Estd. 1889

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CERTIFICATE

I hereby certify that, this is the revised version of the thesis entitled ***"Modified iron-based nanoparticles for the removal of dyes and hexavalent chromium from water"*** *submitted by* ***Ms. Anju Rose Puthukkara P*** *under my guidance after incorporating the necessary corrections/suggestions made by the adjudicators.*

Dr. Sunil Jose T

(Research Guide)

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11-03-2022

CERTIFICATE

This is to certify that the thesis entitled ***"Modified iron-based nanoparticles for the removal of dyes and hexavalent chromium from water"*** *is an authentic record of research work carried out by* ***Ms. Anju Rose Puthukkara P*** *under my supervision in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry of University of Calicut and further that no part thereof has been presented before for any other degree.*

Dr. Sunil Jose T

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DECLARATION

I hereby declare that the thesis entitled ***"Modified iron-based nanoparticles for the removal of dyes and hexavalent chromium from water"****, submitted to the University of Calicut in partial fulfillment of the requirement for the award of the Degree of Doctor of Philosophy in Chemistry is a bonafied research work done by me under the supervision and guidance of* ***Dr. Sunil Jose T****, Assistant Professor, Research and PG Department of Chemistry, St. Thomas College (Autonomous), Thrissur*

I further declare that this thesis has not previously formed the basis of any degree, diploma or any other similar title.

11-03-2022

ANJU ROSE PUTHUKKARA P

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Dedication

To my parents

For raising me to believe that anything is possible

To my husband

For encouraging me to achieve everything possible

To my child

For always being the loving and understanding son

PREFACE

Water pollution is one of the major environmental problems faced by the world, drastically influenced by population stress and industrialisation. Iron-based nanoparticles have a significant role in the remediation of water pollutants as a cost-effective material. Among the iron-based nanoparticles, zero valent iron (Fe^0) particles have had a remarkable position in wastewater treatment for the last few years due to their environmental compatibility, high reactivity, fast kinetics and magnetic property. However, rapid oxidation and agglomeration are the significant drawbacks of Fe^0 nanoparticles. The thesis reports the studies conducted to develop stable and efficient Fe^0 based nanoparticles by incorporating different materials. The efficiency of prepared materials was evaluated by analysing the removal efficiency of organic dyes and hexavalent chromium (Cr(VI)) from water. The factors influencing the removal of Cr(VI) and malachite green dye were also discussed in the thesis.

The whole thesis is divided into eight chapters. A general introduction along with the literature review of properties, synthesis methods, modification routes and application of Fe^0 nanoparticles are discussed in chapter 1. Chapter 2 includes the materials and instruments used for the synthesis, characterisation and application of the studies. In addition, the general method followed for the Cr(VI) and dye removal studies were also discussed here.

In chapter 3, Fe^0 and the second metal (Cu, Ni and Zn) loaded Fe^0 nanoparticles were prepared by the liquid-phase reduction method. The establishment of the second metal on Fe^0 and characteristics of the prepared nanoparticles were studied by HRTEM, XRD and EDAX. This chapter compares the efficiency of Fe^0 and bimetallic iron nanoparticles to remove hexavalent chromium and organic dyes from water. Various techniques were used to confirm the removal mechanism of Cr(VI) and malachite green dye from water.

The application of biopolymer chitosan, as a stabilising agent of Fe^0 and Fe/Ni nanoparticles were discussed in chapter 4. The characteristics of chitosan stabilised Fe nanoparticles were studied by the HRTEM, XPS and FTIR techniques. The prepared nanoparticles were applied to remove Cr(VI) and triphenylmethane dyes and the removal efficiency was evaluated. The influence of chitosan and nickel loading on Fe^0 for removing malachite green dye was also discussed.

Chapter 5 of the thesis mainly focuses on the preparation of novel TiO_2-zeolite composites with different percentages of TiO_2 and their application for Fe^0 stabilisation. The TiO_2-zeolite composite was prepared by sonication of ingredients followed by the hydrothermal method. The incorporation of Fe nanoparticles into TiO_2-zeolite composite was done using wet impregnation method followed by the liquid-phase reduction. For comparative study with TiO_2-zeolite-Fe nanoparticles, TiO_2-Fe and zeolite-Fe nanoparticles were also prepared. The characterisation of TiO_2 and zeolite modified Fe nanoparticles were done by XRD, HRTEM, EDAX, FTIR and UV-visible spectroscopy. The study evaluated the efficiency of prepared TiO_2-Fe, zeolite-Fe and TiO_2-zeolite-Fe nanoparticles to remove Cr(VI) and malachite green dye from water. GC-MS/MS was done to identify the malachite green degradation products using TiO_2-zeolite-Fe nanoparticles.

Chapter 6 deals with the preparation of Fe nanoparticles using two novel plant extracts from *Abrus precatorius* (AP) and *Strychnos nux-vomica* (SN). GC-MS/MS analysis has been done to identify the volatile bioactive components present in the plant extracts. The iron nanoparticles were synthesised by simple mixing of iron salt solution and plant extracts and the characterisation of Fe nanoparticles were done by UV-visible spectroscopy, FTIR, HRTEM and EDAX. The efficiency of AP-Fe and SN-Fe nanoparticles for removing Cr(VI) and malachite green dye from water was also analysed.

The preparation of plant extract from *Triphala* (TP), an ayurvedic composition and synthesis of Fe nanoparticles from it were discussed in chapter 7. Fe nanoparticles using *Terminalia chebula, Terminalia belerica* and *Phyllanthus emblica* were also synthesised for comparative study. GC-MS/MS analysis has been done to identify bioactive components in *Triphala* extract. The UV-visible spectroscopy, FTIR, HRTEM and EDAX techniques were used to characterise the prepared Fe nanoparticles. The Cr(VI) and malachite green dye removal efficiency of prepared nanoparticles are also analysed.

Chapter 8 includes the brief conclusion of all the previous chapters and it also contains the practical significance of the work and the future scope of our investigation.

LIST OF ABBREVIATIONS

Fe^0	Zero valent iron
UV	Ultraviolet
HRTEM	High-resolution transmission electron microscopy
FTIR	Fourier-transform infrared spectroscopy
EDAX	Energy-dispersive X-ray spectroscopy
XRD	X-ray powder diffraction
XPS	X-ray photoelectron spectroscopy
GC-MS/MS	Gas chromatography coupled with triple quadrupole tandem mass spectrometry
LC-MS/MS	Liquid chromatography coupled with triple quadrupole tandem mass spectrometry
MG	Malachite green
MB	Methyl blue
MO	Methyl orange
MLB	Methylene blue
Cr(VI)	Hexavalent Chromium
Cr(III)	Trivalent Chromium
CS	Chitosan
T-Z	TiO_2-zeolite
AP	*Abrus precatorius*
SN	*Strychnos nux-vomica*
TP	*Triphala*
TB	*Terminalia belerica*
PE	*Phyllanthus emblica*
TC	*Terminalia chebula*

ABSTRACT

Industrialisation and urbanisation led to the contamination of groundwater and surface water to a large extent. Zero valent iron nanoparticle (Fe^0) is a promising material for water contaminants remediation due to its large surface area to volume ratio coupled with greater reactivity. However, the Fe^0 rapidly reacts with air and water and results in reduced reactivity due to oxidation and agglomeration. Our work aims to prepare modified iron-based nanoparticles with improved reactivity, stability and dispersibility without much secondary pollution. The reactivity of modified iron-based nanoparticles was evaluated by measuring the removal efficiency of hexavalent chromium and malachite green dye from water. Iron nanoparticle modification was done by depositing catalytic metal to the Fe^0 surface, encapsulating it with polymer and depositing Fe^0 on solid support. Green synthesis of Fe nanoparticles was done using plant extracts, which neither requires additional energy nor produces any hazardous by-products.

The specific objectives of our work include (1) synthesise Fe^0 and bimetallic Fe based nanoparticles using the chemical reduction method, (2) prepare chitosan stabilised Fe^0 and Fe/Ni nanoparticles, (3) develop zeolite and TiO_2 based novel composites as supporting and stabilising material for Fe^0 nanoparticles, (4) prepare Fe nanoparticles using plant extracts as green reducing agents, (5) evaluate the efficiency of synthesised nanoparticles in the removal of toxic hexavalent chromium and toxic dyes under different reaction conditions such as initial pollutant concentration, nanoparticle dosage, contact time and solution pH.

The synthesis of modified iron nanoparticles was carried out under an inert atmosphere and the collected samples were lyophilised. The characterisation of prepared nanoparticles was performed using UV-visible spectroscopy, HRTEM, EDAX, FTIR, XRD and XPS. UV-visible spectroscopy was used to analyse the remaining concentration of the pollutant after treating with Cr(VI) and toxic dyes. The degradation product of malachite green was analysed by LC-MS/MS and GC-MS/MS. The various modifications done on iron nanoparticles in our study improved the reactivity and stability of the iron nanoparticles.