Use of Nanoparticles in Disinfection of Desalinated Water in United Arab Emirates

Laila Masoud Rashid Al-Issai

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Use of Nanoparticles in Disinfection Of Desalinated Water In United Arab Emirates

Laila Masoud Rashid AL-Issai

This thesis is submitted in partial fulfillment of the requirements for the Master of Science in Water Resources

Under the direction of Doctor. Walid EL-Shorbagy

February 2014
Declaration

I, Laila Masoud Rashid Al-Issai, the undersigned, a graduate student at the United Arab Emirates University (UAE) and the author of the thesis “Evaluating the Usage of Nanoparticles in Disinfection of Desalinated Water in United Arab Emirates”, hereby solemnly declare that this thesis is an original work done and prepared by me under the guidance of Dr. Walid Elshorbagy, in the College of Civil Engineering at UAEU. This work has not been previously formed as the basis for the award of any degree, Bachelor or similar title at this or any other university. The materials borrowed from other sources and included in my thesis have been properly acknowledged.

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Copy ___ of ___
ABSTRACT

United Arab Emirates (UAE) as well as most Gulf Countries depends mostly on desalinated sea water as the main source of drinking water. The drinking water disinfection process has been routinely carried out since the turn of the century to destroy pathogenic organisms and prevent waterborne diseases. When chemical disinfection is applied before or after desalination, a number of harmful compounds are formed posing potential risks to the health of human or aesthetic quality of drinking water. As such, a tremendous number of studies have been conducted to identify new alternative methods of disinfecting water without formation of harmful Disinfection by-products (DBPs). Several metal and metal oxide nanoparticles (NPs) have shown significant advantages as potent bactericidal agents. In this study, seven nanoparticles (Silver, Silver-Cupper, Copper, Carbon Nanotubes, Silicon Dioxide, Magnesium Oxide, and Zinc Oxide) were evaluated in disinfecting drinking water produced from two desalination technologies; namely Multi-Stage Flash (MSF) and Reverse Osmosis (RO). All particles were applied to the water samples in suspension mode and the disinfection strength was evaluated by inspecting the degradation percentages of four types of bacteria; E.coli, Enterobacter, Salmonella, and Enterococci. The levels of four inorganic byproducts; chlorite, chlorate, bromate, and iodate, were identified in all tested samples. A major result found from this study indicated that Ag and Ag-Cu NPs had the highest disinfection efficiency among the tested nanoparticles and chlorate was the most inorganic byproduct formed in desalinated samples but with lower levels than the regulated limit.
ACKNOWLEDGMENTS

Praise be to Allah who enable me to complete this work. Thanks and deepest appreciation to my supervisor, Dr. Walid Elshorbagy for his guidelines, support and great help throughout this research. I am grateful to Prof. Yousef Haik and his staff for their great help in preparing the nano-particles. Also I address my acknowledgment to Dr. Khalid Tarably and Dr. Mohamed Taha for their support and advice. I would also like to extend my gratitude to Dr. Tiber for his cooperation and providing the Salmonella bacteria. I acknowledge the food control center for providing the bacteria and cooperation. Thanks are due to Mr. Tariq in the college of medicine and health sciences for his cooperation in TEM tests and to Dr. Ahmed Suliman for his help in analyzing IDBPs.
DEDICATION

To UAE University, To My Managers in PAWE, to my family, to my Friends. And to my Supervisor for his continuous support with my appreciation
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<td>Cupper</td>
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<td>CFU</td>
<td>Colonies Forming Units</td>
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<td>Graphene Oxide</td>
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<td>HLOL</td>
<td>High Limit Of Linearity</td>
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<td>Hypochlorous acid</td>
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<td>IO₃</td>
<td>Iodate</td>
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<td>Inorganic Disinfection By-products</td>
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<td>LDR</td>
<td>Linear Dynamic Range</td>
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<td>LLOL</td>
<td>Low Limit Of Linearity</td>
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<td>Linear Detection Limit</td>
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<td>Lipopolysaccharides</td>
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<td>Public Health Service</td>
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<td>Peptido glycan</td>
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<td>Part per million</td>
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<tr>
<td>RO</td>
<td>Reverse Osmosis</td>
</tr>
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<td>ROS</td>
<td>Reactive Oxygen Species</td>
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<td>SiO₂</td>
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<td>St.Sp MSF</td>
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<td>Silt Density Index</td>
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<td>SLED</td>
<td>System Lactose Electrolyte Deficient</td>
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<td>THMs</td>
<td>Trihalomethanes</td>
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<tr>
<td>UAE</td>
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<td>Zinc Oxide</td>
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Chapter 1
INTRODUCTION

1.1 General

One of the most pervasive problems affecting people throughout the world is inadequate access to clean water and sanitation. Problems with water are expected to grow worse in the coming decades, with water scarcity occurring globally, even in regions currently considered water-rich. The many problems worldwide associated with the lack of clean, fresh water are well known as 1.2 billion people lack access to safe drinking water, 2.6 billion have little or no sanitation, millions of people die annually, 3.900 children die every day from diseases transmitted through unsafe water or human excreta. Countless more are sickened from disease and contamination [1].

Water borne diseases are among one of the major public health problems in developing countries. According to World Health Organization, 3 million deaths occur every year from diarrheal diseases worldwide. The problem of water borne disease is especially prevalent where general hygiene and environmental sanitation are poor and where there is a shortage of protected water supply. It is believed that 80% of all diseases in the world are caused by inadequate sanitation, polluted water or unavailability of water [2].
In both developing and industrialized nations, a growing number of contaminants are entering water supplies from human activity: industrialization and urbanization. Contaminants may pose health risk if they are present in large quantities. These organic contaminants need to be removed from water if the water is to be used in homes for human consumption.

Disinfection of drinking water was introduced as a treatment step at the beginning of the 20 century in developed countries. This led to a dramatic decrease of water borne diseases. Chlorination is the most widely used technique for disinfection of drinking water. Chlorine is currently the most common disinfectant because it is the cheapest of all chemical disinfectant, it is relatively easy to use, and it is highly effective for killing most microorganisms. However, water chlorination leads to the formation of a wide range of halogenated compounds due to the reaction of halogens with naturally occurring organics such as humic, fulvic acids and other components of natural organic matter. These chemical products referred to as disinfection by-products (DBPs). Approximately 600-700 DBPs have been reported in the literature for the major disinfectants used (chlorine, ozone, chlorine dioxide, chloramines), as well as their combinations [3].
Drinking water production from desalination

Desalination is increasingly being used to provide drinking water under conditions of fresh water scarcity. Water scarcity is estimated to affect one in three people on every continent of the globe, and almost one fifth of the world’s population living in areas where water is physically scarce. This situation is expected to worsen as competing needs for water intensify along with population growth, urbanization, climate change impacts and increases in household and industrial uses. Many countries in the arid regions like most of the countries in the Arabian peninsula are now increasing dependence on sea water desalination as the major source of drinking water. Two desalination techniques are most widely employed: thermal desalination and membrane desalination. Thermal desalination includes Multi Stage Flash Method (MSF) and Multi effect desalination method (MED) while membrane desalination is mostly adapted via reverse osmosis (RO) technology. In these plants, source sea water and the product water; distillates in thermal desalination and permeates in membrane desalination, are disinfected to control pathogenic bacteria. Gaseous chlorine and sodium hypochlorite are considered as the most widely used disinfectants in the desalination industry [4].
The main goal for the future of desalination is to increase the fresh water supply via desalination of seawater and saline aquifers with as much reduced cost as possible. These sources account for 97.5% of all water on the earth, so capturing even a tiny fraction could positively have a major impact on water scarcity. Through continual improvements, particularly in the last decade, desalination technologies can be reliably used to desalinate sea water as well as brackish water from saline aquifers. Desalination of all types though is often considered a capital and energy intensive process and typically requires the conveyance of the water to the desalination plant, pretreatment of the intake water, disposal/treatment of the concentrate (brine) and process maintenance.

Desalination may be applied to waters of varying level of salinity, such as brackish groundwater, estuarine water, or seawater. At its origins, desalination technological advanced membrane has become a more cost-effective alternative that is increasingly being selected for new systems. Yet many thermal plants still remain in use and undergo expansion, rehabilitation, and upgrade.

There are notable differences between fresh water sources and brackish or saline sources. In particular, the survival of many microbial pathogens is significantly reduced in saline waters, especially in combination with a high level of solar radiation. While the desalination process usually provides a significant barrier to both pathogens and chemical contaminants conveyed with the source water, this barrier is not necessarily absolute, and a number of issues could potentially have
an impact on public health. Some of these are similar to the challenges encountered in most piped water systems, but others such as those related to stabilizing and remineralizing the water to prevent it from being excessively aggressive, are different and therefore must be addressed within the context of a site specific health risk management plan [4].

The efficiency of desalination plants in removing or inactivating microbial contaminants can be assessed by examining the expected performance and factors affecting the quality of each stream or combined final treated water. The potential for survival of microorganisms depends upon the capability and operating conditions of each process unit for their removal or inactivation. Evaluation should include any pretreatment processes, the water produced by membrane processes or by thermal treatment processes.

Chemical disinfectants are used in desalination plants for pre-treatment and for disinfection of water after desalination. Chemical disinfectants are applied during pre-treatment to control bio-fouling on intake structures, to improve the performance of filters and to control biofouling on membranes. In plants equipped with reverse osmosis, many of the DBPs formed during pre-treatment. In some cases, DBPs may be formed when desalinated water is blended with water from other sources prior to disinfection or when desalinated water and water from other sources mix in the presence of a residual disinfectant in the distribution system [3].
The kinetics of DBP formation and the nature of DBPs formed are affected by the presence of bromide and iodide. For example, elevated concentrations of bromide lead to enhanced production of brominated DBPs during chlorination and enhanced bromate production during ozonation. Brominated and iodinated DBPs are particularly problematic because they often are more carcinogenic or mutagenic than their chlorinated analogs [3].

### Nanotechnology in drinking water treatment:

Nanotechnology is the manipulation of matter on an atomic, molecular, and supramolecular scale (1–100 nm). Particles of such sizes have some unique physicochemical and surface properties that lend themselves to novel uses. Indeed, advocates of nanotechnology suggest that this area of research could contribute to solutions for one of the major problems we face on the global scale which is ensuring a supply of safe drinking water for a growing population. The rapid growth in nanotechnology has spurred significant interest in the environmental applications of nanomaterials. In particular, its potential to revolutionize century-old conventional water treatment processes has been enunciated recently.
Nanomaterials are excellent adsorbents and catalysts due to their large specific surface area and high reactivity. More recently, several natural and engineered nanomaterials have also been shown to have strong antimicrobial properties, including carbon nanotubes [5] and metals such as silver [6] and copper [7]; metal oxides such as MgO [8], SiO₂ [9] and CaO [10], and photocatalytic such as ZnO [11] and TiO₂. Unlike conventional chemical disinfectants, these antimicrobial nanomaterials are not strong oxidants and are relatively inert in water. Therefore, they are not expected to produce harmful DBPs [12]. If properly incorporated into treatment processes, they have the potential to replace or enhance conventional disinfection methods.

1.2 Problem Statement

Water treatment and provision of safe potable water are tasks that most developing countries struggle to undertake. Some of the methods for water treatment have some significant disadvantages. For instance, when water is treated with chlorine or chloramines, the chlorine may react with trace organic matter and produce several by-products; many of which are carcinogenic.

Nanotechnology has been found to play an important role in solving many of the problems encountered in water purification and disinfection. This study tests the effectiveness of a number of selected nanoparticles in disinfecting desalinated water when applied in suspension mode. This includes Silver nanoparticles [6].
Silver-Cupper nanoparticles [13], Cupper nanoparticles [7], Carbon nanotubes [5], Silicon dioxide nanoparticles [8], Magnesium Oxide nanoparticles [8] and Zinc Oxide nanoparticles [10]. The desalinated water is tested when infected with different microbes and in particular *Escherichia coli*, *Enterobacter aerogenes*, *Salmonella* typhimurium and *Enterococcus faecalis*. The particles showing acceptable disinfection properties will be tested in forming a number of common regulated inorganic byproduct compounds, particularly bromate, chloride, chlorite and iodate.

### 1.3 Aims and Objectives

The overall goal of this study is to evaluate the usage of nanoparticles in disinfection of desalinated water in UAE. Specific objectives are:

1. Evaluate seven metal and metal oxide nanoparticles in disinfecting drinking water produced from two main desalination technologies: RO and MSF, and applied in suspension mode. The evaluation is made via eliminating four major microbes usually tested in drinking water: *E.coli*, *Enterobacter*, *Salmonella* and *Enterococci*.

2. Assess the impacts of nanoparticles sizes, dosages, and residence time upon their efficiency of disinfecting desalinated water.

3. Identify the inorganic disinfection byproducts formed with the applied nanoparticles.
1.4 Delineation and delimitation of the study

In this study, the disinfection ability of NPs applied in suspension mode on two types of processed water: RO and MSF is tested. Other fixation methods used in applying NPs in water disinfection are not considered in the study. Multi Effect Desalination, (MED), is not considered here and assumed to behave in similar way to the other thermal desalination technology; that is MSF technology.

Furthermore, detailed and exact mechanisms of interaction between selected NPs and microorganisms are not investigated here. In addition, the study investigates the formation of inorganic DBPs only upon the application of NPs and doesn’t consider other potential organic DBPs (ODBPs) that may deserve to be studied in further studies.

Also photo-catalytic NPs such as TiO$_2$ were not considered in this study or were evaluated under dark conditions only (case of ZnO). Finally, analysis and management of wastes produced from the disinfection process using the considered nanoparticles is not considered and needs further analysis too.
1.5 Thesis outline

The thesis consists of six chapters. A general introduction is presented in Chapter 1 including problem statement and objectives. Chapter 2 presents the literature review of different relevant topics: mainly disinfection methods, disinfection byproducts, properties of the nanoparticles considered in the study, their applications in drinking water treatment, common fixation methods used in applying nanoparticles in water purification.

Chapter 3 explains the methods used in different analytical tasks. This includes chemical analyses (test of physical parameters, anions and cations tests and analysis of formed IDBPs. This chapter also describes the morphology test used in characterizing the seven considered nanoparticle by (TEM) and the methods used in synthesizing the seven nanoparticles. Also, it describes the preparation methods of different culture media used in the experiments and methods used in evaluating the disinfection efficiency of the seven nanoparticles in different water samples; tap, permeate and distillate.

Chapter 4 reports the results of physical, chemical and bacteriological analysis. It also presents the characterization of the seven nanoparticles used in this study. Chapter 5, has a discussion of the results obtained from the experimental work.

Finally, chapter 6 presents a summary of concluding remarks along with recommendations for future work.
Chapter II

LITERATURE REVIEW

This chapter reviews the recent publications addressing different aspects of drinking water infection along with traditional and emerging disinfection technologies. Also it reviews the nanoparticles considered in this study; their structures, application methods and antimicrobial mechanisms against different bacteria. In addition, DBPs formed by current disinfectants were also reviewed. Finally, different fixation methods applied in previous studies were summarized.

II.1 Water borne diseases and microorganisms in drinking water

Water borne diseases are caused by pathogenic microorganisms that most commonly are transmitted in contaminated fresh water. Infection commonly results during bathing, washing, drinking; in the preparation of food or the consumption of food thus infected. The pathogens involved including a wide verity of viruses, bacteria and protozoan parasites. Due to differences in size, structure, composition and excretion by human and animals, their incident and behavior in water environment are not alike. This constitutes difficult challenge for testing safety of water and the efficiency of treatment processes.
The detection of many water born and water related pathogens requires expensive and time consuming techniques, while others are not detectable by conventional method at all. It would, therefore hardly be possible to include tests for all or even a meaningful representation of these pathogens in routine quality surveillance. Water quality monitoring therefore usually based on tests for indicator organisms. The primary objective of the indicators is commonly used to indicate fecal pollution. Therefore, indicators of fecal pollution were much needed. As early as 1914, the U.S. Public Health Service (U.S.PHS) adopted the coliform group as an indicator of fecal contamination of drinking water [14].

The criteria for an ideal indicator organism are the following [15]:

- It should be a member of the intestinal microflora of warm-blooded animals.
- It should be present when pathogens are present, and absent in uncontaminated samples.
- It should be present in greater numbers than the pathogen.
- It should be at least equally resistant as the pathogen to environmental factors and to disinfection in water and wastewater treatment plants.
- It should not multiply in the environment.
- It should be detectable by means of easy, rapid, and inexpensive methods.
- The indicator organism should be non-pathogenic.
Many microorganisms have attractive indicator features. The reliability of indicators is evaluated by comparison of their incidence and survival in water environment and treatment process to that of pathogens as well as epidemiological studies on the consumer of water supplies calculation based on minimal infectious dose of pathogens and experiment using human volunteers. The following is a summary of key features of commonly used indicator:

**Total Coliform Bacteria:** Total coliform bacteria refer to a vaguely defined group of gram negative bacteria primarily identified by the ability to ferment lactose with the production of acid and gas or aldehyde within 24 hours at 35 °C to 37 °C. Total coliform bacteria include *Escherichia coli, Enterobacter, Klebsilla* and *Citrobacter*. These coliforms are discharged in relatively high number (2*10⁹) coliform/day/capita) in human and animal feces, but not all of them of fecal origin.

These organisms have long history in water quality assessment, mainly because of their association with fecal contamination, and relatively easy and rapid detection. Coliform bacteria are described and grouped based on their common origin or characteristics, as either total of fecal coliform. Some members of the group are almost conclusively of fecal origin, while other may also multiply in suitable water environment. They are commonly found in environment for example in soil or vegetation, as well as the intestines of mammals, including humans. Total coliform bacteria are not likely to cause illness, but their presence
indicates that the water supply may be vulnerable to contamination by more harmful microorganisms. Therefore, total coliform are primary used for assessment of the general sanitary quality of finally treated and disinfected drinking water [16].

*Enterobacter aerogenes*: *Enterobacter* is a genus of common gram negative facultative anaerobic rod shaped non spore forming bacteria of the family Enterobacteriaceae. Several strains of these bacteria are pathogenic and cause opportunistic infections in immune-compromised host and in those who are on mechanical ventilation. The urinary and respiratory tracts are the most common sites of infection. The genus *Enterobacter* is a member of the coliform group of bacteria. It does not belong to the fecal coliform because it is incapable of growth at 44.5°C in the presence of bile salts.

**Fecal Coliform Bacteria**: Fecal coliform bacteria refer to certain members of the group of total coliform bacteria which are more closely related to fecal or sewage pollution and which generally not readily multiply in water environment. This group of bacteria is also known as the most tolerant coliforms or presumptive *E.coli*. Fecal coliforms are primary used for the assessment of the fecal pollution in waste water and raw water sources. Because the origins of fecal coliform are more specific than origins of the more general total coliform group of bacteria, fecal coliform are considered a more accurate indication of animal or human
waste than the total coliforms. They are detectable simple and inexpensive test and widely used in routine water quality monitoring.

*Escherichia Coli (E.Coli):* *E.coli* is the major species in the coliform group. Of the five general groups of bacteria that comprise the total coliforms, only *E.coli* is generally not found growing and reproducing in the environment. Consequently, *E.coli* is considered to be the species of coliform bacteria that is the best indicator of fecal pollution the possible presence of pathogens.

*E.coli* in drinking water indicates the water has been contaminated with fecal material that may contain disease-causing microorganisms, such as certain bacteria, viruses or parasites. The health effects of exposure to disease causing bacteria viruses and parasites in drinking water are varied. The most common symptoms of water borne illness include nausea, vomiting, and diarrhea. Infants, the elderly and those with compromised immune systems may suffer more severe effects. In extreme cases some pathogens may infect the lungs, skin eyes nervous system, kidney or liver and effects may be more severe chronic or even fatal [14].

*Enterococcus faecalis:* *Enterococci, also referred to fecal streptococci, are related groups of bacteria which are more closely associated with fecal pollution that total coliform bacteria because member typically present in feces of human and animals do not readily multiply in water environments. Recently the term fecal *enterococci* have been proposed for a group consisting exclusively of *Enterococcus faecalis*, which are highly specific for human and animal fecal
pollution. These spherical gram positive bacteria tend to be most resistance than fecal coliform [15].

**Salmonella typhimurium**: *Salmonella typhimurium* is a pathogenic gram-negative bacteria predominately found in the intestinal lumen. Its toxicity is due to an outer membrane consisting largely of lipopolysaccharides (LPS) which protect the bacteria from the environment.

Water borne typhoid fever outbreaks cause by another species of *Salmonella* has devastating public health implications. Transmission has been associated with the consumption of contaminated ground water and surface water supplies.

**Other indicators**: A variety of other indicators has been used in water quality assessment including *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Legionella* species, and *Candida albicans* and endotoxins. All of these have advantages for certain purposes [15].
11.2 Traditional Disinfection Methods

Chlorine, considered as the most popular drinking water disinfectant for the last several decades, met its first challenge in 1974 when THMs were discovered as its disinfection by-products. Water utilities almost immediately started looking for alternative disinfectants mainly to avoid the occurrence of THMs in the finished water. Ozonation started gaining prominence in Europe and Canada, and become popular in many utilities. Though Ozone is known to be a very strong oxidizing and disinfecting agent, produces little THMs, removes taste and odor from the treated water its main drawback are high capital cost and inability to impart residual protection in the distribution mains. Chlorine dioxide was considered as another potential disinfectant for drinking water treatment. Chlorine dioxide is similar to Ozone in its disinfection power and taste/odor removal qualities and in addition, has longer residence time. However, due to the difficulties in handling chlorine dioxide it has to be locally produced close to the dosing point and leaves toxic inorganic residuals such as chlorite and chlorate. Chloramine though produces very low levels of THMs and has much longer residence time than the other three disinfectants considered here, is a mild disinfectant, by itself is environmentally hazardous and does not have odor and taste removal properties [16].
11.3 Disinfection Byproducts

Disinfectants are also applied prior to sending the water into the distribution system. In some cases, DBPs may be formed when desalinated water is blended with water from other sources prior to disinfection or when desalinated water and water from other sources mix in the presence of a residual disinfectant in the distribution system. In most existing desalination plants, free chlorine (HOCl/OCl) is used for pre-treatment and final disinfection [17].

Chlorine, considered as the most popular drinking water disinfectant for the last several decades, met its first challenge in 1974 when THMs were discovered as its disinfection by product. Disinfection of drinking water by chlorine produces several disinfection byproducts (DBPs) including the well documented Trihalomethanes (THMs). As some of these compounds are harmful to health, stringent limits have been imposed by regulatory bodies on their permissible levels in potable water.

Water utilities almost immediately started looking for alternative disinfectants mainly to avoid the occurrence of THMs in the finished water. Treatments based on pre-ozonation followed by post-chlorination became popular in many utilities. But recent study shows that also ozone form organic and inorganic by-product. Aldehydes, ketones, ketoaldehydes, carboxylic acids, aldo acids, keto acids, hydroxyl acids, alcohols and esters are examples of organic by-product. Inorganic by-products also form including bromate and hypobromite [18].
Though several other compounds with disinfection properties are available today: chlorine, chloramine, ozone, Ultraviolet and chlorine dioxide, but all formed DBPs. Each has its own advantages and limitation with respect to disinfection efficiency, post-disinfection biocidal activity, cost, ease of handling and by-product formation etc.

In seawater desalination, disinfection of seawater and product water is mostly carried out by chlorination and very few studies have been carried on the use of alternative disinfect in this field. Water samples from desalination differ from those originating from natural sources such as rivers and lakes in one important aspect which is relevant to THM formation, i.e. its bromide content. High bromide content in seawater and possibility of carryover of bromine and brominated THMs into desalinated water may alter both the quantity and species distribution of THMs [19].
II.4 Regulation of Disinfection By-Products in Drinking Water

Since the discovery of chloroform as a DBP in drinking water in the early 1970s, significant research efforts have been made to improve our understanding of DBP formation and control. To date, more than 600 DBPs have been identified in drinking waters. To minimize consumer exposure to hazardous DBPs while maintaining an adequate disinfection and control of targeted pathogens, the World Health Organization (WHO) and the authorities in most developed countries have introduced drinking water guidelines and standards [20].

Table II.1: WHO regulation of inorganic disinfection by product

<table>
<thead>
<tr>
<th>IDBPs</th>
<th>WHO standard in mg/L</th>
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<tbody>
<tr>
<td>Iodate</td>
<td>Not regulated</td>
</tr>
<tr>
<td>Bromate</td>
<td>0.01</td>
</tr>
<tr>
<td>Chlorite</td>
<td>0.7</td>
</tr>
<tr>
<td>Chlorate</td>
<td>0.7</td>
</tr>
</tbody>
</table>
11.5 DBPs in Arabian Gulf Countries

Many countries in the region, like most of the countries in the Arabian Peninsula, are now increasingly depending on sea water desalination as the major source of drinking water. Two most widely employed desalination techniques in these countries are Multistage Flash Distillation (MSF) and Reverse Osmosis (RO). In these plants, sources sea water and the product water (distillates from MSF and permeates from RO) are disinfected to control pathogenic bacteria. Gaseous chlorine and hypochlorite solutions as the most widely used disinfectants in the desalination industry.

Studies on the nature and extent of DBPs in desalination derived drinking water supplies are very scanty in literature. A study [21] determined the concentrations of THMs in the distillates produced from synthetic sea water containing varying concentration of humic acid and chlorine. Their result indicated that the distillation process is very effective in removing THMs and TOC from chlorinated sea water. But post chlorination of the distillates caused the formation of traces of THMs. Another study [22], THMs and extractable organics in the distillates were measured from three MSF plants in Eastern Province of Saudi Arabia. Samples of drinking water prepared by blending brackish water with distillates from one of these plants were also monitored for similar organics for a period of one year. Later the same group extended the study by determining THMs in potable water sample from 13 distribution points in 10 cities in Eastern Province of Saudi Arabia and Riyadh.
In Saudi Arabia, the concentrations of THMs found in the distillates and the makeup water were much lower, i.e. <1 and 20 μg/L, respectively. These studies also indicated that THMs in chlorinated distillates and chlorinated blended water process capable of removing high molecular weight humic substance present in sea water as reported in that study [21]. But some traces of total organic carbon still could be detected in the distillates (usually less than 0.1 ppm).

In Kuwait, a study [23] studied the effects of various process parameters such as pH, Temperature, chlorine concentration and anti-scalant additives on the formation of THMs in the product distillates and other process streams in MSF plant at Doha East. Studies from Kuwait concluded that approximately 11% of THMs initially present in the chlorinated make up sea water (29.2 μg/L) appeared in the distillates. Kuwait also had reported bromoform as the largest fraction in the total THMs [23].

A study [24] analyzed the seawater in Umm AL Nar desalination plant in Abu Dhabi, the capital city of UAE and examined its potential to form trihalomethane compounds after chlorination. The study showed that bromoform represented 95% of the formed THM in seawater and in the final distilled as well. Another study [25] has also identified the dominance of bromoform as DBPs in Abu Dhabi; water distribution system known to receive a major portion of its drinking water from the same plant mentioned above Um Al Nar.
In another study [26], chlorination byproducts in drinking water produced from a thermal desalination plant in the UAE were investigated. Trihalomethanes and haloacetic acids were both tracked at the plant’s influent and effluent and after several distillation stages inside the plant. And the result showed that trace levels of Haloacetic acids were reported in the effluent water, tangible levels of bromoform were reported in the final distillate especially after post chlorination. Results reported in the above studies indicated that in general, THMs levels in the desalination derived potable water were lower by an order of magnitude in comparison with concentration found in drinking water from natural sources. Also, the results indicate that the thermal processes do not totally remove the DBPs precursors originally found in the seawater.

The kinetics of DBPs formation and the nature of DBPs formed are affected by the presence of bromide and iodide. For example, elevated concentrations of bromide lead to enhanced production of brominated DBPs during chlorination and enhanced bromate production during ozonation [17].

Iodide is usually present in natural waters at concentrations that are significantly lower than those of chloride or bromide. Nevertheless, its presence can lead to formation of elevated concentrations of iodinated DBPs when chloramines are employed for disinfection. In addition to their potential adverse health effects, iodinated DBPs are a concern because the taste and odor threshold of iodinated organic compounds is often very low [3]. Iodide concentrations in desalinated
waters are usually lower than those of chloride and bromide because iodide occurs at lower concentrations in seawater. Moreover, in seawater, iodine is usually present in its oxidized form, iodate (IO₃). As a result, iodide concentrations are not always correlated with concentrations of chloride and bromide. The highest iodide concentrations usually occur in arid regions and in groundwater where the local geology is rich in iodide. Thus, formation of iodinated DBPs may be localized to desalination systems in which the source water is enriched in iodide [3].

Ensuring the availability of clean, abundant fresh water for human use is among the most pressing issues facing the United Arab Emirates and the world. In the United Arab Emirates as in the rest of the world, drinking water disinfection is conducting by chlorination. On top of the impending supply crisis, the United Arab Emirates face a host of water quality issues that demand improved treatment methods to resolve.

One global scale water borne diseases are still a major cause of death in developing countries where access to safe drinking water is often limited. With the introduction of disinfection process (mainly chlorine), water borne infectious diseases have been significantly reduced. However, it is known that the application of disinfection agents such as chlorine, chlorine dioxide or ozone is associated with the formation of disinfection by product, e.g. trihalomethane, halo-phenol, ketones, aldehydes) some with a high mutagenic and or carcinogenic
potential. Chlorination also affects the taste and odor of drinking water. Therefore, there is still a need for new concepts to reduce the release of toxic byproducts resulting from disinfection processes [26].

We also need to improve disinfection to inactivate pathogens and prevent creating disinfection byproducts that are themselves highly toxic. There is a clear and urgent need for new more effective methods to purify water for the people of the United Arab Emirates and the world. The application of modern nanotechnology could be one approach to improve this situation. Addressing these problems calls out for a tremendous amount of research to be conducted to identify robust new methods of purifying water at lower cost and with less energy, while at the same time minimizing the use of chemicals and impact on the environment. More effective, lower-cost, robust methods to disinfect and decontaminate waters from source to point-of-use are needed, without further stressing the environment or endangering human health by the treatment itself.
II.6 Pretreatment and Removal of Precursors of Disinfection Byproducts

Membranes need to be protected from particulates to prevent clogging so particulate removal processes are employed, while oxidants and biocides may be employed to prevent fouling of the RO membranes. Although these pretreatments are not necessarily employed to reduce the numbers of waterborne pathogens they will have an impact on numbers particularly through particle removal.

Pretreatment include the use of membranes for microfiltration (MF) and nanofiltration (NF) to prepare the water for the subsequent desalination process. MF and NF have a subsequent capacity to physically remove a large proportion of particulate associated microorganisms as well as some dissolved solids. They can effectively remove at least 6 logs of microorganisms according to their pore size distribution, but the actual removal should be validated before application as a pretreatment.

Pretreatment of the source water after the intake is normally designed to remove contaminants that will interfere with the desalination process by scale formation or membrane fouling. This treatment can include coagulation and filtration or membrane filtration processes that will remove particulate and organic matter, including a significant reduction of NOM. A disinfectant such as chlorine is normally applied to minimize fouling and reduce the risk of pathogens carrying over the product water.
Humic and fulvic acids and other related substances that constitute NOM can react with chlorine (and other disinfectants) to produce a wide range of halogenated and oxidation by-products. In the presence of the high bromide concentrations found in seawater and many brackish water, the bromide is oxidized to bromine or hypobromite, which will take part in the halogenation reactions and produce organobromine products as the predominant by-products.

Here we highlight some of the science and technology being developed to improve the disinfection and decontamination of water, without formation for harmful disinfection by product. This technology is using nanoparticles in water disinfection.

Nanotechnology has been found to play an important role in solving many of the problems that are encountered in water purification. The recent development of nanotechnology has proved that nanomaterials such as nano-sized metal oxide catalysts can have high activity in degradation of a wide range of organic and inorganic contaminants in water.

**II.7 Application of Nanoparticles in Water Disinfection**

The removal of pathogens using nanotechnology is an emerging area of research and it is a promising alternative to existing processes such as chlorination. Effective treatment processes for drinking water production are major prerequisites for a developing and growing economy. Therefore, it is crucial to develop and implement innovative water technologies treating water with high
efficiency and low energy consumption. To date major challenges for water
treatment are pathogens and chemical pollutants. On a global scale; water-borne
diseases are still a major cause of death in developing countries where access to
safe drinking water is often limited. With the introduction of disinfection
processes; mainly chlorine, water borne infectious diseases have been
significantly reduced. However, it is known that the application of disinfection
agents such as chlorine, chlorine dioxide or ozone is associated with the
formation of disinfection by products some with a high mutagenic and or
carcinogenic potential.

Chlorination also affects the taste and odor of drinking water. Therefore, there is
still a need for new concepts to reduce the release of toxic byproducts resulting
from disinfection processes. The application of modern nanotechnology could be
one approach to improve this situation.

The utilization of nanomaterials has received much attention due to their unique
properties such as extremely small size, high surface area to volume ratio, surface
modification excellent magnetic properties and great biocompatibility [27].
Nanomaterials are excellent adsorbents, catalysts and sensors due to their large
specific surface area and high reactivity. More recently several natural and
engineered nanomaterials have also been shown to have strong antimicrobial
properties.
Unlike conventional chemical disinfectants, these antimicrobial nanomaterials are not strong oxidants and are relatively inert in water. Therefore, they are not expected to produce harmful DBPs. If properly incorporated into treatment processes, they have the potential to replace or enhance conventional disinfection method [28].

Antibacterial activity is related to compounds that locally kill bacteria or slow down their growth, without being in general toxic to surrounding tissue. Most current antibacterial agents are chemically modified natural compounds [11].

Several nanoparticles have been synthesized tested for their application in water treatment. These include carbon nanotubes, metal nanoparticles, nano-sponges and zeolites.

II.8 Types of Nanomaterials Used in Water Treatment

The nanomaterials used for water treatment on research can be classified into four groups: Nanosorbents, Metals and Metal oxide nanoparticles, Zeolites, and Nanosponges.

Nano-sorbents are nanosized particles onto which some inorganic and organic molecules can be adsorbed. They are working as a separation medium in water treatment. These have received great attention worldwide because they have a
very large surface area to volume ratio and can also be functionalized for specific application in the removal of pollutants in water [29].

**Metal and Metal oxide nanoparticles** such as silver, magnesium oxide and copper. These nanoparticles are receiving attention for their potential application in water treatment and disinfection.

**Zeolites** are inorganic crystalline porous materials that have a high order structure and are generally comprised of silicon, aluminum and oxygen. Their physicochemical characteristic such as high mechanical and chemical resistance in addition to their high surface area, have formed the basis for their widespread use in catalysis, separation, and ion-exchange. Zeolites are used as an ionexchange media for metal ions and effective sorbents for removal of metal ions [30]. Zeolites have been reportedly used in the removal of heavy metals such as Cr(III), Ni(II), Zn(II), Cu(II) and Cd(II) from metal electroplating and acid mine wastewaters [29]. These are inorganic crystalline porous materials with a highly ordered structure.

**Polymeric nanosponges** have been developed and have been used for the removal of organic pollutants. An example is cyclodextrin polyurethanes. These have a powdery granular morphology and have a large surface area. They have been conjugated with functional monomers such as ionic liquids and functionalized carbon nanotubes. Upon conjugation, cyclodextrin based
Polyurethanes can remove inorganic and organic pollutants. Moreover, further addition of components such as metal nanoparticles such as silver and copper nanoparticles can add an antibacterial characteristic to the cycloextrin polyurethane based polymers [29].

**Nanopowder Properties**

Nanopowders are three dimensional uni-axial nanosized objects at a level intermediate between atom/molecule and bulk. The nanopowders have a tendency to grow into micro-powders or macroscopic materials instantaneously and then lose their specific features. Therefore, the production of a nanopowder with controlled particle size and degree of aggregation is the main attraction for the many research efforts. Recently, significant progress in the diversity of preparative methods has been made. Powder size is the primary driver for the growing synthetic interest as it affects photocatalyst properties. In general, nanoparticles have different classical properties from the bulk material.
11.9 The toxicity mechanisms of NPs against bacteria

The exact mechanisms of NPs toxicity against various bacteria are not understood completely. NPs are able to attach to the membrane of bacteria by electrostatic interaction and disrupt the integrity of the bacterial membrane. Non-toxicity is generally triggered by the induction of oxidative stress by free radical formation that is the reactive oxygen species (ROS) following the administration of NPs [31].

Role of the cell wall:

The bacterial cell wall is designed to provide strength rigidity, and shape and to protect the cell from osmotic rupture and mechanical damage. According to their structure components and functions the bacteria cell wall can be divided into the two main categories: Gram positive and gram negative. The wall of gram positive cells contains a thick layer (20-50 nm) of peptidoglycan (PG) which is attached to teichoic acids that are unique to the gram positive cell walls. By contrast gram negative cell wall is more complex, both structurally and chemically. More specifically, in gram negative bacteria the cell wall comprises a thin PG layer and contains an outer membrane, which covers the surface membrane. The outer membrane of gram negative bacteria often confers resistance to hydrophobic compounds, including detergents and contains as a unique component lipopolysaccharides which increase the negative charge of cell membranes and are essential for structural integrity and viability of the bacteria [11].
Species sensitivity is not only related to the structure of the cell wall in gram-positive and gram-negative bacteria. Several additional factors can influence the susceptibility or tolerance of bacteria to NPs. For example, *E. coli* is highly susceptible whereas *Staphylococcus aureus* and *Bacillus subtilis* are less susceptible to CuO NPs. The antibacterial effect of Ag NPs is higher than Cu NPs against *E. coli* and *S. aureus* bacteria. *S. aureus* and *B. subtilis* are more susceptible than *E. coli* to NiO and ZnO NPs [11].

**Role of growth rate:**

Another factor can influence the tolerance of bacteria against NPs is the rate of bacterial growth. Fast-growing bacteria are more susceptible than slow-growing bacteria to antibiotics and NPs. It is possible that the tolerance property of slow-growing bacteria is related to the expression of stress-response genes. Consequently, antibacterial effects high depend on the particular strain.

The recent development of nanotechnology has raised the possibility of environmental decontamination through several nanomaterials, processes and tools. To keep pace with this extremely rapid growth in nanotechnology in the field of remediation, it is necessary to critically assess the current knowledge of environmental decontamination where prominent scientist and researchers have provided insight in their areas of expertise, thus offering an overall picture of state-of-art of the field. These following lines summarize the expertise of
decontamination for the successful realization of remediation in drinking water from microbes through nanotechnology [32].

II.10 Characteristics of Examined Nanoparticles

This section summarizes the main characteristics of nanoparticles considered in this study and elaborates on their effectiveness in disinfection of drinking water. The selection of these nanoparticles was made by considering the nanoparticles widely studied in previous literature and found to have potential efficiency in water disinfection. In most of these studies, the nanoparticles were applied in matrix or used with different fixation methods. Those studies also overlooked the regulated limits of used nanoparticles in drinking water. On the contrary, this study accounted for the standard limits of each of these particles in drinking water since the nanoparticle were tested in suspension mode and applied directly into different water samples. Table II.2 list the standard limits of the used nanoparticles.
Table II.2 Standard limits of used nanoparticles regulated by WHO

<table>
<thead>
<tr>
<th>no</th>
<th>Nanoparticles</th>
<th>Standard limits (mg/L)</th>
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<tbody>
<tr>
<td>1</td>
<td>Ag</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>Ag-Cu</td>
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</tr>
<tr>
<td>3</td>
<td>Cu</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>CNTS</td>
<td>NA</td>
</tr>
<tr>
<td>5</td>
<td>ZnO</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>SiO₂</td>
<td>NA</td>
</tr>
<tr>
<td>7</td>
<td>MgO</td>
<td>50</td>
</tr>
</tbody>
</table>

Silver Nano particles:

Properties of silver NPs: Silver nanoparticles have unique optical, electrical and thermal properties and being incorporated into products that range from photovoltaics to biological and chemical sensors. Examples include conductive inks, pastes and fillers which utilize silver nanoparticles for their high electrical conductivity, stability and low sintering temperatures. Additional applications include molecular diagnostics and photonic devices, which take advantage of the novel optical properties of these nanomaterials. An increasingly common application is the use of silver nanoparticles for antimicrobial coatings and many textiles, keyboards wound dressing and biomedical devices now contain silver nanoparticles that continuously release a low level of silver ions to provide protection against bacteria [18].
Antimicrobial properties of silver compounds and silver ions have been historically recognized and applied in a wide range of application from disinfecting medical devices and home appliances to water treatment. The antibacterial effects of metallic silver have been known for centuries. This beneficial property originates from silver ions dissolving from the surface of bulk silver. In contrast to the use of silver ions, the biocidal effect of bulk silver is long lasting and stable. However, it is difficult to apply bulk silver in industrial or domestic applications because of its high price and low ion release rate. Recently, the application of silver nanoparticles has ushered in a new approach to the application of silver antimicrobial agents [33].

Several investigations have been carried out to find out the bactericidal effect of nanoparticles and their applications in the plastics, health, textile and paint industries. In comparison with bulk silver, silver nanoparticles release of silver ions with a controllable rate. Therefore nanoparticles are expected to play a crucial role in the food industry, water disinfection and other applications related to disinfection.

Physicochemical properties play an important role in the antimicrobial activity of Ag NP. In general particles of less than 10 nm are more toxic to bacteria such as E. coli and Pseudomonas aeruginosa. However, the mechanism of toxicity is still only partially understood. Silver ions interact with thiol groups in proteins, resulting in inactivation of respiratory enzymes and leading to the production of
ROS. It was also shown that Ag ions prevent DNA replication and affect the structure and permeability of the cell membrane.

A study [34], the treatment of *E.coli* bacteria was investigated using two common disinfectants, phenol and hypochlorite with various concentrations to compare with the bactericidal activity of Ag NPs. The full bactericidal activity of the three agents was assessed by culturing samples after 10 min and or 2 h of treatment with various concentrations of the disinfectants. Phenol disinfectants showed a MBC of 16 ppt for the 10 min treatment while the hypochlorite showed a MBC of 16 ppm under the same operational conditions. Although Ag NPs did not show a full bactericidal activity for the 10 min treatment, they displayed a MBC of 40 ppm after 2 h. With increase in the treatment time period to 6h, the Ag NPs exhibited MBC of 0.6 ppm. It was also found that the Ag NPs exhibited long term and persistent effect on *E.coli* inactivation with high efficiency (100% effective). The Ag nanoparticles may provide new opportunities for water treatment [34].

**The toxicity mechanisms of Ag NPs against bacteria:** Regarding the similarities and differences in bactericidal mechanisms of action by silver and other chemical disinfectants, it has been proposed that inhibition of microbes involves interaction of cysteine residues in critical regions of proteins, resulting in their inactivation. Other studies indicate that the silver caused leakage of potassium cations from the membrane, thereby disrupting cellular transport or respiration. Other effects observed were inhibition of growth or abnormal growth...
that caused cellular defects. Importation into the cellular body also lead to interactions with negatively charged deoxyribonucleic acid (DNA) causing nucleic acid damage. Intriguingly greater lethality was observed from electrochemically generated silver compared to ionic silver with concomitant formation of silver ions. These ions interact with lipid conjugates of polysaccharides and lead to deformation of the membrane [34].

A comparison of the bactericidal activity of Ag NPs on two types of bacteria, Gram negative (*E.coli*) and Gram positive (*S.aureus*) was performed [25]. In that study, the Gram positive bacteria *S.aureus* were used as a model microbe and treated with various concentrations of Ag NPs to determine whether the Ag NPs exhibit bactericidal activity. The bactericidal behavior was assessed by culturing sample after 2, 4, 6 and 8 h of treatment. The Ag-NPs were capable of inactivating Gram positive bacteria, however they display a high MBC to inactivating the *S.aureus* (10 ppm) compared to *E.coli* (0.6 ppm) with the same treatment time (4h). To achieve the same MBCs (2.5ppm), *S.aureus* requires longer treatment time period (8 h) to damage its cell wall/membrane and to cause cell death, whereas for *E.coli* approximately 4 h were needed. Compared to *E.coli*, *S.aureus* displayed higher resistance to Ag NPs. This may be due to the inactivation mode of the microbe being different or due to the fact that *S.aureus* has a thicker peptidoglycan layer in its cell wall. This cell wall has been demonstrated to provide resistance to chemical disinfections and allowed the cell to survive under condition, which would terminate *E.coli*. The differences in
composition of the cell wall between Gram positive/ negative bacteria could result in diminished interactions of Ag NPs with the *S. aureus*, requiring greater interaction time before the treatment was effective [34].

The mechanism of *E. coli* inactivation using Ag NPs could involve multiple processes including:

1. Indirect generation of reactive oxygen species (ROS)
2. Direct interaction of silver with proteins and lipids in the cell wall and proteins in the cytoplasmic membrane involved in transport and respiration metabolism, compromising their function.
3. Once the wall and plasma membrane are compromised potential interaction with DNA, although our results did not detect lingering nanoparticles in the cytoplasm [34].

A study [35] reported that, Graphene Oxide (GO) nanosheets impregnated with silver nanoparticles (Ag NP/GO) performed efficiently in bringing down the count of *E. coli* from $10^6$ cfu/ml to zero with 45 mg/L GO in water. The micron-scale GO nano-sheets enable them to be easily deposited on porous ceramic membranes during water flirtation, making them a promising biocide material for water disinfection.
Another study [36] investigated biosynthesis of silver nanoparticles and its activity on waterborne bacterial pathogens. In this study, silver nanoparticles showed effective inhibitory activity against waterborne pathogens Viz, *E.coli* and *Vibrio cholera*. Silver nanoparticles 10 µg/ml was recorded as the minimal inhibitory concentration (MIC) against *E.coli* and *V.cholerae*.

**Silver and copper NPs:** The use of silver in water disinfection was investigated in recent study [37] where silver and copper were supported on activated carbon by impregnation method. Further 0.1g of the catalyst was dipped in 50 cm³ raw water (pond water, which contains plenty of microorganisms with *E.coli* as main bacterial type present) taken in a 100 ml sterile transparent vessel with screw cap and stirred for 1 h in a batch mode at room temperature. After 1 h, the catalyst was filtered off and the water tested for the presence of bacteria quantitatively. The data of quantitative analysis of microorganisms present in the water samples after treating with Ag-Cu catalysts clearly indicates the highly efficient nature of 0.5 Ag-0.5 Cu/C catalysts toward controlling the microorganism. The raw water i.e. without a catalyst that is tested has shown the presence of large number of bacterial colonies. Even, with activated carbon, the catalytic activity in controlling the microorganisms is negligible. The High activity (nearly 80 %) possessed by 0.5 Ag-0.5 Cu/C catalysts was due to the strong interaction between Ag and Cu, presence of smaller particles of Ag and Cu and more amount surface composition of Ag and Cu [37].
Copper (Cu) NPs: Copper nanoparticles have already been considered for a range of uses based on their antimicrobial properties and they are widely used in lubricants, inks and other applications that make use of their anti-microbial properties. However, the biological effects of Cu-NPs can vary based on their physicochemical properties, and on their oxide content and primary size. Cu-NPs can be oxidized and exist as copper oxide nanoparticles (CuO-NPs) [38].

Copper nanoparticles have large specific surface area and a number of surface active centers. Due to its high conductivity and surface area, copper nanoparticles can be used for electromagnetic shielding and heat sinks. Cu nanoparticles can serve as catalysts for chemical reactions [39].

The exact mechanism of bacterial disinfection by CuO is not clear. However, limited proposed mechanisms are reported, one of these mechanisms is the released Cu ions from the nanoparticles going in contact with the bacteria cell membrane. The released Cu ions may lead to disorder in DNA molecules helical structure by interaction of the ions with DNA molecules.

Another proposed mechanism is the nano-effect where [37] reported that the size of nano copper oxide plays an important role on the toxicity and therefore, on the disinfection efficiency. The latest proposed mechanism is the oxidative stress [40], where reported that ROS may be induced by CuO NPs, depending on CuO
NPs dissolution rate, where ROS may cause damage to bacteria cell structure. However, the mechanism was applied to *E. coli* bacteria only [40].

**Carbon Nano Tubes (CNTs):** Carbon nanotubes are very thin, hollow cylinders made of carbon atoms. They are about 10,000 times thinner than human hair. Carbon nanotubes are produced using various thermal processes to strip carbon atoms from carbon-bearing materials and use them to form a hexagonal network of carbon atoms that is rolls up into a cylinder, or tube.

Carbon nanotubes, a new form of carbon are attracting great research interest due to their exceptional adsorption and mechanical properties and unique electrical property, highly chemical stability and large specific surface area mainly because of their extremely small sizes, uniform pore distribution and large specific surface area [41]. Carbon nanotubes adsorption technology has the potential to remove bacterial pathogens, natural organic matter (NOM), and cyanobacterial toxins from water system. Unlike many micro-porous adsorbents, CNTs possess fibrous shape with high aspect ratio, large accessible external surface area and well developed mesoporose, all contribute to the superior removal capacities of these macromolecular biomolecules and microorganisms.

Carbon nanotubes are hollow graphitic layers rolled up into cylinders. There are several types of carbon nanotubes but two types are prominent. These are multiwalled carbon nanotubes and single walled carbon nanotubes. Carbon
nano tubes possess special mechanical, electrical and structural properties and they have been exploited for use in electronics biosensing and chemical sensing. Their large surface area makes them an ideal adsorbent. Carbon nanotubes have been functionalized with cerium dioxide hydroxyl, phosphate functional groups to remove heavy metals and organics from water [41].

Properties of CNTs: Carbon nanotubes form aggregated pores due to the entanglement of tens and hundreds of individual tubes that are adhered to each other as a result of van der Waals forces of attraction. The aggregated pores have the dimensions of a mesopore or higher and are able to provide large external surface areas that can immobilize large biological contaminants including bacteria and viruses. In CNTs adsorption can occur at four regions in CNTs, at hollow interiors of nanotubes they are open ended at interstitial pore spaces between the tube bundles, at groves present at the boundary of nanotube bundles or at the external surface of the outermost CNTs. At the groove edges of nanotube bundles and the external surface area of outermost nanotubes are potential adsorption sites and provide large pore spaces that well be fully utilized by microorganisms. Thus with respect to adsorption of biological contaminants on CNTs, accessible external surface area and presence of aggregated pores with volumes greater than mesopore are considered important [42].
Cytotoxic nature of CNTs plays an indirect role in improving the microbial sorption efficiency because CNTs offers simultaneous capture and deactivation of pathogens. Antimicrobial effect of CNTs is due to its fibrous shape. Thin fibers of CNTs impinge bacterial cell surface disrupt the intracellular metabolic pathways and subsequently, the internal content are released due to the cell rupture caused by oxidative stress after impingement. It was initially though that the metal impurities (coming from catalyst source during synthesis) are responsible for cytotoxicity. However later it was established that physiochemical properties greatly influence the cytotoxic nature of CNTs. The size and length of the tubes dispersivity impurity content and number of layers (single or multi walled) are identified to influence the cytotoxic properties [42].

The toxicity mechanisms of CNTs against bacteria: In general, single walled carbon nanotubes (SWNTs), due to their short length are able to easily penetrate through the cell membrane and display higher cell toxicity than multi walled nanotubes (MWNTs). But dispersivity of CNTs is a more important parameter than length. Highly dispersed CNTs facilitate greater cell contact and thus the rate of lysing of cells is high. The semi-dispersible and partially hydrophobic CNTs exhibit greater affinity towards bacteria than both completely dispersed or weakly dispersed CNTs. Therefore, the capture and precipitation efficiency of bacteria depends on the balance between adequate dispensability and aggregation activity of CNTs, which in turn a function of its diameter [42].
Bacterial adsorption on CNTs is characterized by having three unique features. Firstly, microbial adsorption capacity on CNTs so far reported is higher than any other commercially available adsorbent media. Secondly, CNTs express selective adsorption of bacteria, a feature which is not generally seen in other adsorbents. Finally, adsorption kinetic of bacteria on CNTs is almost instantaneous suggesting their use in applications such as pathogen sensors, where it is desired to rapidly concentrate the target contaminant [42].

Research has shown carbon nanotubes have a strong ability to adsorb many types of chemical and microbial contaminants. Adsorption is one of the simplest techniques that can be used for removal of biological contaminants from raw drinking water. Majority of adsorbent media used in water treatment applications are microporous in nature. In spite of their large surface areas, these microporous media register low efficiencies in concentrating microbes simply because the pore surface area is not accessible by them. On the other hand CNTs have exceptionally high bacterial adsorption capacities. The unique properties of carbon nanotubes would allow water molecules to pass through the interior of the cylinders while chemical and microbial contaminants could not. This is filtration process called size exclusion. This could be accomplished at a higher rate of flow with very little energy (pressure) input to push the water through the nanotubes—thus a big advantage over current membrane technologies [43].
Antimicrobial properties and the efficient removal of bacterial from contaminated waters have also been demonstrated. A study [44], demonstrated that a SWNT Bucky-paper was effective in completely retaining E.coli cells due to size exclusion and also exhibited exceptionally high removal of the model virus MS2 bacteriophage due to depth filtration. Furthermore the SWNT Bucky-paper promoted the inactivation of E.coli cell which was attributed to cell membrane damage on direct contact with SWNT aggregates [44].

Surprisingly, the effect of CNTs on bacteria and viruses has not received particular attention, probably due to the difficulty of dispersing CNTs in water [34]. The antimicrobial activity of CNTs requires direct contact between CNTs and the target microorganism. Because CNTs are highly hydrophobic materials, this finding suggests that the suspension of nano-functionalized CNTs in water is very difficult and does not provide enough CNT-microbe contact for disinfection [44].

Removal of E.coli bacteria using SWCNTs interaction with microwave radiation was evaluated [45] and the main results are as follow:

- A low removal (3-5%) of E.coli bacteria was observed when CNTs alone were used, indicating that the CNTs alone do not cause bacterial death.
- A high removal of E.coli bacteria was obtained when microwave radiation was used.
Almost complete removal of *E.coli* bacteria (100%) was obtained using CNTsC\textsubscript{18}

CNTs functionalized with carbon-18 functional groups with microwave radiation generally showed the highest antibacterial activity when compared with non-functionalized carbon nanotubes interacting with microwave radiation and microwave radiation without a carbon source. This significant result were obtained due to multiple chains of C\textsubscript{18} (C–C bonds), which increased the absorption rate of the microwave heat. As an innovative application, the combination of microwaves with modified and unmodified CNTs appears to be promising and can complement the currently employed disinfection methods [45].

In another study, the use of CNTs in removal of bacterial pathogens, natural organic matter (NOM) and cyanobacterial toxins from water systems was reviewed [46]. This paper concludes that, the physiochemical properties greatly influence the cytotoxic nature of CNTs. The size and the length of the tubes, dispersivity, impurity content and number of layers (single or multi walled) are identified to influence the cytotoxic properties. It is evident that bacterial toxicity is high in case of uncapped, de-bundled, short length and highly dispersed MWNTs. In general, single walled carbon nanotubes (SWNTs), due to their short length are able to easily penetrate through the cell membrane and
display higher cell toxicity than multi walled carbon nanotubes. But dispersivity of CNTs is a more important parameter than length. High dispersed CNTs facilitate greater cell contact and thus the rate of lysing of cells is high.

CNTs are characterized by selective adsorption of bacteria. This is conformed from pure and mixed culture studies using Staphylococcus aureus and E.coli pathogens at different concentrations on pristine SWNTs. Based on that study, it appears that:

- Sorption capacity of S.aureus is 100 times greater than E.coli suggesting a size dependent and adsorption similar to others but with large magnitude of difference.
- CNTs can selectively concentrate one bacterium over the other.
- In addition to high sorption capacities adsorption of bacteria on SWNTs is also characterized by having extremely rapid kinetic rates.

The adsorption kinetic rates of B.subtilis, S.aureua and E.coli at concentration greater than 10^7 CFU/ml, suggest that more than 95% of the bacteria in the solution are concentrated by SWNTs in a time between 5 and 30 min. The enormous potential of CNTs, as represented by rapid kinetics and high sorption capacities over a wide range of bacteria [46].
Adsorption of natural organic matter (NOM):

The adsorption of NOM on carbon surface is a function of both the physical properties of the carbon material and chemical composition of NOM. Presence of micropores or mesopores, presence of specific functional groups on surface and having a net positive charge on the adsorbent surface affecting the NOM removal are mainly responsible that can dictate the sorption effectiveness of NOM. In addition, the average size of NOM and its chemical composition also play an important role [42].

Adsorption of cyanobacterial toxins:

The kinetics of sorption is also rapid in CNTs because the adsorbent molecules need to diffuse from the bulk solution to external surface of the mesopores, where they face a minimal resistance of diffusion.

Zink Oxide (ZnO) NPs: ZnO NPs can also serve as photo-catalysts. The antimicrobial mechanism of ZnO nanoparticles is unclear, but it has been postulated that hydrogen peroxide generated through photocatalysis plays a primary role. ZnO nanoparticles also inhibit microbial growth by cell membrane damage and intracellular accumulation [47].
Nanostructured zinc Oxide was investigated in water treatment by grown ZnO nanorods in a wide variety of membranes made from polyethylene, polypropylene, glass, metal, cellulose based materials like paper [48]. The authors found that the inactivation efficiencies for both \( E.\) coli and staphylococcus aureus in aqueous matrix by ZnO under illuminated conditions were almost double that under dark conditions. Inactivation in the dark was attributed to the bactericidal effect of Zn2+ ions, while under illuminated conditions the inactivation is alleviated due to photocatalytic electron injection process. The Zn ions released through dissolution binds to the tip of pili of bacteria and prolong the lag phase of the bacterial growth cycle thereby checking reproduction. Strong radicals generated through photocatalysis can disrupt bacterial cell wall creating permanent damage. In this study, the water purifier was tested on two model bacteria \( E.\) coli and S.aureus. Up to 99% \( E.\) coli and S.aureus in spiked water containing about \( 10^{10}\) colony forming units of bacteria cells could be immobilized under sunlight, while under room lighting conditions.80% of \( E.\) coli and 59 % of S.aureus cell could be inactivated. Two mechanisms come play roles in the antibacterial activity of the ZnO and the formation of reactive oxygen species (ROS) through photo-catalysis [49].

Another study [50] reported that, \( E.\) coli removal efficiency of the ZnO/UV process was approximately 45% better than that of UV alone because of the photocatlytic effect. They also found that, Photocatalytic removal of \( E.\) coli increased with increased amount of loaded ZnO due to the increased adsorption
sites on ZnO as well as the increased generation of free electrons in the conduction band. Maximum disinfection of E. coli was observed at neutral pH because of the reduced photocatalytic activity of ZnO at low and high pH values due to either acidic/photochemical corrosion of the catalyst and/or surface passivation with Zn(OH)₂. Rate of E. coli removal decreased as initial E. coli concentration increased. The presumed reason is that when the initial E. coli concentration increased, E. coli molecules obstructed the impact of UV irradiation from reaching the surface of ZnO.

Silicon Dioxide NPs: Nano SiO₂ has the features of small particle size, narrow particle size distribution, porous, large surface area and owns a large number of hydroxyl groups and unsaturated residual bonds on its surface and shows high reflectivity to long wave, visible light and ultraviolet ray [51].

The toxicity of SiO₂ may be related to the mechanisms by which the particles act on the cells. It is documented that these particles are photosensitive and produce reactive oxygen species (ROS) in the presence of light [52].

Silver nanoparticles inlaid Fe₃O₄-SiO₂ magnetic composite (Fe₃O₄-SiO₂-Ag) was investigated in water disinfection [53]. In this study, silver nanoparticles with diameter of about 10nm, were anchored homogeneously and tightly onto the silica coat of Fe₃O₄-SiO₂ magnetic nanoparticles, which increased the antibacterial abilities by avoiding the aggregation of Ag nanoparticles. The
minimum inhibitory concentrations of Fe3O4-SiO2-Ag magnetic composite to E.coli and Staphylococcus aureus were 15.625 mg/L and 31.25 mg/L respectively, and the minimum bactericidal concentrations were 250 mg/L and 500mg/L respectively. In inactivation experiment, 15 mg/L of Fe3O4-SiO2-Ag disinfectant in 150 ml of normal saline solution could kill 99.9% of the tested bacteria within 60 min. The silica coat not only acted as a supporting matrix, but also enhanced the stability of the disinfectant.

Another study [54] reported that; high concentration of SiO2 was required to achieve a reduction in cell growth. Addition of SiO2 at 5000 ppm resulted in 99% growth reduction of B.subtilis, while E.coli was less susceptible to the effects of SiO2 with 5000ppm achieving only 48% growth reduction. Although antibacterial activity increased with dose the two bacterial species behaved differently upon exposure to the same levels of nanoparticle suspensions. In this study they also report that; cell growth inhibition with SiO2 was similar under both dark and light condition, indicating that light had an insignificant effect in increasing the toxicity of SiO2.

**Magnesium Oxide (MgO) NPs:** The antibacterial activity of metal oxide appeared on the surface. Active superoxide ions are generated on the surface of the oxide, which can react with the peptide linkages in the cell wall of bacteria and thus disrupt them. The bacterial action of MgO may results from attack of these superoxide ions on carbonyl group in the peptide linkages, leading to
degradation of the proteins. As the surface area of the particles increases, it leads to an increase of the O₂ concentration in solution of the cell wall of bacteria.

Due to very high surface energy of nanoparticles, the aggregation becomes very significant due to interparticle interaction from van Der Wall's, electrostatic force. Consequently, the interaction between oxide particle and bacterium is reduced and the bactericidal efficiency tends to be lower.

A study [55] reported that the nanoparticles tend to form agglomerates inside the bacterial cell. The intimate contact between the cell and the particle seems to be more important because metal oxide particles do not necessarily have to enter the cells.

Nano-MgO is a functional material that has been widely used in various areas and recently it has been reported that MgO has a good bactericidal performance in aqueous environments [56]. Nano-MgO exhibits high activity against bacteria, spores and viruses because of its large surface area.

The positively charged particles can interact strongly with negatively charged bacteria. Compared with TiO₂, silver, copper and other kinds of solid bactericides nano-MgO has the advantage of being prepared from readily available and economical precursors and solvents, and therefore has considerable potential as a solid bactericidal material under simple conditions [36].

53
A combined system using nano-MgO and nanofiltration (NF) membrane was established to purify polluted water [57]. The combined nano-MgO-NF system could efficiently remove many kinds of pollutants in this study, including organic matter, nitrogen species, heavy metals, suspended solids and bacteria.

In addition, nano MgO has good bactericidal performance in aqueous environments due to the formation of superoxide (O$^{2-}$) anions on its surface. Furthermore, increasing the nano-MgO dosage could not elevate the removal ratio of the pollutants, but only increase the Mg content of the effluent. Thus, 0.05g/L of nano-MgO may be a suitable dosage for 2,000 L of polluted water treatment [56].

Many researchers have pointed out that NF separation was primarily caused by size exclusion and electrostatic interactions. Unfortunately, membrane fouling is still a critical problem for efficient commercialization of NF plants, which results in flux decline with operating time. Combined nano MgO-NF treatment system may offer significant potential advantages over approaches where either process is used alone. On one hand, the NF membrane supply security. On the other hand, the rejected nano MgO can remove the pollutants rejected on the surface of the NF membrane to slow down membrane fouling. Nano MgO could remove about 20% of PI, 10 % of ammonium, 95% of bacteria and all of Fe and Mn. Except for adsorption, there were two possible reasons for pollutant removal by MgO nanoparticles. One explanation is that the existence of large amounts of OH-
which were generated in the reaction between MgO and water could enhance the oxidization of superoxide (O$^-$) anions. The other is that the positive electrostatic surface charge of the formed Mg (OH)$_2$ enabled the nanoparticles to act as a powerful and efficient coagulant [57].

II.11 Removal of Nanoparticles from Treated Waters

The growing use and applications of engineered nanoparticles in a variety of industrial products and their potential for wastewater purification and drinking water treatment raise the question how these nanoparticles can be removed in the urban water cycle.

Conventional methods for the removal of particulate matter during wastewater treatment include sedimentation and filtration. However, due to the small size of nanoparticles, the sedimentation velocities are relatively low and a significant sedimentation will not occur as long as there is no formation of larger aggregates or flocculants are not added.

The stability of nanoparticle dispersions depends on the properties of the surrounding solution, namely pH and ionic strength which influence the surface charge of the particles and thus the repulsive forces between them. Furthermore, the stability can be increased by surface modifications of the particles (due to sorption of molecules). For example, an increasing ionic strength of nanoparticles
solution leads to a reduction of zeta potential and a decreased thickness of the diffuse part of the electrical double layer. The solution becomes unstable and the particles agglomerate.

The influence of sorption on the dispersive behavior of nanoparticles is also utilized in many industrial applications. In many commercial nanoparticles, suspensions surfactants are used to obtain stable dispersions. This might have a string of environmental impacts. If the surfactant-nanoparticle bonds are strong enough to persist in wastewater and the aqueous environment, an inhibition of the agglomeration should be the consequence leading to a very limited sedimentation during wastewater treatment and enhanced groundwater mobility.

Only few studies have investigated the influence of coagulants on the aggregation behaviour of nanoparticles. In conventional WWTPs, various coagulants such as aluminium sulphate, aluminium hydroxide, polystyrene sulphate, iron chloride or negatively and positively charged polymers are used for the removal of suspended matter. A study [49], investigated the influence of polyaluminium chloride (PACl) addition as a coagulant on the removal of nanoparticles from an aqueous solution. Even high concentrations of the coagulants (10.4 mg/L as Al) yielded only a small reduction of the silt density index (SDI) from 65 to 27, indicating that a significant proportion of particles remained in solution.
Aluminium sulphate (alum) was tested as potential coagulant and the influence of high electrolyte concentrations was also investigated in removal of commercial nanoparticles (TiO₂, Fe₂O₃, ZnO, NiO and SiO₂) [58]. At an alum dosage of 20 mg/L, 20-80% of commercial nanoparticles (TiO₂, Fe₂O₃, ZnO, NiO and SiO₂) were removed in nanopure water and tap water by sedimentations (following coagulation-flocculation). A further increase of the coagulant concentrations up to 60 mg/L did not enhance removal of nanoparticles.

A reduction of the zeta potential below 10 mV was observed for all investigated nanoparticles when the ionic strength was increased up to 10 mg/L (using MgCl₂). Nevertheless, 8h and 30 min, only 23-30% and 40-70% of the nanoparticles were removed. Common technologies such as flocculation might be inappropriate to remove engineered nanoparticles from water indicating the need of finding new technical solutions.

Several organic nanoparticles exhibit strong hydrophobic properties (logKow > 6). Therefore, it is likely that these particles are removed from the water phase by sorbing to suspended solids as long as they are not biodegraded. However, carbon nanomaterials such as CNTs can undergo environmental degradation, when exposed to light yielding to a modification of the surface and the introduction of hydroxyl groups in the molecule. Due to the enhanced polarity caused by the functional groups, the sorption affinity to suspended solids is reduced and mobility is increased.
Electrocoagulation has been applied for removal of fine dispersed particles from various types of wastewater. This technique is based on the continuous release of metal ions into the solution by anodic electrodes, typically made of iron and aluminum. These metal ions form hydroxides which are capable of destabilizing the particles in dispersion. However, electrocoagulation strongly depends on the type of the nanoparticles and the electric conductivity of the suspension. The magnetic properties of nanoparticles such as hematite can be utilized for their removal when applying a magnetic field. However, this technique can also be employed for nano-magnetic particles such as SiO$_2$ via magnetic seeding aggregation. Hematite and Silica particles are oppositely charged and thus aggregation can occur enabling both to be removed together from solution with magnetic fields [59].

### 11.12 Fixation Methods

Metals and metal oxide nanoparticles can be used in drinking water disinfection in different application method, they can be applied as free nanoparticles suspended in aqueous solution, or they can be fixed in different forms of matrixes. Utilization of specific nanoparticles either embedded in membranes or on other structural media that can effectively, inexpensively disinfect drinking water; has been investigated in different studies.
The stabilization and immobilization of metallic nanoparticles in different matrixes has gained increased importance since such nanoparticles purportedly present high antibacterial activity, low toxicity, chemical stability, a long-lasting action period, and thermal resistance [60].

Nanoparticles fixation could be by:

1. Bound NPs to the surface of another solid structure
2. Composites.
3. Coatings
4. Thin films
Table II.3: Summary of different fixation methods and their application in drinking water disinfection

<table>
<thead>
<tr>
<th>#</th>
<th>Fixation Method</th>
<th>Fixation procedure</th>
<th>Conclusion</th>
<th>Applied in</th>
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<tr>
<td>1</td>
<td>Bound NPs to the surface of another solid structure</td>
<td>Son et al. (2004) prepared ultrafine cellulose acetate (CA) fibers by direct electrospinning of a CA solution with 0.05 wt. % AgNO₃, followed by UV irradiation photoreduction.</td>
<td>The CA fibers with embedded Ag nanoparticles (average diameters 15.4 nm) were reported to be effective biocides against Gram-positive (S. aureus) and Gram-negative (E. coli, Klebsiella pneumoniae, and P. aeruginosa) bacteria.</td>
<td>Drinking Water</td>
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<td>Commercially available activated carbon Support has been used for silver-copper catalysts. Silver and copper are supported on activated carbon by impregnation method. Cu (NO₃)₂·3H₂O and AgNO₃ (M/s. Loba Chemie, India) are the metal precursors used for copper and silver respectively. The catalysts were prepared with varied composition of silver and copper taking increments of one metal and decrements of other metal by 0.25% by weight. Requisite amount of Ag and Cu salts are dissolved in water and the support has been dipped in this solution followed by heating to remove excess water. The resultant mass was dried in the oven for 12 hours. The samples were subjected to calcination in the flow of nitrogen (30cm³min⁻¹) at 673K for 4 hours.</td>
<td>Both Ag and Cu catalysts are known to possess good anti-bacterial activity. However in the present investigation, the catalytic activity of 0Ag-1Cu/C catalyst is better compared to that of 1Ag-0Cu/C catalyst. This is due to the smaller particle size of Cu compared to the silver particle size. No Cu particle is visible in the TEM picture of 0Ag-1Cu/C catalyst, indicating that Cu particle size is very small. On the other hand, Ag particle size in 1Ag-0Cu/C catalyst is in the range of 50nm. XRD and TEM data supports this evidence. The data of quantitative analysis of microorganisms present in the water samples after treating with Ag-Cu catalysts clearly indicates the highly efficient nature of 0.5Ag-0.5Cu/C catalyst towards controlling the</td>
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<td></td>
<td>Thin films</td>
<td>Thin film nanocomposite (TFN) membranes</td>
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<tr>
<td>Water &amp; Waste water</td>
<td>Development of TFN membranes mainly focuses on incorporating nanomaterials into the active layer of thin film composite (TFC) membranes via doping in the casting solutions or surface modification. Nanomaterials that have been researched for such applications include nano-zeolites, nano-Ag, nano-TiO₂, and CNTs. The impact of nanoparticles on membrane permeability and selectivity depends on the type, size and amount of nanoparticles added.</td>
<td>The raw water, i.e., without a tested catalyst has shown the presence of large number of bacterial colonies. CNTs (unaligned) found their application in TFN membranes due to their antimicrobial activities. Tiraferri et al. covalently bonded SWNTs to a TFC membrane surface. This approach is advantageous as it uses relatively small amount of the nanomaterial and minimizes perturbation of the active layer. The resulting TFN membrane exhibited moderate anti-bacterial properties (60% inactivation of bacteria attached on the membrane surface in 1 h contact time), potentially reducing or delaying membrane biofouling.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1- Preparation of silver nanoparticle/graphene oxide composite suspension
Silver nitrate was used as the salt precursor, hydroquinone as the reductant, and citrate as the stabilizer. Graphite oxide powder (30 mg) was dispersed in the citrate buffer solution (15 mL) by sonication for 2 h to form a stable GO colloid solution. Silver nitrate aqueous solution (10 mM, 15 mL) was then added into the solution under stirring. Hydroquinone was dissolved in the citrate buffer solution to form a 20 mg/mL solution. The hydroquinone solution was mixed with the GO and silver-containing solution. The final mixture was left undisturbed at room temperature for 75 min. The slurry-like product was centrifuged and washed with water repeatedly to remove excess reagents.

2- Preparation of paper-like materials
The Ag NP/GO composite paper was fabricated using the prepared Ag NP/GO stock suspension under vacuum filtration-induced directional flow. The obtained Ag NP/GO composite suspension was slowly filtered through a cellulose acetate membrane (47 mm in diameter, 0.22 μm pore size). GO sheets were then assembled into a paper-like material under directional flow. The films were air dried, peeled off the membrane, and cut into the desired shape for the antibacterial tests. For the blank control experiment, GO paper was prepared in a similar method as Ag NP/GO paper.

Antibacterial activity was tested using *Escherichia coli* and *Staphylococcus aureus* as model strains of Gram negative and Gram positive bacteria, respectively. The as-prepared composites exhibit stronger antibacterial activity against both. The Ag NP/GO composites performed efficiently in bringing down the count of *E. coli* from 106 cfu/mL to zero with 45 mg/L GO in water. The micron-scale GO nanosheets (lateral size) enable them to be easily deposited on porous ceramic membranes during water filtration; making them a promising biocidal material for water disinfection.
Some titanium dioxide nanoparticles were so small that they were difficult to separate from the solution. Even after centrifugation for some time, the nanoparticles did not settle down. To overcome this problem, polymer powder was added to the solution so that the polymer became coated with the nanoparticles. After the gelation process, PAN (2 g) was added followed by centrifugation and washing several times with water and anhydrous ethanol. Washing with ethanol helped to prevent agglomeration between the precipitates. The PAN/Ti(OH)$_4$ complex was then air dried. The above procedure was repeated at 25 $^\circ$C, 40 $^\circ$C, 80 $^\circ$C and 120 $^\circ$C. At each of the above temperatures, the precursor concentrations were also varied and 1.3 M, 0.7841 M, 0.392 M and 0.0492 M were used. The ratio of water to ethanol was varied so as to keep the percentage of water which brings about hydrolysis the same in all experiments.

15.00 g of CuSO$_4$·5H$_2$O with 2.34 g of TOAB (Tetraoctylammonium bromide) surfactant dissolved in 150 mL of distilled water in 250 mL round-bottom flask installed with condenser heated at about 65, 75 and 85 $^\circ$C separately to produce different NPs size, after 15 min of heating and shaking at 150 rpm, 100 mL of 2M sodium hydroxide as reducing agent rapidly added to the solution, black precipitate was formed, the black precipitate was collected, washed with distilled water and then dried.

In this study, the prepared TiO$_2$ photocatalyst was immobilized on carbon nanofibres to allow isolation and reuse of catalyst. The photocatalytic activity of the catalyst was tested using methyl orange as a model pollutant and was based on the decolourization of the dye as it was degraded. The doped TiO$_2$ exhibited higher photocatalytic activity than the undoped TiO$_2$.

CuO-TOAB stabilized NPs showed higher antibacterial activity more than that without TOAB surfactant, where it was less than 100 and 1000 $\mu$g/ml for CuO NPs with and without TOAB surfactant, respectively.
Chapter III

MATREIALS AND METHODS

III.1 Introduction

The objective of this study was to directly apply the nanoparticles in water for disinfection of desalinated water in UAE without using any matrix or supports for the NPs so that they can be easily adopted toward any ppt-treatment system. The major parameters related to the considered NPs (size, morphology, the contact time, and dosage) were determined so they can applied in practice.

NPs were first applied to sterilized tap water spiked with four types of bacteria which are commonly found and usually tested in drinking water. These are *Escherichia coli*, *Enterobacter aerogenes*, *Salmonella Typhimurium*, and *Enterococci Faecalis*. Different contact times and dosages were tested to determine their optimum values achieving the best disinfection and removal of bacteria. It is worth mentioning that the tested tap water is originated from different sources of desalinated water conveyed from Abu Dhabi and Fujaira city few hundreds of meters away from Al-Ain City; the location of undertaken lab work. The conveyed water to Al-Ain underwent chlorination at the source and at other intermediate locations along its path to Al-Ain. Sterilization was undertaken to warrant no bacteria other than the spiked ones exist in the water. The results were inspected as...
guidelines to identify suitable initial dosages and contact times of NPs applied later to non-chlorinated desalinated water. The desalinated water considered later was also tested with two conditions: one after being sterilized and spiked with specific bacteria and one as is without sterilization.

In this chapter, the synthesis methods of seven nanoparticles used in this study are described. Then the morphology characteristics of synthesized NPs are tested by Transmission Electron Microscopy (TEM). Then, the methods of chemical and bacteriological characterizations of used water samples are presented. Also the preparation method and used materials of different culture media used for the four types of spiked bacteria are described. Finally, the spiking method of four types of bacteria in the three used water samples; tap water samples, Spiked MSF water and Spiked RO water are presented along with the methods of applying NPs in the water.

The objective of spiking different bacteria in tap water was to establish the suitable conditions for application of NPs in water disinfection for both MSF (Multi Stage Flash) water samples and RO (Reverse Osmosis) water samples from UAE. And because tap water is free of any bacteria, most common tested bacteria in drinking water were selected for spiking purpose, in order to evaluate the antimicrobial efficiency of synthesized NPs in eliminating these bacteria.
In view of the previous literatures, which indicated that, the chemical composition of water can affect antimicrobial efficiency of NPs [61]. So in order to evaluate the antimicrobial efficiency of synthesized NPs for each used bacteria, spiked samples of MSF water samples and RO water were examined. Finally, the synthesized NPs were also tested in natural water samples collected from MSF plant and RO plant after the desalination and before chlorination to evaluate the efficiency of synthesized NPs in disinfection of raw water and to evaluate the possibility of using these NPs in practice as available alternative disinfection technology in desalination industries in UAE.

III.2 Syntheses of Nanoparticles

Metal nanoparticles can be prepared by chemical methods such as chemical reduction and electrochemical techniques and physical methods such as condensation and laser ablation. In this study chemical reduction method was used in synthesizing all the nanoparticles. To prevent undesired oxidation of some nanoparticles during nanoparticles preparation L-ascorbic acid was added.

Simple, inexpensive and quick chemical methods for nanoparticles synthesis is salt reduction method. This is the most common process for nanoparticles synthesis, where metal salts dissolve in a solvent such as alcohol or water. Salt then dissociates to metal cations and non-metal anion. By adding a reducing agent, the metal cations are reduced to zero-valent metal aggregate to form particles by
nucleation and growth. The particles are stabilized by adding stabilizing agent like citrate to prevent the nanoparticles from non-desired aggregation, then the final nanoparticles form precipitate. Size of the nanoparticles can be controlled by varying pH, temperature, solvent type and reducing agent type [51]. More detailed description of the synthesis procedures for the NPs considered in this study are presented below.

**Ag NPs:** 0.1 M of silver nitrate is prepared using deionized water and its solution is heated to 90 °C. The heating is undertaken under sonication followed by dropwise addition of sodium hydroxide (8M) until a brown black precipitate of silver nanoparticles is obtained. The solution is centrifuged followed by washing of the precipitate five times with deionized water. The obtained nanoparticles are freeze dried. To obtain the suspension of Ag nanoparticles, the required amount of silver nanoparticles is sonicated in deionized water containing small amounts of 1% citric acid.

**Ag-Cu NPs (70:30):** 0.1 M of silver nitrate and 0.1 M of copper Sulphate pentahydrate are prepared using deionized water. 70 ml of 0.1 M silver nitrate solution and 30 ml of 0.1 M copper sulphate solution are mixed together and heated to 90 °C. The solution is heated under sonication followed by drop wise addition of 2 M sodium hydroxide until a brown black precipitate of Ag-Cu (70:30) nanoparticles is obtained. The solution is centrifuged followed by washing of the precipitate five times with deionized water. The obtained nanoparticles are freeze
dried. To obtain the suspension of Ag nanoparticles, the required amount of silver nanoparticles is sonicated in deionized water containing small amount of 1% citric acid.

**Cu NP:** CuCl₂·2H₂O (Sinopharm Chemical reagent Co., Ltd) aqueous solution was prepared by dissolving CuCl₂·2H₂O (10 mmol) in 50 ml deionized water. A flask containing CuCl₂·2H₂O aqueous solution was heated to 80 °C in an oil bath with magnetic stirring. A 50 ml L-ascorbic acid (Sinopharm chemical Reagent Co., Ltd) aqueous solution of various concentrations (0.4, 0.6, 0.8 and 1.0 M) was dropwise added into the flask while stirring. The mixture was kept at 80 °C until a dark solution was obtained. The resulting dispersion was centrifuged at 8000 rpm for 15 min. L-ascorbic acid acted both as reducing agent and capping agent.

**CNTs:** The required sample of CNTs (Nanolab, Inc., USA) was suspended in the mixture of concentrated nitric acid (65%) and sulfuric acid (95-97%) by the volume ratio of 1:3 and boiled at 140 °C for 30 min. The chemically treated nanotubes were washed with deionized water until the supernatant attained a pH around 7 and the sample was dried in a hot air oven at 100°C. The required amount of modified CNTs is sonicated in water to obtain the required amount of modified CNTs is sonicated in water to obtain CNTs suspension.
ZnO NP: 1.48 g of Zn (OAc)$_2$$ \cdot $2H$_2$O was dissolved in 62.5 ml of methanol (Fisher Scientific Inc) and heated to 60 °C while stirring. To this solution, 0.74 g of KOH dissolved in 32.5 ml of methanol was added. After 3-5 hrs, the reaction was stopped, and the final product of a white precipitate was collected, washed twice using acetone (Sigma-Aldrich) and dried at room temperature.

SiO$_2$ NP: First, ethanol (99.99%, Aldrich) was taken and kept in a sonication bath. After 10 min, a known volume of Tetraethyl orthosilicate (99.99%, Aldrich) was added while sonicating and after 20 min, 28% ammonium hydroxide (28%, Wako) was added as a catalyst to promote the condensation reaction. Sonication was continued for a further 60 min to get a white turbid suspension.

MgO NP: 12.30 g of Mg (NO$_3$)$_2$$ \cdot $6H$_2$O (Mallinckrodt Baker Inc, ACS) were dissolved in 25 ml of 99% ethylene glycol solution (BDH Inc)). 12.5 ml of NaCO$_3$ (2.70 g) was added into above mixture under sonication (Sonicafier 450, Branson Ultrasonic Corporation, USA). After sonication for 15 min, the solution obtained was kept at rest for about 5 hrs. Then it was filtered and washed using water and dried at 50 °C. Finally, the samples were obtained under calcination.
III.3 TEM Characterization

III.3.1 Size and Morphology of NPs

TEM is a powerful technique for the determination of particle size and morphology.

The analysis was done on a CM10 PHILIPS TEM instrument. In this study, particle size determination was based on direct measurement of the particles on the TEM image. The following formulas were used to calculate the size:

\[
\text{Actual particle size (nm)} = \frac{\text{(size of particle in micrograph (mm)} \times 10^6)}{\text{final micrograph magnification}}.
\]

Final magnification = the instrument magnification at which the specimen was photographed \* enlarged magnification of the negative.

III.3.2 Surface Charge of NPs

The analysis of surface charge for used NPs was done on Zetasizer Nano-series (Malvern, UK) instrument.
III.4 Characterization of Tested Water

III.4.1 Chemical characteristics

pH, EC and TDS Analysis: Samples of tap water, MSF, and RO water were tested for pH, EC and TDS. The PH test was conduct by pH meter Orion 410 A+. EC and TDS were tested using EC meter Therom Orion 150.

Analysis of Cations: Measurements of Cations, such as Ca, K, Na, and Mg were conducted using a Flam photometer CORNING 410. The lower detection limit of the followed analysis was 0.22 ppm. The instrument was first calibrated using a calibration curve constructed for every tested cation in the range of 1 ppm to 100 ppm. Sea water samples were diluted 1000 times for Na, Ca, and K determination and diluted 250 times for Mg determination.

Analysis of anions: Anions in different water samples were determination by using ICS-90 (Dionex) ion chromatography system, AS9HCcolumn for oxyhalids (DBPs) and inorganic anions. The suppressor used is Dionex AMMS300 and carbonate anion is used as an eluent anion measurements.

Standard calibration curve is constructed for every anion included with the using DIONEX seven anions standard solutions and for every tested IDBBs. The detection limit, the linear dynamic range (LDR), low limit of linearity (LLOL), high limit of linearity (LLOL) and correction coefficient $R^2$ for each anion are all listed in Table III.1.
Table III.1: Determination limit, the linear dynamic range (LDR) and correction coefficient (r²) for each anion.

<table>
<thead>
<tr>
<th>Anions</th>
<th>Determination limit (ppm)</th>
<th>LDR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(L.L.O.L.) ppm</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.001</td>
<td>0.05</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.004</td>
<td>0.04</td>
</tr>
<tr>
<td>Nitrite</td>
<td>0.001</td>
<td>0.04</td>
</tr>
<tr>
<td>Sulphate</td>
<td>0.001</td>
<td>0.05</td>
</tr>
<tr>
<td>Fluoride</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Phosphate</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Bromide</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Bromate</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>Chlorate</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>Chlorite</td>
<td>0.010</td>
<td>0.010</td>
</tr>
<tr>
<td>Iodate</td>
<td>0.01</td>
<td></td>
</tr>
</tbody>
</table>

The analysis involved sample filtration then dilution to suitable range depending on conductivity measurements (less than 500μs). For example, RO water was diluted 10 times to achieve that. Then 1 ml of water sample is manually injected in the instrument for half an hour to cover the chromatogram of all target parameters.
III.4.2 Bacteriological characteristics of tested water

Filtration membrane method for bacteriological analysis was conducted to detect and enumerate different types of bacteria in different water samples (MFS) and permeate water samples (RO samples). 100 mL of water was filtered through a 0.45 μm membrane in each test and the whole test was repeated three times (replicates) to account for count variability.

For **Enterococci** isolation, the membrane containing the bacteria cells was placed on a selective medium, mEl agar, and incubated for 24 h at 37°C. All colonies with a blue halo are recorded as **Enterococci** colonies.

For **E.coli** isolation, the membrane containing the bacteria cells is placed on a selective medium, EMB agar, and incubated for 24 h at 44°C. All colonies with a green metallic color are recorded as **E.coli** colonies.

For **Coliform Bacilli** Isolation, the membrane containing the bacteria cells is placed on a pad saturated with 2 ml of M-Endo broth MF, and incubated for 24 h at 35°C.

For **Aerobic colony Isolation**, the membrane containing the bacteria cells is placed on a nutrient agar, and incubated for 24 h at 37°C.
For *Pseudomonas aeruginosa* Isolation, the membrane containing the bacteria cells is placed on SLED (System Lactose Electrolyte Deficient) agar, and incubated for 24 h at 42°C.

For *Sulphite reducing clostridia* Isolation, the membrane containing the bacteria cells is placed on *Sulphite reducing clostridia* selective agar media, and incubated for 24 h at 37°C.

### III.5 Micro-organisms and Bacterial Cultures Media

For water disinfection experiments, the most common bacteria strains which can contaminate drinking water were determine. These are: *Escherichia coli*, *Enterobacter aerogenes* TPC129, *Salmonella* Typhimurium ATCC 14028, and, *Enterococcus Faecalis* NCTC775, were selected.

**Bacterial Culture media:** Different selective media were prepared according to the standard procedure. XLD agar (Fluka analytical) for Salmonella bacterium was prepared by dissolving 56.7 g in 1 litter distilled water and heat the solution slightly without autoclave. Then, cooling to 60°C it was distributed to Patri-Plates and left for solidification.

**EMB agar** (Fluka analytical) for *E.Coli* bacterium was prepared by suspending 37.5g in 1 liter of distilled water. This solution then, sterilized in autoclave at 121°C for 15 minutes. Then, the medium was cooled to 60°C and shaking to oxidize the
methylene blue and to suspend the predicate. Finally, the media distributed in to Patri-Plates and left for solidification.

**MacConkey agar** (SIGMA) for *Enterobacter* bacterium was prepared by dissolving 54.5 g in to 1 liter distillated water. This solution then, sterilized in autoclave at 121°C for 15 minutes. Then, the medium was cooled to 60°C. Finally, it distributed in to Patri-Plates and left for solidification.

**Kf-Streptococcus agar** (Fluka analytical) for *enterococci* bacterium was prepared by dissolving the 76g to 1 liter in distilled water. This solution then, sterilized in autoclave at 121°C for 10 minutes. Then, it cooled to 50°C and 1ml of 1% triphenyltetrazolium chloride solution was added. Finally, it distributed in to Patri-Plates and left for solidification.

Nutrient Broth (LAB M) was prepared by dissolving 13 g into 100 ml deionized water then allows soaking for 10 minutes. Then, it dispended in to 10 bottles, 100ml in each bottle. Finally, it sterilized by autoclaving at 121°C for 15 minutes.

**Broth Culture**: Each bacterium was cultivated in 100ml nutrient broth and incubated at 37°C for 24 hrs.

**III.6 Spiked experiment with Tap Water**:

Spiked experiments were conducted for the three types of tested water; tap water, MSF water and RO water. Different NPs dosages were applied to each type of
water considering the standard limit for each metal in drinking water regulated by WHO, and for different contact times as illustrated in tables III.2 and III.3.

Table III.2: Different contact times for different used bacteria.

<table>
<thead>
<tr>
<th></th>
<th>E coli</th>
<th>Enterobacter</th>
<th>Salmonella</th>
<th>Enterococci</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact Time 1</td>
<td>1 hour</td>
<td>30 minutes</td>
<td>30 minutes</td>
<td>1 hour</td>
</tr>
<tr>
<td>Contact Time 2</td>
<td>2 hours</td>
<td>1 hour</td>
<td>1 hour</td>
<td>2 hours</td>
</tr>
</tbody>
</table>

Table III.3: Different NPs dose (µl/100ml) for different water samples.

<table>
<thead>
<tr>
<th>Water Samples</th>
<th>Standard Limit</th>
<th>Standard limit</th>
<th>Spiked Tap water</th>
<th>Spiked MSF water</th>
<th>Spiked RO water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µg/l</td>
<td>µl/100ml</td>
<td>Conc. µl/100ml</td>
<td>Dose µl/100ml</td>
<td>Conc. µl/100ml</td>
</tr>
<tr>
<td>Ag NPs</td>
<td>0.1</td>
<td>1</td>
<td>0.053</td>
<td>2</td>
<td>0.1</td>
</tr>
<tr>
<td>Ag-Cu NPs</td>
<td>2</td>
<td>2</td>
<td>0.2</td>
<td>4</td>
<td>0.4</td>
</tr>
<tr>
<td>Cu NPs</td>
<td>2</td>
<td>20</td>
<td>0.2</td>
<td>4</td>
<td>0.4</td>
</tr>
<tr>
<td>CNTs</td>
<td>5</td>
<td>10</td>
<td>0.5</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>ZnO NPs</td>
<td>5</td>
<td>50</td>
<td>0.5</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>SiO₂ NPs</td>
<td>5</td>
<td>10</td>
<td>5</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>MgO NPs</td>
<td>50</td>
<td>500</td>
<td>5</td>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>
Spiking Water Samples with 4 bacteria strains

Three sets of water samples: Tap Water, MSF water and RO water, were sterilized and spiked with four types of bacteria as per the following procedures:

1. Stock solution was prepared by taking full loop of colonies from each strain type and cultivated in 100 ml nutrient broth for 24 hrs at 37°C.

2. Serial dilution was done by taking 0.8 ml from the stock solution and diluted into 1000 ml sterilized water samples. Then 0.1 ml was taken from that dilution and added to 2700 ml sterilized water samples. The diluted water was shaken in order to obtain homogenous sample. Then, the diluted water was distributed to 9 sterilized beakers, 200ml in six beakers and 300 ml in three beakers (control beakers).

3. Two different dosages (as illustrated in table III.3) of nano-particles were distributed to six 200ml beakers while three 300ml beakers left as a control.

4. 100 ml from each control beakers was filtered as a control at time zero by using Millipore filtration device and 0.45 μm filter papers. Then the filter papers were placed in petri plates containing selective agar media for each bacteria.

5. The water samples were incubated in 37°C and shacked in reciprocating shaker at 60 rpm for different contact times (as illustrated in tableIII.2).

6. The 100 ml from each sample was filtered using 0.45 μm filter papers. Then the filter papers were placed on to petri plates containing selective agar media for different bacteria. The petri plates contains the filters were incubated at 37°C for 24 hrs.
7- Then the remaining samples retain back to the incubator for second contact time (as illustrated in table III.2) and the above steps are repeated.

II.7 Non-Spiked MSF distillate and RO permeate samples with 7 nanoparticles:

The bacteriological analysis of water samples collected from MSF plant and RO plant show high concentration of bacteria so the dose (µl/100ml) of NPs was increased (but still under the standard limit) as shown in table III.3. And the contact time was same as in table III.2.

Table III.4: NPs dose applied to distillate and permeate samples (µl/100ml)

<table>
<thead>
<tr>
<th>Water samples</th>
<th>Distillate</th>
<th>Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPs dose</td>
<td>Dose 1</td>
<td>Dose 2</td>
</tr>
<tr>
<td>Ag NPs</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Ag-Cu NPs</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Cu NPs</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>CNTs</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>ZnO NPs</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>SiO₂ NPs</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Mg NPs</td>
<td>10</td>
<td>20</td>
</tr>
</tbody>
</table>
Experiment of Non-Spiked MSF distillate and RO permeate samples with 7 nano-particles:

1. The water samples were distributed into 9 sterilized beakers.

2. Two different dosages of nano-particles (as illustrated in Table 4) were added to 6 beakers and 3 beakers were left as a control.

3. 100 ml from control beakers were filtered as a control at time zero by using Millipore filtration device and 0.45 μm filter papers. Then the filter papers were placed in petri plates containing nutrient agar media.

4. The plates containing the membrane incubated at 37°C for 24 hours. Then the water samples (with different nanoparticles dose) incubated in 37°C and shacked in reciprocating shaker at 60 rpm for 1 hour.

5. Then 100 ml from each sample were filtered using 0.45 μm filter papers. Then the filter papers were placed onto petri plates containing nutrient agar media. The petri plates contain the filters were incubated at 37°C for 24 hrs.

6. Then the remaining samples retain back to the incubator for one more hour. Then the above steps repeated.
Chapter IV
RESULTS

Results obtained from the analyses and experiments conducted in this study are illustrated in this chapter including: NPs size and morphology by TEM, chemical and bacteriological analysis of the tested water samples, antibacterial experiments with spiked samples and with non-spiked samples. Finally, the result of formed IDBPs (In Organic By-Products), mainly chlorate, chlorite, bromate and iodate, in the tested desalinated water are presented.

IV.1 TEM Results of NPs

TEM characterization was used to show the surface morphology and estimated the sizes of prepared NPs. The TEM images of considered NPs in the first and second batches are in the in figures. IV.1 and IV.2; respectively. While several images reflect clear and segregated particles (mostly in batch II), many others reflect collided particles agglomerated at different levels at different times; mostly in Batch II whose particles are larger than those in batch I. The shape of particles was determined by visual inspection: either spherical or irregular. Finally, the sizes of
Different NPs in both batches were determined as per the method described in section III and using the image scale shown at the top. Sizes, morphology and surface charge of all NPs in both batches are listed in Table IV.1

Table IV.1: Size and morphology of used NPs

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>Size in nm</th>
<th>Surface Charge</th>
<th>Morphology of NPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>First batch</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>17.5</td>
<td>Negative</td>
<td>Irregular</td>
</tr>
<tr>
<td>Ag-Cu</td>
<td>36.5</td>
<td>Negative</td>
<td>Irregular</td>
</tr>
<tr>
<td>CuO</td>
<td>12.9</td>
<td>Negative</td>
<td>Irregular</td>
</tr>
<tr>
<td>CNTs</td>
<td></td>
<td>Negative</td>
<td>Cylindrical</td>
</tr>
<tr>
<td>ZnO</td>
<td>17.5</td>
<td>Positive</td>
<td>Irregular</td>
</tr>
<tr>
<td>SiO₂</td>
<td>15.5</td>
<td>Negative</td>
<td>Spherical</td>
</tr>
<tr>
<td>MgO</td>
<td>42.4</td>
<td>Positive</td>
<td>Irregular</td>
</tr>
<tr>
<td>Second batch</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>29.6</td>
<td>Negative</td>
<td>Irregular</td>
</tr>
<tr>
<td>Ag-Cu</td>
<td>34.8</td>
<td>Negative</td>
<td>Irregular</td>
</tr>
<tr>
<td>Cu</td>
<td>37.8</td>
<td>Negative</td>
<td>Irregular</td>
</tr>
<tr>
<td>CNTs</td>
<td>11.99</td>
<td>Negative</td>
<td>Cylindrical</td>
</tr>
<tr>
<td>ZnO</td>
<td>11.99</td>
<td>Positive</td>
<td>Irregular</td>
</tr>
<tr>
<td>SiO₂</td>
<td>386.8</td>
<td>Negative</td>
<td>Spherical</td>
</tr>
<tr>
<td>MgO</td>
<td>229.2</td>
<td>Positive</td>
<td>Irregular</td>
</tr>
</tbody>
</table>
Figure IV. 1: TEM images of NPs in the first batch
Figure IV. 2 TEM images of NPs in the second batch
IV.2 Characteristics of water samples

This section presents the results of chemical and bacteriological analyses for different tested water samples. Chemical parameters (quoted in mg/l) were analyzed for three sets of water samples: tap water samples, MSF water samples, and RO water samples.

Table IV.2: Results for the intake seawater before and after pretreatment for both MSF and RO desalination plants.

<table>
<thead>
<tr>
<th>Water Sample ID</th>
<th>Intake sea water before pretreatment for MSF water samples</th>
<th>Intake sea water after pretreatment for MSF water samples</th>
<th>Intake sea water before pretreatment for RO water samples</th>
<th>Intake sea water after pretreatment for RO water samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>24700</td>
<td>24500</td>
<td>23700</td>
<td>23850</td>
</tr>
<tr>
<td>Br⁻</td>
<td>80</td>
<td>81</td>
<td>66</td>
<td>68</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>5200</td>
<td>5102</td>
<td>4750</td>
<td>4760</td>
</tr>
<tr>
<td>Na⁺</td>
<td>16890</td>
<td>16710</td>
<td>15500</td>
<td>15900</td>
</tr>
<tr>
<td>K⁺</td>
<td>533</td>
<td>521</td>
<td>477</td>
<td>479</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>502</td>
<td>490</td>
<td>487</td>
<td>492</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>2400</td>
<td>2350</td>
<td>1600</td>
<td>1650</td>
</tr>
<tr>
<td>EC ms/cm</td>
<td>73.4</td>
<td>73.4</td>
<td>62</td>
<td>62.8</td>
</tr>
<tr>
<td>TDS</td>
<td>44700</td>
<td>44500</td>
<td>35000</td>
<td>35600</td>
</tr>
<tr>
<td>Salinity</td>
<td>44.4</td>
<td>44.2</td>
<td>38.6</td>
<td>35.6</td>
</tr>
<tr>
<td>pH</td>
<td>7.2</td>
<td>7.3</td>
<td>7.8</td>
<td>7.6</td>
</tr>
</tbody>
</table>
Table IV.3: Results for Tap water, MSF distillate, and RO permeate.

<table>
<thead>
<tr>
<th>Water Sample ID</th>
<th>Tap Water</th>
<th>MSF Distillate</th>
<th>RO Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>F⁻</td>
<td>0.02</td>
<td>0.0087</td>
<td>0.025</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>75</td>
<td>10.6</td>
<td>103</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.5</td>
<td>0.24</td>
<td>0.2</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>4.96</td>
<td>1.3</td>
<td>4.2</td>
</tr>
<tr>
<td>Na⁺</td>
<td>60</td>
<td>12</td>
<td>80</td>
</tr>
<tr>
<td>K⁺</td>
<td>5</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>10</td>
<td>4</td>
<td>12</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>Less than 1 ppm</td>
<td>Less than 1 ppm</td>
<td>Less than 1 ppm</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>20</td>
<td>15</td>
<td>Less than 1 ppm</td>
</tr>
<tr>
<td>EC μS/cm</td>
<td>268</td>
<td>80</td>
<td>148</td>
</tr>
</tbody>
</table>

Bacteriological characteristic of distillate water and permeate water after desalination and before chlorination are shown in table IV.4 and IV.5; respectively.

Table IV.4: Results of bacteriological analyses for distillate waters (CFU/100ml)

<table>
<thead>
<tr>
<th>No</th>
<th>Bacterial strain</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><em>E.coli</em></td>
<td>ND</td>
</tr>
<tr>
<td>2</td>
<td><em>Pseudomonas aeruginosa</em></td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td><em>Coliform bacilli</em></td>
<td>2.4*10¹⁰</td>
</tr>
<tr>
<td>4</td>
<td>Aerobic colony count</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td><em>Enterococci</em></td>
<td>ND</td>
</tr>
<tr>
<td>6</td>
<td><em>Sulphite reducing clostridia</em></td>
<td>ND</td>
</tr>
</tbody>
</table>
Table IV.5: Results of bacteriological analyses for permeate water (CFU/100ml)

<table>
<thead>
<tr>
<th>No</th>
<th>Bacterial strain</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><em>E. coli</em></td>
<td>ND</td>
</tr>
<tr>
<td>2</td>
<td><em>Pseudomonas aeruginosa</em></td>
<td>$5.6 \times 10^5$</td>
</tr>
<tr>
<td>3</td>
<td><em>Coliform bacilli</em></td>
<td>$8.3 \times 10^4$</td>
</tr>
<tr>
<td>4</td>
<td>Aerobic colony count</td>
<td>$5.9 \times 10^4$</td>
</tr>
<tr>
<td>5</td>
<td><em>Enterococci</em></td>
<td>ND</td>
</tr>
<tr>
<td>6</td>
<td><em>Sulphite reducing clostridia</em></td>
<td>ND</td>
</tr>
</tbody>
</table>

IV.3 Antimicrobial activity of NPs against microorganisms

The antimicrobial activity of considered NPs applied in water samples in suspension mode are represented by bacterial degradation percentages referenced to blank samples (not spiked with any NPs). Each test and bacterial count was carried out three times (three replicates) and the averages and standard deviations of bacterial counts for all scenarios are reported in Appendix A for the seven considered NPs. The detailed results reported in Appendix A are summarized in Tables IV.6 to IV.12 by reporting the averages of bacterial degradation percentages for different doses of suspended NPs in 100 ml Spiked tap water, Spiked distillate water; Spiked permeate water, MSF water, and RO water and for two different contact times (T1 and T2 reported earlier in Table IV)

Although antibacterial activity increased with dose and contact time for all treatments, the four bacterial species behaved differently upon exposure to the same levels of nanoparticle suspensions.
Table IV.6: Bacterial degradation percentages for different water samples spiked with different doses of Ag NPs and for different contact times.

<table>
<thead>
<tr>
<th>Ag NPs</th>
<th>Tap Water</th>
<th>MSF</th>
<th>RO</th>
<th>Distillate</th>
<th>Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact Time</td>
<td>T1</td>
<td>T2</td>
<td>T1</td>
<td>T2</td>
<td>T1</td>
</tr>
<tr>
<td>First dose (µl/100ml)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>E.coli</td>
<td>84.5</td>
<td>100</td>
<td>95.8</td>
<td>100</td>
<td>99.2</td>
</tr>
<tr>
<td>Enterobacter</td>
<td>85.9</td>
<td>100</td>
<td>87.96</td>
<td>89.2</td>
<td>98.9</td>
</tr>
<tr>
<td>Salmonella</td>
<td>85.96</td>
<td>100</td>
<td>72.9</td>
<td>97.4</td>
<td>46.9</td>
</tr>
<tr>
<td>Enterococci</td>
<td>62.7</td>
<td>92.8</td>
<td>97.2</td>
<td>100</td>
<td>69.5</td>
</tr>
<tr>
<td>Second dose (µl/100ml)</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>E.coli</td>
<td>99.5</td>
<td>100</td>
<td>98.9</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Enterobacter</td>
<td>99.7</td>
<td>100</td>
<td>96.1</td>
<td>100</td>
<td>99.9</td>
</tr>
<tr>
<td>Salmonella</td>
<td>91.2</td>
<td>100</td>
<td>84.9</td>
<td>100</td>
<td>61.7</td>
</tr>
<tr>
<td>Enterococci</td>
<td>71.3</td>
<td>100</td>
<td>99.4</td>
<td>100</td>
<td>98.97</td>
</tr>
</tbody>
</table>

Table IV.7: Bacterial degradation percentages for different water samples spiked with different doses of Ag-Cu NPs and for different contact times.

<table>
<thead>
<tr>
<th>Ag-Cu NPs</th>
<th>Tap Water</th>
<th>MSF</th>
<th>RO</th>
<th>Distillate</th>
<th>Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact Time</td>
<td>T1</td>
<td>T2</td>
<td>T1</td>
<td>T2</td>
<td>T1</td>
</tr>
<tr>
<td>First dose (µl/100ml)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>E.coli</td>
<td>46</td>
<td>84</td>
<td>55.7</td>
<td>100</td>
<td>32.9</td>
</tr>
<tr>
<td>Enterobacter</td>
<td>100</td>
<td>100</td>
<td>90.0</td>
<td>96.4</td>
<td>91.8</td>
</tr>
<tr>
<td>Salmonella</td>
<td>95.3</td>
<td>100</td>
<td>56.9</td>
<td>89.7</td>
<td>56.5</td>
</tr>
<tr>
<td>Enterococci</td>
<td>78.4</td>
<td>78.7</td>
<td>73.6</td>
<td>94</td>
<td>46.4</td>
</tr>
<tr>
<td>Second dose (µl/100ml)</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>E.coli</td>
<td>66.9</td>
<td>100</td>
<td>93.4</td>
<td>100</td>
<td>73.2</td>
</tr>
<tr>
<td>Enterobacter</td>
<td>100</td>
<td>100</td>
<td>96.1</td>
<td>100</td>
<td>94.6</td>
</tr>
<tr>
<td>Salmonella</td>
<td>97.9</td>
<td>100</td>
<td>84.9</td>
<td>100</td>
<td>81.3</td>
</tr>
<tr>
<td>Enterococci</td>
<td>88.9</td>
<td>98.1</td>
<td>88.1</td>
<td>96.9</td>
<td>58.7</td>
</tr>
</tbody>
</table>
Table IV.8: Bacterial degradation percentages for different water samples spiked with different doses of Cu NPs and for different contact times

<table>
<thead>
<tr>
<th>Cu NPs</th>
<th>Tap Water</th>
<th>MSF</th>
<th>RO</th>
<th>Distillate</th>
<th>Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact Time</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>First dose</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(µl/100ml)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. coli</td>
<td>7</td>
<td>19.4</td>
<td>24</td>
<td>32.2</td>
<td>77.8</td>
</tr>
<tr>
<td>Enterobacter</td>
<td>51.5</td>
<td>81</td>
<td>70.5</td>
<td>70.8</td>
<td>73.3</td>
</tr>
<tr>
<td>Salmonella</td>
<td>74.4</td>
<td>100</td>
<td>61.5</td>
<td>72.5</td>
<td>89.9</td>
</tr>
<tr>
<td>Enterococci</td>
<td>36.4</td>
<td>41.9</td>
<td>49</td>
<td>51</td>
<td>62.4</td>
</tr>
<tr>
<td>Second dose</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(µl/100ml)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. coli</td>
<td>18.1</td>
<td>23.5</td>
<td>51.8</td>
<td>56.99</td>
<td>100</td>
</tr>
<tr>
<td>Enterobacter</td>
<td>74.3</td>
<td>91.1</td>
<td>60.8</td>
<td>70.5</td>
<td>99.7</td>
</tr>
<tr>
<td>Salmonella</td>
<td>94.4</td>
<td>100</td>
<td>79.3</td>
<td>81.7</td>
<td>94.7</td>
</tr>
<tr>
<td>Enterococci</td>
<td>52.8</td>
<td>57.3</td>
<td>67.4</td>
<td>71.5</td>
<td>100</td>
</tr>
</tbody>
</table>

*100% because the control had only 3 colonies

Table IV.9: Bacterial degradation percentages for different water samples spiked with different doses of CNTs and for different contact times.

<table>
<thead>
<tr>
<th>CNTs</th>
<th>Tap Water</th>
<th>MSF</th>
<th>RO</th>
<th>Distillate</th>
<th>Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact Time</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>First dose</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(µl/100ml)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. coli</td>
<td>17</td>
<td>18</td>
<td>52</td>
<td>75</td>
<td>48.6</td>
</tr>
<tr>
<td>Enterobacter</td>
<td>41.2</td>
<td>*100</td>
<td>33.9</td>
<td>42.3</td>
<td>32</td>
</tr>
<tr>
<td>Salmonella</td>
<td>23.2</td>
<td>0</td>
<td>29.1</td>
<td>67.2</td>
<td>50.7</td>
</tr>
<tr>
<td>Enterococci</td>
<td>11.9</td>
<td>12.9</td>
<td>36.3</td>
<td>62</td>
<td>33.3</td>
</tr>
<tr>
<td>Second dose</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(µl/100ml)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E. coli</td>
<td>21.9</td>
<td>27.7</td>
<td>72.9</td>
<td>93.8</td>
<td>81.4</td>
</tr>
<tr>
<td>Enterobacter</td>
<td>85.3</td>
<td>100</td>
<td>52.1</td>
<td>65</td>
<td>36</td>
</tr>
<tr>
<td>Salmonella</td>
<td>55.4</td>
<td>0</td>
<td>57.8</td>
<td>77.97</td>
<td>58.9</td>
</tr>
<tr>
<td>Enterococci</td>
<td>17.9</td>
<td>22.9</td>
<td>67.2</td>
<td>82.95</td>
<td>68.1</td>
</tr>
</tbody>
</table>
Table IV.10: Bacterial degradation percentages for different water samples spiked with different doses of ZnO NPs and for different contact times.

<table>
<thead>
<tr>
<th>ZnO NPs</th>
<th>Tap Water</th>
<th>MSF</th>
<th>RO</th>
<th>Distillate</th>
<th>Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact Time</td>
<td>T1</td>
<td>T2</td>
<td>T1</td>
<td>T2</td>
<td>T1</td>
</tr>
<tr>
<td>First dose (µl/100ml)</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td><em>E.coli</em></td>
<td>20</td>
<td>23.9</td>
<td>43.3</td>
<td>92</td>
<td>45.8</td>
</tr>
<tr>
<td><em>Enterobacter</em></td>
<td>23</td>
<td>28.3</td>
<td>50</td>
<td>65.8</td>
<td>36.4</td>
</tr>
<tr>
<td><em>Salmonella</em></td>
<td>3.1</td>
<td>3.7</td>
<td>33</td>
<td>50.5</td>
<td>56.7</td>
</tr>
<tr>
<td><em>Enterococci</em></td>
<td>7.9</td>
<td>11.9</td>
<td>11.5</td>
<td>17</td>
<td>3.2</td>
</tr>
<tr>
<td>Second dose (µl/100ml)</td>
<td>10</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td><em>E.coli</em></td>
<td>33.4</td>
<td>48.3</td>
<td>73.3</td>
<td>98.4</td>
<td>73.5</td>
</tr>
<tr>
<td><em>Enterobacter</em></td>
<td>33</td>
<td>45</td>
<td>90.5</td>
<td>100</td>
<td>90.9</td>
</tr>
<tr>
<td><em>Salmonella</em></td>
<td>6.25</td>
<td>70.4</td>
<td>73.3</td>
<td>75.7</td>
<td>73.6</td>
</tr>
<tr>
<td><em>Enterococci</em></td>
<td>11.6</td>
<td>17.1</td>
<td>22.3</td>
<td>29.8</td>
<td>21.2</td>
</tr>
</tbody>
</table>

*100% because the control had only 2 colonies.

Table IV.11: Bacterial degradation percentages for different water samples spiked with different doses of SiO₂ NPs and for different contact times.

<table>
<thead>
<tr>
<th>SiO₂ NPs</th>
<th>Tap Water</th>
<th>MSF</th>
<th>RO</th>
<th>Distillate</th>
<th>Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact Time</td>
<td>T1</td>
<td>T2</td>
<td>T1</td>
<td>T2</td>
<td>T1</td>
</tr>
<tr>
<td>First dose (µl/100ml)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td><em>E.coli</em></td>
<td>34</td>
<td>34.8</td>
<td>8.9</td>
<td>16.8</td>
<td>14.6</td>
</tr>
<tr>
<td><em>Enterobacter</em></td>
<td>0.4</td>
<td>52</td>
<td>37.2</td>
<td>49.2</td>
<td>27.8</td>
</tr>
<tr>
<td><em>Salmonella</em></td>
<td>6</td>
<td>36.6</td>
<td>8.6</td>
<td>35.3</td>
<td>10.9</td>
</tr>
<tr>
<td><em>Enterococci</em></td>
<td>23.8</td>
<td>26.2</td>
<td>28.2</td>
<td>30</td>
<td>11.6</td>
</tr>
<tr>
<td>Second dose (µl/100ml)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td><em>E.coli</em></td>
<td>35.7</td>
<td>44.4</td>
<td>23.5</td>
<td>30.9</td>
<td>30.2</td>
</tr>
<tr>
<td><em>Enterobacter</em></td>
<td>32.6</td>
<td>72.7</td>
<td>56.96</td>
<td>62.6</td>
<td>50.8</td>
</tr>
<tr>
<td><em>Salmonella</em></td>
<td>17.5</td>
<td>40.9</td>
<td>24.8</td>
<td>49.9</td>
<td>14.7</td>
</tr>
<tr>
<td><em>Enterococci</em></td>
<td>33.7</td>
<td>40.4</td>
<td>33.1</td>
<td>36.1</td>
<td>13.8</td>
</tr>
</tbody>
</table>

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Table IV.12: Bacterial degradation percentages for different water samples spiked with different doses of MgO NPs and for different contact times

<table>
<thead>
<tr>
<th>MgO NPs</th>
<th>Tap Water</th>
<th>MSF</th>
<th>RO</th>
<th>Distillate</th>
<th>Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact Time</td>
<td>T1</td>
<td>T2</td>
<td>T1</td>
<td>T2</td>
<td>T1</td>
</tr>
<tr>
<td>First dose (µl/100ml)</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>E. coli</td>
<td>12.3</td>
<td>25.5</td>
<td>19.7</td>
<td>19.8</td>
<td>41.5</td>
</tr>
<tr>
<td>Enterobacter</td>
<td>40</td>
<td>*100</td>
<td>21.5</td>
<td>69.3</td>
<td>2.5</td>
</tr>
<tr>
<td>Salmonella</td>
<td>12.7</td>
<td>28</td>
<td>89.7</td>
<td>92.2</td>
<td>15.6</td>
</tr>
<tr>
<td>Enterococci</td>
<td>6.9</td>
<td>11</td>
<td>15</td>
<td>15</td>
<td>8.1</td>
</tr>
<tr>
<td>Second dose (µl/100ml)</td>
<td></td>
<td></td>
<td>10</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>E. coli</td>
<td>36.4</td>
<td>46.4</td>
<td>63.1</td>
<td>82.9</td>
<td>45.6</td>
</tr>
<tr>
<td>Enterobacter</td>
<td>100</td>
<td>100</td>
<td>68.9</td>
<td>96</td>
<td>6.6</td>
</tr>
<tr>
<td>Salmonella</td>
<td>15.1</td>
<td>39.8</td>
<td>94.6</td>
<td>98.8</td>
<td>23.3</td>
</tr>
<tr>
<td>Enterococci</td>
<td>9.6</td>
<td>17.1</td>
<td>61.6</td>
<td>64.9</td>
<td>9.8</td>
</tr>
</tbody>
</table>

*100% because the control had only 3 colonies

The results reported in Tables IV.6 to IV.12 are summarized and reproduced in another set of tables for the four types of considered water samples: Table IV.13 for tap water, Table IV.14 for Spiked MSF water, Table IV.15 for Spiked RO water, Table IV.16 for non-spiked desalinated water (distillate and permeate). Table IV.17 combine all the average results reported in these tables (Dose II and Contact time II) for easy reference and comparison.
Table IV.13: Overall bacterial degradation percentage for tap water spiked by 4 indicators and treated by synthesized NPs at second dose and second contact time.

<table>
<thead>
<tr>
<th>Tap Water</th>
<th>E.coli</th>
<th>Enterobacter</th>
<th>Salmonella</th>
<th>Enterococci</th>
<th>Average removal percentage of all indicators</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag NPs</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Ag-Cu NPs</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>98.1</td>
<td>99.5</td>
</tr>
<tr>
<td>CuO NPs</td>
<td>23.5</td>
<td>91</td>
<td>100</td>
<td>57.3</td>
<td>67.95</td>
</tr>
<tr>
<td>ZnO NPs</td>
<td>48.3</td>
<td>45</td>
<td>70.4</td>
<td>11.6</td>
<td>43.83</td>
</tr>
<tr>
<td>MgO NPs</td>
<td>36.4</td>
<td>100</td>
<td>39.2</td>
<td>17.1</td>
<td>48.18</td>
</tr>
<tr>
<td>SiO₂ NPs</td>
<td>44.4</td>
<td>72.2</td>
<td>40.8</td>
<td>40.6</td>
<td>49.5</td>
</tr>
<tr>
<td>CNTs</td>
<td>27.7</td>
<td>100</td>
<td>55.4</td>
<td>22.96</td>
<td>51.52</td>
</tr>
</tbody>
</table>

Table IV.14: Overall bacterial degradation percentage for MSF water spiked by 4 indicators and treated by synthesized NPs at second dose and second contact times

<table>
<thead>
<tr>
<th>Spiked MSF Water</th>
<th>E.coli</th>
<th>Enterobacter</th>
<th>Salmonella</th>
<th>Enterococci</th>
<th>Average removal percentage of all indicators</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag NPs</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Ag-Cu NPs</td>
<td>100</td>
<td>100</td>
<td>98.3</td>
<td>96.9</td>
<td>99</td>
</tr>
<tr>
<td>Cu NPs</td>
<td>56.99</td>
<td>53.7</td>
<td>79.3</td>
<td>71.5</td>
<td>65.37</td>
</tr>
<tr>
<td>ZnO NPs</td>
<td>98.4</td>
<td>75.7</td>
<td>70.4</td>
<td>29.8</td>
<td>68.58</td>
</tr>
<tr>
<td>MgO NPs</td>
<td>82.9</td>
<td>96</td>
<td>98.8</td>
<td>64.9</td>
<td>85.65</td>
</tr>
<tr>
<td>SiO₂ NPs</td>
<td>30.9</td>
<td>62.2</td>
<td>49.9</td>
<td>36.1</td>
<td>44.78</td>
</tr>
<tr>
<td>CNTs</td>
<td>92.8</td>
<td>65</td>
<td>77.97</td>
<td>82.95</td>
<td>79.68</td>
</tr>
</tbody>
</table>
Table IV.15: Overall Bacterial degradation percentages for RO water spiked by 4 indicators and treated by synthesized NPs at second dose and second contact times.

<table>
<thead>
<tr>
<th>Spiked RO Water</th>
<th>E.coli</th>
<th>Enterobactor</th>
<th>Salmonella</th>
<th>Enterococci</th>
<th>Average removal percentage of all indicators</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag NPs</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>89.1</td>
<td>97.3</td>
</tr>
<tr>
<td>Ag-Cu NPs</td>
<td>100</td>
<td>100</td>
<td>68.3</td>
<td>68.1</td>
<td>84.1</td>
</tr>
<tr>
<td>Cu NPs</td>
<td>100</td>
<td>100</td>
<td>98.4</td>
<td>100</td>
<td>99.6</td>
</tr>
<tr>
<td>ZnO NPs</td>
<td>84.2</td>
<td>100</td>
<td>75.8</td>
<td>22.8</td>
<td>70.7</td>
</tr>
<tr>
<td>MgO NPs</td>
<td>48.7</td>
<td>54</td>
<td>36.3</td>
<td>12.7</td>
<td>37.93</td>
</tr>
<tr>
<td>SiO₂ NPs</td>
<td>30.4</td>
<td>51.7</td>
<td>19.6</td>
<td>19.9</td>
<td>30.40</td>
</tr>
<tr>
<td>CNTs</td>
<td>90.9</td>
<td>59.1</td>
<td>80.3</td>
<td>84.7</td>
<td>78.75</td>
</tr>
</tbody>
</table>

Table IV.16: Bacterial degradation percentages of distillate water and permeate water

<table>
<thead>
<tr>
<th>Water type</th>
<th>Distillate</th>
<th>Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag NPs</td>
<td>100</td>
<td>99.6</td>
</tr>
<tr>
<td>Ag-Cu NPs</td>
<td>99.9</td>
<td>99.2</td>
</tr>
<tr>
<td>Cu NPs</td>
<td>82.9</td>
<td>NI</td>
</tr>
<tr>
<td>ZnO NPs</td>
<td>92.7</td>
<td>NI</td>
</tr>
<tr>
<td>MgO NPs</td>
<td>90.5</td>
<td>NI</td>
</tr>
<tr>
<td>SiO₂ NPs</td>
<td>81.3</td>
<td>NI</td>
</tr>
<tr>
<td>CNTs</td>
<td>69.6</td>
<td>NI</td>
</tr>
</tbody>
</table>

Table IV.17: Overall Bacterial degradation percentages with different water samples spiked by all synthesized NPs at second dose and second contact time

<table>
<thead>
<tr>
<th>NPs</th>
<th>Tap water samples</th>
<th>MSF water samples</th>
<th>RO water samples</th>
<th>Distillate</th>
<th>Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag NPs</td>
<td>100</td>
<td>100</td>
<td>97.3</td>
<td>100</td>
<td>99.6</td>
</tr>
<tr>
<td>Ag-Cu NPs</td>
<td>99.5</td>
<td>99</td>
<td>84.1</td>
<td>99.9</td>
<td>99.2</td>
</tr>
<tr>
<td>Cu NPs</td>
<td>67.95</td>
<td>65.37</td>
<td>99.6</td>
<td>82.9</td>
<td>NI*</td>
</tr>
<tr>
<td>ZnO NPs</td>
<td>43.83</td>
<td>68.58</td>
<td>70.7</td>
<td>92.7</td>
<td>NI</td>
</tr>
<tr>
<td>MgO NPs</td>
<td>48.18</td>
<td>85.65</td>
<td>37.93</td>
<td>90.5</td>
<td>NI</td>
</tr>
<tr>
<td>SiO₂ NPs</td>
<td>49.5</td>
<td>44.78</td>
<td>30.4</td>
<td>81.3</td>
<td>NI</td>
</tr>
<tr>
<td>CNTs</td>
<td>51.52</td>
<td>79.68</td>
<td>78.75</td>
<td>69.6</td>
<td>NI</td>
</tr>
</tbody>
</table>

*Not identified
Figure IV.3: Overall bacterial degradation percentage for tap water samples spiked by 4 indicators and treated by synthesized NPs at second dose and second contact time.

Figure IV.4: Overall bacterial degradation percentage for MSF water samples spiked by 4 indicators & treated with 7 NPs at (D2&T2)
Figure IV.5: Overall bacterial degradation percentage for RO water samples spiked by 4 indicators and treated by synthesized NPs at second dose and second contact time.

Figure IV.6: Overall bacterial degradation percentage for different water samples spiked by 4 indicators and treated by synthesized NPs at second dose and second contact time.
IV.4 Disinfection by-products Identification

Four different inorganic IDBPs were analyzed in the desalinated water after treated by different NPs and the results (produced as average of three injections in IC) are reported here. : Table IV.18 for spiked MSF water, Table IV.19 for spiked RO water, Table IV.20 for non-spiked MSF water, and Table IV.21 for non-spiked RO water.

Table IV.18: Detected IDBPs in spiked MSF water after treated by different NPs in mg/l for two doses and two contact times

<table>
<thead>
<tr>
<th>IDBPs</th>
<th>Chlorate</th>
<th>Chlorite</th>
<th>Bromate</th>
<th>Iodate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CT</td>
<td>T1</td>
<td>T2</td>
<td>T1</td>
</tr>
<tr>
<td>Ag NPs</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Ag-Cu NPs</td>
<td>0.02</td>
<td>0.02</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Cu NPs</td>
<td>0.17</td>
<td>0.24</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>CNTs</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>ZnO NPs</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>SiO₂ NPs</td>
<td>0.02</td>
<td>0.02</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>MgO NPs</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>Dose I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag NPs</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Ag-Cu NPs</td>
<td>0.02</td>
<td>0.03</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Cu NPs</td>
<td>0.21</td>
<td>0.24</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>CNTs</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>ZnO NPs</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>SiO₂ NPs</td>
<td>0.02</td>
<td>0.02</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>MgO NPs</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>Dose II</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag NPs</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Ag-Cu NPs</td>
<td>0.02</td>
<td>0.03</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Cu NPs</td>
<td>0.21</td>
<td>0.24</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>CNTs</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>ZnO NPs</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>SiO₂ NPs</td>
<td>0.02</td>
<td>0.02</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>MgO NPs</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

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Table IV.19: Detected IDBPs in spiked RO water after treated by Different NPs in mg/l for two doses and two contact times

<table>
<thead>
<tr>
<th>IDBPs</th>
<th>Chlorate</th>
<th>Chlorite</th>
<th>Bromate</th>
<th>Iodate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T1</td>
<td>T2</td>
<td>T1</td>
<td>T2</td>
</tr>
<tr>
<td>Dose I</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag NPs</td>
<td>0.02</td>
<td>0.02</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Ag-Cu NPs</td>
<td>0.04</td>
<td>0.04</td>
<td>0.02</td>
<td>0.06</td>
</tr>
<tr>
<td>Cu NPs</td>
<td>0.18</td>
<td>0.24</td>
<td>ND</td>
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</tr>
<tr>
<td>CNTs</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>ZnO NPs</td>
<td>0.02</td>
<td>0.02</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>SiO₂ NPs</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>MgO NPs</td>
<td>0.01</td>
<td>0.01</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Dose II</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag NPs</td>
<td>0.02</td>
<td>0.02</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Ag-Cu NPs</td>
<td>0.04</td>
<td>0.05</td>
<td>0.06</td>
<td>0.12</td>
</tr>
<tr>
<td>Cu NPs</td>
<td>0.23</td>
<td>0.24</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>CNTs</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>ZnO NPs</td>
<td>0.02</td>
<td>0.03</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>SiO₂ NPs</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>MgO NPs</td>
<td>0.01</td>
<td>0.02</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>
Table IV.20: Detected IDBPs in distillate water after treated by Different NPs in mg/l for two doses and two contact times

<table>
<thead>
<tr>
<th>IDBPs</th>
<th>Chlorate</th>
<th>Chlorite</th>
<th>Bromate</th>
<th>Iodate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CT</td>
<td>T1</td>
<td>T2</td>
<td>T1</td>
</tr>
<tr>
<td>Dose I</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag NPs</td>
<td>0.07</td>
<td>0.07</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Ag-Cu NPs</td>
<td>0.03</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Cu NPs</td>
<td>0.03</td>
<td>0.03</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>CNTs</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>ZnO NPs</td>
<td>0.05</td>
<td>0.05</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>SiO₂ NPs</td>
<td>0.02</td>
<td>0.03</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>MgO NPs</td>
<td>0.03</td>
<td>0.04</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Dose II</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag NPs</td>
<td>0.07</td>
<td>0.07</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Ag-Cu NPs</td>
<td>0.03</td>
<td>0.03</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>Cu NPs</td>
<td>0.23</td>
<td>0.25</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>CNTs</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>ZnO NPs</td>
<td>0.05</td>
<td>0.05</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>SiO₂ NPs</td>
<td>0.03</td>
<td>0.06</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>MgO NPs</td>
<td>0.04</td>
<td>0.05</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

Table IV.21: Detected IDBPs in permeate water after treated by different NPs in mg/l for two doses and two contact times.

<table>
<thead>
<tr>
<th>IDBPs</th>
<th>Chlorate</th>
<th>Chlorite</th>
<th>Bromate</th>
<th>Iodate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CT</td>
<td>T1</td>
<td>T2</td>
<td>T1</td>
</tr>
<tr>
<td>Dose I</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag-Cu NPs</td>
<td>0.02</td>
<td>0.03</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Dose II</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag-Cu NPs</td>
<td>0.03</td>
<td>0.05</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>

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The above results reporting detected IDBPs for different types of desalinated water samples are summarized in Table IV.22 and Table IV.23 at first dose/first contact time and second dose/second contact time, respectively.

Table IV.22: Detected IDBPs for all tested water samples after treated by different NPs in mg/l at first dose and first contact time.

<table>
<thead>
<tr>
<th>Water type</th>
<th>St.Sp.MSF</th>
<th>St.Sp. RO</th>
<th>Distillate</th>
<th>Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag NPs</td>
<td>ND</td>
<td>Chlorate=0.02</td>
<td>Chlorate=0.07</td>
<td>ND</td>
</tr>
<tr>
<td>Ag-Cu NPs</td>
<td>Chlorate=0.02</td>
<td>Chlorate=0.04</td>
<td>Chlorate=0.03</td>
<td>Chlorate=0.03</td>
</tr>
<tr>
<td>Cu NPs</td>
<td>Chlorate=0.17</td>
<td>Chlorate=0.23</td>
<td>Chlorate=0.23</td>
<td>Chlorate=0.03</td>
</tr>
<tr>
<td>CNTs</td>
<td>ND</td>
<td>ND</td>
<td>Chlorate=0.23</td>
<td>NI</td>
</tr>
<tr>
<td>ZnO NPs</td>
<td>ND</td>
<td>Chlorate=0.02</td>
<td>Chlorate=0.05</td>
<td></td>
</tr>
<tr>
<td>SiO₂ NPs</td>
<td>Chlorate=0.02</td>
<td>ND</td>
<td>Chlorate=0.03</td>
<td></td>
</tr>
<tr>
<td>MgO NPs</td>
<td>ND</td>
<td>Chlorate=0.01</td>
<td>Chlorate=0.04</td>
<td></td>
</tr>
</tbody>
</table>

Table IV.23: Detected IDBPs all tested water samples after treated by different NPs in mg/l at Second dose and second contact time.

<table>
<thead>
<tr>
<th>Water Type</th>
<th>St.Sp.MSF</th>
<th>St.Sp. RO</th>
<th>Distillate</th>
<th>Permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag NPs</td>
<td>ND</td>
<td>Chlorate=0.02</td>
<td>Chlorate=0.07</td>
<td>ND</td>
</tr>
<tr>
<td>Ag-Cu NPs</td>
<td>Chlorate=0.02</td>
<td>Chlorate=0.04</td>
<td>Chlorate=0.03</td>
<td>Chlorate=0.03</td>
</tr>
<tr>
<td>Cu NPs</td>
<td>Chlorate=0.21</td>
<td>Chlorate=0.23</td>
<td>Chlorate=0.25</td>
<td>Bromate=0.04</td>
</tr>
<tr>
<td>CNTs</td>
<td>ND</td>
<td>ND</td>
<td>Chlorate=0.06</td>
<td>NI</td>
</tr>
<tr>
<td>ZnO NPs</td>
<td>ND</td>
<td>ND</td>
<td>Chlorate=0.02</td>
<td>Chlorate=0.05</td>
</tr>
<tr>
<td>SiO₂ NPs</td>
<td>Chlorate=0.02</td>
<td>ND</td>
<td>Chlorate=0.04</td>
<td></td>
</tr>
<tr>
<td>MgO NPs</td>
<td>ND</td>
<td>Chlorate=0.01</td>
<td>Chlorate=0.04</td>
<td></td>
</tr>
</tbody>
</table>
Chapter V

DISCUSSION

V.1 TEM Characterization

TEM was used to determine the size and morphology of the used nanoparticles. Zetasizer was used to determine the surface charge of the used nanoparticles. Table IV.1 reports the size, morphology and the surface charge of these nanoparticles. There were no significant differences between the size for almost all the nanoparticles except SiO$_2$ and MgO. SiO$_2$ used with spiked tap water was 12.5 nm, while the one used with Spiked MFS water, Spiked RO water, non-spiked distillate and permeate was 386.8 nm. For MgO used with tap water, the size was 42.4 nm it was 229.2 nm with other water samples. Despite the differences in particles size of SiO$_2$ NPs and MgO NPs used with first and second batch, there was no significant effect on the antimicrobial effect of these nanoparticles as shown in Table IV.17. The surface charge of all used nanoparticles was negative except ZnO NPs and MgO NPs, have positive charge.

V.2 Bacterial Degradation by NPs in Different Water Samples

Antimicrobial performance with four considered indicators; E. coli, Enterobacter, Salmonella and Enterococci was evaluated in different drinking water samples with seven selected nanoparticles. The results showed that Ag NPs can achieve up to 100% in both tap water samples and MSF water samples for all four indicators, while Spiked RO water samples had slightly lower removal percentage (97.3%) as
shown in table IV.15. Previous studies have reported a reduction in antibacterial properties of Ag NPs with increased size of nanoparticles clusters due to aggregation in the presence of divalent ions such as Ca\(^{2+}\) and Mg\(^{2+}\) [59]. In this study, Spiked RO water contained 12 mg/L Ca\(^{2+}\) and 80 mg/L Mg\(^{2+}\) while Spiked MSF water contained 4 mg/L Ca\(^{2+}\) and 12 mg/L Mg\(^{2+}\) as shown in table IV.3.

Ionic strength and presence of divalent or multivalent cations result in aggregation of Ag NPs. Large aggregates exhibit lower toxicity compared with mono-dispersed NPs. Because cations in aqueous solution can adsorb on the surface of the nanoparticles and neutralize the negative surface, this results in removing the energy barriers between particles which allow particles to aggregate easily [59]. On the other hand presence of specific anions such as Cl\(^-\) and SO\(_4\)\(^{2-}\) in water can form complexes with the released Ag ions. The presence of Cl\(^-\) in particular enhances dissolution of Ag NPs and formation of AgCl\(_2\) and AgCl\(_3\) complexes. The complexes are usually less toxic than Ag\(^+\)[50] and this may explain the lower toxicity of Ag NPs in Spiked RO samples which contained 103 mg/L Cl\(^-\) and 4.2 SO\(_4\)\(^{2-}\) mg/L compared to Spiked MSF samples that contained 10.6 mg/L Cl\(^-\) and 1.3 mg/L SO\(_4\)\(^{2-}\) as shown in table IV.3.

The noticed removal percentage of Ag for Spiked tap water and Spiked MSF water (100%) was very close to that of Ag-Cu NPs for Spiked tap water and Spiked MSF water; 99.5% and 99% respectively. However, the same NPs had slightly lower removal percentage, 84.1% for Spiked RO water samples and that can be
contributed to the difference in chemical composition of Spiked MSF water and Spiked RO water. Furthermore, the removal percentage was the same for Ag and Ag-Cu NPs for all the used indicators which is 100% for both tap water and Spiked MSF water. However, *Enterococci* had slightly lower removal percentage with Ag-Cu NP for tap water and Spiked MSF water; 98.1% and 96.9% respectively. The previous studies [53, 54] reported that the cell wall plays an important role in tolerance or susceptibility of bacteria in presence to NPs as per structure, components, and functions. The gram positive cells contain a thick layer (20-80 nm) of peptidoglycan, which is attached to teichoic acids that are unique to the gram positive wall. By contrast, gram negative cell walls comprise a thin PG layer (5-10nm) and contains unique component, lipopolysaccharides, which increase the negative charge of cell membrane [57]. The differences in the composition of the cell wall between Gram positive/ negative bacteria could result in diminished interactions of Ag NPs with the gram positive, requiring greater interaction time before the treatment was effective [62].

Some researchers claim that released Ag⁺ ions from the nanoparticle are the more active species, whereas in some studies the nanoparticles itself was assumed to lead to a higher toxicity [58]. Species sensitivity is not only related to the structure of the cell wall in gram negative and gram positive bacteria. Another factor that can influence the tolerance of bacteria against NPs is the rate of bacterial growth. Fast growing bacteria are more susceptible than slow-growing bacteria to NPs. It is possible that the tolerance property of slow-growing bacteria is related to the
expression of stress-response genes. Consequently, antibacterial effects highly depend on the particular strain [57].

The removal percentage was same (100%) for Cu NPs with Spiked RO water for all the used indicator except Salmonella (98.4%). While Spiked MSF water, the overall removal by Cu NPs was 65.4% with high levels for both Salmonella and Enterococci compared to those with E.coli and Enterobacter. Previous studies [58] reported that several naturally adapted bacteria are tolerant to specific NPs. The tolerance mechanism of bacteria may be related to physical properties of their PG layer and or products of genes that are located in the plasmids and are able to stabilize the plasma membrane or efflux of NPs. In addition, the toxicity of ions released from NPs is not significant while the toxicity strength of the particles themselves depends on the natural toxic properties of the Cu metal [58].

ZnO NPs had very close removal percentage for both Spiked MSF water and Spiked RO water for all indicators, 68.6% and 70.7%; respectively. Furthermore, the noticed removal percentages were high and close to each other for E.coli, Enterobacter and Salmonella, markedly low for Enterococci. The electrostatic attraction and repulsion between the NPs and microorganisms play an important role in the adhesion of the NP to the microorganisms and eventually the observed toxicity. In both MSF water samples and RO water samples, low removal percentages for gram positive bacteria; Enterococci were attained; 29.8% and 22.8 respectively. Such result can be attributed to the repulsion between positive charge
on ZnO PNs and *Enterococci* cell wall. Also, the toxicity of oxide NPs, e.g. ZnO and CuO does not always depend on the bacteria internalizing the NPs; these NPs can locally change microenvironments near the bacteria and produce ROS or increase the NPs solubility which can induce bacterial damage [57].

MgO NPs removed 85.7% of all indicators with MSF water and only removed 37.9% with Spiked RO water. In both cases, the noticed removal percentage was high for *E. coli*, *Salmonella* and *Enterobacter* compared to *Enterococci*.

Previous studies reported that the action of metal oxides against bacteria appears to be really close to the surface of the particle. Contact between MgO particles and bacteria are also an important factor in their activity. In both MSF water samples and RO water samples the removal percentage of gram positive bacterial; *Enterococci* was 64.9% and 12.8% respectively. The positive surface charge of MgO NPs and *Enterococci* may interfere with the adhesion and thus prevent contact. On the other hand, the alkalinity of the surface is another major microbicidal effect against bacteria. Furthermore, the existence of active oxygen, such as $O_2^-$, on the surface of MgO (and CaO as well) has been observed. When the particle comes into contact with a bacterial cell at neutral or slightly acidic, the active oxygen would increase the antimicrobial activity. A difference in the antimicrobial activity of MgO and ZnO comes from active oxygen species generated by the powder in solution. Indeed, every bacterium responds unevenly to oxidative stress due to differences in the permeability of cell membranes [11].
SiO2 removed 44.8% of all indicators in Spiked MSF water and slightly lower percentage with Spiked RO water (30.4%). While the noticed removal percentage of CNTs was high and close to each other for both Spiked RO and Spiked MSF water, 78.75% and 79.7%; respectively. Enterobacter had slightly lower removal percentage among the 4 indicators for both water samples, and that may be attributed to the bacterial susceptibility to CNTs. It was reported that cell damage by CNTs was caused by direct cell contact and physicochemical/mechanical interaction with the outer cell membrane of E.coli [58]. For raw non-spiked water: after desalination and before chlorination, Ag and Ag-Cu NPs almost removed 100% of all the bacteria in MSF distillate samples. However the removal percentage was slightly lower for RO permeate water by same NPs (99.6 % and 99.2% respectively). Such results can be similarly explained due to the difference of chemical quality of MSF and RO water samples. ZnO and MgO NPs had the second highest removal percentage for MSF distillate water, 92.7% and 90.5%; respectively while Cu NPs and SiO2 had slightly lower removal percentages, 82.9% and 81.3%. CNTs achieved the least removal percentage (69.6%) with MSF distillate water.
V.3 Inorganic Disinfection By-Products

The formation of IDDBPs was investigated for different doses and contact times of the considered seven NPs applied to the desalinated water (spiked and non-spiked). In general, the result of all used nanoparticles show that all the formed DBPs were under the WHO standard limit except the Bromate (0.04mg/L), which formed with Cu NPs after 2 hrs contact time and with 20μl/100 with MSF samples. This can be attributed to higher initial concentration of bromide ion 81 mg/L (in raw water) compared to bromide in raw water of RO sample (68 mg/l). In addition to bromide concentration, previous studies indicated that Cu (II) enhance HOBr/OBr decay in alkaline solution (pH 8.6) [63]. In another study [64], they reported that, CuO catalyzes the disproportionation of HOBr leading to significant formation of chlorate and bromate. The same study, reported that, in the absence of CuO, no significant bromate was formed, while in the presence of CuO, a significant bromate formation was observed and enhanced with increasing CuO dose. This may explain the formation of bromate with Cu NPs only but not with others NPs. The formation of Bromate in MSF sample and not in RO samples may be attributed to the rejection of bromide ion by NF in Reverse Osmosis Plant. A study [58] reported that NF membrane achieved 94-96% bromide rejection and 84-91% iodide rejection.
All used NPs formed chlorate ranging between 0.02 - 0.2 mg/L. The highest concentration was formed with Cu NPs in MSF samples but was still below WHO standards (0.7 mg/L). Chlorite was formed with Cu in distillate water sample (0.06mg/L) and with Ag-Cu NPs in RO water sample, distillate water samples, and permeate water samples 0.06 mg/L, 0.06 and 0.03 mg/l; respectively that were still below the WHO standards.

Among the seven considered nanoparticles, Ag NPs achieved the highest percentage removal with all used bacterial indicators for both RO & MSF samples and had the lowest DPBs. However, Ag-Cu achieved close to 100% removal with less dose than that of Ag when used with RO water. This can be attributed to the oxidizing effect of the Copper portion contained in the Ag-Cu composite.

**V.4 Cost Implications**

There are currently two approaches to address the cost issue. One proposed approach is to use low purity nanomaterials without significantly compromising efficiency as much of the production cost is related to separation and purification. Alternatively, the cost-effectiveness can be improved by retaining and reusing nanomaterials. Most desalination plants are expected to remain in place for decades to come. As a result, it is important to be able to implement nanotechnology with
minimal changes to existing infrastructure in the near term and this explains the focus put into this study in applying the nanoparticles in suspension mode.

Although nanotechnology sounds promising in several treatment processes as per the results attained from intensive laboratory studies, their readiness for commercialization and application in practice are still questionable. The adoption of innovative technologies in practice strongly depends on the cost effectiveness and the potential risk involved. The current cost of nanomaterials is prohibitively high with few exceptions such as nano TiO₂, nanoscale ion oxide and polymeric nanofibers.

Table V.1 compares the estimated costs of current and widely used disinfectant (free chlorine applied in form of Sodium Hypochlorite salt) and the nanoparticles found in this study to be effective disinfectants for both desalination technologies (MSF and RO) with minimum formed IDBPs; these are Ag NPs and Ag-Cu NPs (70:30). The costs were calculated for an amount of 10,000 m3 of desalinated water employing the dosages of NPs effective with desalinated water (Table IV.16). Such dosages are 5 μg/100ml and 10 μg/100ml for Ag NPs applied to MSF and RO water; respectively and 5 μg/100ml for Ag-Cu NPs (70:30) applied to both of MSF and RO water. It is worth noting as the removal efficiency was 100% for the case
of applied Ag NPs to MSF water only while other cases reported little less than that (99.2% to 99.8%). Achievement of 100% of bacterial removal percentage is assumed to be achieved easily in practice by slight increase of the contact times found for each case. Such increase will eventually result in increasing the capital cost of disinfection tanks due to the associated enlarged sizes. The costs listed in Table V.1 ignores that and considers only the cost of materials needed to produce the disinfectant: NaOCl for free chlorine, AgNO₃ for Ag NPs, and AgNO₃/CuCl for Ag-Cu NPs.

Table V.1: Estimates costs (AED) for different disinfectant techniques applied to 10,000m³

<table>
<thead>
<tr>
<th>Disinfectant</th>
<th>Free Chlorine</th>
<th>Ag NPs</th>
<th>Ag-Cu NPs 70:30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desalination plant</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MSF/RO</td>
<td>MSF</td>
<td>RO</td>
<td></td>
</tr>
<tr>
<td>Estimated Cost</td>
<td>50.2</td>
<td>2928</td>
<td>5856</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2212 2212</td>
</tr>
</tbody>
</table>
Cost of free chlorine was calculated based on an estimated cost of 2.51 AED/kg of NaOCl to deliver a concentration of 2.0 mg/L of free chlorine in the water required for initial disinfection. The cost of Ag NPs is based on the usage of 170 mg of AgNO₃ to produce 50 mg Ag NPs used to produce an applied Ag suspended solution of 0.535 mg/mL concentration. The cost of CuCl₂ is based on the use of 170 mg of CuCl₂ to produce 50 mg of Cu NPs used to produce an applied Cu suspended solution of 1.0 mg/mL concentration. Commercial prices of materials considered in these calculations were 2.51 AED/kg of NaOCl, 4590 AED/kg of AgNO₃, and 320 AED/kg of CuCl₂. Even though the cost of NPs is in general much higher than traditional chlorine disinfection, a significant health advantage exists with the elimination of harmful DBPs. It should also be noted that major saving is achieved in using the Ag-Cu composite instead of Ag NPs. That was clearly related to the reduced dosage required for Ag-Cu compared to that of Ag NPs and this exemplifies the importance of further investigation of Ag and Cu based composite NPs in disinfection of desalinated water.
Although water plays a critical role in every facet of human activity, it is becoming an increasingly scarce resource in many parts of the world. Besides utilization of non-traditional sources for production of high-quality fresh water and conservation and protection of water bodies from pollution, equally important is the development of innovative new technologies and materials whereby challenges associated with the provision of safe potable water can be addressed. It is widely recognized that nanotechnology and applications thereof may play an important role in resolving issues relating to water shortage and water quality. Due to their large surface areas and their size and shape dependent catalytic properties, considerable efforts are underway to explore uses of nanomaterials in applications such as membrane separations, catalysis and adsorption. Moreover, nanomaterials can be functionalized with various different chemical groups to increase their affinity toward a given compound, thus resulting in ligands that are not only recyclable but also have a high capacity and selectivity for organic and inorganic solutes, as well as toxic metal ions and inorganic anions in aqueous solution [58].

Effective treatment processes for drinking water production are major prerequisites for a developing and growing economy. Therefore, it is crucial to develop and implement innovative water technologies treating water with high efficiency, with low energy consumption and with low over all cost. The application of modern
nanotechnology could be one approach to improve this situation. The removal of pathogens using nanotechnology is an emerging area of research and it is a promising alternative to existing processes such as chlorination.

This research evaluated seven nanoparticles in disinfecting desalinated drinking water produced by different desalination technologies spiked by four types of bacteria: *E. coli, Enterobacter, Salmonella* and *Enterococci*. Various parameters were tested including: size of nanoparticles, contact time and different dosage of suspended nanoparticles. The present approach examined the treatment protocol associated with utilization of NPs in colloidal suspension that can be easily adopted in drinking water pretreatment as well as post-treatment systems. Also, four inorganic disinfection by products were analyzed.

Several conclusions can be drawn from the results of this study as follows:

(i) All used indicators behave in the same manner, as the NPs dose and/or contact time increase, the removal percentage increase.

(ii) The antimicrobial performance of Ag NPs was the best among all tested nanoparticles and for tested water samples followed by Ag-Cu NPs.

(iii) The cost of adopting Ag-Cu in disinfecting RO water was less that of Ag NPs due to its less required dose (5 µg/100mL) than that required with
Ag NPs (10 μg/100 mL). However, same required dose was found for both of Ag and Ag-Cu NPs used with MSF water.

(iv) 100% removal was achieved by Ag NPs for all spiked indicators with MSF water samples while; with RO water samples it was slightly lower 97.3%. Also in non-spiked distillate water sample the removal percentage of microorganisms was 100%, while in non-spiked permeate samples it was slightly lower 99.6%, but as illustrated in table IV.16 and IV.17, a slight increase in Ag NPs dose and/or contact time can easily achieve 100% removal.

(v) The most frequent IDBP formed was chlorate and it was under the standard limits by 10 times even with high dose of Ag NPs.
RECOMMENDATIONS

There are two major researches needed for full-scale applications of nanotechnology in water treatment. First, cost-effectiveness and potential environmental and human risk need to investigate. Secondly, the long-term efficacy of these nanotechnologies is largely unknown as most lab studies were conducted for relatively short period of time. Research addressing the long-term performance of water treatment nanotechnologies is in great need. As a result, side-by-side comparison of nanotechnology enabled systems and existing technologies is challenging. The compatibility between aforementioned nanotechnologies and current water treatment processes and infrastructure also needs to be addressed. Most treatment plants and distribution systems in developed countries are expected to remain in place for decades to come. As a result, it is important to be able to implement nanotechnology with minimal changes to existing infrastructure in the near term.

Metals and metal oxide nanoparticles can be used in drinking water disinfection in different application method, they can be applied as free nanoparticles suspended in aqueous solution, or they can be fixed in different forms of matrixes. Utilization of specific nanoparticles either embedded in membranes or on other structural media that can effectively, inexpensively disinfect drinking water; has been investigated in different studies.
Nano-Ag has good potential for application at Point-of-Use (POU) treatment. It can improve water quality for high-end use or provide another barrier against waterborne pathogens for vulnerable population. Nano-Ag has also been incorporated into ceramic micro filters as barriers for pathogens, which can be employed in remote area in developing countries. Another potential application of fixing nanoparticles is the development of thin film Nano composite membrane (TFM), which mainly focus on incorporating nanomaterials (e.g. Ag NPs) into the active layer of thin film composite membranes via doping in the casting solutions or surface modification.

The main recommendation driven from this study is to evaluate the use of NPs in disinfecting NPs applied in matrix forms using native and cheap local adsorbent materials. Also the cost savings achieved with Ag-Cu compared to that of Ag NP suggests further investigation of Ag and Cu based composite NPs.
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APPENDIX A

<table>
<thead>
<tr>
<th>Tap water Ag (0.535 mg/ml)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>E.coli</strong></td>
<td></td>
</tr>
<tr>
<td>T0</td>
<td>T1</td>
</tr>
<tr>
<td>R1</td>
<td>398</td>
</tr>
<tr>
<td>R2</td>
<td>399</td>
</tr>
<tr>
<td>R3</td>
<td>399</td>
</tr>
<tr>
<td>Avg</td>
<td>398.66</td>
</tr>
<tr>
<td>RP%</td>
<td>84.52</td>
</tr>
<tr>
<td>σ</td>
<td>992.33</td>
</tr>
<tr>
<td>SD</td>
<td>31.50</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Tap water Ag (0.535 mg/ml)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Enterococci</strong></td>
<td></td>
</tr>
<tr>
<td>T0</td>
<td>T1</td>
</tr>
<tr>
<td>R1</td>
<td>399</td>
</tr>
<tr>
<td>R2</td>
<td>397</td>
</tr>
<tr>
<td>R3</td>
<td>399</td>
</tr>
<tr>
<td>Avg</td>
<td>398.33</td>
</tr>
<tr>
<td>RP%</td>
<td>62.69</td>
</tr>
<tr>
<td>σ</td>
<td>217</td>
</tr>
<tr>
<td>SD</td>
<td>14.73</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Tap water Ag (0.535 mg/ml)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Enterobacter</strong></td>
<td></td>
</tr>
<tr>
<td>T0</td>
<td>T1</td>
</tr>
<tr>
<td>R1</td>
<td>399</td>
</tr>
<tr>
<td>R2</td>
<td>398</td>
</tr>
<tr>
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### Tap water Ag (0.535 mg/ml)

#### Salmonella

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#### St.Sp.MSF Ag (0.535 mg/ml)

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127
### St. Sp. RO Ag (0.535 mg/ml)

#### Enterococci

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#### Salmonella

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### Distillate Ag (0.535 mg/ml)

#### NoN-Spiked

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#### RR%

|         | 91.79 | 91.32 | 92.55 | 92.71 |

#### SD

|         | 11.30 | 31.13 | 28.15 | 9.29 |

### Permeate Ag (0.535 mg/ml)

#### NON-Spiked

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#### RR%

|         | 91.41 | 99.36 | 99.56 | 99.58 |

#### SD

|         | 2.88 | 7.57 | 4.16 | 1.52 |

### Tap water Ag-Cu (0.535 mg/ml)

#### E.coli

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#### RP%

|         | 45.96 | 84.14 | 66.88 | 100 |

#### SD

|         | 11.53 | 14.18 | 17.15 | 0 |

129
### Tap water Ag-Cu (0.535 mg/ml)

#### Enterococci

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130
### St. Sp. MSF Ag-Cu (0.535 mg/ml)

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131
### St.Sp.MSF Ag-Cu (0.535 mg/ml)

#### Salmonella

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### St.Sp.RO Ag-Cu (0.535 mg/ml)

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### St.Sp.RO Ag-Cu (0.535 mg/ml)

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### Distillate Ag-Cu (0.535 mg/ml)

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### Permeate_Ag -Cu(0.535 mg/ml)

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### Tap water_Cu (1 mg/ml)

#### E.coli

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#### Enterococci

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### E. coli

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### Enterobacter

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### Tap water CNTs (1 mg/ml)

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### Tap water_CNTs (1 mg/ml) - *Enterobacter*

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### Tap water CNTs (1 mg/ml)

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### St.Sp.MSF CNTs (1 mg/ml)

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#### Enterococci

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### Salmonella

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### St.Sp.RO_CNTs (1 mg/ml) Enterococci

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### St.Sp.RO_CNTs (1 mg/ml) Enterobacter

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### St.Sp.RQ_CNTs (1 mg/ml)

#### Salmonella

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### Distillate_CNTs (1 mg/ml)

#### NON-Spiked

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### Tap Water ZnO (1 mg/ml)

#### E.coli

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145
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### Tap Water SiO2 (1 mg/ml)

#### E. coli

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### Tap Water SiO2 (1 mg/ml) - Enterobacter

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151
### St.Sp RO_SiO2(1 mg/ml)

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### Disttialte_SiO2(1 mg/ml)

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### St.Sp.RO_MgO(1 mg/ml)

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Appendix B

**Figure 1:** Bacterial degradation percentages for Tap Water samples spiked by 4 indicators and tested with 7 NPs at (D1&T1)

**Figure 2:** Bacterial degradation percentages for Tap Water samples spiked by 4 indicators and tested with 7 NPs at (D2&T2)
Bacterial degradation percentages for MSF water samples spiked by 4 indicators & 7 NPs at (D1&T1)

Figur3: Bacterial degradation percentages for MSF Water samples spiked by 4 indicators and testes with 7 NPs at (D1&T1)

Bacterial degradation percentages for MSF water samples spiked by 4 indicators & treated with 7 NPs at (D2&T2)

Figur4: Bacterial degradation percentages for MSF Water samples spiked by 4 indicators and testes with 7 NPs at (D2&T2)
Figur 5: Bacterial degradation percentages for RO water samples spiked by 4 indicators and testes with 7 NPs at (D1&T1)

Figur 6: Bacterial degradation percentages for RO water samples spiked by 4 indicators & treated with 7 NPs at (D2 &T2)
Overall bacterial degradation percentages for different water samples spiked by 4 indicators and treated by 7 NPs at (D2&T2)

Figur 7: Bacterial degradation percentages for different water samples and testes with 7 NPs at (D2&T2)
تعتمد معظم دول الخليج العربي بما فيها دولة الإمارات العربية المتحدة على تحلية مياه البحر كمصادر رئيسية لمياه الشرب. ومنذ قرون عديدة اعتمدت عملية تطهير المياه كعملية أساسية للقضاء على الكائنات الحية الدقيقة المرضية وللوقاية من الأمراض المنقلة عن طريق المياه. وعلى الرغم من كفاءة عمليات التفتيت المستخدمة حاليا في تطهير مياه البحر قبل أو بعد عملية التحلية، إلا أن هناك تركيزات ضارة وتشكل مخاطر على صحة الإنسان.

وقد أجريت العديد من الدراسات لإيجاد طرق بناء لمعايير مياه الشرب ولهد من المركبات الضارة والناجحة من عمليات التفتيت التقليدية. وقد أظهرت الدراسات أن المعايير وأقسام المعايير النانوية لها مزايا كبيرة، إذ تقول بأنها قد تمثل عديدة من بينها قد تكون على مدى الميكروربات دون تكون المركبات ضارة.

في هذه الدراسة تم تقسيم سبعة من المعايير وأقسام المعايير النانوية (الفترة، الفضاء النحاسي، النحاس، ثاني أكسيد السيليكا، ثاني أكسيد المغنيسيوم، ثاني أكسيد الكربون النانوية وأكسيد الزئبق) في تعقيم مياه الشرب المنتجة من نوعين من تقنيات تحلية المياه وهي التناسخ العكسي والتبخر الوضعي، وتم تقييم قدرة هذه العناصر في إزالة اربعة انواع من الباكتيريا وتشمل: البكتيريا الفولونية والسانمرايلا والانتروكيكاي، والبكتيريا العضوية. تم تحليل المياه بعد معالجتها والمياه وتم قياس تركيز كل من المركبات الكيميائية الضارة بالغرضية والتي تحمل كوكليتاز، والكوليات، والبروتامينات، والبروتينات، والمواد الأيضية. وقد أظهرت النتائج هذه الدراسة أن معدن الفضة النانوي ومكثف الفضة النحاس النانوي لديهما كفاءة عالية في تعقيم مياه الشرب وآكلات الكوليات كان المركب الأكثر مفعولية نتيجة عملية التفتيت للمياه المحلاة ولكن بتركيزات أقل من الحد المسموح به في مياه الشرب.

الملخص

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استخدام الجسيمات النانوية في تعقيم مياه التحلية في دولة الإمارات العربية المتحدة

ليلى مسعود راشد العيسائي

رسالة مقدمة لاستكمال متطلبات الحصول على درجة الماجستير في الهندسة
قسم الهندسة المدنية والبيئية

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