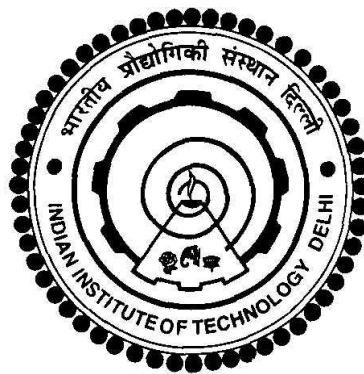


**STABILITY OF MIXTURE OF NANOPARTICLES AND  
ASSOCIATED HEALTH RISKS FROM ENVIRONMENT**

**TANUSHREE PARSAI**



**DEPARTMENT OF CIVIL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

**JANUARY, 2021**

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ASSOCIATED HEALTH RISKS FROM ENVIRONMENT**

*by*

**TANUSHREE PARSAI**

**DEPARTMENT OF CIVIL ENGINEERING**

*Submitted*

**in fulfilment of the requirements of the degree of Doctor of Philosophy**

*to the*



**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

**JANUARY 2021**

## **Dedication**

*This thesis is dedicated to my beloved Parents...*

*Mumma and Papa*

*And*

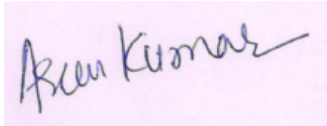
*To my Brother and Sister*

*for their endless love, support and encouragement...*

## THESIS CERTIFICATE

This is to certify that the thesis entitled “**Stability of mixture of nanoparticles and associated health risks from environment**” submitted by **Tanushree Parsai** to the Indian Institute of Technology, Delhi for the award of the degree of **Doctor of Philosophy** is a bona fide record of research work carried out by her under my supervision. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

**Prof. Arun Kumar**

A handwritten signature in blue ink on a light pink rectangular background. The signature reads "Arun Kumar" in a cursive script.

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## ABSTRACT

This research was carried out to understand the stability of mixture of nanoparticles in aquatic system and risk associated with these mixtures of nanoparticles. Stability of mixture in different suspension chemistry was studied to understand role of various factors such as pH, ionic strength, presence of clay, humic acid (HA) and organic compound. For ZnO and CuO nanoparticles, model equations were developed for predicting values of their (i) aggregation rate constant, (ii) settling rate constant, (iii) difference in zeta potential, (iv) percentage change of metal in suspension function of pH, ionic strength and NP concentration. In another experiment, heteroaggregation of mixture of ZnO and CuO nanoparticles (NPs) with clay was analysed by determining aggregation rate constant (0.281-8.63nm/min), critical coagulation concentration (120.7mM,1144mM), and attachment efficiency for mixture system. This study provided information on aggregate characterization of mixture of metal oxide nanoparticles (ZnO and CuO) in HA and clay presence, which is useful in understanding aggregation formation and in characterizing exposure dose for environmental risk assessment. Effect of organic pollutant (Bisphenol A) on stability of mixture of nanoparticles (TiO<sub>2</sub>+ZnO) released from sunscreen in seawater was also determined and presence of BPA was found to increase or decrease the aggregation state of system depending on pH condition and NPs ratio condition. The information about aggregation rate constant and size change may help in assessing aquatic risk and human health risk due to mixture of nanoparticles in seawater. Human health risk assessment framework to estimate health risks due to exposure of mixture of nanoparticles (NP) and ions from surface water, exposure of nanoparticles through fish grown in NP contaminated water was developed for the first time in this study. Maximum allowable concentration of NPs in various exposure medium as single NPs and mixture of NPs were determined in this study (value= 0.207mg/L for ZnO NPs as well as CuO NPs when present in mixture). Similarly, maximum allowable values of NP were found to be 0.115mg/L, 0.152mg/L, and  $1.77 \times 10^7$  mg/L for single ZnO, CuO, and TiO<sub>2</sub> NP, respectively for oral ingestion route. Top three most hazard causing NPs were suggested in various medium which require urgent monitoring and also values of their revised guidelines in mixture condition were also proposed. The identified top three risk-posing NPs can be used for conducting toxicity studies for mixture of NPs and long-term monitoring so that it can be used in the proposed framework for setting up guideline values for NPs in mixture for environment. Overall, stability of mixture of nanoparticles considering various transformation process needs to be analysed to determine various kinetic parameters for aggregation, dissolution process and

incorporate these nanoparticle characteristics for predicting their fate in aquatic system and defining risk.

**Keywords: Nanoparticles, Mixture, Health risks, Stability**

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## सार

यह शोध जलीय प्रणाली में नैनोकणों के मिश्रण की स्थिरता और नैनोकणों के इन मिश्रणों से जुड़े जोखिम को समझने के लिए किया गया था। विभिन्न निलंबन रसायन विज्ञान में मिश्रण की स्थिरता का अध्ययन पीएच, आयनिक शक्ति, मिट्टी की उपस्थिति, ह्यूमिक एसिड (एचए) और कार्बनिक यौगिक जैसे विभिन्न कारकों की भूमिका को समझने के लिए किया गया था। ZnO और CuO नैनोकणों के लिए, मॉडल समीकरणों को उनके (i) एकत्रीकरण दर स्थिर (एग्रीगेशन रेट कांस्टेंट), (ii) स्थिरांक दर स्थिर (सेटलिंग रेट कांस्टेंट), (iii) जीटा पोटेन्शियल में अंतर, (iv) पीएच के निलंबन समारोह में धातु का प्रतिशत परिवर्तन, आयनिक शक्ति और नैनोकणों की एकाग्रता के सांद्रता की भविष्यवाणी करने के लिए विकसित किया गया था। एक अन्य प्रयोग में, क्ले के साथ ZnO और CuO नैनोकणों के मिश्रण एकत्रीकरण का विश्लेषण एकत्रीकरण दर स्थिर (0.281-8.63nm/ min), क्रिटिकल कागुलेशन कॉन्सेंट्रेशन (120.7mM, 1144mM) और मिश्रण प्रणाली के लिए अनुलग्नक दक्षता (अटैचमेंट एफिफिकेन्सी) का निर्धारण करके किया गया था। इस अध्ययन ने ह्यूमिक एसिड और मिट्टी की उपस्थिति में धातु ऑक्साइड नैनोकणों (ZnO और CuO) के मिश्रण के समग्र लक्षण वर्णन पर जानकारी प्रदान की, जो एकत्रीकरण गठन को समझने और पर्यावरणीय जोखिम मूल्यांकन के लिए जोखिम की खुराक को चिह्नित करने में उपयोगी है। समुद्री जल में सनस्क्रीन से जारी नैनोकणों (TiO<sub>2</sub> और ZnO) के मिश्रण की स्थिरता पर कार्बनिक प्रदूषक (बिस्फेनॉल ए) का प्रभाव भी निर्धारित किया गया था और पीएच स्थिति और नैनोकण अनुपात स्थिति के आधार पर प्रणाली के एकत्रीकरण की दर को बढ़ाने या घटाने के लिए बीपीए (बिस्फेनॉल ए) की उपस्थिति पाई गई थी। समुद्री जल में नैनोकणों के मिश्रण से जलीय जोखिम और मानव स्वास्थ्य जोखिम का आकलन करने में एकत्रीकरण दर स्थिर और आकार परिवर्तन की जानकारी मदद कर सकती है। सतह के पानी से नैनोकणों और आयनों के मिश्रण के संपर्क में आने के कारण स्वास्थ्य जोखिमों का अनुमान लगाने के लिए मानव स्वास्थ्य जोखिम मूल्यांकन ढांचा, दूषित पानी में उगाई गई मछली के माध्यम से नैनोकणों का प्रदर्शन इस अध्ययन में पहली बार नैनोकणों के लिए किया गया था। नैनोकण के मिश्रण के रूप में विभिन्न संसर्ग माध्यमों में नैनोकणों की अधिकतम स्वीकार्य एकाग्रता इस अध्ययन में निर्धारित की गई थी (ZnO नैनोकण के साथ ही CuO नैनोकण के लिए सांद्रण = 0.207mg / L)। इसी प्रकार, नैनोकण के अधिकतम स्वीकार्य सांद्रण क्रमशः 0.115mg /L, 0.152mg / L और  $1.77 \times 10^7$  mg/L एकल ZnO, CuO, और TiO<sub>2</sub> नैनोकण के लिए मौखिक अंतर्ग्रहण (ओरल एक्सपोज़र) मार्ग के लिए पाए गए। नैनोकणों के शीर्ष तीन सबसे खतरनाक नैनोकण का सुझाव विभिन्न माध्यमों में दिया गया था, जिसमें तत्काल निगरानी की आवश्यकता होती है और मिश्रण स्थिति में उनके संशोधित

दिशानिर्देशों के सांद्रण को भी प्रस्तावित किया गया था। पहचान किए गए शीर्ष तीन जोखिम वाले नैनोकण का उपयोग नैनोकण के मिश्रण और दीर्घकालिक निगरानी के लिए विषाक्तता अध्ययन करने के लिए किया जा सकता है ताकि पर्यावरण के लिए नैनोकण मिश्रण में दिशानिर्देश मान स्थापित करने के लिए प्रस्तावित ढांचे में इसका उपयोग किया जा सके। कुल मिलाकर, विभिन्न रूपांतरण प्रक्रिया पर विचार करने वाले नैनोकणों के मिश्रण की स्थिरता को एकत्रीकरण, विघटन प्रक्रिया के लिए विभिन्न गतिज मापदंडों को निर्धारित करने और जलीय प्रणाली में अपने भाग्य की भविष्यवाणी करने और जोखिम को परिभाषित करने के लिए इन नैनोकणों की विशेषताओं को शामिल करने के लिए विश्लेषण करने की आवश्यकता है।

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## List of Abbreviations

NP	Nanoparticle
pH <sub>zpc</sub>	Point of zero charge
HDD	Hydrodynamic diameter(nm)
ΔZP	Zeta potential difference
RfD	Reference Dose
CuO NP	Copper Oxide Nanoparticles
ZnO NP	Zinc Oxide Nanoparticles
Ext Zn	Background Zinc ion
Ext Cu	Background copper ion
UF	Uncertainty Factor
HHRA	Human Health Risk Assessment
BAF	Bio accessible fraction
SSD	Species Sensitivity Distribution
RQ	Risk quotient
HQ	Hazard Quotient
HI	Hazard Index
IR	Ingestion rate
ADD	Average Daily Dose
GF	Gastric Fluid
NOAEL	No observed Adverse Effect Level
LOAEL	Lowest Observed Adverse Effect Level
WOE	Weight-of-evidence
POD	Point of Departure
ECHA	European Chemical Agency
ATSDR	Agency for Toxic Substances and Disease Registry
HSDB	Hazardous Substances Data Bank
TOXNET	Toxicology Data Network
BCF	Bio-Concentration Factor
BAF	Bio-Assimilation Factor
PEC	Predicted Environmental Concentration

ADD	Average Daily Dose
CDF	Cumulative Density Function
TEM	Transmission Electron Microscopy
ATSDR	Agency for Toxic Substances and Disease Registry
IRIS	Integrated Risk Information System
OECD	The Organization for Economic Co-operation and Development
HSDB	Hazardous Substances Data Bank
FDA	Food and Drug Administration
USEPA	United States Environmental Protection Agency
OSHA	Occupational Safety and Health Administration
WHO	World health Organization
ECHA	European Chemicals Agency
EFSA	European Food Safety Authority
EU	European Union
GV	Guideline Value
RQ	Risk Quotient
RfD	Reference Dose
RfC	Reference Concentration
MCL	Maximum Contaminant Level
PEL	Permissible Exposure Limit
NIOSH	National Institute for Occupational Safety and Health