the synthesized CeO₂ NPs especially the aggregation and dissolution of the NPs. Increased in HA concentration and pH resulted into an increased stability of CeO₂ NPs. At acidic pH, the amount of dissolved Ce⁴⁺ when using 10 mg/L HA was found to be lower compared to the 5 mg/L HA. This was due to the higher aggregation and adsorption rates between HA molecules and CeO₂ NPs.

Hence, results from this study have shown that spherical CeO₂ NPs was able to be synthesized using the hydrothermal method at 70 °C for 4 hours. However, it is recommended to study effects of different temperature and heating time on the physicochemical properties of CeO₂ NPs because the different synthesis conditions may produce different properties of NPs which behaves differently in the environment. This study also was limited to the effects of pH, HA and ionic strength without the presence of sunlight which might be another important factor that affects the dissolution of CeO₂ NPs. Therefore, the effects of pH, HA and ionic strength under sunlight towards CeO₂ NPs of different sizes, shapes and surface area can be studied in future research.

REFERENCES

- Agboola, O.D., & Benson, N. U. (2021). Physisorption and Chemisorption Mechanisms Influencing Micro (Nano) Plastics-Organic Chemical Contaminants Interactions: A Review. *Frontiers in Environmental Science*, 9, 1-27. <https://doi.org/10.3389/fenvs.2021.678574>
- Ahmad, N. S., Radiman, S., & Yaacob, W. Z. W. (2019). Aggregation and Stability of Iron Oxide and Alumina Nanoparticles: Influences of pH And Humic Acid Concentration. *Sains Malaysiana*, 48(2), 435-442. <https://doi.org/10.17576/jsm-2019-4802-22>
- Ahmed, I. M., Gamal, R., Helal, A. A., Abo-El-Enein, S. A., & Helal, A. A. (2017). Kinetic Sorption Study of Cerium (IV) on Magnetite Nanoparticles. *Particulate Science and Technology*, 35(6), 643–652. <https://doi.org/10.1080/02726351.2016.1192572>
- Akduman, C., & Kumbasar, A.E.P., (2018). Nanofibers in Face Masks and Respirators to Provide Better Protection. *IOP Conference Series: Materials Science and Engineering*, 460, 1-5, Istanbul, Turkey, 20-22 June 2018. Institute of Physics Publishing <https://doi.org/10.1088/1757-899X/460/1/012013>
- Akrawi, H. S. Y., Al-Obaidi, M. A., & Abdulrahman, C. H. (2021). Evaluation of Langmuir and Frenlich Isotherm Equation for Zinc Adsorption in some Calcareous Soil of Erbil Province North of Iraq. *IOP Conference Series: Earth and Environmental Science*, 761, 1-11, Iraq, 24-25 March 2021. IOP Publishing Ltd. <https://doi.org/10.1088/1755-1315/761/1/012017>

- Alhalili, Z. (2023). Metal Oxides Nanoparticles: General Structural Description, Chemical, Physical, and Biological Synthesis Methods, Role in Pesticides and Heavy Metal Removal through Wastewater Treatment. *Molecules*, 28(7), 3086. <https://doi.org/10.3390%2Fmolecules28073086>
- Ali, K. (2021). Hydrothermal Synthesis of Cerium Oxide Nanostructures. *Global Scientific Journals*, 9(4), 429–444.
- Altaf, M., Manoharadas, S., & Zeyad, M. T. (2021). Green Synthesis of Cerium Oxide Nanoparticles Using *Acorus calamus* Extract and Their Antibiofilm Activity Against Bacterial Pathogens. *Microscopy Research and Technique*, 84(8), 1638-1648. <https://doi.org/10.1002/jemt.23724>
- Ampong, K., Thilakaranthna, M. S., & Gorim, L. Y. (2022). Understanding the Role of Humic Acids on Crop Performance and Soil Health. *Frontiers in Agronomy*, 4, 1-14. <https://doi.org/10.3389/fagro.2022.848621>
- Asgari, G., Mohammadi, A. S., Ebrahimi, A., & Hosseinzadeh, E. (2012). Adsorption of Phenol from Aqueous Solution by Modified Zeolite with FeCl₃. *International Journal of Environmental Health Engineering*, 1(7), 1-6. <https://doi.org/10.4103/2277-9183.107915>
- Bajaj, N. S., & Joshi, R. A. (2021). Energy Materials: Synthesis and Characterization Techniques. *Energy Materials: In Energy Materials: Fundamentals to Applications*, pp. 61-82. Elsevier. <https://doi.org/10.1016/B978-0-12-823710-6.00019-4>

- Basumallick, S., & Santra, S. (2017). Monitoring of ppm Level Humic Acid in Surface Water using ZnO–Chitosan Nano-Composite as Fluorescence Probe. *Applied Water Science*, 7(2), 1025-1031. <https://doi.org/10.1007/s13201-015-0291-1>
- Bathi, J. R., Moazeni, F., Upadhyayula, V. K. K., Chowdhury, I., Palchoudhury, S., Potts, G. E., & Gadhamshetty, V. (2021). Behavior of Engineered Nanoparticles in Aquatic Environmental Samples: Current Status and Challenges. *Science of the Total Environment*, 793, 1-13. <https://doi.org/10.1016/j.scitotenv.2021.148560>
- Bayda, S., Adeel, M., Tuccinardi, T., Cordani, M., & Rizzolio, F. (2020). The History of Nanoscience and Nanotechnology: From Chemical-Physical Applications to Nanomedicine. *Molecules*, 25(1), 112-126. <https://doi.org/10.3390/molecules25010112>
- Belkacem, I., Helali, A., Khardi, S., Chrouda, A., & Slimi, K. (2022). Road Traffic Nanoparticle Characteristics: Sustainable Environment and Mobility. *Geoscience Frontiers*, 13(1), 1-16. <https://doi.org/10.1016/j.gsf.2021.101196>
- Bhuiyan, M.H.U., Saidur, R., Amalina, M.A., Mostafizur, R.M., Islam, A.K.M.S. (2015). Effect of Nanoparticles Concentration and their Sizes on Surface Tension Nanofluids. *Procedia Engineering*, 105(2015), 431-437. doi: 10.1016/j.proeng.2015.05.030
- Bohinc, K., Korade, K., Jerin, K., Lešić, N., Đaković, M., Dražić, G., Dufrêche, J. F., & Kovačević, D. (2021). Experimental and Theoretical Study of Morphological and Charging Properties of Truncated Octahedron and Cubic Ceria Nanoparticles: Implications for Biomedical Applications. *ACS Applied Nano Materials*, 4(2), 1434-1444. <https://doi.org/10.1021/acsanm.0c02960>

- Boxall, A., Tiede, K., Chaudhry, Q., Aitken, R., Jones, A., & Jefferson, B.J.L. (2007). Current and Future Predicted Environmental Exposure to Engineered Nanoparticles. *Environment*, 89. <https://doi.org/196111>
- Bunghez, I. R., Patrascu, M. E. B., Badea, N., Doncea, S. M., Popescu, A., & Ion, R. M. (2012). Antioxidant Silver Nanoparticles Green Synthesized Using Ornamental Plants. *Journal of Optoelectronics and Advanced Materials*, 14(11-12), 1016-1022.
- Buzea, C., Pacheco, I. I., & Robbie, K. (2007). Nanomaterials and Nanoparticles: Sources and Toxicity. *Biointerphases*, 2(4), 17-71. <https://doi.org/10.1116/1.2815690>
- Caballero-Guzman, A., & Nowack, B. (2016). A Critical Review of Engineered Nanomaterial Release Data: Are Current Data Useful for Material Flow Modeling? *Environmental Pollution*, 213, 502-517. <https://doi.org/10.1016/j.envpol.2016.02.028>
- Celardo, I., Pedersen, J. Z., Traversa, E., & Ghibelli, L. (2011). Pharmacological Potential of Cerium Oxide Nanoparticles. *Nanoscale*, 3(4), 1411-1420. <https://doi.org/10.1039/c0nr00875c>
- Chavali, M.S. & Nikolova, M.P. (2019). Metal Oxide Nanoparticles and their Applications in Nanotechnology. *SN Applied Sciences*, 1(607), 607-637. <https://doi.org/10.1007/s42452-019-0592-3>
- Chelliah, M., Rayappan, J. B. B., & Krishnan, U. M. (2012). Synthesis and Characterization of Cerium Oxide Nanoparticles by Hydroxide Mediated

- Approach. *Journal of Applied Sciences*, 12(16), 1734-1737.
<https://doi.org/10.3923/jas.2012.1734.1737>
- Chen, Y., Gao, Q., Chen, W., Wu, F., Yang, Y., Werner, D., Tao, S., & Wang, X. (2018). A Mechanistic Study of Stable Dispersion of Titanium Oxide Nanoparticles by Humic Acid. *Water Research*, 135, 85-94.
<https://doi.org/10.1016/j.watres.2018.02.018>
- Choudhury, S., Paul, S., Goswami, S., & Deb, K. (2022). Methods for Nanoparticle Synthesis and Drug Delivery. In *Advances in Nanotechnology-Based Drug Delivery Systems*, pp. 21-44. Elsevier. <https://doi.org/10.1016/B978-0-323-88450-1.00005-3>
- Collin, B., Auffan, M., Johnson, A.C., Kaur, I., Keller, A.A., Lazareva, A., Lead, J.R., Ma, X., Merrieffield, R.C., Svendsen, C., White, J.C., & Unrine, J.M. (2014). Environmental Release, Fate and Ecotoxicological Effects of Manufactured Ceria Nanomaterials. *Environmental Science: Nano*, 1, 533-548.
<https://doi.org/10.1039/C4EN00149D>
- Da Silva, R. R., Lucena, G. N., MacHado, Â. F., De Freitas, G. A., Matos, A. T., & Abrahão, W. A. P. (2018). Spectroscopic and Elementary Characterization of Humic Substances in Organic Substrates. *Comunicata Scientiae*, 9(2), 264-274.
<https://doi.org/10.14295/CS.v9i2.2734>
- Dahle, J. T., & Arai, Y. (2015). Environmental Geochemistry of Cerium: Applications and Toxicology of Cerium Oxide Nanoparticles. *International Journal of Environmental Research and Public Health*, 12, 1253-1278.
<https://doi.org/10.3390/ijerph120201253>

- Dahle, J. T., Livi, K., & Arai, Y. (2015). Effects of pH and Phosphate on CeO₂ Nanoparticle Dissolution. *Chemosphere*, 119, 1365-1371. <https://doi.org/10.1016/j.chemosphere.2014.02.027>
- Darr, J. A., Zhang, J., Makwana, N. M., & Weng, X. (2017). Continuous Hydrothermal Synthesis of Inorganic Nanoparticles: Applications and Future Directions. *Chemical Reviews*, 117, 11125-11238. <https://doi.org/10.1021/acs.chemrev.6b00417>
- Davis, J. (2021). *What is High-Resolution TEM (HR-TEM)?* [online] Available at: [https://www.azolifesciences.com/article/What-is-High-Resolution-TEM-\(HR-TEM\).aspx](https://www.azolifesciences.com/article/What-is-High-Resolution-TEM-(HR-TEM).aspx). [Assessed on 20 September 2023]
- Dhall, A., & Self, W. (2018). Cerium Oxide Nanoparticles: A Brief Review of their Synthesis Methods and Biomedical Applications. *Antioxidants*, 7(8), 97-100. <https://doi.org/10.3390/antiox7080097>
- Divya, T., Anjali, C., Sunajadevi, K. R., Anas, K., & Renuka, N. K. (2021). Influence of Hydrothermal Synthesis Conditions on Lattice Defects in Cerium Oxide. *Journal of Solid State Chemistry*, 300, 1-9. <https://doi.org/10.1016/j.jssc.2021.122253>
- Duncan, T. V. (2011). Applications of Nanotechnology in Food Packaging and Food Safety: Barrier Materials, Antimicrobials and Sensors. *Journal of Colloid and Interface Science*, 363(1), 1-24. <https://doi.org/10.1016/j.jcis.2011.07.017>
- Eka Putri, G., Rilda, Y., Syukri, S., Labanni, A., & Arief, S. (2021). Highly Antimicrobial Activity of Cerium Oxide Nanoparticles Synthesized Using *Moringa oleifera* Leaf Extract by a Rapid Green Precipitation Method. *Journal of*

Materials Research and Technology, 15, 2355-2364.

<https://doi.org/10.1016/j.jmrt.2021.09.075>

El-Sayed, G. O., Mohammed, T. Y., & Salama, A.A.A. (2013). Batch Adsorption of Maxilon Red GRL from Aqueous Solution by Natural Sugarcane Stalks Powder. *ISRN Environmental Chemistry*, 2013, 1-8. <https://doi.org/10.1155/2013/514154>

Farré, M., Gajda-Schranz, K., Kantiani, L., & Barceló, D. (2009). Ecotoxicity and Analysis of Nanomaterials in the Aquatic Environment. *Analytical and Bioanalytical Chemistry*, 393(1), 81-95. <https://doi.org/10.1007/s00216-008-2458-1>

Ghosh, S., Mashayekhi, H., Pan, B., Bhowmik, P., & Xing, B. (2008). Colloidal Behavior of Aluminum Oxide Nanoparticles as Affected by pH and Natural Organic Matter. *Langmuir*, 24(21), 12385-12391. <https://doi.org/10.1021/la802015f>

Gosens, I., Post, J. A., de la Fonteyne, L. J. J., Jansen, E. H. J. M., Geus, J. W., Cassee, F. R., & de Jong, W. H. (2010). Impact of Agglomeration State of Nano- and Submicron Sized Gold Particles on Pulmonary Inflammation. *Particle and Fibre Toxicology*, 7, 37-44. <https://doi.org/10.1186/1743-8977-7-37>

Gupta, K., Khandelwal, N., & Darbha, G. K. (2020). Removal and Recovery of Toxic Nanosized Cerium Oxide Using Eco-Friendly Iron Oxide Nanoparticles. *Frontiers of Environmental Science and Engineering*, 14(1), 15-25. <https://doi.org/10.1007/s11783-019-1194-4>

Gutierrez, A. M., Dziubla, T. D., & Hilt, J. Z. (2023). The Impact of Solution Ionic Strength, Hardness, and pH on the Sorption Efficiency of Polychlorinated

- Biphenyls in Magnetic Nanocomposite Microparticle (MNM) Gels. *Gels*, 9(4), 344-355. <https://doi.org/10.3390/gels9040344>
- Handy, R. D., Von Der Kammer, F., Lead, J. R., Hassellöv, M., Owen, R., & Crane, M. (2008). The Ecotoxicology and Chemistry of Manufactured Nanoparticles. *Ecotoxicology*, 17, 287-314. <https://doi.org/10.1007/s10646-008-0199-8>
- Hoecke, V. K., Schamphelaere, D. K. A. C., Meeren, V. D. P., Smagghe, G., & Janssen, C. R. (2011). Aggregation and Ecotoxicity of CeO₂ Nanoparticles in Synthetic and Natural Waters with Variable pH, Organic Matter Concentration and Ionic Strength. *Environmental Pollution*, 159(4), 170-176. <https://doi.org/10.1016/j.envpol.2010.12.010>
- Hosokawa, S. (2016). Synthesis of Metal Oxides with Improved Performance Using a Solvothermal Method. *Journal of the Ceramic Society of Japan*, 124, 870-874. <https://doi.org/10.2109/jcersj2.16109>
- Idrus, F. A., Chong, M. D., Abd Rahim, N. S., Mohd Basri, M., & Musel, J. (2017). Physicochemical Parameters of Surface Seawater in Malaysia Exclusive Economic Zones Off the Coast of Sarawak. *Borneo Journal of Resource Science and Technology*, 7(1), 1-10. <https://doi.org/10.33736/bjrst.388.2017>
- Inyinbor, A. A., Adekola, F. A., & Olatunji, G. A. (2016). Kinetics, Isotherms and Thermodynamic Modeling of Liquid Phase Adsorption of Rhodamine B Dye onto *Raphia Hookerie* Fruit Epicarp. *Water Resources and Industry*, 15, 14-27. <https://doi.org/10.1016/j.wri.2016.06.001>
- Iqbal, M. W., Yu, Y., & Simakov, D. S. A. (2021). Enhancing the Surface Area Stability of the Cerium Oxide Reverse Water Gas Shift Nanocatalyst via Reverse

- Microemulsion Synthesis. *Catalysis Today*, 407, 230-243.
<https://doi.org/10.1016/j.cattod.2021.11.029>
- Jayalath, S., Wu, H., Larsen, S. C., & Grassian, V. H. (2018). Surface Adsorption of Suwannee River Humic Acid on TiO₂ Nanoparticles: A Study of pH and Particle Size. *Langmuir*, 34(9), 3136-3145. <https://doi.org/10.1021/acs.langmuir.8b00300>
- Jiang, C., Aiken, G. R., & Hsu-Kim, H. (2015). Effects of Natural Organic Matter Properties on the Dissolution Kinetics of Zinc Oxide Nanoparticles. *Environmental Science and Technology*, 49(19), 11476-11484.
<https://doi.org/10.1021/acs.est.5b02406>
- Ju-Nam, Y., & Lead, J. R. (2008). Manufactured nanoparticles: An Overview of their Chemistry, Interactions and Potential Environmental Implications. *Science of the Total Environment*, 400(1-3), 396-414.
<https://doi.org/10.1016/j.scitotenv.2008.06.042>
- Kang, W., Ozgur, D. O., & Varma, A. (2018). Solution Combustion Synthesis of High Surface Area CeO₂ Nanopowders for Catalytic Applications: Reaction Mechanism and Properties. *ACS Applied Nano Materials*, 1(2), 675-685.
<https://doi.org/10.1021/acsanm.7b00154>
- Keller, A. A., Wang, H., Zhou, D., Lenihan, H. S., Cherr, G., Cardinale, B. J., Miller, R., & Zhaoxia, J. I. (2010). Stability and Aggregation of Metal Oxide Nanoparticles in Natural Aqueous Matrices. *Environmental Science and Technology*, 44(6), 1962-1967. <https://doi.org/10.1021/es902987d>
- Khan, A. J., Hanif, M., Javed, M. S., Hussain, S., Zhong, W., Saleem, M., & Liu, Z. (2020). Energy Storage Properties of Hydrothermally Processed, Nanostructured,

- Porous CeO₂ Nanoparticles. *Journal of Electroanalytical Chemistry*, 865, 1-23.
<https://doi.org/10.1016/j.jelechem.2020.114158>
- Khan, I., Saeed, K., Khan, I. (2019). Nanoparticles: Properties, Applications and Toxicities, *Arabian Journal of Chemistry*, 12(7), 908-931,
<https://doi.org/10.1016/j.arabjc.2017.05.011>.
- Khan, S. A., Khan, S. B., Khan, L. U., Farooq, A., Akhtar, K., & Asiri, A. M. (2018). Fourier transform infrared spectroscopy: Fundamentals and application in functional groups and nanomaterials characterization. In *Handbook of Materials Characterization*, pp. 317-344. Springer International Publishing.
https://doi.org/10.1007/978-3-319-92955-2_9
- Kumar, S., Ahmed, F., Shaalan, N. M., & Saber, O. (2021). Biosynthesis of CeO₂ Nanoparticles Using Egg White and their Antibacterial and Antibiofilm Properties on Clinical Isolates. *Crystals*, 11(6), 584-596.
<https://doi.org/10.3390/cryst11060584>
- Kurajica, S., Minga, I., Guliš, M., Mandić, V., & Simčić, I. (2016). High Surface Area Ceria Nanoparticles via Hydrothermal Synthesis Experiment Design. *Journal of Nanomaterials*, 2016, 1-8. <https://doi.org/10.1155/2016/7274949>
- Li, C., Jin, S., Guan, W., Tsang, C. W., Chu, W. K., Lau, W. K., & Liang, C. (2018). Chemical Precipitation Method for the Synthesis of Nb₂O₅ Modified Bulk Nickel Catalysts with High Specific Surface Area. *Journal of Visualized Experiments*, 2018(132), 1-8. <https://doi.org/10.3791/56987>

- Linse, P., & Wennerstrom, H. (2012). Adsorption versus Aggregation. Particles and Surface of the Same Material. *Soft Matter*, 8(8), 2486-2493. <https://doi.org/10.1039/c2sm07000f>
- Liu, B., Luo, H., Rong, H., Zeng, X., Wu, K., Chen, Z., Lu, H., & Xu, D. (2019). Temperature-Induced Adsorption and Desorption of Phosphate on Poly(Acrylic Acid-Co-N-[3-(Dimethylamino)Propyl]Acrylamide) Hydrogels in Aqueous Solutions. *Desalination and Water Treatment*, 160, 260-267. <https://doi.org/10.5004/dwt.2019.24351>
- Liu, Z., Wang, C., Hou, J., Wang, P., Miao, L., Lv, B., Yang, Y., You, G., Xu, Y., Zhang, M., & Ci, H. (2018). Aggregation, Sedimentation, and Dissolution of CuO and ZnO Nanoparticles in Five Waters. *Environmental Science and Pollution Research*, 25(31), 31240-31249. <https://doi.org/10.1007/s11356-018-3123-7>
- Loosli, F., Le Coustumer, P., & Stoll, S. (2015). Effect of Electrolyte Valency, Alginate Concentration and pH on Engineered TiO₂ Nanoparticle Stability in Aqueous Solution. *Science of the Total Environment*, 535, 28-34. <https://doi.org/10.1016/j.scitotenv.2015.02.037>
- Lv, X., Gao, B., Sun, Y., Shi, X., Xu, H., & Wu, J. (2014). Effects of Humic Acid and Solution Chemistry on the Retention and Transport of Cerium Dioxide Nanoparticles in Saturated Porous Media. *Water, Air, and Soil Pollution*, 225(10), 2167-2176. <https://doi.org/10.1007/s11270-014-2167-7>
- Farahmandjou, M. & Zarinkamar, M. T. F. (2016). Synthesis of Cerium Oxide (CeO₂) Nanoparticles Using Simple CO-Precipitation Method. *Revista Mexicana de Fisica*, 62, 496-499.

- Ma, X., Wang, Q., Rossi, L., & Zhang, W. (2016). Cerium Oxide Nanoparticles and Bulk Cerium Oxide Leading to Different Physiological and Biochemical Responses in *Brassica rapa*. *Environmental Science and Technology*, 50(13), 6793–6802. <https://doi.org/10.1021/acs.est.5b04111>
- Mahato, J. K., & Gupta, S. K. (2021). Exceptional Adsorption of Different Spectral Indices of Natural Organic Matter (NOM) by Using Cerium Oxide Nanoparticles (CONPs). *Environmental Science and Pollution Research*, 28(33), 45496-45505. <https://doi.org/10.1007/s11356-021-13964-w>
- Matilainen, A., Gjessing, E. T., Lahtinen, T., Hed, L., Bhatnagar, A., & Sillanpää, M. (2011). An Overview of the Methods Used in the Characterisation of Natural Organic Matter (NOM) in Relation to Drinking Water Treatment. *Chemosphere* 83, 1431-1442. <https://doi.org/10.1016/j.chemosphere.2011.01.018>
- Maurer-Jones, M. A., Gunsolus, I. L., Murphy, C. J., & Haynes, C. L. (2013). Toxicity of Engineered Nanoparticles in the Environment. *Analytical Chemistry*, 85(6), 3036-3049. <https://doi.org/10.1021/ac303636s>
- Mittal, S., & Pandey, A.K. (2014). Cerium Oxide Nanoparticles Induced Toxicity in Human Lung Cells: Role of ROS Mediated DNA Damage and Apoptosis. *BioMed Research International*. 24(1), 1-14. <https://doi.org/10.1155/2014/891934>
- Mohamad, S., Bakar, N. K. A., Ishak, A. R., Surikumaran, H., Pandian, K., Raoov, M., Zain, N. N. M., & Chandrasekaram, K. (2014). Removal of Phosphate by Paper Mill Sludge: Adsorption Isotherm and Kinetic Study. *Asian Journal of Chemistry*, 26(12), 3545-3552. <https://doi.org/10.14233/ajchem.2014.16227>

- Muduli, S. K., Wang, S., Chen, S., Ng, C. F., Huan, C. H. A., Sum, T. C., & Soo, H. Sen. (2014). Mesoporous Cerium Oxide Nanospheres for the Visible-Light Driven Photocatalytic Degradation of Dyes. *Beilstein Journal of Nanotechnology*, 5(1), 517-523. <https://doi.org/10.3762/bjnano.5.60>
- Nalabotu, S. K., Kolli, M. B., Triest, W. E., Ma, J. Y., Manne, N. D. P. K., Katta, A., Addagarla, H. S., Rice, K. M., & Blough, E. R. (2011). Intratracheal Instillation of Cerium Oxide Nanoparticles Induces Hepatic Toxicity in Male Sprague-Dawley Rats. *International Journal of Nanomedicine*, 6, 2327-2332. <https://doi.org/10.2147/ijn.s25119>
- Nandiyanto, A. B. D., Hofifah, S. N., Anggraeni, S., & Kurniwan, T. (2022). Isotherm Adsorption of 40-µm Zeolite Particles for Treatment of Dye Wastewater. *Journal of Engineering Science and Technology*, 17(2), 1265-1275.
- Nanja, A. F., Focke, W. W., & Musee, N. (2020). Aggregation and Dissolution of Aluminium Oxide and Copper Oxide Nanoparticles in Natural Aqueous Matrixes. *SN Applied Sciences*, 2(7), 1164-1180. <https://doi.org/10.1007/s42452-020-2952-4>
- Nikam, A. V., Prasad, B. L. V., & Kulkarni, A. A. (2018). Wet Chemical Synthesis of Metal Oxide Nanoparticles: A Review. *CrystEngComm*, 20(35), 5091-5107. <https://doi.org/10.1039/C8CE00487K>
- Nile, S. H., Baskar, V., Selvaraj, D., Nile, A., Xiao, J., & Kai, G. (2020). Nanotechnologies in Food Science: Applications, Recent Trends, and Future Perspectives. *Nano-Micro Letters*, 12, 45-79. <https://doi.org/10.1007/s40820-020-0383-9>

- Nurhasanah, I., Kadarisman, Gunawan, V., & Sutanto, H. (2020). Cerium Oxide Nanoparticles Application for Rapid Adsorptive Removal of Tetracycline in Water. *Journal of Environmental Chemical Engineering*, 8(1), 1-25. <https://doi.org/10.1016/j.jece.2019.103613>
- Nyoka, M., Choonara, Y. E., Kumar, P., Kondiah, P. P. D., & Pillay, V. (2020). Synthesis of Cerium Oxide Nanoparticles Using Various Methods: Implications for Biomedical Applications. *Nanomaterials*, 10, 1-22. <https://doi.org/10.3390/nano10020242>
- Ogholaja, T., Njobuenwu, D. O., & Fairweather, M. (2017). Particle Size Effects on Collision and Agglomeration in Turbulent Channel Flows. In *Computer Aided Chemical Engineering*, Vol.40, pp. 79-84, Elsevier B.V. <https://doi.org/10.1016/B978-0-444-63965-3.50015-5>
- Osmari, T. A., Gallon, R., Schwaab, M., Barbosa-Coutinho, E., Severo, J. B., & Pinto, J. C. (2013). Statistical Analysis of Linear and Non-Linear Regression for the Estimation of Adsorption Isotherm Parameters. *Adsorption Science and Technology*, 31(5), 433-458. <https://doi.org/10.1260/0263-6174.31.5.433>
- Pang, J. H., Liu, Y., Li, J., & Yang, X. J. (2019). Solvothermal Synthesis of Nano-CeO₂ Aggregates and its Application as a High-Efficient Arsenic Adsorbent. *Rare Metals*, 38(1), 73-80. <https://doi.org/10.1007/s12598-018-1072-4>
- Park, E. J., Choi, J., Park, Y. K., & Park, K. (2008). Oxidative Stress Induced by Cerium Oxide Nanoparticles in Cultured BEAS-2B Cells. *Toxicology*, 245(1-2), 90-100. <https://doi.org/10.1016/j.tox.2007.12.022>

- Piccin, J. S., Dotto, G. L., & Pinto, L. A. A. (2011). Adsorption Isotherms and Thermochemical Data of FDandC RED N° 40 Binding by Chitosan. *Brazilian Journal of Chemical Engineering*, 28(2), 295-304. <https://doi.org/10.1590/S0104-66322011000200014>
- Plakhova, T. V., Romanchuk, A. Y., Yakunin, S. N., Dumas, T., Demir, S., Wang, S., Minasian, S. G., Shuh, D. K., Tylliszczak, T., Shiryaev, A. A., Egorov, A. V., Ivanov, V. K., & Kalmykov, S. N. (2016). Solubility of Nanocrystalline Cerium Dioxide: Experimental Data and Thermodynamic Modelling. *Journal of Physical Chemistry C*, 120(39), 22615-22626. <https://doi.org/10.1021/acs.jpcc.6b05650>
- Pop, O. L., Mesaros, A., Vodnar, D. C., Suharoschi, R., Tăbăran, F., Mageruşan, L., Tóodor, I. S., Diaconeasa, Z., Balint, A., Ciontea, L., & Socaciu, C. (2020). Cerium Oxide Nanoparticles and their Efficient Antibacterial Application in vitro Against Gram-Positive and Gram-Negative Pathogens. *Nanomaterials*, 10(8), 1-15. <https://doi.org/10.3390/nano10081614>
- Prabaharan, D. M. D. M., Sadaiyandi, K., Mahendran, M., & Sagadevan, S. (2016). Structural, Optical, Morphological and Dielectric Properties of Cerium Oxide Nanoparticles. *Materials Research*, 19(2), 478-482. <https://doi.org/10.1590/1980-5373-MR-2015-0698>
- Putri, G. E., Arief, S., Jamarun, N., Gusti, F. R., & Zainul, R. (2019). Microstructural Analysis and Optical Properties of Nanocrystalline Cerium Oxides Synthesized by Precipitation Method. *Rasayan Journal of Chemistry*, 12(1), 85-90. <https://doi.org/10.31788/RJC.2019.1215029>

- Quik, J. T. K., Lynch, I., Hoecke, K. V., Miermans, C. J. H., Schamphelaere, K. A. C. D., Janssen, C. R., Dawson, K. A., Stuart, M. A. C., & Meent, D. V. D. (2010). Effect of Natural Organic Matter on Cerium Dioxide Nanoparticles Settling in Model Fresh Water. *Chemosphere*, 81(6), 711-715. <https://doi.org/10.1016/j.chemosphere.2010.07.062>
- Quik, J. T. K., Vonk, J. A., Hansen, S. F., Baun, A., & Meent, D. V. D (2011). How to Assess Exposure of Aquatic Organisms to Manufactured Nanoparticles? *Environment International*, 37, 1068-1077. <https://doi.org/10.1016/j.envint.2011.01.015>
- Rajeshkumar, S., & Naik, P. (2018). Synthesis and Biomedical Applications of Cerium Oxide Nanoparticles – A Review. *Biotechnology Reports*, 17, 1-5. <https://doi.org/10.1016/j.btre.2017.11.008>
- Rasmi, Y., Saloua, K. S., Nemati, M., & Choi, J. R. (2021). Recent Progress in Nanotechnology for Covid-19 Prevention, Diagnostics and Treatment. *Nanomaterials*, 11, 1788-1813. <https://doi.org/10.3390/nano11071788>
- Raval, N., Maheshwari, R., Kalyane, D., Youngren-Ortiz, S. R., Chougule, M. B., & Tekade, R. K. (2018). Importance of Physicochemical Characterization of Nanoparticles in Pharmaceutical Product Development. In *Basic Fundamentals of Drug Delivery*, pp. 369-400, Elsevier. <https://doi.org/10.1016/B978-0-12-817909-3.00010-8>
- Rogers, S., Rice, K. M., Manne, N. D., Shokuhfar, T., He, K., Selvaraj, V., & Blough, E. R. (2015). Cerium Oxide Nanoparticle Aggregates Affect Stress Response and

- Function in *Caenorhabditis elegans*. *SAGE Open Medicine*, 3, 1-9.
<https://doi.org/10.1177/2050312115575387>
- Ruiz-Hitzky, E., Darder, M., Wicklein, B., Ruiz-Garcia, C., Martín-Sampedro, R., del Real, G., & Aranda, P. (2020). Nanotechnology Responses to COVID-19. *Advanced Healthcare Materials*, 9, 1-26.
<https://doi.org/10.1002/adhm.202000979>
- Sabouri, Z., Sabouri, M., Amiri, M. S., Khatami, M., & Darroudi, M. (2020). Plant-Based Synthesis of Cerium Oxide Nanoparticles Using *Rheum turkestanicum* Extract and Evaluation of their Cytotoxicity and Photocatalytic Properties. *Materials Technology*, 37(8), 555-568.
<https://doi.org/10.1080/10667857.2020.1863573>
- Sahoo, T. R., & Prelot, B. (2020). Adsorption Processes for the Removal of Contaminants from Wastewater: The Perspective Role of Nanomaterials and Nanotechnology. In *Nanomaterials for the Detection and Removal of Wastewater Pollutants*, pp. 161-222, Elsevier. <https://doi.org/10.1016/B978-0-12-818489-9.00007-4>
- Saikia, H., Hazarika, K. K., Chutia, B., Choudhury, B., & Bharali, P. (2017). A Simple Chemical Route toward High Surface Area CeO₂ Nanoparticles Displaying Remarkable Radical Scavenging Activity. *ChemistrySelect*, 2(11), 2369-2375
<https://doi.org/10.1002/slct.201700354>
- Sankar, J., & Kumar, S. S. (2021). Synthesis and Characterization of Nano Cerium Oxide Using Hydrothermal Technique. *INCAS Bulletin*, 13(11), 173-181.
<https://doi.org/10.13111/2066-8201.2021.13.1.18>

- Sathyamurthy, S., Leonard, K. J., Dabestani, R. T., & Paranthaman, M. P. (2005). Reverse Micellar Synthesis of Cerium Oxide Nanoparticles. *Nanotechnology*, 16, 1960-1964. <https://doi.org/10.1088/0957-4484/16/9/089>
- Scirè, S., & Palmisano, L. (2020). Cerium and Cerium Oxide: A Brief Introduction. In *Cerium Oxide (CeO₂): Synthesis, Properties and Applications*, pp. 1-12, Elsevier. <https://doi.org/10.1016/b978-0-12-815661-2.00001-3>
- Shamhari, N. M., Wee, B. S., Chin, S. F., & Kok, K. Y. (2018). Synthesis and Characterization of Zinc Oxide Nanoparticles with Small Particle Size Distribution. *Acta Chimica Slovenica*, 65(3), 578-585. <https://doi.org/10.17344/acsi.2018.4213>
- Sharma, R., Sharma, K. S., & Kumar, D. (2022). Introduction to Nanotechnology. *Nanomaterials in Clinical Therapeutics: Synthesis and Applications*, 3-31. <https://doi.org/10.1002/9781119857747.ch1>
- Singh, A. K. (2016). Nanoparticle Ecotoxicology. In *Engineered Nanoparticles*, pp. 343-450, Elsevier. <https://doi.org/10.1016/b978-0-12-801406-6.00008-x>
- Singh, K. R. B., Nayak, V., Sarkar, T., & Singh, R. P. (2020). Cerium Oxide Nanoparticles: Properties, Biosynthesis and Biomedical Application. In *RSC Advances*, 10, 27194-27214. <https://doi.org/10.1039/d0ra04736h>
- Siqueira, J.R., Oliveira, O.N.J.R. (2017). 9 - Carbon-Based Nanomaterials. In *Nanostructures*, pp. 233-249, Elsevier Inc. <https://doi.org/10.1016/B978-0-323-49782-4.00009-7>
- Smith, D. J. (2015). CHAPTER 1: Characterization Of Nanomaterials Using Transmission Electron Microscopy. In *RSC Nanoscience and Nanotechnology*,

pp.1-29, Royal Society of Chemistry. <https://doi.org/10.1039/9781782621867-00001>

Tharayil, A., Rajakumari, R., Chirayil, C. J., Thomas, S., & Kalarikkal, N. (2021). A Short Review on Nanotechnology Interventions Against COVID-19. *Emergent Materials*, 4, 131-141. <https://doi.org/10.1007/s42247-021-00163-z>

Thomas, C. E., & Aust, S. D. (1986). Free Radicals and Environmental Toxins. *Annals of Emergency Medicine*, 15(9), 1075-1083. [https://doi.org/10.1016/S0196-0644\(86\)80132-9](https://doi.org/10.1016/S0196-0644(86)80132-9)

Tian, R., Xu, J., Luo, Q., Hou, C., & Liu, J. (2021). Rational Design and Biological Application of Antioxidant Nanozymes. *Frontiers in Chemistry*, 8, 1-21. <https://doi.org/10.3389/fchem.2020.00831>

Valsaraj, P. V., & Divyarthana., 2019. Structural, Optical and Antimicrobial Properties of Green Synthesized Cerium Oxide Nanoparticles. In: Sadasivuni, K.K., Kurian, J., Damodaran, S.V., Joseph, J., Joseph, D., Tom, E., and Thomas, D. *AIP Conference Proceedings*, Kerala, India, 12-14 June 2019, AIP Publishing. <https://doi.org/10.1063/1.5130232>

Walkey, C., Das, S., Seal, S., Erlichman, J., Heckman, K., Ghibelli, L., Traversa, E., McGinnis, J. F., & Self, W. T. (2015). Catalytic Properties and Biomedical Applications of Cerium Oxide Nanoparticles. *Environmental Science: Nano*, 2, 33-35. <https://doi.org/10.1039/c4en00138a>

Walton, R. I. (2011). Solvothermal Synthesis of Cerium Oxides. *Progress in Crystal Growth and Characterization of Materials*, 57(4), 93-108. <https://doi.org/10.1016/j.pcrysgrow.2011.10.002>

- Wang, J., Liu, Q., & Liu, Q. (2008). Ceria- and Cu-Doped Ceria Nanocrystals Synthesized by the Hydrothermal Methods. *Journal of the American Ceramic Society*, 91(8), 2706-2708. <https://doi.org/10.1111/j.1551-2916.2008.02418.x>
- Wu, C. Y. (2005). Nanoparticles and the Environment. *Journal of the Air and Waste Management Association*, 55(6), 708-746. <https://doi.org/10.1080/10473289.2005.10464656>
- Xu, C., & Qu, X. (2014). Cerium Oxide Nanoparticle: A Remarkably Versatile Rare Earth Nanomaterial for Biological Applications. *NPG Asia Materials*, 6, 1-16. <https://doi.org/10.1038/am.2013.88>
- Yan, M., Wei, W., & Zuoren, N. (2007). Influence of pH on Morphology and Formation Mechanism of CeO₂ Nanocrystalline. *Journal of Rare Earths*, 25(1), 53-57. [https://doi.org/10.1016/S1002-0721\(07\)60044-1](https://doi.org/10.1016/S1002-0721(07)60044-1)
- Yang, K., Lin, D., & Xing, B. (2009). Interactions of Humic Acid with Nanosized Inorganic Oxides. *Langmuir*, 25(6), 3571-3576. <https://doi.org/10.1021/la803701b>
- Yap, C. K., Chee, M. W., Shamarina, S., Edward, F. B., Chew, W., & Tan, S. G. (2011). Assessment of Surface Water Quality in the Malaysian Coastal Waters by Using Multivariate Analyses. *Sains Malaysiana*, 40(10), 1053-1064.
- You, G., Hou, J., Xu, Y., Miao, L., Ao, Y., & Xing, B. (2021). Surface Properties and Environmental Transformations Controlling the Bioaccumulation and Toxicity of Cerium Oxide Nanoparticles: A Critical Review. In *Reviews of Environmental Contamination and Toxicology*, pp. 155-206, Switzerland, Springer Nature. https://doi.org/10.1007/398_2020_42

- Younus, H. (2018). Younus, H. (2018). Therapeutic potentials of superoxide dismutase. *International Journal of Health Sciences*, 12(3), 88-93.
- Yurova, P. A., Tabachkova, N. Y., Stenina, I. A., & Yaroslavtsev, A. B. (2020). Properties of Ceria Nanoparticles with Surface Modified by Acidic Groups. *Journal of Nanoparticle Research*, 22(11). <https://doi.org/10.1007/s11051-020-05049-5>
- Zhang, M., Li, D., Ye, Z., Wang, S., Xu, N., Wang, F., Liu, S., Chen, J., & Gu, H. (2020). Effect of Humic Acid on the Sedimentation and Transport of Nanoparticles Silica in Water-Saturated Porous Media. *Journal of Soils and Sediments*, 20(2), 911-920. <https://doi.org/10.1007/s11368-019-02444-x>
- Zhu, X., Liu, J., Li, L., Zhen, G., Lu, X., Zhang, J., Liu, H., Zhou, Z., Wu, Z., & Zhang, X. (2023). Prospects for Humic Acids Treatment and Recovery in Wastewater: A Review. *Chemosphere*, 312(2), 137192. <https://doi.org/10.1016/j.chemosphere.2022.137193>

APPENDICES

Appendix A: Journal Publication

1. Wee, B.S., **Halim, S.A.b.E.** & Choo, T.F. (2024). Simple Hydrothermal Synthesis of Ultra-Small Cerium Oxide Nanoparticles. *Journal of Cluster Science*.
<https://doi.org/10.1007/s10876-024-02644-7>

Appendix B: Multi-point linear BET plot of CeO₂ NPs

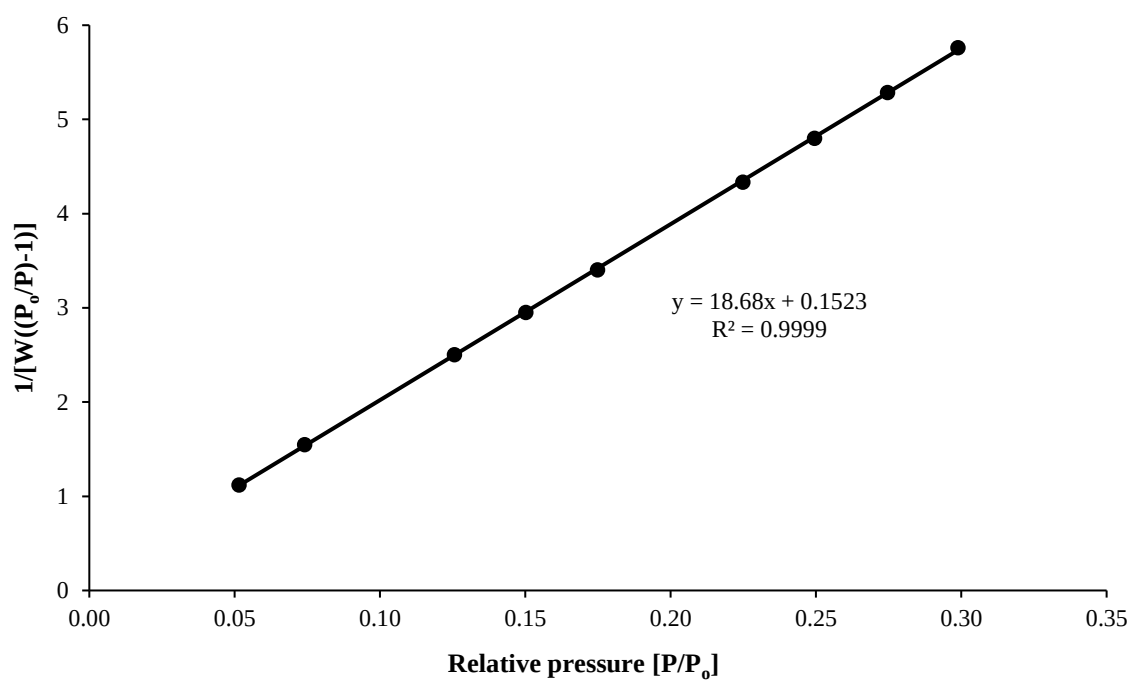


Figure 1: Multi-point linear BET plot of CeO₂ NPs

Appendix C: Standard Calibration Curve from ICP-OES Analysis

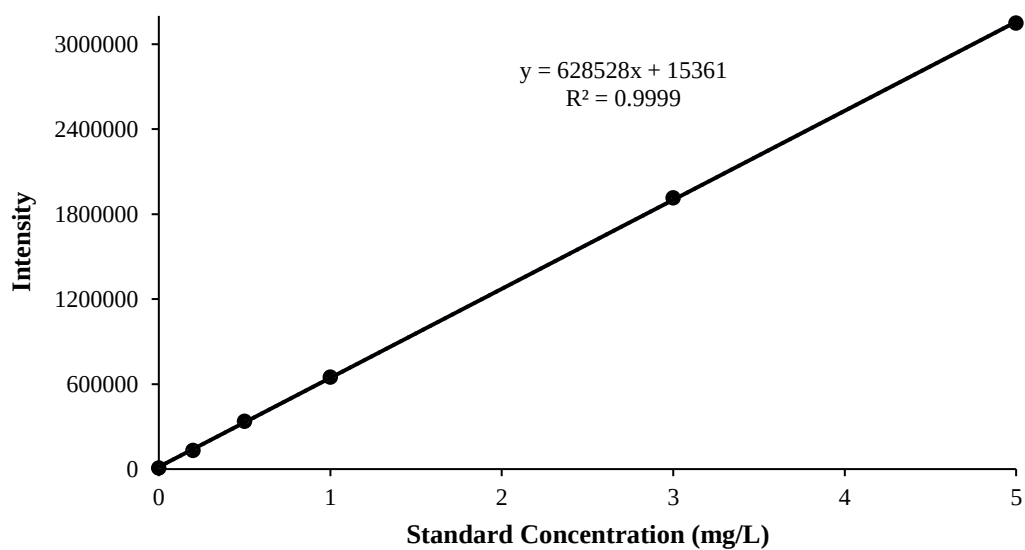


Figure 2: Standard calibration curve of Ce standards

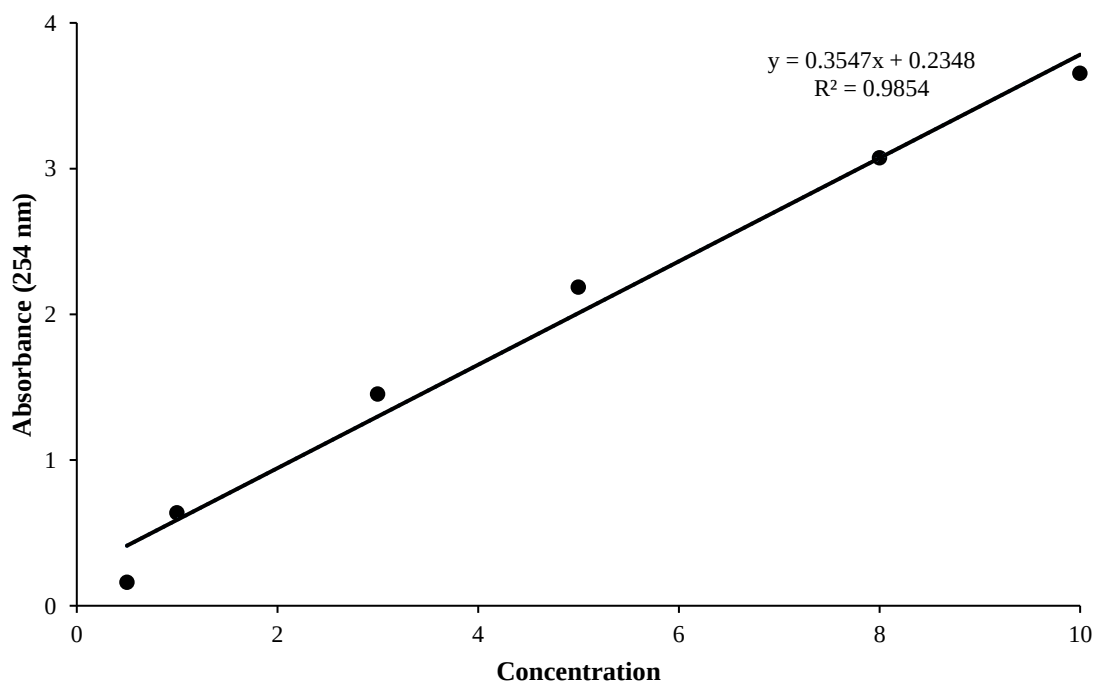


Figure 3: Standard calibration curve of humic acid

Appendix D: Amount of HA adsorbed on CeO₂ NPs at different pH and time.

Table 1. Amount of HA adsorbed on CeO₂ NPs at different pH and time.

Initial Humic Acid Concentration (mg/L)	Time (hour)	Amount of Humic Acid Adsorbed (mg/g)			
		pH 5	pH 6	pH 7	pH 9
5	0.5	24.53	19.83	19.80	15.54
	6	22.43	16.87	21.46	15.16
	12	18.84	16.37	19.76	14.63
	18	30.31	21.13	17.82	15.56
	24	23.67	18.20	20.38	17.42
	30	22.24	16.14	19.12	18.85
	36	16.49	14.14	15.09	13.56
	42	15.49	13.44	14.24	12.91
	48	16.18	14.02	14.49	13.77
10	0.5	54.74	41.23	37.03	24.94
	6	40.93	32.45	37.17	21.02
	12	48.92	30.63	37.98	16.17
	18	45.24	33.37	24.04	27.56
	24	36.30	33.37	30.19	25.84
	30	40.08	26.42	22.37	32.04
	36	40.93	28.65	22.13	21.99
	42	43.52	28.31	21.38	23.31
	48	34.76	33.01	20.23	24.12

Appendix E: Amount of Dissolved Ce^{4+} for the Influence of IS and pH on CeO_2 NPs.

Table 2. Dissolved Ce^{4+} under different IS and pH

Ionic Concentration (mM)	Time (hour)	pH				
		3	5	6	7	9
0	0.5	0.447	2.593	0.079	0.118	0.184
	2	0.276	2.211	0.105	0.211	0.290
	4	0.053	0.921	< LOD	0.310	0.362
	6	< LOD	0.711	0.066	0.290	0.276
	24	< LOD	0.355	< LOD	< LOD	0.382
	26	< LOD	0.092	< LOD	< LOD	0.513
	28	< LOD	< LOD	< LOD	< LOD	0.658
	30	< LOD	< LOD	< LOD	< LOD	0.547
	48	< LOD	< LOD	< LOD	< LOD	0.632
	50	< LOD	< LOD	< LOD	< LOD	0.645
	52	< LOD	< LOD	< LOD	< LOD	0.691
	54	< LOD	< LOD	< LOD	< LOD	0.711
3	0.5	0.553	3.764	1.671	0.184	1.619
	2	0.513	1.105	0.895	0.184	1.013
	4	0.368	0.290	0.592	< LOD	0.053
	6	0.461	0.026	0.487	< LOD	< LOD
	24	0.342	< LOD	0.329	< LOD	< LOD
	26	0.579	< LOD	0.290	< LOD	< LOD
	28	0.619	< LOD	0.184	< LOD	< LOD
	30	0.658	< LOD	0.276	< LOD	< LOD
	48	0.605	< LOD	< LOD	< LOD	< LOD
	50	1.053	< LOD	< LOD	< LOD	< LOD
	52	1.342	< LOD	< LOD	< LOD	< LOD
	54	1.527	< LOD	< LOD	< LOD	< LOD

< LOD: below the limit of detection of ICP-OES analysis (0.006 mg/L)

Appendix E1: Amount of Dissolved Ce^{4+} under the Influence of 0 mM IS and pH on CeO_2 NPs for every 3 replicates used.

Table 3: Amount of Dissolved Ce^{4+} under the influence of 0 mM IS and pH on CeO_2 NPs for every 3 replicates used.

pH	pH 3					pH 5				
Time (h)/ Replicate No.	1	2	3	Average	SD	1	2	3	Average	SD
0.5	0.038	0.038	0.039	0.038	0.0006	0.043	0.041	0.043	0.042	0.0012
2	0.079	0.077	0.081	0.079	0.0020	0.059	0.061	0.063	0.061	0.0020
4	0.094	0.090	0.069	0.084	0.0134	0.062	0.061	0.061	0.061	0.0006
6	0.079	0.077	0.087	0.081	0.0053	0.057	0.051	0.060	0.056	0.0046
24	0.095	0.099	0.098	0.097	0.0021	0.088	0.088	0.091	0.089	0.0017
26	0.102	0.102	0.107	0.104	0.0029	0.093	0.142	0.102	0.112	0.0261
28	0.119	0.119	0.117	0.118	0.0012	0.103	0.103	0.100	0.102	0.0017
30	0.138	0.126	0.157	0.140	0.0156	0.102	0.102	0.107	0.104	0.0029
48	0.135	0.131	0.138	0.135	0.0035	0.103	0.105	0.104	0.104	0.0010
50	0.132	0.129	0.128	0.130	0.0021	0.123	0.125	0.125	0.124	0.0012
52	0.128	0.126	0.130	0.128	0.0020	0.128	0.126	0.130	0.128	0.0020
54	0.127	0.124	0.122	0.124	0.0025	0.151	0.153	0.154	0.153	0.0015

Appendix E1: continued

pH	pH 6					pH 7				
Time (h)/ Replicate No.	1	2	3	Average	SD	1	2	3	Average	SD
0.5	0.000	0.000	0.000	0.000	0.0000	0.001	0.002	0.000	0.001	0.0010
2	0.000	0.000	0.000	0.000	0.0000	0.003	0.007	0.005	0.005	0.0020
4	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
6	0.000	0.000	0.000	0.000	0.0000	0.001	0.004	0.001	0.002	0.0017
24	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
26	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
28	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
30	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
48	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
50	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
52	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
54	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000

Appendix E1: continued

pH	pH 9				
Time (h)/ Replicate No.	1	2	3	Average	SD
0.5	0.059	0.059	0.060	0.059	0.0006
2	0.017	0.015	0.016	0.016	0.0010
4	0.003	0.004	0.002	0.003	0.0010
6	0.005	0.005	0.006	0.005	0.0006
24	0.000	0.000	0.000	0.000	0.0000
26	0.000	0.000	0.000	0.000	0.0000
28	0.000	0.000	0.000	0.000	0.0000
30	0.000	0.000	0.000	0.000	0.0000
48	0.000	0.000	0.000	0.000	0.0000
50	0.000	0.000	0.000	0.000	0.0000
52	0.000	0.000	0.000	0.000	0.0000
54	0.000	0.000	0.000	0.000	0.0000

Appendix E2: Amount of Dissolved Ce^{4+} under the Influence of 3 mM IS and pH on CeO_2 NPs for every 3 replicates used.

Table 4: Amount of Dissolved Ce^{4+} under the influence of 3 mM IS and pH on CeO_2 NPs for every 3 replicates used.

pH	pH 3					pH 5				
Time (h)/ Replicate No.	1	2	3	Average	SD	1	2	3	Average	SD
0.5	0.540	0.566	0.553	0.553	0.0132	4.053	3.751	3.487	3.764	0.2832
2	0.526	0.487	0.526	0.513	0.0228	1.224	1.184	0.908	1.105	0.1721
4	0.355	0.382	0.368	0.368	0.0132	0.513	0.197	0.158	0.290	0.1948
6	0.461	0.461	0.461	0.461	0.0000	0.053	0.000	0.026	0.026	0.0263
24	0.342	0.368	0.316	0.342	0.0263	0.000	0.000	0.000	0.000	0.0000
26	0.605	0.579	0.553	0.579	0.0263	0.000	0.000	0.000	0.000	0.0000
28	0.579	0.697	0.579	0.619	0.0684	0.000	0.000	0.000	0.000	0.0000
30	0.632	0.645	0.697	0.658	0.0348	0.000	0.000	0.000	0.000	0.0000
48	0.579	0.592	0.645	0.605	0.0348	0.000	0.000	0.000	0.000	0.0000
50	1.040	1.066	1.053	1.053	0.0132	0.000	0.000	0.000	0.000	0.0000
52	1.342	1.342	1.342	1.342	0.0000	0.000	0.000	0.000	0.000	0.0000
54	1.540	1.527	1.513	1.527	0.0132	0.000	0.000	0.000	0.000	0.0000

Appendix E2: continued

pH	pH 6					pH 7				
Time (h)/ Replicate No.	1	2	3	Average	SD	1	2	3	Average	SD
0.5	1.553	1.803	1.658	1.671	0.1255	0.132	0.211	0.211	0.184	0.0456
2	0.895	0.934	0.855	0.895	0.0395	0.184	0.171	0.197	0.184	0.0132
4	0.579	0.697	0.500	0.592	0.0994	0.000	0.000	0.000	0.000	0.0000
6	0.500	0.474	0.487	0.487	0.0132	0.000	0.000	0.000	0.000	0.0000
24	0.355	0.316	0.316	0.329	0.0228	0.000	0.000	0.000	0.000	0.0000
26	0.290	0.329	0.250	0.290	0.0395	0.000	0.000	0.000	0.000	0.0000
28	0.132	0.211	0.211	0.184	0.0456	0.000	0.000	0.000	0.000	0.0000
30	0.290	0.263	0.276	0.276	0.0132	0.000	0.000	0.000	0.000	0.0000
48	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
50	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
52	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
54	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000

Appendix E2: continued

pH	pH 9				
Time (h)/ Replicate No.	1	2	3	Average	SD
0.5	1.474	1.619	1.763	1.619	0.1448
2	0.869	1.355	0.816	1.013	0.2975
4	0.039	0.039	0.079	0.053	0.0228
6	0.000	0.000	0.000	0.000	0.0000
24	0.000	0.000	0.000	0.000	0.0000
26	0.000	0.000	0.000	0.000	0.0000
28	0.000	0.000	0.000	0.000	0.0000
30	0.000	0.000	0.000	0.000	0.0000
48	0.000	0.000	0.000	0.000	0.0000
50	0.000	0.000	0.000	0.000	0.0000
52	0.000	0.000	0.000	0.000	0.0000
54	0.000	0.000	0.000	0.000	0.0000

Appendix F: Amount of Dissolved Ce^{4+} for the Influence of HA and pH on CeO_2 NPs.

Table 2. Dissolved Ce^{4+} under the influence of different pH and HA concentrations

Humic Acid Concentration (mg/L)	Time (hour)	pH				
		3	5	6	7	9
5	0.5	0.038	0.042	< LOD	0.001	0.059
	2	0.079	0.061	< LOD	0.005	0.016
	4	0.084	0.061	< LOD	< LOD	0.003
	6	0.081	0.056	< LOD	0.002	0.005
	24	0.097	0.089	< LOD	< LOD	< LOD
	26	0.104	0.112	< LOD	< LOD	< LOD
	28	0.119	0.102	< LOD	< LOD	< LOD
	30	0.140	0.104	< LOD	< LOD	< LOD
	48	0.135	0.104	< LOD	< LOD	< LOD
	50	0.129	0.125	< LOD	< LOD	< LOD
	52	0.128	0.128	< LOD	< LOD	< LOD
	54	0.124	0.153	< LOD	< LOD	< LOD
10	0.5	0.046	0.007	< LOD	< LOD	0.329
	2	0.030	< LOD	< LOD	< LOD	0.211
	4	0.016	< LOD	< LOD	< LOD	0.092
	6	0.030	0.003	< LOD	< LOD	0.082
	24	0.053	0.020	< LOD	< LOD	0.039
	26	0.079	0.020	< LOD	< LOD	0.036
	28	0.125	0.030	< LOD	< LOD	0.016
	30	0.160	0.026	< LOD	< LOD	0.012
	48	0.184	0.030	< LOD	< LOD	0.007
	50	0.176	0.053	< LOD	< LOD	0.010
	52	0.196	0.046	< LOD	< LOD	0.023
	54	0.193	0.053	< LOD	0.004	0.007

< LOD: below the limit of detection of ICP-OES analysis (0.006 mg/L)

Appendix F1: Amount of Dissolved Ce^{4+} under the Influence of 5 mg/L HA and pH on CeO_2 NPs for every 3 replicates used.

Table 5: Amount of dissolved Ce^{4+} under the influence of 5 mg/L HA and different pH on CeO_2 NPs for every 3 replicates used.

pH	pH 3					pH 5				
Time (h)/ Replicate No.	1	2	3	Average	SD	1	2	3	Average	SD
0.5	0.038	0.038	0.039	0.038	0.0006	0.043	0.041	0.043	0.042	0.0012
2	0.079	0.077	0.081	0.079	0.0020	0.059	0.061	0.063	0.061	0.0020
4	0.094	0.090	0.069	0.084	0.0134	0.062	0.061	0.061	0.061	0.0006
6	0.079	0.077	0.087	0.081	0.0053	0.057	0.051	0.060	0.056	0.0046
24	0.095	0.099	0.098	0.097	0.0021	0.088	0.088	0.091	0.089	0.0017
26	0.102	0.102	0.107	0.104	0.0029	0.093	0.142	0.102	0.112	0.0261
28	0.119	0.119	0.117	0.118	0.0012	0.103	0.103	0.100	0.102	0.0017
30	0.138	0.126	0.157	0.140	0.0156	0.102	0.102	0.107	0.104	0.0029
48	0.135	0.131	0.138	0.135	0.0035	0.103	0.105	0.104	0.104	0.0010
50	0.132	0.129	0.128	0.130	0.0021	0.123	0.125	0.125	0.124	0.0012
52	0.128	0.126	0.130	0.128	0.0020	0.128	0.126	0.130	0.128	0.0020
54	0.127	0.124	0.122	0.124	0.0025	0.151	0.153	0.154	0.153	0.0015

Appendix F1: continued

pH	pH 6					pH 7				
Time (h)/ Replicate No.	1	2	3	Average	SD	1	2	3	Average	SD
0.5	0.000	0.000	0.000	0.000	0.0000	0.001	0.002	0.000	0.001	0.0010
2	0.000	0.000	0.000	0.000	0.0000	0.003	0.007	0.005	0.005	0.0020
4	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
6	0.000	0.000	0.000	0.000	0.0000	0.001	0.004	0.001	0.002	0.0017
24	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
26	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
28	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
30	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
48	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
50	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
52	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
54	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000

Appendix F1: continued

pH	pH 9				
Time (h)/ Replicate No.	1	2	3	Average	SD
0.5	0.059	0.059	0.060	0.059	0.0006
2	0.017	0.015	0.016	0.016	0.0010
4	0.003	0.004	0.002	0.003	0.0010
6	0.005	0.005	0.006	0.005	0.0006
24	0.000	0.000	0.000	0.000	0.0000
26	0.000	0.000	0.000	0.000	0.0000
28	0.000	0.000	0.000	0.000	0.0000
30	0.000	0.000	0.000	0.000	0.0000
48	0.000	0.000	0.000	0.000	0.0000
50	0.000	0.000	0.000	0.000	0.0000
52	0.000	0.000	0.000	0.000	0.0000
54	0.000	0.000	0.000	0.000	0.0000

Appendix F2: Amount of Dissolved Ce^{4+} under the Influence of 10 mg/L HA and pH on CeO_2 NPs for every 3 replicates used.

Table 6: Amount of Dissolved Ce^{4+} under the influence of 10 mg/L HA and different pH on CeO_2 NPs for every 3 replicates used.

pH	pH 3					pH 5				
Time (h)/ Replicate No.	1	2	3	Average	SD	1	2	3	Average	SD
0.5	0.044	0.045	0.049	0.046	0.0026	0.007	0.008	0.007	0.007	0.0006
2	0.030	0.030	0.029	0.030	0.0006	0.000	0.000	0.000	0.000	0.0000
4	0.017	0.015	0.016	0.016	0.0010	0.000	0.000	0.000	0.000	0.0000
6	0.030	0.033	0.028	0.030	0.0025	0.004	0.003	0.001	0.003	0.0015
24	0.080	0.043	0.035	0.053	0.0240	0.020	0.026	0.014	0.020	0.0060
26	0.079	0.077	0.082	0.079	0.0025	0.020	0.018	0.021	0.020	0.0015
28	0.122	0.127	0.125	0.125	0.0025	0.031	0.030	0.028	0.030	0.0015
30	0.157	0.159	0.163	0.160	0.0031	0.026	0.028	0.024	0.026	0.0020
48	0.180	0.185	0.186	0.184	0.0032	0.030	0.027	0.032	0.030	0.0025
50	0.179	0.156	0.194	0.176	0.0191	0.053	0.053	0.054	0.053	0.0006
52	0.194	0.197	0.196	0.196	0.0015	0.044	0.045	0.049	0.046	0.0026
54	0.196	0.191	0.193	0.193	0.0025	0.051	0.056	0.053	0.053	0.0025

Appendix F2: continued

pH	pH 6					pH 7				
Time (h)/ Replicate No.	1	2	3	Average	SD	1	2	3	Average	SD
0.5	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
2	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
4	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
6	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
24	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
26	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
28	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
30	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
48	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
50	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
52	0.000	0.000	0.000	0.000	0.0000	0.000	0.000	0.000	0.000	0.0000
54	0.000	0.000	0.000	0.000	0.0000	0.003	0.003	0.007	0.004	0.0023

Appendix F2: continued

pH	pH 9				
Time (h)/ Replicate No.	1	2	3	Average	SD
0.5	0.357	0.313	0.316	0.329	0.0246
2	0.226	0.169	0.237	0.211	0.0365
4	0.095	0.093	0.089	0.092	0.0031
6	0.077	0.084	0.084	0.082	0.0040
24	0.037	0.041	0.039	0.039	0.0020
26	0.033	0.038	0.037	0.036	0.0026
28	0.017	0.015	0.016	0.016	0.0010
30	0.012	0.013	0.011	0.012	0.0010
48	0.007	0.008	0.007	0.007	0.0006
50	0.009	0.009	0.011	0.010	0.0012
52	0.024	0.023	0.021	0.023	0.0015
54	0.006	0.009	0.007	0.007	0.0015