Development of UF membrane by coating using Green synthesized Copper oxide nanoparticle for remediation of heavy metals

A thesis submitted in partial fulfilment of the requirements for the award of the degree of

Master of Engineering in Metallurgical Engineering

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By

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WEST BENGAL

DEDICATED

TO MY BELOVED PARENTS

Certificate

This is to certify that the thesis entitled **"Development of UF membrane by coating using Green synthesized metal oxide nanoparticle for remediation of heavy metals**" has been carried out by **Indrajit Bag (Examination Roll No.** M4MET24004 **and Registration No. 163721 of 2022-23)** under my guidance and supervision and accepted in partial fulfillment for the degree of Master of Engineering in Metallurgical and Material Engineering from Jadavpur University. To the best of our knowledge the content of this thesis or any parts thereof have not been previously submitted for the award of any degree or diploma.

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Declaration of Originality and Compliance of Academic Ethics

I hereby declare that this thesis "**Development of UF membrane by coating using Green synthesized metal oxide nanoparticle for remediation of heavy metals**" contains literature survey and original research work by me, as a part of my M.E. Degree in Metallurgical Engineering during the academic session 2022-2024. All information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by this rules and conduct, I have fully cited and referred all material and results that are not original to this work.

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The foregoing thesis is hereby approved as a creditable study of an engineering subject and presented in a manner satisfactory to warrant acceptance as a pre- requisite to the degree for which it has been submitted. It is understood that by this approval the undersigned does not necessarily endorse or approve any statement made, opinion expressed or conclusion drawn there in but approve the thesis only for which it is submitted.

Committee on final examination for the evaluation of the thesis

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Signature of Examiners

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Abstract

Copper Oxide Nanoparticles were green synthesized using extracts of *Anabaena variabilis*. The synthesized nanoparticles were washed, dried and kept for further use. Samples were characterized in terms of X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscope (FESEM), Energy Dispersive X-Ray Spectroscopy (EDS), Brunauer-Emmett-Teller (BET) etc. Average crystallite size of Nano powders was calculated from full width at half maxima of XRD Peaks. Debye-Scherrer formula was used for the calculation of crystallite size which was found to be 22.0684 nm. Spherical morphology of the NPs was confirmed from FESEM micrographs. BET surface area of CuO NPs was 3.718 m^2/g. Phthalates and Paraben were used to observe removal efficiency of synthesized CuO NPs. CuO nanoparticle was used for development of UF ceramic membrane by coating on inside wall of 300mm length ceramic support (OD/ID 10/7 mm). BET Surface area of unsupported membrane was determined to be 6.355 m^2/g. Flux Values of 249LMH and 230LMH for Phthalates and paraben respectively was obtained after 120mins of filtration study. Removal Efficiency of 92% & 96.3 % for phthalates and paraben was obtained.

Keywords: Nanoparticles, Copper Oxide, Green synthesis, FTIR, XRD, FESEM, EDS, Adsorption, PPCPs removal.

Chapter 1

INTRODUCTION

Chapter 1

1.1 Nano scale Technology

Nanoscience is emerging as a cutting-edge technology that has the potential to create new revolutions in every field of science [1]. Nanotechnology can be seen as one of the most challenging areas of recent research. Nanoparticles, unlike many of their counterparts, have become very popular among researchers in recent years due to their unique and interesting properties that can be used in various applications. These technologies include 'research and technology advances' at the atomic, molecular or macromolecular level. It is related to nanoparticles consisting of atoms or molecules between 1 nm and 100 nm in size in at least one dimension [2,3]. According to the UK Standards Institutions [4], the definitions of the various scientific terms used are:

- **Nanoscale:** approximately 1 to 1000 nm in size.
- **Nanoscience:** It is the science that deals with the study of objects at the atomic, molecular and macromolecular scale and understanding their sizes and other factors that affect their structure and properties.
- **Nanotechnology:** It is a technology that concerns the design, characterization, production and use of structures, materials and systems by using the size and shape of materials at the nanoscale.
- **Nanomaterials:** Materials that have at least one dimension at the nanoscale (<100nm).
- **Nanomaterials:** Materials that have one or more dimensions on the nanoscale.
- **Nanoparticles (NPs):** Nanoparticles with three external dimensions on the nanoscale. Nanorod or nanoplate is a convenient term used in the field of nanoparticles when long and short length nanomaterials are different.
- **Nanofiber:** When there are two similar dimensions at the nanoscale and a third dimension emerges in the nanomaterial, it is called nanofiber.

Observing and using materials at the nanoscale has been available since 1931, when Knoll and Ruska invented the electron microscope. A famous lecture by Richard P. (“There's Plenty of Room at the Bottom”). Feynman's work in 1959 [5] was a great inspiration for future research.

Nanotechnology has provided many new solutions in various fields such as material science, biology, optics and electronics [6]. Nanotechnology provides fundamental knowledge of materials and materials at the nanoscale to create and use structures, materials, and systems with new properties, functions, dimensions. It has inspired researchers and technologists to work in the field of nanotechnology in many ways like Engineering, biology, science and chemistry. The application of functional nanostructures and nanosystems can lead to significant changes in industry, agriculture, medicine, healthcare and especially the environment [7].

1.2 Green technology

Green technology and **nanotechnology** intersect in fascinating ways, and the adoption of green principles in nanotechnology has gained momentum. Let's explore why green technology is increasingly favoured over traditional chemical processes in the realm of nanotechnology:

1.2.1 Environmental Impact

- Green nanotechnology emphasizes environmentally friendly practices. It aims to reduce contaminants, minimize waste, and prevent harmful processes.
- By incorporating green chemistry and engineering principles, nanotechnology strives to create products with less environmental impact.
- Traditional chemical processes often involve hazardous chemicals, whereas green nanotechnology focuses on safer alternatives.

1.2.2 Principles of Green Chemistry

- The 12 Green Chemistry Principles, initially published in 1998, provide a framework accepted not only by chemists but also by designers and policymakers.
- These principles guide the synthesis and manufacture of engineered nanomaterials (ENMs) to minimize environmental harm and health risks.
- Green nanotechnology aligns with these principles, ensuring responsible design, production, and disposal of nanomaterials.

1.2.3 Economic and Social Benefits

- Green nanotechnology aims to create energy-efficient products and processes that are both environmentally and economically sustainable.
- By using renewable inputs, minimizing energy consumption, and reducing toxic ingredients, it contributes to a more sustainable society.
- The concept of the 'Green Economy' recognizes the interplay between the environment and the economy, emphasizing proper management of this relationship [8].

1.2.4 Specific Applications

- Nanoscale membranes can separate desired chemical reaction products from waste materials, promoting efficiency.
- Nanoscale catalysts enhance chemical reactions while minimizing waste.
- Nano sensors play a crucial role in process control systems.
- These applications demonstrate how green nanotechnology integrates principles of green chemistry and engineering to create innovative solutions [9].

1.3 Classification of Nanomaterials

Nanomaterials (NM) can be both naturally occurred or man-made i.e., engineered nanomaterials. Based on the chemical composition engineered NMs can be classified broadly in three major groups:

- Inorganic materials; such as metal NPs and quantum dots (QDs)
- Organic NMs; such as carbon-based materials
- Mixed organic– inorganic NMs, for example, gold NPs functionalized with cyclodextrins.

However, in general, five major groups are distinguished [9]:

- carbon NMs,
- metal oxide nanoparticles,
- zero-valence metal NPs,
- Quantum Dots
- dendrimers.

1.3.1 Metal Oxide Nanoparticles

Among different nanomaterials metal-oxide NPs are most important from their usage frequency [10]. In spite of long-term presence in the bulk form, nano-sized forms of titanium dioxide, alumina and iron oxides have entered the market recently and are being used in different consumer products. Zinc oxide (ZnO) and TiO_2 are widely exploited due to their photolytic properties [11]. Nanoparticles like alumina (Al_2O_3) derivatives are applied in materials science (e.g., polymer composites and core–shell NPs for different applications, including catalysis [12], or to improve the mechanical characteristics of different materials), for example, use of Al_2O_3 NPs up to maximum replacement level of 2.0% in cement mortar produces concrete with improved split tensile strength [13].

Copper Oxide NPs (CuO) also finds extensive applications in sunscreens, cosmetics and bottle coatings because of their ultraviolet blocking capability [14,15]. Other relevant metal-oxide NPs are based on cerium dioxide (CeO_2,) chromium dioxide (CrO_2) molybdenum trioxide (MoO_3), bismuth trioxide (Bi_2O_3) and binary oxides {e.g., lithium-cobalt dioxide ($LiCoO_2$) or indium-tin oxide (InSnO)} [16,17]. CeO_2 is finding major uses as a combustion catalyst in diesel fuels to improve emission quality [18], and in solar cells, gas sensors, oxygen pumps, and metallurgical and glass or ceramic applications.

1.4 Different synthesis methods for Metal Oxide nanoparticles

There are different synthesis routes available for synthesis of metal oxide nanoparticles. They can be mainly classified into three main types, viz.:

- Chemical synthesis.

- Physical synthesis.
- Biological synthesis.

A graphical representation of different available synthesis routes is shown below:

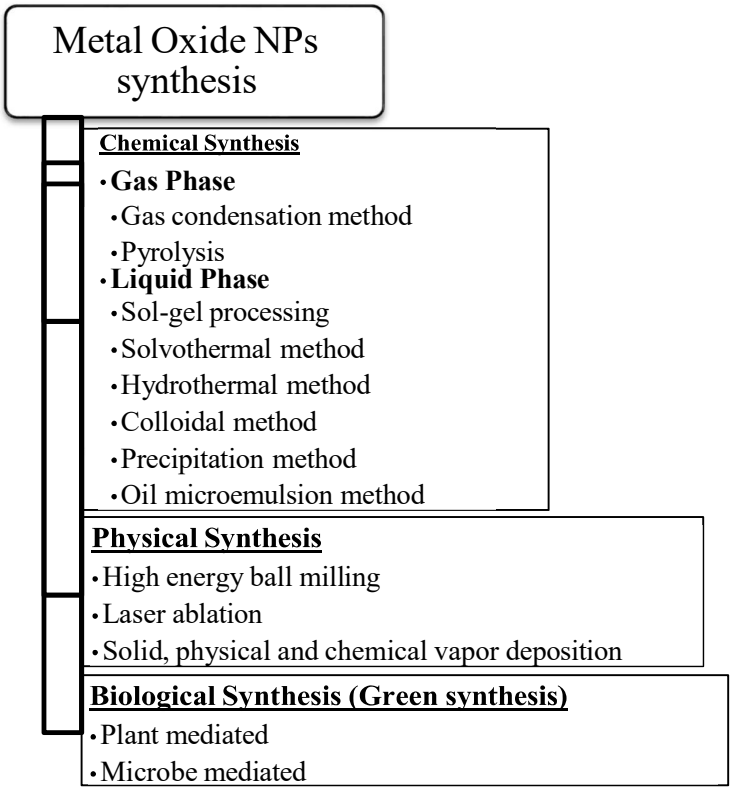

Fig 1: Different synthesis routes of Metal oxide NPs

Based on the starting phase of synthesis these routes can further be grouped into two methods:

1. Top-down approach: Here bulk material is used as starting material for nanoparticle synthesis. These bulk materials are further processed to reduce its size up to Nano size via different physical, chemical and mechanical processes. E.g. Mechanical milling (Ball milling, Mechanochemical method), Laser ablation, Sputtering. E.g. Mechanical milling (Ball milling, Mechanochemical method), Laser ablation, Sputtering [19].

2. Bottom-up approach: Here the synthesis starts from atoms and molecules. E.g., Solid state methods (Physical vapor deposition Chemical vapor deposition), Liquid state synthesis methods (Sol gel methods Chemical reduction Hydrothermal method Solvothermal method), Gas phase methods (Spray pyrolysis Laser ablation Flame pyrolysis), Biological or green synthesis methods (Bacteria Fungus Yeast Algae Plant extract) and other methods like

Electrodeposition process Microwave technique Supercritical fluid precipitation process Ultrasound technique. [19]

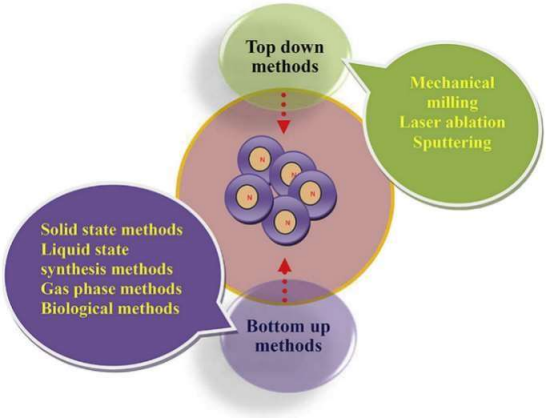

Fig 2: Top down and bottom-up approach

However, nanoparticles manufactured by physical methods usually require more control to obtain the desired shape and size [20]. Chemical parameters (e.g., pH, temperature, synthesis) can produce NPs with different desired properties. Size, shape and crystal structure of NPs, as well as composition (single or complex), determine their mobility, chemical and physical properties in different systems. Despite the fact that the majority of NPs are produced by physical methods such as arc discharge, evaporation, laser ablation, among others, chemical methods have demonstrated to be more effective in controlling size and shape [21]. Physical processes require high vacuum and they are energy consuming. Chemical methods such as precipitation, co-precipitation, solvothermal, sol–gel, sonochemical, spray pyrolysis, hydrothermal, and electrodeposition processes [22-26] have an advantage of being cost effective and they are mass-production oriented. In contrast, their disadvantage lies in their uncongenial nature to the environment.

On other hand greener approaches are environmentally friendly and also easy to synthesis methods. Biosynthesis of nanoparticles using plant-based extracts is one such promising method. Indeed, this biosynthesis approach has been proved to be effective in the synthesis of metal oxide nanoparticles [27-29].

Copper Oxide nanoparticles like other metal oxide NPs can be synthesized via many of the above-mentioned synthesis routes. Looking at the above-mentioned advantages and disadvantages, Plant (Algae) mediated method under bio synthesis (**green synthesis)** are chosen as economic, scalable and sustainable options to synthesize Copper Oxide NPs for the present study.

1.4.1 Algae mediated (green synthesis) method

This method comes under the biological synthesis method. Here degradation and metabolization of chemical substances are done by environmentally friendly biological processes. Here plants or plant parts are used to synthesize the NPs. In

this case plant part (e.g., leaf) extracts are used as precursors instead of chemical agents. The green synthesis method employing biological plant extracts is one of the more extensively acknowledged routine due to its several advantages, such as requiring no additional chemicals, simple, environmentally friendly, inexpensive and reliable method. [30-39].

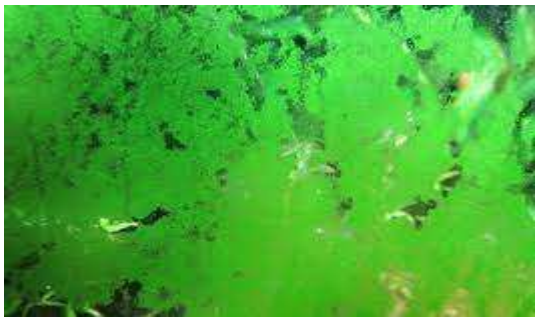

Fig 3: Cultured Algae medium

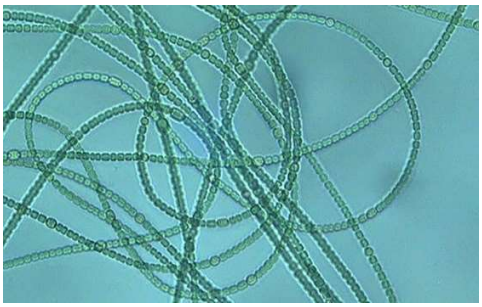

Fig 4: Microscopic view of Algae

1.5 Application of CuO NPs in Waste Water Treatment

Copper oxide nanoparticles (CuO NPs) have been found to have significant applications in wastewater treatment. Here are some key points:

- **Sorption of Contaminants**: CuO NPs have shown promising characteristics as a sorbent to remove arsenic from water [30].
- **Effect on Biological Wastewater Treatment**: A study conducted at the Czestochowa University of Technology investigated the effect of CuO NPs on wastewater treatment in a sequencing batch reactor (SBR) bioreactor [31]. It was found that at a concentration of 3 mg/L CuO NPs, the degree of wastewater treatment decreased from 92.17% to 71.9% (based on the Total Organic Carbon - TOC) [31]. This suggests that while CuO NPs can be effective in treating wastewater, their concentration needs to be carefully managed to avoid negatively affecting the activity of activated sludge in SBR reactors[31].
- **Nanotechnology in Wastewater Treatment**: The use of nanomaterials, including CuO NPs, is a promising solution to the problem of residual contaminants in wastewater [32]. Nanoparticles have unique properties that allow them to efficiently remove residual contaminants while being cost-effective and environmentally friendly [32].
- **Environmental Impact**: The widespread use of nanoparticles inevitably leads to their release into the environment, particularly from wastewater treatment plants [32]. During wastewater treatment, nanoparticles undergo aggregation, sedimentation, and transformation, which may cause their concentration in effluents and the sludge [32].

1.6 Application of CuO NPs in remediation of Pharmaceutical and Personal Care Products (PPCPs) from wastewater

Copper oxide nanoparticles (CuO NPs) have a wide range of applications in pharmaceutical and personal care products. Here are some key points:

- **Antimicrobial Activity**: CuO NPs are known for their tremendous antimicrobial activity and are used as potential disinfectants against nosocomial infections [33]. They are applied in wound dressings due to their strong bactericidal property against different Gram +ve and Gram -ve bacterial strains [33].
- **Biomedical Applications**: The versatile nature of CuO NPs has made them an imperative nanomaterial being employed in nanomedicine [33]. They have been used in various biomedical applications highlighting antimicrobial, anticancer, and antioxidant studies[33].
- **Antiviral, Antidiabetic, and Antiparasitic Applications**: Despite the aforementioned applications of CuO NPs, they can be widely used in many other applications, such as antiviral, antidiabetic, and antiparasitic [33]. However, only limited reports are available regarding these applications of CuO NPs [33].
- **Photocatalytic Degradation of Pharmaceuticals**: As part of the degradation process of pharmaceuticals, photocatalytic nanomaterials such as CuO are used[34]. A photocatalyst is a semiconductor material that is activated by light and breaks down pollutants, transforming them into harmless materials [34].

1.7 Harmful Phthalates and Paraben

Phthalates and parabens are commonly used in a variety of products, but they have been linked to several health concerns. Here's why they can be harmful:

Phthalates:

- Phthalates are chemicals found in many products, including food sources and personal care products [35].
- They are linked to serious health issues, especially for pregnant women, unborn babies, and young children [35].
- Studies have connected phthalates to health conditions related to the liver, kidneys, lungs, and the endocrine and reproductive systems [35].
- Phthalates are linked to reduced testosterone levels and low sperm counts in males. In all sexes, high phthalate exposure may lead to reduced fertility [35].
- Despite these concerns, the Food and Drug Administration (FDA) doesn't discourage the use of all phthalates [35].

Parabens:

- Parabens are man-made chemicals that prevent mold and bacteria growth. They are used to preserve cosmetics, medicines, foods, drinks, and personal care items [36].
- Early research showed parabens affect hormone function. This can cause changes in cholesterol, blood sugar, thyroid, and immune function[36].
- The risk of allergies, obesity, and infertility has also been associated with the use of parabens [36].
- Parabens are endocrine-disrupting chemicals (EDCs) that cause problems to the endocrine system[36].
- Other identified risks of paraben exposure include the risk of cancer. Parabens can activate the hormone estrogen. High levels of estrogen have been found in breast cancer tumors [36].

1.8 Role of CuO NPs in remediation of Phthalates and Paraben

Copper oxide (CuO) nanoparticles have shown potential in the remediation of phthalates and parabens, which are common contaminants in the environment. Here are some key points:

- **Phthalates Remediation**: Phthalates are high production volume chemicals used extensively as plasticizers. They are reported to leach into their surroundings from plastic products and are now a ubiquitous environmental contaminant [37]. Current remediation strategies for phthalate removal such as adsorption, advanced oxidation, and microbial degradation have been highlighted [37].
- **Parabens Remediation**: Similar to phthalates, parabens can also be remediated using CuO nanoparticles. However, the specific mechanisms and effectiveness of CuO in paraben remediation are not well-documented and require further research.
- **Photocatalytic Degradation**: CuO nanoparticles, often in combination with other materials like ZnO, have been used as effective photocatalysts for environmental remediation [38]. Photocatalysts are activated by light and break down pollutants, transforming them into harmless materials [38]. This process could potentially be applied to the degradation of phthalates and parabens.
- **Membrane separation**: An indigenous development of CuO/TiO_2 coated ceramic ultrafiltration membrane has been reported for the removal of emerging contaminants like phthalates and parabens [39].

1.9 Hybrid Technology

Hybrid technology involving ceramic membranes and nanoparticles has shown significant potential in various fields, particularly in water treatment and environmental remediation. Here are some key points:

- **Nanoparticles Functionalized Ceramic Membranes**: These are used intensively for desalination and wastewater treatment [40]. Water filtration using ceramic membranes

exhibits high performance compared to polymeric membranes due to properties such as high resistance to fouling, permeability, rejection rate, and chemical stability [40]. The performance of nanocomposite ceramic membranes has been improved due to the development in nanotechnology [40].

- **Clay-Based Nanocomposites and Hybrid Membrane**: These are getting attention among researchers in the field of water treatment [41]. The chapter focuses on the clay-based hybrid membrane potentials in the removal of different types of wastewater pollutants and discusses the approaches involved in the clay-based hybrid membrane synthesis, characterization, and their application in wastewater treatment [41].
- **Hybrid Cell Membrane-Coated Nanoparticles**: The process involves the fusion of membranes originating from distinct cell types and their subsequent coating onto nanoparticle cores, forming hybrid cell membrane-coated nanoparticles [42].
- **Nanoparticle/C Hybrid CMS Membranes**: This review discusses the hybridized nanoparticle selection and effect of the species, quantities, and particle sizes of the foreign materials on CMS membrane characteristics and performance [43].
- **Hybrid Ceramic Materials for Environmental Applications**: Ceramic nanocomposites or hybrids have emerged as novel materials to create multi-functional engineered materials for various applications such as self-cleaning devices, filters for water purification and industrial applications, adsorbents, sensors, photocatalysts and photovoltaics, electronic devices, corrosion protective coatings, bactericide surfaces, coatings for biomedical applications, porous carriers, and bioactive scaffolds [44].

In the present study, algae mediated green synthesis of CuO NPs was conducted. *Anabaena* sp. was used which was cultured in the laboratory aseptically. Algal extract acted as reducing agent for synthesizing CuO NPs from $CuSO_4.5H_2O$. The prepared nanoparticles were then used for coating on inside wall of single channel ceramic membrane. Membranes were then fired at 550℃ and studied for removal of phthalates and parabens. Domestic wastewater was collected from nearby sewage pumping station and simulated by adding phthalate and paraben. Nanoparticles were added in the feed tank (20L) and operated in recirculation mode. Permeate was collected at specific time interval and subjected to characterization for removal of phthalate and paraben. Flux profile and percent removal was calculated and noted.

Chapter 2

LITERATURE REVIEW

Metal oxide nanoparticles represent a group of chemical materials of great interest, considering the potential technological applications of these materials. Research towards the synthetic approach to nanostructures has been greatly influenced by the impact of these materials on industries such as pharmaceuticals, information technology, catalysis, energy storage and sensing. This review discusses advancement in traditional metal oxide nanoparticle techniques as well as investments in green synthetic procedures. This new method could make it possible to reduce the energy power of metal oxide nanoparticles synthesis and the characteristics of the results can be exploited for use in different technologies. This is because the final structures and morphology are closely related to the chosen synthesis route. This work will also present some examples of high-level characterization techniques that will help us understand these structure-property-function relations with nano-sized metal oxides.

The surface, optical, thermal, and electrical properties of metal and metal oxide nanoparticles are among the many physicochemical traits that set them apart from their original bulk counterparts. Reducing or oxidizing/precipitating agents are used while synthesizing metal and metal oxide nanoparticles accordingly. [45]

The noble metal-incorporated materials are created using modified hydrothermal processes. Clusters of colloidal nanocrystals are typically produced by solvothermal techniques. This synthesis technique makes use of non-aqueous solutions. The benefit that is present on both the hydrothermal and sol-gel methods will be present in the product that is synthesized utilizing this process. [46-48]

AgNPs are gaining popularity due to their extensive use in a variety of products, including antimicrobial agents, food packaging materials, food storage containers, fabrics, room sprays, detergents, shampoo, soap, toothpaste, paint, waste water treatment and so on. [49]

The citrate method is a traditional technique for creating gold nanoparticles. It is a very common technique; however, it once had a lot of problems, such stability and dispersity. It's also known as the Turkevich approach. As time passed, new techniques for synthesis emerged. By using new techniques, the method of regulating the synthesis's circumstances have produced outcomes that are better controlled in terms of size. [50]

TiO_2 nanoparticles are among the most widely used nanoparticles, with applications including cosmetic and skin care products, antibacterial and cleaning air products, paints, and organic matter decomposition in wastewater. [51] Several other

nanoparticles are used in various industries to improve the quality of products and services. For example, Cerium dioxide nanoparticles (CeO_2 NP) are primarily used in the automotive and semiconductor industries.

Copper nanoparticles (Cu NPs) are widely used in a variety of commercial applications, including antimicrobial agents, catalysts, gas sensors, electronics, batteries, heat transfer fluids etc. [52]. Dey et al. studied about the synthesis and characterization of mango leaves biosorbents for removal of iron and phosphorous from contaminated waste water. The optimal preparation of mango leaves as biosorbents for iron and phosphorous sorption processes was associated with the modification in inherent textural and morphological characteristics and they also do not show any specific change in their adsorption capacity even after reusing for iron and phosphorous removal [53].

Melkamu et al. provided a fast and simple green synthesis method for the synthesis of Copper oxide nanoparticles using non-toxic *Justicia Schimperiana* plant leaf extract (JSPLE) from Ethiopia. Presence of various functional groups responsible for reducing and stabilizing during the biosynthesis process is confirmed by FTIR analysis. From XRD analysis it was confirmed that the synthesized NPs were crystalline in nature with monoclinic structure and the average size of the crystallite particles were found to be 21.8 nm [54].

Rajabai et al. synthesized Paracetamol- CuO nano particles using microwave method. Precursor was prepared using aqueous solution of paracetamol, copper sulphate and NaOH in the molar ratio of 0.1:0.1:0.2 and it was prepared in 100 ml of double distilled UV – treated water. The mixture was constantly stirred for an hour and then heated in a domestic microwave oven (480W, 92^0C) for 10 mins. And the precipitate was separated, dried to form CuO NPs. Using X-ray diffraction analysis, particle size of paracetamol-CuO NPs was determined as 18.527 nm. SEM micrograph of CuO NPs shows well defined, spherical particles of NPs and the grain size is in the range of 20 nm [55].

CuO NPs were synthesized using the leaf extract of Justicia adhatoda and it was observed that the leaf extract has good capability of acting as reducing agent for conversion of Copper ions to CuO NPs. In this method, Justicia adhatoda leaf extract and $CuCl_2$ solution in different concentrations were taken in a beaker and heated for several minutes at room temperature and after few hours formation of NPs started. From the XRD analysis it was noticed that CuO NPs formation faces central to the cubic assembly. From FESEM analysis, it was observed that size of synthesized NPs was found to be 45.07 nm and is of spherical shape [56]. An eco-friendly technique was adopted by Ijaz et al. to synthesize CuO NPs and to evaluate their antimicrobial, antioxidant and photo-catalytic dye degradation potentials. Aqueous extract of *Abutilon indicum* was used for the synthesis. After successful synthesis of CuO NPs, it was confirmed that NPs with hexagonal, wurtzite and sponge crystal structure was formed [57].

The leaf extract of *Ocimum basilicum* was used by Katoglu et al. for the synthesis of CuO NPs. Synthesis of NPs was carried out by mixing copper sulphate dehydrate ($CuSO_4.5H_2O$) with the leaf extract. NPs exhibited antibacterial activity against pathogenic bacterial strains *Escherichia coli* and *Staphylococcus aureus*. Size of the NPs was found to be ranging under 70 nm [58].

Leaf extract of Eucalyptus Globoulus was used by Alhalili et al. to synthesize copper oxide nanoparticles. Using SEM analysis, mean particle size of 88 nm was obtained and the average crystalline size was found to be around 85.80 nm was observed by the Debye–Scherrer formula. Crystalline and monoclinic phase of CuO NPs was obtained by this method. Methyl orange was used to investigate the adsorption characteristics of the nano-adsorbents and adsorption efficiency of 95 mg/g was attained at room temperature [59].

Similar research work was carried out by Sylvia Devi et al. to demonstrate the adsorption capacity of CuO NPs by using leaf extracts of *Centella asiatica* (L.). [60] This technique can be utilized to create copper oxide NPs that can be utilized for the photocatalytic destruction of methyl orange. In the absence of reducing agents, these NPs can convert methyl orange to its leuco form in an aqueous solution. It is more economical than alternative methods. Because of their small size, copper oxide nanoparticles have a catalytic effect. Because they have a high surface to volume ratio, nanoparticles have more active sites than bulk materials. Such produced copper oxide nanoparticles have effective catalytic capabilities.

Mahmoud et al. prepared two samples of CuO NPs by using extracts of mint leaves and orange peels. For the elimination of Pb(II), Ni(II), and Cd(II) using CuO NPs, several batch experiment parameters, including nanosorbent dose, contact time, pH, and initial metal concentration, were taken into consideration. [61]. In this study by Hassan et al., the modified sol-gel process is used to create copper oxide nanoparticles. Its surface was examined and characterized using a variety of methods, including XRD, SEM, TEM, and AFM. The presence of CuO is indicated by all of the reflection peaks from the XRD study, and the spectrum showed that the particle size produced was around (21.11 nm), which was in agreement with estimates from SEM and TEM. CuO examination using SEM, TEM, and AFM revealed that the particle sizes are in the nanometer range. Through the use of an adsorption batch approach, these oxides were employed to separate Cd (II) and Ni (II) ions from their aqueous solutions (binary system) [62].

Tsegaye et al. reported the synthesis of CuO NPs using aqueous extract of *Prunella vulgaris* flower. Synthesized NPs were crystalline in nature with spherical shape and average particle size is in the range of 41 – 76 nm. FCC structure of the particles was reported by XRD analysis. The biomolecules and functional groups found in NPs, however, were identified via FTIR analysis. This study further highlights the fact that CuO NPs made using green technique show effective antibacterial activity against the tested strains of *S.aureus* and *K.pneumoniae*. Therefore, CuO NPs

antibacterial activity has demonstrated the biological importance of NPs and will be important in the search for new treatments to address the problem of these organisms developing drug resistance [63].

Hybrid technology for membrane refers to the combination of different materials or processes to create a membrane with improved properties. This approach allows for the creation of membranes with enhanced performance, durability, and functionality. Hybrid membranes are developed by combining different materials, such as polymers, ceramics, and metals, metal oxides etc. to synthesize membrane with improved properties like enhanced separation performance, increased durability, and improved chemical resistance.

These membranes have various applications in industries such as water and wastewater treatment, biotechnology, and pharmaceuticals. They can be used for separation, filtration, and purification of liquids and gases.

The advantages of hybrid membranes include:

a. Improved separation performance
b. Increased durability and lifespan
c. Enhanced chemical resistance
d. Ability to operate at high temperatures and pressures
e. Reduced fouling and cleaning requirements

Some examples of hybrid membranes include:

a. Hybrid ceramic-polymer membranes for water treatment
b. Hybrid metal-polymer membranes for biotechnology applications
c. Hybrid carbon-polymer membranes for gas separation

Although there are several advantages of polymeric membranes like low cost, easy fabrication process, suitability for a range of application, there are certain limitations that are discussed below-

1. As they are made of two of many products, the products may be contaminated with impurities. They may also have chemical incompatibilities, especially those who have high organic compound concentrations.
2. Polymeric membranes also show low mechanical, thermal, and chemical suitability thus makes them less suitable for various industries [64].
3. Emitting volatile organic compounds, wastewater with high toxicity, a large number of non-cyclable waste, polymeric membranes involves a great environmental impact [65].
4. Suffers from trade-off between selectivity and permeability [66].

Ceramic membranes have several advantages over polymeric membranes:

a. Chemical, Mechanical, and Thermal Stability**:** Ceramic membranes offer exceptional chemical, thermal, mechanical, and physical stability [67]. They can withstand high temperatures, a wide pH range (0 to 14), and operating pressures up to 10 bar without compaction or swelling [67].
b. Fouling Resistance**:** Ceramic membranes are known for their outstanding fouling resistance [68]. This makes them more suitable for applications where fouling is a significant concern, such as wastewater treatment [69].
c. High Permeability**:** Ceramic membranes have high permeability, which allows for efficient separation processes [69].
d. Self-Cleaning Properties**:** Some ceramic membranes have self-cleaning properties, which can reduce maintenance requirements and improve operational efficiency [69].
e. Long Shelf Life**:** Ceramic membranes have a longer shelf life compared to polymeric membranes [70]. This makes them a more cost-effective choice for long-term applications [70].
f. Applicability in Harsh Environments**:** Ceramic membranes have much better performance, extra-long service life, mechanical robustness, and high thermal and chemical stabilities [70]. They have also been applied in gas, petrochemical, food-beverage, and pharmaceutical industries, where most polymeric membranes cannot perform properly [70].

Though different synthesis methods and applications of CuO NPs have been reported in the literature, but most of them were energy consuming. Also, very few studies were reported for the application of CuO NPs in dye removal. These facts inspired the author to carry out the present study.

Chapter 3

MATERIALS AND METHODS

3.1 MATERIALS AND EQUIPMENT USED

3.1.1 Chemicals

- Copper Sulphate ($CuSO_4$)
- Sodium Hydroxide (NaOH) (mfd. by GR India)
- Ethanol (CH_3CH_2OH) (mfd. By GR India)

3.1.2 Plant

- **General name:** Algae
- **Scientific name:** *Anabaena variabilis*
- **Type of tree:** all seasoned water type
- **Source of collection:** Jadavpur University campus

Fig 5: Algae *(Anabaena variabilis)*

3.1.3 Apparatus

- Weighing Machine (Sartorius, Germany, 0.0001-220gm)
- Magnetic stirrer (Remi, India)
- Centrifuge machine (Tarsons, India,0-1400 rpm)
- Hot air oven (G.B. Enterprise, India)
- Tube furnace (K. Furnace, India, Room temperature to 1100℃)

3.2 METHODOLOGY

CuO NPs was synthesized via green synthesis of nanoparticles using Copper Sulphate as precursors. The synthesized NPs were characterized in terms of XRD, FTIR, FESEM & EDS, and DGA/DTA. Phthalates and Parabens were taken as a model carcinogenic product to evaluate the efficiency of synthesized CuO NPs. Removal of phthalate and paraben was determined by HPLC.

3.2.1 Green Synthesis of CuO NPs

3.2.1.1 Preparation of Precursors

Copper Sulphate pentahydrate ($CuSO_4.5H_2O$) was taken as the main source of Copper in CuO NPs for our study.

- Molecular Weight of $CuSO_4.5H_2O$ is:
(63.546 + 32.06+ 64) + 5× (1.00794×2 + 15.9994)) = 249.68 grams.
- To prepare 1 M solution of $CuSO_4.5H_2O$, 159.61 gm of $CuSO_4.5H_2O$ (S) was weighed and dissolved in distilled (deionozed) water. The solution was stirred with a stirring rod until it is completely dissolved.
- The solution is then diluted with distilled water to get the final volume of 1000 ml. Prepared Copper Sulphate solution was kept in a glass container for further use.

O.1M Sodium Hydroxide (NaOH) solution was prepared as (NaOH) solution acted as the precipitating agent in our synthesis.

- Molecular weight of NaOH is (23+16+1) =40 grams.
- 0.4 grams of Sodium hydroxide pellets were weighed and dissolved in distilled (deionized) water. The solid was stirred with a stirring rod until it completely dissolved.

- The solution is then diluted with distilled water to get the final volume of 100ml and stirred again to get homogeneous. Prepared Sodium hydroxide solution was kept in a glass container for further use.

During green synthesis of nanoparticles, Algal extract along with small amount of NaOH (0.1M) was used as a precipitating agent.

- Algae was collected and cultured in aseptic condition in aquarium under proper illumination.
- Algae was boiled 1gm per 100ml distilled water for algal extract.
- The extract was filtered using Whatman 42 filter paper and kept in for further use.

3.2.1.2 Synthesis of Nanoparticles

- $CuSO_4$ solution was taken in a Borosil 250 ml conical flask and it was mixed thoroughly with the help of a magnetic stirrer.
- Algal extract that was prepared earlier was added drop wise in the $CuSO_4$ Solution in systematic manner and stirred at 900 rpm.
- NaOH was added to the solution in a drop wise at a regular interval.
- All the steps regarding the synthesis of copper oxide nanoparticles were conducted at room temperature. (30 ± 2 ℃).
- The solution turned brownish and deep brown precipitate was formed at pH 8.
- The precipitate is then repeatedly washed with the help of distilled water to remove any traces of dirt and alkali.
- The resultant precipitate was kept for some time undisturbed for the heavy portion to settle down at the bottom of the flask. And the excess non-useful portion of the precipitate was expelled out. The useful portion was centrifuged and was heated in tube furnace (JAY CRUCIBLES, India) at around 500℃ for 15 mins.
- After that the heated material was collected from the furnace and left in open atmosphere to cool down. Then, the material was hand grinded using mortar-pestle.

The resultant nanoparticles were stored for further use.

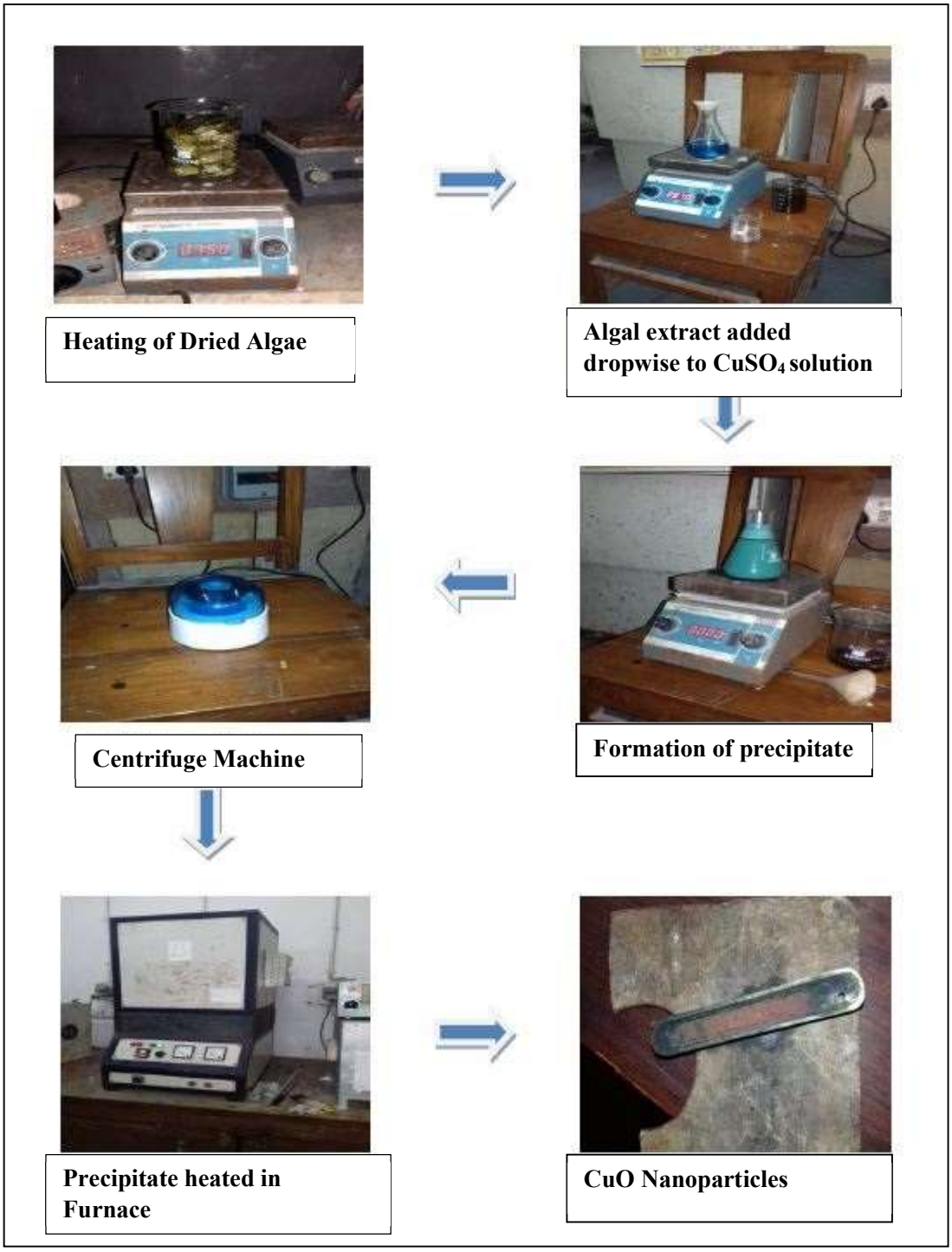

Fig 6: Steps involved in synthesis of CuO NPs

3.2.1.3 Characterization of CuO NPs

[1] X-Ray Diffraction is an important non-destructive technique in the characterization of nanoparticles. The XRD phenomena obeys the Bragg's law i.e.,

$$2D_{hkl}sin\theta = n\lambda$$

The XRD analysis for the present study was carried out in *SmartLabSE (Rigaku Corporation, Japan)* XRD machine. Scan parameters for the analysis were set to-

2θ range: 20-80°; Step: 0.01°; Scan Speed: 0.4°/ min

Fig 7: SmartLab SE XRD set up

[2] Fourier Transform Infrared (FTIR) spectrometer, based on infrared spectroscopy, is an instrument for the characterization of unknown materials. FTIR analysis in the present study was carried out in IRPrestige-21(Shimadzu, Japan). For FTIR analysis sample was mixed with KBr and a pellet was made by using hydraulic press. For baseline correction of the spectrum a KBr pellet was taken as a reference material. FTIR operation was carried out in 4000–400 cm^{-1} wavenumber range, in the absorbance mode. The absorbance data was transformed in to percentage transmittance using Beer-Lambert law.

Fig 8: IRPrestige-21 FTIR Machine set up

[3] Field emission scanning electron microscope (FESEM) is used to investigate the morphology (e.g., particle sizes and shapes), metallographic details, imperfections, and

topology of nanocrystalline powders and bulk materials. The FESEM & EDS analysis for the present study was carried out in Inspect F50 (FEI, USA) FESEM machine. Gold coating was used for sample preparation for FESEM & EDS.

Fig 9: FESEM & EDS set up

[4] Thermal gravimetric analysis (TGA) is a thermal analysis technique that measures changes in physical and chemical properties of materials as a function of increasing temperature (with constant heating rate) or time (with constant temperature and/or constant mass loss). TGA is done to determine specific properties of materials that display mass loss or gain owing to decomposition, oxidation, or volatile loss (such as moisture). In a TGA curve, the y-axis represents the percentage of mass loss and the x- axis represents temperature (or time, and most of the time a direct heating rate).

This technique has been used to characterize different metal oxide nanoparticles including CuO NPs.

In DTA, the differential temperature change between the specimen and reference for a fixed amount of heat input is measured. Here, ΔT signal is referred to as the DTA signal. α-alumina is used as reference material in DTA. TGA-DTA techniques are preferably performed all together, in order to determine the range of thermal characteristics with a single sample run.

DTA is an important characterization tool to determine

- Heat change measurements and whether the process and endothermic or exothermic.
- decomposition behavior in various atmospheres.

The TGA/DTA analysis for the present study was carried out in EXSTAR 6000 TG/DTA 630(Seiko Instruments Inc., Japan) machine.

Fig 10: TG/DTA set up

[5] BET analysis was done in order to get the surface area and porosity distribution of the synthesized nanoparticles.

Fig 11-
BET set up

3.2.2 PPCP's REMOVAL STUDY

3.2.2.1 Preparation of phthalate and paraben solution:

Sodium Phthalate and Methyl paraben was taken as starting material for preparation of solution. Initial 1000 ppb solution was prepared which was diluted for further use.

3.2.2.2 Preparation of UF membrane

For synthesis of ultrafiltration membrane Titanium dioxide (TiO_2) and green synthesized copper oxide nanoparticle (CuO NP) composite were used and coated over clay/alumina support. TiO_2-CuO Nano powders was evenly dispersed in HEC as binder, Dolapix as dispersant (2wt%) and PEG as plasticizer and the slurry was stirred for 1hour at 100rpm for uniform dispersion. It was followed by addition of hydroxyethyl cellulose (2wt%) and PEG (4 wt.%) under stirring condition of

100rpm and ambient temperature. Stirring was continued for 24h until a stable, bubble free suspension having uniform solid loading is produced. Based on the sedimentation rate and viscosity and experiments, optimized ratio of CuO and TiO2 NP was selected for coating on support.

UF membrane was developed using optimized CuO and TiO_2 composition over clay-alumina support purchased from Johnson's and Johnson. The support is hollow, tubular, single-channeled having 10mm/7mm (outer diameter/inner diameter) and 300mm length, developed by extrusion method from cost effective composition of clay and alumina. Tubes were subjected to ultrasonication with acetone followed by oven drying at 100°C to remove any surface impurities. It was dip coated using the prepared slurry for contact time of 5min. Tubes were then left for curing at room temperature followed by sintering at 550°C at slow heating rate. Balance slurry was used for characterization of unsupported membrane.

3.3.2.3 Application of synthesized membrane for removal of PPCP's

The developed UF membrane was used for removal of Phthalate and paraben from synthetic solution in cross flow filtration mode. The membrane was conditioned by immersing in clean water overnight for obtaining stable flux. The membrane was then housed in stainless steel module of dimensions 10mm/7mm (O.D/I.D) and 300mm length. The average pore size of membrane was about 0.6 μm. The feed tank was of 20 L capacity made of S. steel 304L with stirring arrangement. Ceramic membrane filtration module was made of Steel 316L with flow rate 0-7 LPM measured through Rotameter differential pressure showing with glycerin pressure gauge for both upstream & downstream. The setup has 2-way valves for reverse connection and total setup was mounted on a moveable trolley. Flux was studied at constant transmembrane pressure of 2 bar for duration of 120 min and 2 LPM CFV. Permeate was collected at regular intervals and was characterized for organic and inorganic components and removal of PPCP's. Membrane fouling constant was obtained by fitting the flux data in cake resistance model and pore blocking models - both complete and intermediate blocking model. The equations are depicted in equation 1,2 and 3.

$$\frac{1}{J_t^2} = \frac{1}{J_0^2} + 2k_c t \ldots\ldots\ldots\ldots\ldots \text{(Equation- 1)}$$

$$LnJ_t = LnJ_0 - k_b t \ldots\ldots\ldots\ldots\ldots \text{(Equation- 2)}$$

$$\frac{1}{J_t} = \frac{1}{J_0} + k_i t \ldots\ldots\ldots\ldots\ldots \text{(Equation- 3)}$$

Fig 12- Filtration Unit for membrane study

3.2.2.4 Characterization of unsupported and used membrane

- To determine the phase of the ceramic membrane XRD analysis was done. The experiment was conducted under the scan parameters for the analysis -

  2θ range: 20-80°; Step: 0.01°; Scan Speed: 0.4°/ min

- To determine the pore density, surface area BET analysis was done.
- To determine phase transitions, chemical reactions-DTA, and to determine the thermal stability, composition of the material- TGA was done. The temperature was set from room temperature to 80°C.
- FESEM was done to show the presented functional groups in that prepared membrane. The FESEM & EDS analysis for the present study was carried out in Inspect F50 (FEI, USA) FESEM machine. Gold coating was used for sample preparation for FESEM & EDS.

Chapter 4

RESULTS AND DISCUSSION

- **XRD**

XRD pattern of metal nanoparticles revealed that peaks position at 33°, 35°, 42° and 52° corresponded to the monoclinic phase of copper oxide (CuO, JCPDS-80-1916) developed at stirring 900 rpm respectively [67]. Peaks at 33 corresponded to (110) plane present in CuO NPs before and after adsorption of phthalate and paraben. High stirring speed destabilized the crystal growth in a particular plane as well as restricted the crystal growth leading to the lower particle size. Crystallite size was calculated using Scherer's formula,

$$D = \frac{k\lambda}{\beta} Cos\theta$$

where D is the crystallite size, λ is wavelength (1.5418 Å), constant k is 0.9–1, β is the full width and half maxima and θ is the Bragg angles of diffraction peak. Average crystallite size calculated for CuO NPs about 22.06 nm. Figure (13)-(15) depicted XRD of CuO NPs before adsorption and after adsorption of phthalate and paraben respectively.

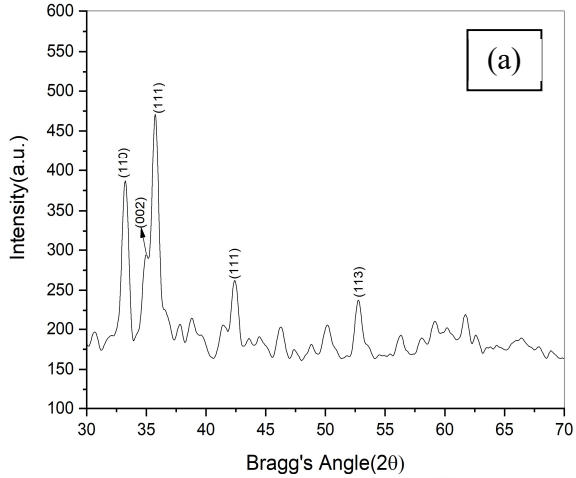

Fig 13- XRD analysis of CuO NPS

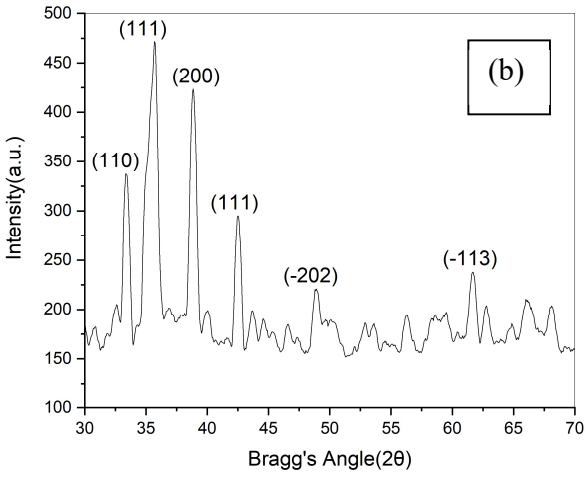

Fig. 14- XRD analysis of Phthalates added CuO

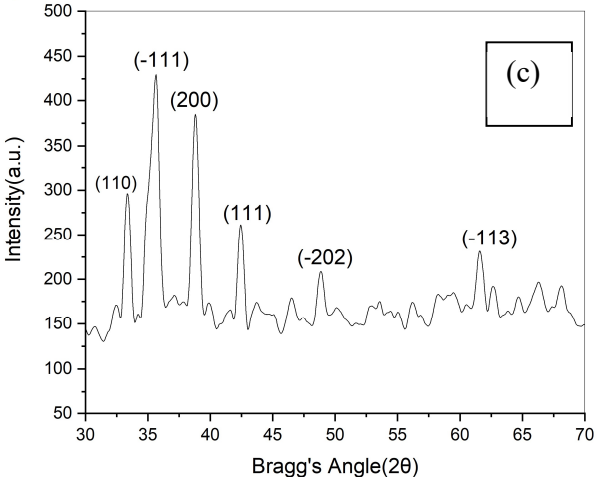

Fig. 15- XRD analysis of Parabens added CuO

- **FTIR**

Figure 16 depicted FTIR spectra of CuO NPs. Bands at 3488 cm^{-1}, 3572 cm^{-1}, 4247 cm^{-1} and 4332 cm^{-1} was due to the -OH stretching of moisture as nanoparticles easily absorb moisture due to their high surface to volume ratio. Bands at 2057 and 2892 cm−1.were due to C-H and O-H stretch respectively [68]. Stretching at 987 and 1113 cm−1 corresponded to C-O bond of polyols like flavones, terpenoids, polysaccharides, etc. of algal biomass and that at1639 cm−1 corresponded to C=O and N-H bond. Stretching at 886 and 987 cm^{-1} might be attributed to the C-O bonds. Bands at 492, 615 and 799 cm^{-1} corresponded to the Cu-O bond [69]. Sharp peak observed at 615 cm^{-1} was the characteristics peak of Cu-O bond present in CuO NPs. Peak at 492 cm^{-1} corresponded to the stretching of CuO bond. Figure (17) & (18) showed FTIR of CuO NPs after adsorption of phthalate and paraben. There was slight shift in peaks around 600cm-1 and new peak was evident for phthalate at around 811 cm^{-1} which might be due to presence of aromatic compounds like phthalates. Shift around 600cm^{-1} might be attributed to involvement of CuO group in adsorption.

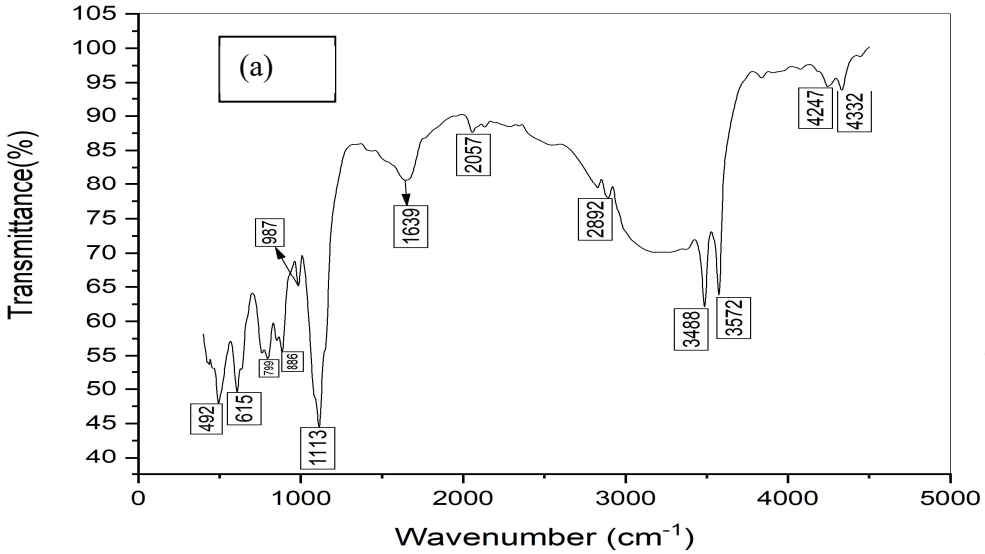

Fig. 16- FTIR analysis of CuO NPs

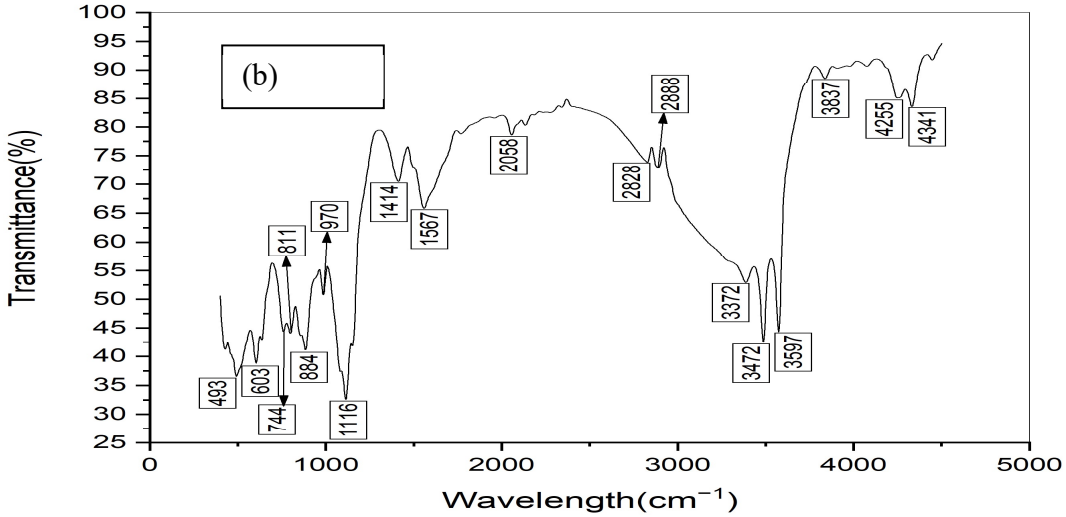

Fig.17- FTIR analysis of Phthalates added CuO NPs

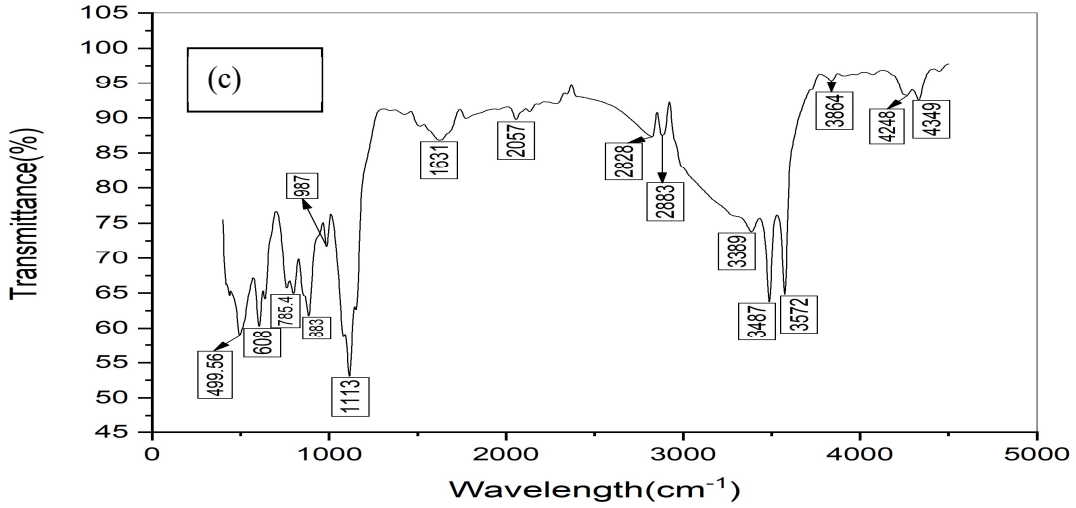

Fig.- 18 FTIR analysis of Parabens added CuO NPs

- **FESEM**

FESEM micrographs of CuO NPs before and after adsorption is shown in Figure (19) – (21) Results confirmed the nano-range of CuO NPs. Results also confirm their spherical shape. After adsorption particles seemed to be agglomerated which may be due to adsorption of phthalates and parabens.

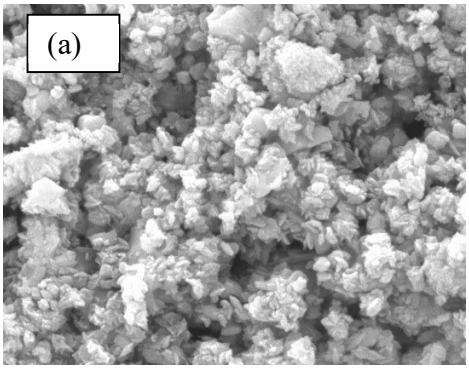

Fig.- 19 FESEM of CuO NPs

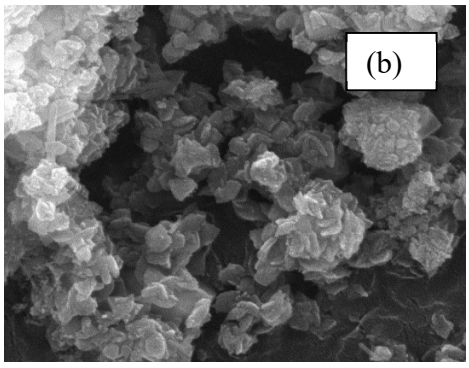

Fig.- 20 FESEM of Phthalates and CuO NPs

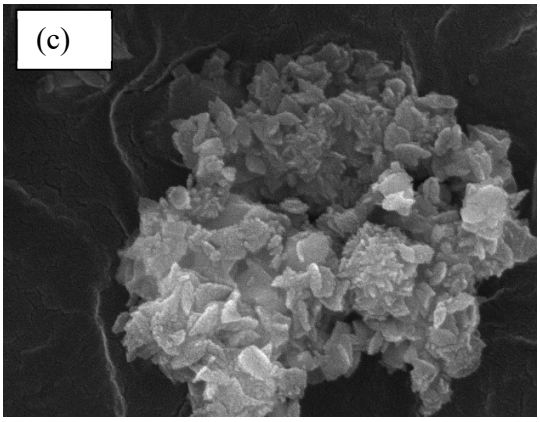

Fig.- 21 FESEM of Paraben and CuO NPs

- **DTA/TGA**

From (Figure 22) TGA curve of CuO NPs it was observed that there was a weight loss around 50-60°C due to removal of surface water. After that no major weight loss was observed upto 480 °C. There was a negligible weight loss around 480–500 °C and second weight loss at around 700°C was observed due to thermal decomposition.

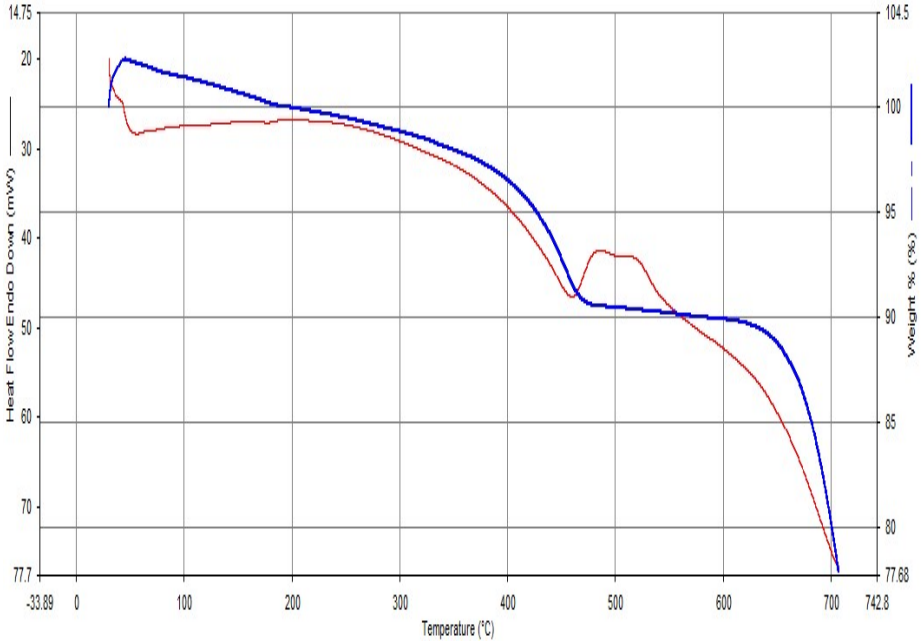

Fig.-22 DTA/TGA of CuO NPs

DTA/ TGA of unsupported membrane (Figure 23) it was observed that there was a weight loss around 100 to 150 °C due to removal of surface water. After that no major weight loss was observed upto 400 °C where negligible weight loss was observed due to decomposition of HEC and other organic polymers.

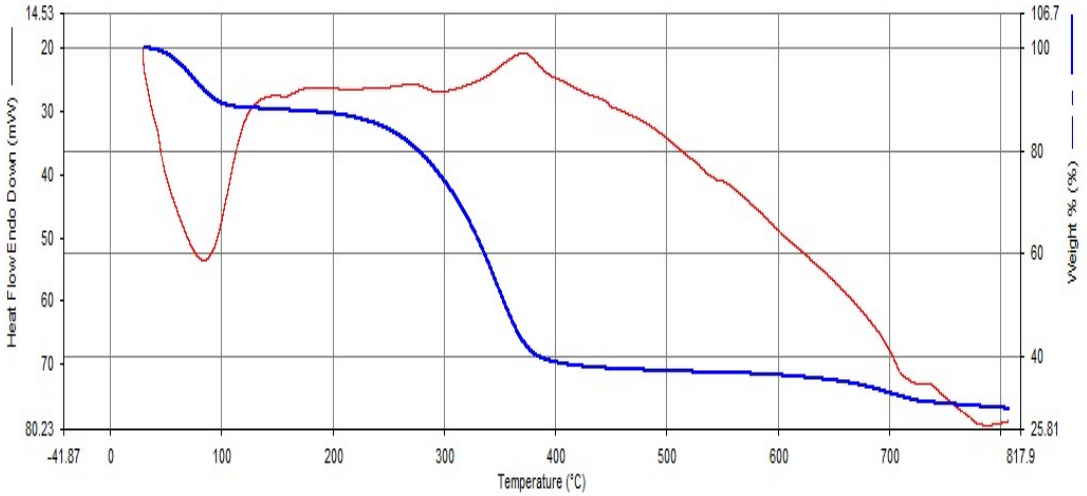

Fig.- 23 DTA/TGA of Ceramic Membrane

- **BET surface area analysis**

Surface area of CuO NPs as calculated from BET analysis was 3.718 m^2/g whereas for unsupported membrane surface area was determined to be 6.355m^2/g. Pore volume of unsupported membrane was 0.012cc/g.

- **Effect of time on membrane flux**

Effect of time on permeates flux has been represented in Figure 24 Study was conducted at 2 bar transmembrane pressure and for 120 minutes each for phthalate and paraben. Membrane was cleaned by backwashing after each run. 20L feed of 500ppb concentration for phthalate and paraben was used. It was observed that with time there was a decline in flux from an initial value of 280LMH to 249LMH for phthalate and 265LMH to 230LMH for paraben respectively at 120 minutes of filtration.

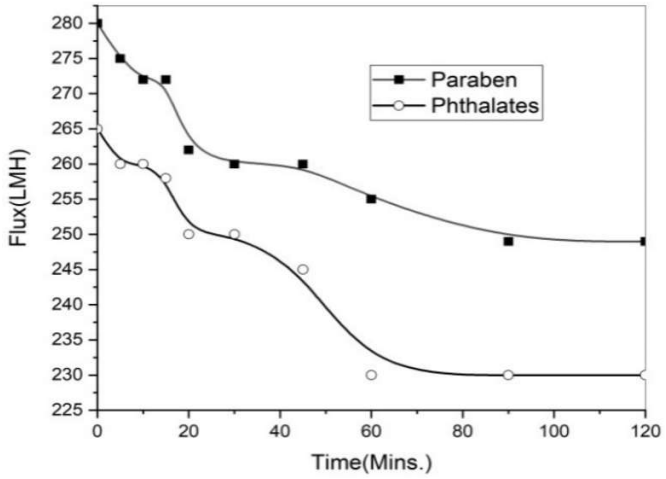

Fig.24- Flux Study of Phthalates and Parabens

- **Effect of time on removal of phthalate and paraben**

Phthalate and paraben removal efficiency of developed UF membrane with time, is reported in Figure 25 Constant increase of PPCPs removal with increasing time is obtained with maximum removal of 92% for phthalate and 96.3% for paraben respectively at 2 bar pressure and 120 minutes of filtration.

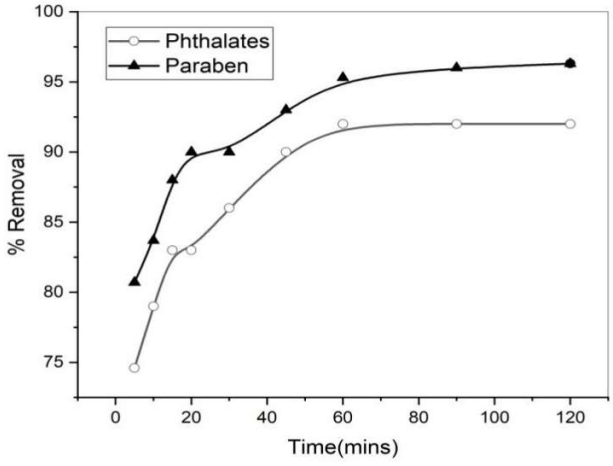

Fig.- 25 Removal % study of PPCPs

Chapter 5

CONCLUSION

Chapter 5

CONCLUSION

The following study is done to understand and analyze the different synthesis methods and characterization of Copper Oxide nanoparticles. Heavy metal removal capacity of the synthesized nanoparticles was also examined during the present study. Phthalates and Parabens were used as model heavy metal solution in this research work.

1) XRD analysis of synthesized CuO NPs showed sharp peaks corresponding to planes (110), (002), (111), (111), (113) confirmed the monoclinic structure of CuO. The average crystallite size (using Debye-Scherrer formula) was found to be 22.0684 nm. Also, when used as absorbent to remove phthalates and paraben the average particle sizes were 13.6848 nm and 14.068 nm.

2) The FTIR test confirmed the presence of bioactive molecules present in the synthesized CuO NPs. It also confirmed different function group and physical interaction of macromolecules with CuO NPs.

3) FESEM results confirmed the nano range of CuO nanoparticles. Results also confirmed their spherical shape. Results from EDX were consistent with the FESEM results and it was evident from the EDS spectrum that the CuO nanoparticles were synthesized successfully. The major constituents of the nanoparticles before adsorption was Cu (28%) and O (8.24%). After adsorption, constituents were Cu (26.59%), H (57.56%), S (4.97%) and O (6.36%) for Phthalate and Cu (25.74%), H (54.86%), S (3.82%) and O (5.68%) respectively.

4) BET surface area of CuO NPs was 3.718 m^2/g. BET Surface area of unsupported membrane was determined to be 6.355 m^2/g. Pore volume of unsupported membrane was 0.012cc/g.

5) Flux Values of 249LMH and 230LMH for Phthalates and paraben respectively was obtained after 120mins of filtration study. Removal Efficiency of 92 & 96.3 % for phthalates and paraben was obtained.

Thus, it may be concluded that UF membrane developed by coating green synthesized CuO NPs and TiO_2 NPs is highly efficient in removing PPCPs (Phthalates and Parabens as model) from waste water. The study proposed single step solution towards harmful constituents from environments which will be further studied in Future.

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