



**ADDIS ABABA UNIVERSITY**  
**ADDIS ABABA INSTITUTE OF TECHNOLOGY**  
**SCHOOL OF MULTIDISCIPLINARY ENGINEERING**  
**CENTER FOR MATERIALS ENGINEERING**

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Synthesis of Cetyltrimethylammonium chloride Coated Diatomite  
Ceramic Membrane Impregnated with  $\text{TiO}_2$  Nanoparticles For the  
Removal of Hexavalent Chromium(VI)

A Thesis Submitted to The Center for Materials Engineering, Addis  
Ababa Institute of Technology in Partial Fulfillment of the  
Requirements for the Degree of Master of Science in Material  
Engineering

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**Addis Ababa, Ethiopia**

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**By: Daniel Getachew**

Approved By the Examining Board

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# DECLARATION

I declare that, this thesis entitled with “Process and Application of Coated, Nano material Modified Ceramic Membrane For the Removal of Hexavalent Chromium(VI)” for the MSc. Degree at Addis Ababa University, hereby submitted by me, is my original work and has not previously been submitted for the degree at this or any other university, and that all resources of materials used in this thesis have been duly acknowledged.

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This thesis has been submitted for examination with my approval as University Advisor.

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## List of Acronyms

CTAC	Cetyltrimethylammonium chloride
EDS	Energy-dispersive X-ray spectroscopy
IE	Ion Exchange
MF	Micro Filtration
MEUF	Micellar enhanced ultrafiltration
NF	Nano filtration
PEUF	Polymer enhanced ultrafiltration
RO	Reverse osmosis
SEM	Scanning electron microscopy
TiO <sub>2</sub>	Titanium dioxide
UF	Ultrafiltration
UV-VIS	Uv Visible spectroscopy
XRD	X-Ray diffraction

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## Abstract

In this study, manufacture of ceramic membranes modified by nanomaterials ( $\text{TiO}_2$ ) and CTAC was done. Materials were synthesized by the application of the sol-gel method with respective amounts measured in the molar ratio of Ti: Ethanol: HCL:  $\text{H}_2\text{O}$  as 1:15:0.3:5. The coating of  $\text{TiO}_2$  was done by two methods. The first method involves coating the sample with the prepared sol and subsequently letting the gelation process to occur. The gel-coated ceramic was then calcinated at  $550^\circ\text{C}$  resulting in a  $\text{TiO}_2$  coated ceramic sample. The second method involves preparing  $\text{TiO}_2$  particles with the formed gel calcination at  $550^\circ\text{C}$  resulting in  $\text{TiO}_2$  powders. Taking the newly formed  $\text{TiO}_2$  powder with Nitric acid ( $\text{HNO}_3$ ) in the ratio of 0.5 gm  $\text{TiO}_2$  powder: 10ml of  $\text{HNO}_3$ ; rigorous mixing for three hours has yielded a solution. Whereby a second sample was Immersed and calcined at the previous temperature. The prepared samples were then Immersed again in a solution formed by CTAC and water at a ratio of 5gm:100ml. The coated samples where finally dried and prepared for the testing. Material characterization and filtration tests were conducted to check whether or not the samples were acceptable. SEM/EDS Mapping as well as XRD tests was done to determine the morphology and phase composition of the manufactured material. Performance in the form of efficiency was also conducted by the use of filtration test as another form of characterization. The results obtained confirmed that the prepared membrane has met all the objectives of the study and has successfully removed hexavalent chromium from water solution. The calculated efficiency value of the respected modified and unmodified membranes has been found to be 73.01% for the unmodified membrane while  $\text{TiO}_2$  modified is found to be 80.05% and CTAC modified 85.44% respectively.

Keywords: Removal of Hexavalent Chromium Ions from wastewater, Sol-gel method,  $\text{TiO}_2$  nanoparticles, Cationic surfactant, Surface modified Ceramic Membrane

# CHAPTER I.

## INTRODUCTION

In recent years, due to the development of industries, there has been a growing concern about environmental issues regarding the effluent waste. Specifically about the presence of heavy metals in wastewater. By nature some of the compounds released from these industries are easily soluble in an aquatic environment and that releasing these toxic materials into the environment has become problematic to the society as well as the ecology. The wastewater, discharged from various industries, As a result of processing, contains different pollutants and toxic substances. One of which is heavy metals. Heavy metals by definition are metals that have a density exceeding 5 g per cubic centimeter with an atomic weight ranging between 63.5 and 200.6 (Barakat, 2011; Fu & Wang, 2011). Due to their diverse application, one can find these metals in a number of industries, from cleaning materials to processing aids. Thus heavy metals in the form of anions and cations are released to the environment causing substantial problems to the ecosystem and ecology in general (N. Abdullah, Yusof, Lau, Jaafar, & Ismail, 2019; Al-Rashdi, Johnson, & Hilal, 2013; Barakat, 2011).

Heavy metals are a serious environmental pollutants because of their toxic nature even in low concentration. They have a tendency to infiltrate and accumulate in the plant, animals as well as human being tissues due to their rapid dissolution in an aquatic environment. The majority of heavy metals found in the aquatic environment comes from industries such as leather tannery, Electroplating, and Electronics industry, as well as mining operations. One such material is Chromium(Kotaś & Stasicka, 2000).

Chromium metal and its compounds can be found commonly in the textile, leather tanning, paint, alloying and plating industries. They are used in different stages, in different processes and in different places within said industries.

Commonly found chromium has two principally dominating oxidation states, i.e.: Cr (III) and Cr (VI). Cr (III) is considered to be a harmless and essential trace element to the ecological system whereas Cr (VI) is extremely toxic (Kotaś & Stasicka, 2000; Memon, Memon, Bhangar, & Khuhawar, 2009; Tugaoen, Hristovski, & Westerhoff, 2015).

This toxic nature has had a negative impact on living things such as bacteria, plants, animals and people. The adverse effects of exposure of humans to hexavalent chromium compounds include cancer, tissue degeneration, kidney, and liver damage. The maximum tolerance limit set for the hexavalent chromium by the Environmental Protection Agency (EPA) is 0.1 ppm or 0.05 mg L<sup>-1</sup> in wastewater. Thus, it is necessary to remove or decrease the amount of chromium from the effluent wastewater originating from these industries (Kotaś & Stasicka, 2000; Memon et al., 2009; Tugaoen et al., 2015). The chromium removal methods currently employed are precipitation, ion exchange, photocatalysis, Membrane separation, and adsorption. Of these adsorption, membrane separation and photocatalysis are showing promising new advancement due to their ease in manufacture and cost-effective nature.

Current technologies in the field of membrane separation has shown the use of modified ceramic membranes. They have been extensively used to separate the chromium ion from wastewater. The need for preference of ceramic membranes over the conventional membranes is a result of the resistant nature of ceramic membranes towards rough environmental conditions. (H. Richter et al 1997; S. Benfer, 2004; Schaep et al., 1999).

What makes the following study unique is that it tries to combine the working ideas of two methods (i.e. adsorption and photocatalysis) for chromium removal and applies them to the current membrane separation technology. It is believed that by taking the photocatalytic material titanium dioxide nanoparticle and impregnating it in a ceramic membrane for adsorption process further modified by surface coating of cationic surfactant drastically improves the efficiency of said ceramic membrane in removal of chromium ions. The method is believed to be cost-effective, simple, easy and highly effective.

## **1.1. Statement of Problem**

As it is known, the use of different removal methods like (Adsorption, Membrane Filtration, IE, etc...) have been applied for heavy metal treatment. Specifically, the application of membrane separation technology with respect to ceramic filter membranes have been tested with regards to efficiently removing hexavalent chromium ions. To mention some:- titanium dioxide-coated ceramic membranes, nanoparticle deposited membranes, and the use of complex membranes to filter wastewater have been tested with varying results. Even though the above membranes have been successfully tested, different compromises arises in each of them. For example coated titanium dioxide membrane is an excellent membrane but suffers from efficiency problems that can be attributed to the low surface area of  $\text{TiO}_2$ , while other similar membranes are difficult to maintain in their operation. Some nanoparticle membranes are expensive to manufacture while others like silver nano membranes have an environmental pollution issue due to the toxic nature of silver. Other Removal methods such as reverse osmosis and ion exchange are costly to maintain and operate as well as not easily applicable in the removal of heavy metals. So the question becomes how to produce a ceramic membrane that has improved performance, is cheap to manufacture and is environmentally safe?. To rectify this issue different modification have been done.

This study tries to answer this question by modifying a titanium dioxide nanoparticle ceramic membrane with the use of cationic surfactant to improve the surface area as well as to enhance performance by acting as a supplement to  $\text{TiO}_2$ .

## **1.2. Objectives**

### **1.2.1. General Objectives**

The main objective of this paper is to develop an efficient cationic surfactant modified ceramic membrane for the removal of hexavalent chromium ions from wastewater. Numerous types of ceramic membranes with different modifications have been done. Consequently, the process of impregnating nanomaterials with additional surface modification into the ceramic membrane is believed to be a creative and new way of manufacturing efficient and cost-effective membranes.

### **1.2.2. Specific Objectives**

- Surface modification and uniform coating of commercial membrane with titanium dioxide nanoparticles and cethyl trimethyl ammonium chloride (CTAC) to enhance its adsorption and photocatalytic property.
- Characterize of modified and unmodified membranes
- Investigation of the Removal efficiency on the prepared membranes

### **1.3. Significance of the study**

The significance of this study arises from the need to make a cheap, reliable, efficient, easily accessible, and easily maintained chromium removal method for commercial application. The current methods of chromium removal are either expensive, are small scale, are less efficient, and are generally complex as well as complicated. Due to the above reasons many industries don't have an adequate chromium removal system in place thus harming the environment. This study is aimed at making an easy and efficient method of chromium removal that can be applied commercially, with the use of ceramic membranes that are modified to improve overall performance.



## CHAPTER II.

### Literature Review

One of the most significant problems our world is facing now is the pollution of water. Which as it is known is causing a considerable amount of damage to the environment. This issue can be attributed to many reasons, one of which is the radical growth of industrialization. The wastewater, discharged from various industries, As a result of processing, contains different pollutants and toxic substances. One of which is heavy metals. Heavy metals by definition are metals that have a density exceeding 5 g per cubic centimeter with an atomic weight ranging between 63.5 and 200.6 (Barakat, 2011; Fu & Wang, 2011). Due to their diverse application, one can find these metals in a number of industries, from cleaning materials to processing aids. Thus heavy metals in the form of anions and cations are released to the environment causing substantial problems to the ecosystem and ecology in general (N. Abdullah et al., 2019; Al-Rashdi et al., 2013; Barakat, 2011).

Heavy metals are a serious environmental pollutants because of their toxic nature even in low concentration. They have a tendency to infiltrate and accumulate in the plant, animals as well as human being tissues due to their rapid dissolution in an aquatic environment. The majority of heavy metals found in the aquatic environment comes from industries such as leather tannery, Electroplating, and Electronics industry, as well as mining operations. Out of the heavy metals encountered in industry the most problematic is Arsenic (As), Lead (Pb), Chromium (Cr) and Mercury (Hg) (Adam et al., 2019).

Lead is one of the heavy metals found in ammunition, battery manufacturing, paint, steel, ceramic and glass industries. Lead metal causes severe damage to the nervous system, kidney, liver, and brain of human beings. Different ways for the infiltration of lead metal into water systems were identified and are being monitored with strict regulation stated by the world health organization (WHO) regarding health and safety(Ajitha P, 2017; Naiya TK, 2009).

Arsenic also is known as "king of poisons" is primarily introduced to aquatic environments by Smelting operations, Gold mining, Pesticide manufacturing, and petroleum industries. Like its sister element chromium, arsenic is also found in two oxidation states. arsenic (III) and arsenic (VI). As (III) is the most toxic of the two to human beings and it's found to be a carcinogenic compound (Adam et al., 2019).

Chromium metal and its compounds can be found commonly in the textile, leather tanning, paint alloying plating industries. They are used in different stages, in different processes and in different places within said industries. Commonly found chromium has two principally dominating oxidation states, i.e.: Cr (III) and Cr (VI). Cr (III) is considered to be a harmless and essential trace element to the ecological system whereas Cr (VI) is extremely toxic. This toxic nature has had a negative impact on living things such as bacteria, plants, animals and people (Almeida et al., 2019; Cheng, Wang, Doudrick, & Chan, 2015).

The adverse effects of exposure of humans to hexavalent chromium compounds include cancer, tissue degeneration, kidney, and liver damage. The maximum tolerance limit set for the hexavalent chromium by the Environmental Protection Agency (EPA) is 0.1 ppm or 0.05 mg L<sup>-1</sup> in wastewater. Thus, it is necessary to remove or decrease the amount of chromium from the effluent wastewater originating from these industries (Almeida et al., 2019; Dehghani, Sanaei, Ali, & Bhatnagar, 2016).

Mercury is commonly encountered in the Electrical, Caustic soda and pharmaceutical industries. The damage done due to the exposure to the metal includes kidney failure, neurotoxicology, and Gastrointestinal problems. As can be seen from the given examples, the risk of any heavy metal poisoning is great and can have an adverse effect on the environment. hence current policies aimed in regards to reducing the amount of heavy metal contamination are being employed to ensure aquatic environmental protection (N. Abdullah et al., 2019; Adam et al., 2019). In recent years the use of different technologies in the ways of combating environmental pollution, have played tremendous roles with regards to minimizing and removing heavy metal contaminants (Al-Rashdi et al., 2013). The occurrence and adverse effects of some heavy metals commonly found are summarized in table 1 as follows:

Type of Metals	Forms of Existence in Water	Occurrence	Risk	Environmental Protection Agency standard
Arsenic	Trivalent arsenic, pentavalent Arsenic	Mining, soil erosion, agricultural activities, medicinal applications	Cardiovascular and peripheral vascular diseases, neurological disorder, cancers,	0.05 mg/L
Chromium	Chromium (III), Chromium (VI)	Metal processing, tannery facilities, chromate production, metallurgical industries, stainless steel welding, pigment production, leather tanning	Respiratory problems, cardiovascular disease, hematological, hepatic, renal effects, neurological disorder	0.05 mg/L
Lead	Lead oxide, divalent lead, lead Chromate	Fossil fuel burning, mining, agricultural activities, domestic activities, metal products piping, ammunitions, X-rays, paint, and ceramic products	Blood level poisoning, lower IQ, impaired neurobehavioral developments, impaired growth, reproductive problems, abortions, brain damage, kidney, and gastrointestinal problems, damage to nervous system	0.006 mg/L
Mercury	Mercury (I), mercurous (II), methyl mercury	Electrical industries, production of caustic soda, solvent, pharmaceutical industries	Gastrointestinal damage, neurotoxicity, kidney problems	0.002 mg/L

Type of Metals	Forms of Existence in Water	Occurrence	Risk	Environmental Protection Agency standard
Cadmium	Cd (II)	Metal and Pigment Industries, Plastic, Polymer Production, Electroplating and Nickel-cadmium Batteries production as well as Photography companies	Renal disorder, Osteomalacia, Cancer, Anemia, Bronchitis	0.005 mg/L
Copper	Cu(II)	Galvanizing, Petroleum refining, Metal finishing, paint, and pigments production, coal mining, smelting, and electroplating	Long term exposure: damage to kidney, liver, pancreas, and brain.	1.0 mg/L
Zinc	Zn(II)	Bioaccumulation, Galvanizing industries	Stomach cramps, Skin irritation, Vomiting, Anemia	5.0 mg/L
Nickel	Ni(II)	The manufacturing process of stainless steel, superalloys, metallic alloys, electroplating, and batteries	Lung and kidney problems as well as Gastrointestinal distress	0.1 mg/L

Table 1 Sources of Release, Potential Risk of Exposure and Regulation standard of some Heavy Metals (Norfadhilatuladha Abdullah, Tajuddin, & Yusof, 2019; Adam et al., 2019; Tchounwou, 2012)

## **2.1. Methods of Heavy Metal Treatment**

Given the dangerous nature of these contaminants, the next question becomes on the issue of how to successfully remove them from industrial wastewater. There are numerous methods used to achieve this and are given as follows:

### **2.1.1. Precipitation**

Precipitation is one of the heavy metal removal methods that are cost-effective in the removal process. It is a process by which certain chemical agents, depending on the heavy metal, are introduced to the system whereby they reduce and precipitate the heavy metals into an insoluble precipitate that later can be removed via simple filtration. Due to the cheap availability of precipitating chemicals and cost-effective operation, compared to the other process, it is by far widely used. (N. Abdullah et al., 2019). The most commonly used precipitation methods involve the use of hydroxides and sulfides as removal mechanisms.

Hydroxide precipitation methods involve the use of hydroxide chemicals to form metal hydroxides at a specified pH range. The solid metal hydroxide precipitates at the bottom and thus can be removed by sedimentation or flocculation methods. The whole process involves knowing the specific pH range to produce low soluble metal hydroxides with the use of efficient hydroxides. The fundamental drawback of this process is the very nature of the heavy metals. Some metals by nature are amphoteric so in a mixed metal system like wastewaters, it is difficult to control the pH of the medium. Some metals become soluble in certain pH where others form precipitates in that very same pH so it becomes difficult to remove all the heavy metals (N. Abdullah et al., 2019; Grace Pavithra, Jaikumar, Kumar, & SundarRajan, 2019).

Sulfide removal methods are just methods to overcome the fundamental drawback of the hydroxide methods. Sulfides can work in a wide range of pH enabling more efficient removal of heavy metals in a broad spectrum. The basic working principles are the same as hydroxides. The only difference being, while hydroxides use hydroxide chemicals, sulfides use sulfate chemicals in the process of achieving metal precipitates. One major drawback in the application of sulfides is that

contact with acidic medium releases toxic hydrogen sulfide (H<sub>2</sub>S) gas and thus care must be taken in applying (Fu & Wang, 2011).

### 2.1.2. Coagulation-Flocculation

Coagulation and flocculation is one of the oldest methods of wastewater treatment. since 2000 BC, mankind has been able to use different materials as a coagulant in the pursuit of purifying water(Fu & Wang, 2011). The process of Coagulation and flocculation can be used as a preliminary filtration or an intermediate stage of wastewater treatment. The process entails the use of certain chemicals to neutralize charges in heavy metals desired to be removed (i.e. It's the destabilization of powers that keep the materials suspended in the water and enabling the neutralized particles to bond), thus enabling the heavy metals to form aggregates. After coagulation takes place flocculation or gentle mixing is conducted in order to form macromolecules of aggregates that can be easily separated by sedimentation (Mohd Ridhwan Adam, Mohamad Izrin Mohamad Esham, Dzarfan Othman, & Ismail, 2019).

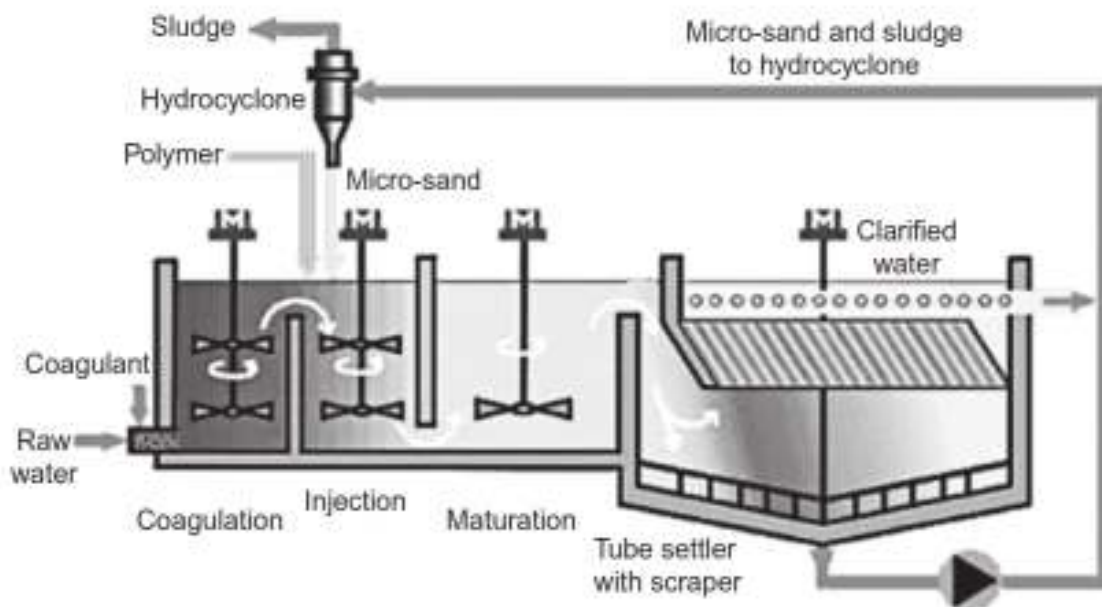


Figure 1: Mechanism of Coagulation and flocculation in wastewater treatment Based on Fig. 1 of (Desjardins C, 2002)

In his study, (Ismail IM, 2002) has found that, the use of Aluminum  $Al_2(SO_4)_3$ , ferrous sulfate  $Fe(SO_4)$ , ferric sulfate  $Fe(SO_4)_3$  and lime  $Ca(OH)_2$  as a low-cost coagulant was a good alternative and that the optimum amount should be 60 mg/l. While (Choumane FZ, 2017) studied the application of biomaterials as a coagulant material in his research. Recent studies in the application of coagulation have yielded the application of electrochemistry in forming aggregates as opposed to the use of conventional chemicals. Electrocoagulation employs the use of anode and cathode materials to attract and neutralize desired metals to form aggregates. Materials such as iron and carbon have been used in the study to determine the effective heavy metal removal. Removal depends on materials, turbidity, conductivity and suspended solids (Barakat, 2011).

### **2.1.3. Ion Exchange**

Ion Exchange is a reversible chemical process that is commonly applied in the removal of heavy metals from industrial wastewater. The mechanism by which removal occurs is the simple kinetic substitution of cation and anion heavy metals with subsequent hydrogen or hydroxide ions on naturally occurring or synthetically manufactured resins. I.e. Ion exchange is simply the application of solid resins in the hopes of substituting metal ions with ions from said solid resins. Ion exchange is used for its advantages with respect to high capacity, high efficiency and fast kinetics in the removal of heavy metals (Kang, 2004).

The efficiency of Ion exchange systems greatly depends on pH as well as the type of resins used (i.e. Natural or Synthetic). Synthetic resins are preferred over the natural due to the specific fabrication of resin materials, to tackle heavy metals, with the latest technologies. One such example is the production of novel ion exchange resin modified by bimetallic Pd-Cu catalyst for the removal of Nitrates in heavy metals (Mendow G, 2017).

In the hopes of cost reduction, some natural ion exchange resins were studied in the removal of heavy metals. Naturally occurring zeolites demonstrated by (Motsi, 2009; Taffarel, 2009) have been used as a cation exchanging material at different circumstances. Though applicable much-needed work must be done to natural resins to match efficiency with synthetic.

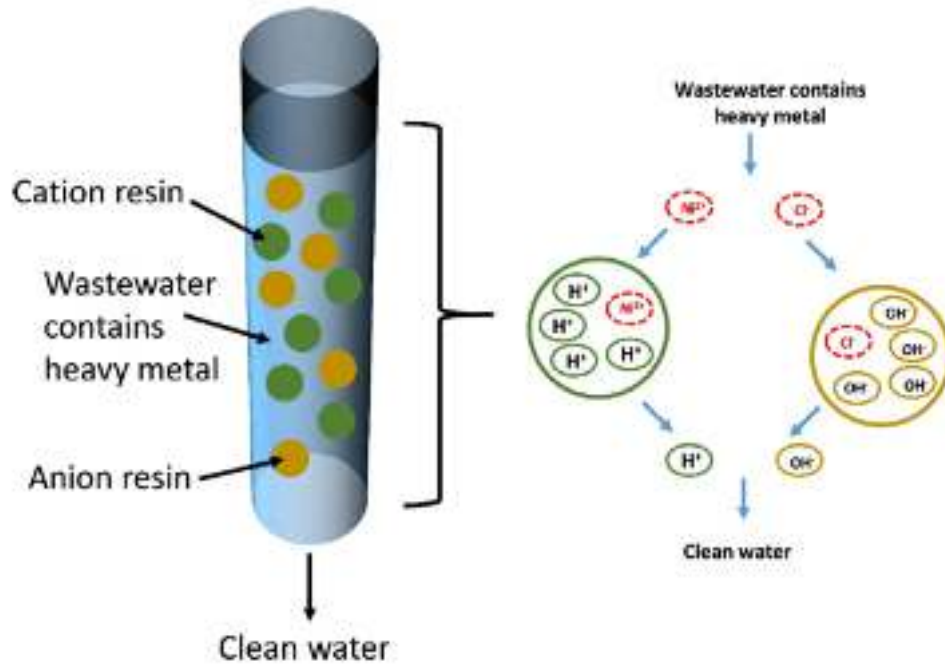


Figure 2: Mechanism of Ion Exchange in wastewater treatment based on fig 12.1 of (Mohd Ridhwan Adam et al., 2019).



#### 2.1.4. Adsorption

Adsorption is one of the most frequently used methods in heavy metal removal because of its ease of availability and cost-effective nature. Adsorption is a process by which pollutant chemicals/materials are attached either by chemical reaction or physical attraction to a solid surface. i.e. it's a process involving a liquid solute contaminant (adsorbate) accumulating on a solid surface of desired material by either a chemical reaction (forming ionic and covalent bonds) or a physical attraction ( by the use of weak van der Waal forces)(N. Abdullah et al., 2019; Barakat, 2011; Fu & Wang, 2011; GracePavithra et al., 2019). Due to its ease of application, many prospecting researches have been done to improve the process. Researches ranging from conventional material selection to application of advanced nanotechnology have been employed not only to improve efficiency but to create a cost-effective easily recoverable method in tackling environmental problems (Fu & Wang, 2011).

Henceforth some of the methods will be discussed in the following literature to give an all-inclusive idea of what has been done in the past. Conventional Adsorption methods are adsorption processes that typically use conventionally available materials and structures to adsorb heavy metals. Adsorption materials consisting of activated carbon are popular due to the nature of activated carbons. They have a high surface area with large mesopores and micropore volumes that makes them ideal for the adsorption process. The most commonly used activated carbon preparation are wood coal and coconut shell (Fu & Wang, 2011). Due to cost and Efficiency, many agricultural wastes are being incorporated into the manufacture of activated carbons.

The most commonly widely used AC in the industry are produced from coal, wood and coconut shell. Due to costs, however, their use has been limited nowadays. Based on this, ACs are being prepared from various agricultural waste. AC made from eucalyptus bark was used in the removal of Cu ions resulting in maximum adsorption capacity for Cu <sup>2+</sup> as 0.45 mmol/g (Kongsuwan et al, 2009).

Zeolites are naturally occurring aluminosilicates that have been used as an adsorption material. Due to their intricate structure, good ion exchange capability and high surface area, zeolites are

among the most effective materials to remove heavy metals (Choi et al., 2016). Clinoptilolite is the most used natural zeolite that has been studied by (Babel and Kurniawan, 2003; Bose et al., 2002; Shaheen et al., 2012) in removing selected materials.

Nanostructure materials Adsorption in the form of several materials like magnetic nanoparticles, Carbon Nano Tubes and Graphene have been used to effectively remove metal ions from wastewater. Limitations in the form of cost and effectiveness, however, have been noticed in these materials and further study is being done to remedy that. Special attention is being given to cationic/ anionic nanoparticles as a form of adsorbent that is being studied for further perspectives (Alexander E. Burakov 2018; Mohd Ridhwan Adam et al., 2019).

#### **2.1.5. Bio removal methods**

Due to the nature of excess toxic wastes, High energy consumption and incomplete removal of heavy metal wastes another sustainable, environmentally safe, low impact as well as low costly method was developed in the form of bioremediation. Microbial remediation or Bioremediation can be broadly defined as the modification and application of specific microorganisms to degrade and/or remove heavy metals from the environment to the acceptable level. Put simply bioremediation is the use of naturally occurring and genetically modified, resistant strains of microorganisms to combat waste materials; in this case heavy metals(Fernández, Viñarta, Bernal, Cruz, & Figueroa, 2018; Jobby, Jha, Yadav, & Desai, 2018; Pradhan, Sukla, Sawyer, & Rahman, 2017; Tchounwou, 2012).

Bioremediation processes due to their safe, efficient and low-cost nature are becoming increasingly the topic of many pieces of research and new trends. Research in all bioremediation methods are being considered a suitable alternative to the aforementioned heavy metal removal methods. Remediation methods fundamentally involve three ways of removal. These are:-

## A) Biosorption

Biosorption is one of the methods by which microorganisms can remove heavy metals from a system. Due to a microorganism's ability to absorb materials, it has been at the forefront of research and study. Based on the condition of the microorganism used (whether or not it's alive or dead) biosorption can either be passive (for dead organisms) or active (absorption through living cells).

Passive absorption is done by the application of dead cells in order to absorb the heavy metals. This has the added benefit of operating in difficult and toxic environments due to the nature of microorganisms being dead as well as easy recoverability and regeneration of biomass. Active absorption occurs due to the fact that cell walls and cells of organisms have different functional groups like carboxylic, amine and such which enables them to absorb the given metallic species. Contact between these groups and heavy metals results in bonds that attach them to the living cells. This opens up new and different mechanisms as well as possibilities to the absorption process. (S. S. Ahluwalia, Goyal, D, 2007; Ajitha P, 2017; Fernández et al., 2018) The rapid application of bio absorbents is attributed to high surface area to volume ratio (making them efficient), minimum cost and easy recoverability of bio absorbent materials.

Research conducted by (S. S. Ahluwalia, Goyal, D., , 2010) have found that in fungi carboxyl, amine, amide, and alkali groups are involved in the absorption of chromium ions while (Bahafid, 2013) have also proven that the functional groups were indeed responsible in chromium absorption found in *Pichia Anomala* involves adsorption on functional groups (e.g. amide I, carboxyl, etc...)

## B) Bioaccumulation

Involves the accumulation of heavy metals in living cells. Many researchers have tried to determine the effects and conditions that are responsible for accumulation. (Fernández et al., 2018; Gutierrez-Corona, 2016) have found that metal accumulation greatly depends on metabolism, metal concentration and contact time. Some also believe that due to the complex nature of membranes found in the bio organism some metals are readily accumulated while others are not. (S. S. Ahluwalia, Goyal, D, 2007) has found that the limitation of this method involves growth inhibition on active cells thus limiting uptake.

### C) Biotransformation

Biotransformation is the last one of the bioremediation process where it involves the reduction of heavy metals to less toxic form (e.g. reduction of chromium (VI) to chromium (III) ). It can simply be viewed as the toxic removal reaction undergone by the body of the biomaterial(Fernández et al., 2018).

#### **2.1.6. Membrane technologies**

Heavy metals as discussed above have been a major problem to society as well as ecology, and many methods shown here have successfully tackled this endeavor in solution-finding. even though there has been tremendous success, these methods are far from being perfect due to limitations like high operation cost, high maintenance, high operation time, high secondary wastes and infeasibility on a large scale. Hence membrane technologies have come into play as an economical and feasible alternative to the above methods. Membrane technologies are technologies that employ a semi-permeable membrane modified in a number of ways to remove said heavy metals without adding unnecessary processes like secondary treatment. They are simple and yet effective methods of removing wastes by the simple application of a selective transport media (N. Abdullah et al., 2019; Barakat, 2011).

Membranes generally work with the belief of separating permeate (the material that passes through the membrane) and retentate (Rejected product) by employing a number of separation techniques like size separation, charge separation and adsorption of specific materials. Size separation as its name suggests involves separating materials based on pore size. Materials that are desired pass through the selective pores while unwanted materials of larger size are hindered. This is the very common and basic separation process of membranes. While size separation is effective against samples of different sizes it becomes ineffective when pitted against materials of the same size (N. Abdullah et al., 2019).

For this, some have proposed the use of specific charge modified membranes that can reject similarly charged unwanted materials (based on Donnan Exclusion principle) while letting though

desired substances. Some also have suggested the use of an adsorbing membrane that can physically hold the unwanted materials by a way of chemical bonding as a form of separating technique as opposed to the use of charged membranes. (Barakat, 2011; Fu & Wang, 2011; GracePavithra et al., 2019)

### Graphical abstract

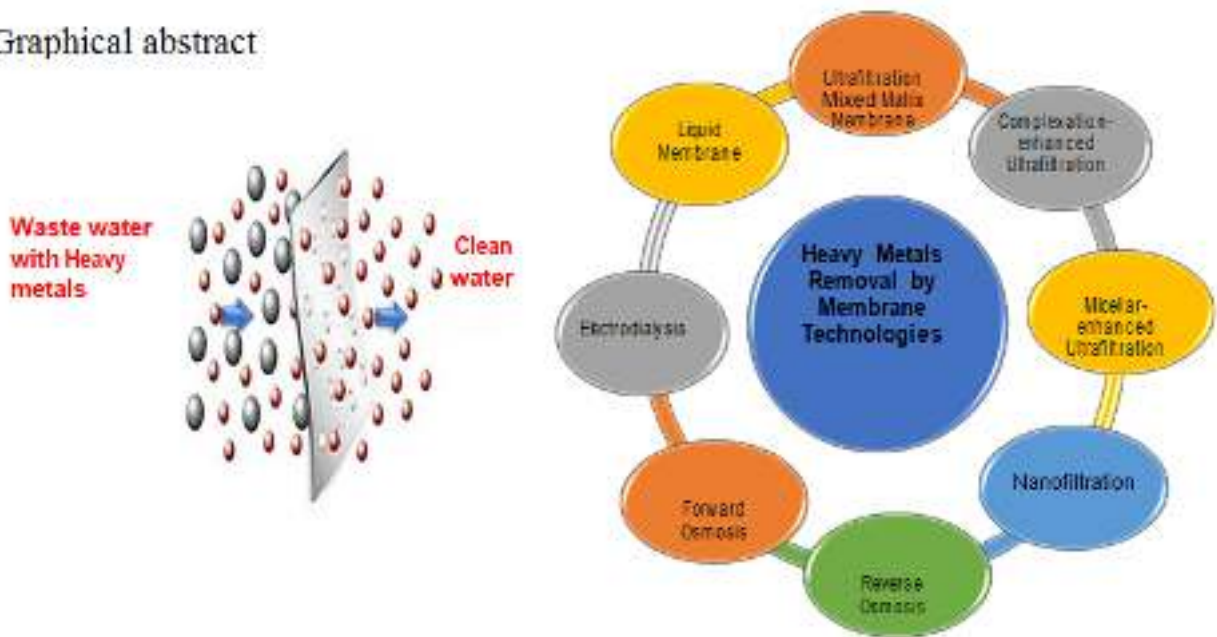


Figure 3. Graphical representation of various membrane technologies(N. Abdullah et al., 2019)

As shown in figure 1 above there are a number of different kinds of membranes modified in some way or another either physically (i.e. Reduced pore sized structures and manufacturing of integrated complex structured membranes) or Chemically (i.e. Modified surface properties by charge manipulation, chemical coatings and attachment of materials to the membrane). Some of these methods will be discussed hereafter.

Ultrafiltration- is a membrane separation technique that utilizes the use of ultra size micropores to remove unwanted materials. Due to the nature of heavy metals ion being smaller than ultra membrane pores, special filter membranes where devised. Micellar enhanced ultrafiltration (MEUF)

and polymer enhanced ultrafiltration (PEUF) were excessively used to improve the heavy metal recovery process. MEUF involves the use of micellar surfactants and compounds to remove heavy metals from wastewater. This is done by adding micellar surfactants and compounds until the critical micellar concentration in the wastewater is surpassed, thereby enabling the formation of bonded micellar and metal ion particles that agglomerate to a large size. Which then incidentally can be removed by the ultra pores of ultrafilters (N. Abdullah et al., 2019; Amin, Hassan, A El-Sherbiny, & Abdallah, 2016; Barakat, 2011).

Polymer enhanced ultrafiltration (PEUF) is the use of water-soluble polymeric compounds that can attach themselves to heavy metals or too complex the heavy metal ions to form macromolecules, which then can be easily removed by the retention of these molecules in the ultrafiltration membrane. Reuse and cleaning of the polymeric compounds are done to reuse the process(Fu & Wang, 2011).

Efficiency of modified ultrafiltration membranes depends on the type of membrane, surfactant, ph and contact time. (Ferella, 2007) used ceramic ultrafiltration membrane to remove  $Pb^{2+}$  and  $AsO_4^-$  metallic ions using Dodecylbenzenesulfonic acid and dodecylamine as a MEUF complexing agent. It was found that at an optimum ph of 7.47 removal efficiency of  $> 99\%$  was achieved for  $Pb^{2+}$  while only 19% was found for Arsenic. Furthermore, PEUF complexing agents of Carboxyl methylcellulose and polyethyleneimine (PEI) were used on Polyethersulfone ultrafilter membranes to remove  $Cu^{2+}$ ,  $Cr^{3+}$ ,  $Ni^{2+}$  at a varying ph range of  $> 6.0$ . PEI yielded an efficiency rate of 94% for removal of  $Cu^{2+}$  and 100% for  $Ni^{2+}$ , while Carboxyl methylcellulose was found to have removed 97.6% of  $Cu^{2+}$ , 99.1% for  $Ni^{2+}$  and 99.5% for  $Cr^{3+}$  thus showing with these results the effect of ph and type of surfactant used (Barakat, 2011; Molinari, 2008).

Reverse osmosis- is the process of removing dissolved solids through the semi-permeable membrane, allowing the desired fluid to pass through while retaining unwanted materials. The process works by the application of pressure. Several methods have been used to remove heavy metals from solutions using reverse osmosis. Table 2 summarizes projects done with reverse osmosis membranes on selected heavy metals with operating conditions as well as efficiencies achieved.

Membrane	Heavy metal	Initial Conc.	Efficiency (%)	Operating Conditions	References
RO	Cu <sup>2+</sup> , Ni <sup>2+</sup>	500 mg/l	99.5	5 atm pressure	Mohsen-Niaet al., 2007
RO	Cu <sup>2+</sup>	20-100 mg/l	70- 95	Low pressure	Zhang et al., 2009
RO	As(III)	<500 µgm/l	20-55	NA	Chan and Dudeney, 2008
RO	Zn <sup>2+</sup> , Ni <sup>2+</sup>	Zn <sup>2+</sup> : 64-170 mg/l Ni <sup>2+</sup> : 44-169 mg/l	98.9 99.3	1100KPa	Ipek, 2005
RO+NF	Cu <sup>2+</sup>	15 mg/l	95-99	3.8bar	Sudilovskiy et al., 2008

Table 2 Operating conditions, Initial Conc., and Efficiency of Reverse osmosis membranes

Nanofiltration- is a removal process much like ultrafiltration that operates based on nano-sized pores. Nano filters are membranes that have become more versatile due to the rise in the use of nanotechnology in heavy metal removal. NF benefits from low manufacturing/operating costs, relatively high efficiency, and versatile modification options (N. Abdullah et al., 2019).

Research done on the use and application of different modifications has yielded promising results in the removal of heavy metals. Removal of hexavalent chromium ion was achieved by using poly (vinylidene fluoride) (PVDF) film supported by thermally treated MoxNiy@N-C catalyst using formic acid as a reducing agent. The membrane in question proved to have better removal efficiency as opposed to MoxNiy@N-C nanoparticle (Choudhury, Mondal, Majumdar, Saha, & Sahoo, 2018). The application of a thin-film composite polyamide NF membrane for the removal of nickel ions was extensively studied by (Murthy and Chaudhari, 2008). Rejection of nickel ion was found to be 98% at the use of the initial feed concentration of 5 mg/L.

Nanoparticle modified membranes - Beyond the conventional use of nano filters the application of nanoparticle incorporated ceramic ultra and nano filter membranes have become increasingly popular due to the various modifications and complementary effects that can be achieved. Effects like bio degeneration increased conductivity and photocatalytic properties.

### 2.1.7. Advantage and Disadvantage in removal technologies

In the endeavor of removing heavy metals from wastewater, there have been a number of methods applied, as each is believed to improve upon one quality or another. The following table tries to summarize the various advantages and disadvantages of methods used in the treatment of heavy metals. the produced membranes

Methods	Description	Advantage	Disadvantage
Precipitation	Conversion of metal ions into precipitates by using chemicals	<ul style="list-style-type: none"> <li>- Simple method</li> <li>- Precipitants are relatively inexpensive</li> </ul>	<ul style="list-style-type: none"> <li>- Ineffective in high concentration</li> <li>- large amount of precipitate agents</li> <li>- Toxic sludge Production</li> <li>- Chemical stabilization and disposal are needed.</li> <li>- Slow metal precipitation</li> </ul>
Coagulation & flocculation	Addition of opposite charges to reduce heavy metals and to form aggregates	<ul style="list-style-type: none"> <li>- Relatively economic in use of inexpensive coagulant</li> <li>- Simple operation</li> </ul>	<ul style="list-style-type: none"> <li>- Incomplete heavy metals removal</li> <li>- Production of sludge</li> </ul>
Adsorption	Use of adsorption materials in absorbing heavy metals	<ul style="list-style-type: none"> <li>- Abundant selection in adsorbents</li> <li>- Relatively inexpensive</li> <li>- Simple operation</li> </ul>	<ul style="list-style-type: none"> <li>- Tedious post-treatment</li> <li>- adsorbents need further modification before treating heavy metals</li> <li>- Complex operation</li> </ul>



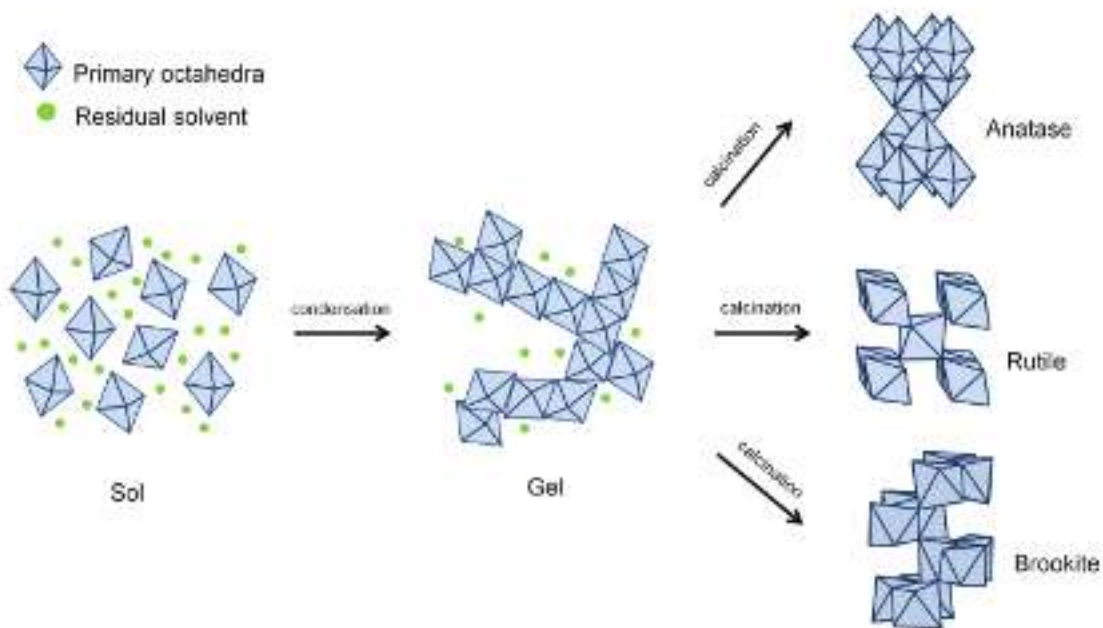
Ion Exchange	Uses resin to exchange ions with metals resulting in water.	<ul style="list-style-type: none"> <li>- Fast kinetic</li> <li>- Convenient process</li> <li>- Effective removal</li> </ul>	<ul style="list-style-type: none"> <li>- Sensitive to pH</li> <li>- Presence of free acids may result in low binding affinity</li> <li>- Small Scale and Expensive</li> <li>- Excessive Fouling</li> <li>- Low concentration of metal removal</li> </ul>
Bio removal	Use of biomaterials in removal	<ul style="list-style-type: none"> <li>- Environmentally friendly</li> <li>- Relatively inexpensive</li> <li>- Abundant options.</li> <li>- Simple operation</li> </ul>	<ul style="list-style-type: none"> <li>- Needs further study</li> <li>- Limited removal</li> <li>- Complex operation</li> </ul>
Membrane technologies	Use semi-permeable membranes to separate metal ions	<ul style="list-style-type: none"> <li>- Multiple options</li> <li>- Relatively inexpensive depending on the membrane</li> <li>- Simple operation</li> <li>- Effective and Efficient</li> </ul>	<ul style="list-style-type: none"> <li>- Fouling</li> <li>- High operating cost on some membranes</li> <li>- Reuse requires additional treatment</li> </ul>

Table 3: Advantage and Disadvantage of different removal methods

## 2.2. Membrane manufacturing process and Sample characterization

Some of the nanomaterials incorporated membranes include Titanium dioxide nanoparticle modified membranes, silver, and carbon modified membranes. Carbon nanotubes and nano fibers incorporated ceramic membranes have been used extensively due to their advantage in structure. Carbon nanotubes membranes were used to remove oil from water, achieving almost 100% removal rate (X. Chen, 2012). The reason for this is given by the unique structural arrangement of nanotubes in the form of grids, enabling the retention of oil much more effectively. Carbon nanofibers supported by carbon- alumina membranes were used in the removal of  $\text{Cu}^{2+}$  ions from chemical treatment wastewater achieving a 90% copper removal rate (G.C.C. Yang, 2008). Silver nanoparticles have been used due to their advantage in combating biofouling as well as their antibacterial properties in wastewater treatment. Attributed to their nature silver nanoparticles require higher adhesive agents as a coupling agent, a phenomenon greatly studied by (Y. Lv, 2009) using amino saline as a coupling agent.

Titanium dioxide nanoparticles have been excessively used in the application of incorporating nanoparticles due to their high photocatalytic properties as well as chemically stable nature. One of the major processing methods of  $\text{TiO}_2$  nanoparticle membranes is the use of the sol-gel method. The sol-gel process is a method of material manufacturing that has been increasingly involved in the material engineering sciences as well as industries. It entails a method of forming specific materials such as metal oxides from a predetermined precursor by the formation of a sol and a gel. Precursors (chemical compounds) are mixed usually with alcohol to form a solution called a sol (Robabeh Bashiri, 2017). The formed sol, as time passes on is turned into a complex integrated matrix of a gel-like substance that can be further treated to give the desired substance. Figure 4 here tries to illustrate what exactly happens in a sol-gel reaction with the corresponding chemical reactions.



*Hydrolysis:*



*Condensation:*

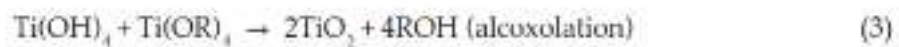
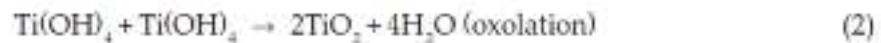


Figure 4. The hydrolysis, condensation and calcination process of the sol-gel method in synthesizing the crystalline anatase, rutile, and brookite TiO<sub>2</sub> nanoparticles (Muhamad Zamri Yahaya, Mohd Asri Mat Teridi, & Mohamad, 2017).

(S.S. Hosseini, 2017; Y. Bessekhoud, 2003) used the sol-gel method to produce TiO<sub>2</sub> nanoparticle membranes in removing chromium ions from industrial wastewater. The rejection efficiency was found to around 80% in removing the ions. Thin-film TiO<sub>2</sub> coated nanoparticle membranes were also synthesized achieving only a removal efficiency of 45% (Litter, 2017). (Z. Song, 2016) used a molecular layer deposition layer to remove methyl blue and has found a removal efficiency of 96% and anti-fouling properties in the produced membranes.

### **2.2.1. Sample Characterization and testing Methods**

The characterization and testing methods involve the use of specialized equipment to determine whether or not the proposed materials have been manufactured. Furthermore, the use of these equipments widely conveys the truth as a notion of proof of what that has been done to what was expected to be done. Characterization of material with XRD and SEM/EDS was done on the sample at SKKU to show the distribution of materials on the ceramic membrane.

#### **A) X-ray diffraction (XRD)**

X-ray diffraction is one of the most commonly used characterization methods in material science. It entails the application of x-rays to determine materials lattice structure and crystalline structure. When a sample is placed in an x-ray diffraction machine, the x-rays diffract giving us a pattern that consists of peaks with various intensities and a spectrum showing peak intensity with the measured angle.

By taking this data values one can match specific patterns to specific materials thus identifying a given sample. In this study sample analysis by XRD was done to determine whether or not the proposed material was manufactured.

#### **B) Scanning Electron Microscope (SEM) with elemental analysis (EDS)**

Scanning Electron microscope is a machine highly capable of magnifying and showing the morphology of materials in a given sample. It is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and measured that give detailed information regarding the sample's surface topography and composition. The working principle involves the application of electrons via tunnel effect to bombard the sample thus giving a picture of the surface structure and morphology of a material. While SEM gives a picture of what the structure might entail EDS gives a precise distribution image for all the elements found on the sample surface. It gives a broad view of what makes up the characteristic samples. SEM and EDS have been done to determine the morphology as well as to show the sample's consisting elements in the study.

### **C) UV-Vis spectrophotometer**

UV-Vis spectrophotometer involves the use of UV/vis light rays in the determination of the constitution of a sample. Samples are subjected to exposure to UV/vis rays at a range or specific wavelengths to determine the measure of absorbance in the materials. Each individual element has its own absorbance value of light rays at a given wavelength and thus the spectrophotometer employs this principle to determine whether or not a certain desired material exists in a sample or not. UV-Vis spectrophotometer analysis was done on the liquid samples to determine the amount of chromium found in them before and after filtration tests in this study. Due to the sensitivity of the given sample Nanodrop 2000 spectrophotometer was used to determine both the calibration curve and the concentration of the respective filtered samples.

### **2.3. Conclusion**

As seen above different treatment methods exist in order to combat heavy metals taking into account different parameters such as cost and availability of technology. This study taking into account flexibility, accessibility, cost, ease of manufacture as well as the merit of the methods for specific condition in particular to the place of application, has selected the use of membrane separation in the removal of heavy metals. Taking into account of the different merits and demerits of membrane separation, emphasis was done on the modification of such membranes in order to enhance the given removal efficiency of the materials.

# CHAPTER III

## Experimental Methods

In this section, based on the objectives of this project, the materials, processing and characterization methods are discussed in the following three parts.

### 3.1. Materials

In the following experiment, different materials were used as a starting material. Titanium (IV)-n-butoxide as well as Cetyltrimethylammonium chloride (CTAC) analytical grade (96%) from DAEJUNG Chemicals, South Korea. Analytical grade Ethanol (98%), Hydrochloric acid (HCL), Nitric acid (HNO<sub>3</sub>) and Commercially available Diatomite Ceramic Membrane were acquired locally. Based on the required objective and taking into account all constraining conditions the materials were prepared.

### 3.2. Processing Methods

In the processing of nanomaterials coated ceramic membranes, there are different methods that can be applied with respect to what is desired ( i.e. Particle size, shape, and structure), Hydrothermal, Chemical vapor deposition(CVD), Sol-gel and such. The simplest and easily available method in this regard is the Sol-gel method. Due to its ease of application, it is one of the broadly used methods.

Here the objective was to manufacture titanium dioxide nanoparticles using titanium n butoxide as a precursor. the overall process and details are given as follows:- Titanium (IV)-n-butoxide was measured according to the given ratio and was mixed with ethanol of half proportion required. the resulting solution was mixed at room temperature for an hour. The advantage for the use of room temperature for this mixing stage was stressed by (Matsoukas, 1998) in their paper as the most optimum and favorable condition for the production titanium dioxide materials out of all the temperatures that have been studied.

While mixing, another solution of HCL, H<sub>2</sub>O and the rest half of the Ethanol was prepared and place in a pipette for the drop wise application that is required in the second phase. At the one hour mark solution in the pipette was added drop wise to the mixture of alcohol and precursor while continuous stirring was still in effect. After the rigorous mixing for two hours, the sol solution was prepared. Based on (Robabeh Bashiri, 2017; T. PHONKHOKKONG & 2016; Y. Bessekhoud, 2003), the amount of materials was measured in the molar ratio of Ti: Ethanol: HCL: H<sub>2</sub>O as 1:15:0.3:5. After the preparation of the sol, diatomite samples were taken and dip-coated in the sol solution before gelation occurred.

Setting the produced sol solution and coated solutions in a furnace, the materials were calcinated at 550<sup>0</sup>c. The result was a TiO<sub>2</sub> nano powder and a TiO<sub>2</sub> coated ceramic sample. Taking the newly formed TiO<sub>2</sub> powder with Nitric acid (HNO<sub>3</sub>) in the ratio of 0.5 gm TiO<sub>2</sub> powder: 10ml of HNO<sub>3</sub>; rigorous mixing for three hours yielded a solution whereby a second sample was dip-coated and calcined at the previous temperature. The prepared samples were then dip-coated again in a solution formed by CTAC and water at a ratio of 5gm:100ml. The coated samples were finally dried and prepared for the testing stage to commence. Figures 5-6 show the overall procedure



Figure 5. First steps of Preparation (A) Raw material preparation (B)The Mixing of Titanium (IV)-butoxide with Ethanol.



C)



D)



E)



F)



G)

Figure 6. Overall manufacture process of modified ceramic membranes with next steps, (C) Drop wise addition of second solution, (D) Gel formed from sol-gel synthesis, (E) Preparation of CTAC solution,(F) Samples prepared for characterization, (G) Samples prepared for Filtration



### 3.3. Filtration test

In order for the filtration test to commence wastewater sample stock solution had to be prepared using data obtained from the Ethiopian leather institute as a reference to leather industry effluent.

Based on the data obtained, a stock solution was prepared with a concentration of 71mg/500ml of chromium from chromium sulfate salt. Figure 8 below show the concentration of heavy metals in tannery wastewater as well as prepared stock solutions.



Figure 7. Chromium containing stock solution

Filtration was done in specially prepared samples under UV rays to promote photocatalytic properties in both  $\text{TiO}_2$  and CTAC. Photocatalytic properties promote the reduction of chromium (VI) to chromium (III) as shown by (Litter, 2017). As discussed in (Karl M.Kadish), the use of UV comes from CTAC property of improving photocatalytic reactions in materials due to its nature. Figure 9 shows the filtration process in the presence of UV light.

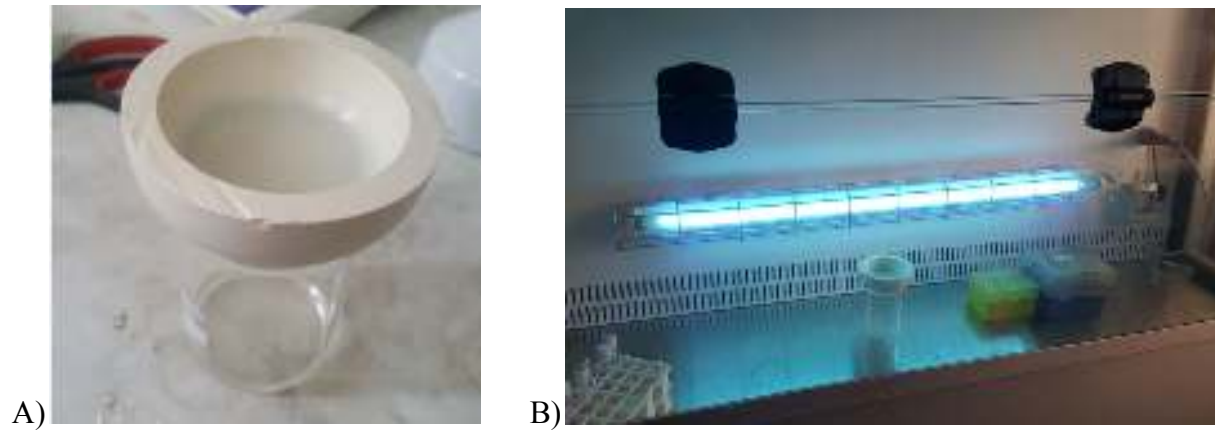


Figure 8: Filtration process (A) Filtration setup and (B) Filtration in the presence of UV light

Filtration test was done according to (A. Sanchez-Hachair, 2018) on the basis of sensitivity rather than the commonly used diphenylcarbazide colorimetry method. The method involves the use of direct UV analysis to determine the concentration of chromium in waste water.

# CHAPTER IV

## Results and Discussion

As shown above, CTAC coated titanium dioxide modified ceramic membrane was produced in order to fulfill the objective of chromium removal from the wastewater effluent. Data on the amount of chromium expected in the waste material was procured from the Ethiopian leather institute and accordingly, a stock solution was produced to use for the tests that follow. At first, the samples have undergone different characterization testes before the final filtration test. In order to determine which method of sample preparation is relatively better, preliminary characterization was done. Henceforth let it be known that sample 1 is given as the sample that has been manufactured with a sol dip-coating procedure whereas sample 2 is sample coated in acid  $\text{TiO}_2$  solution. In order to proceed with the tests required, selection of the best method in regards to coating must be completed. This was achieved by the analysis of SEM and EDS results regarding manufactured materials.

As seen below in the corresponding results, there was a significant difference in the distribution of specific elements throughout the ceramic surface. As such was the requirement of uniform coating, the selection of sample 2 for further tests was deemed acceptable. Based on the results, sample 2 was taken as the primary sample for further tests in this project. The results of the tests performed are as follows.

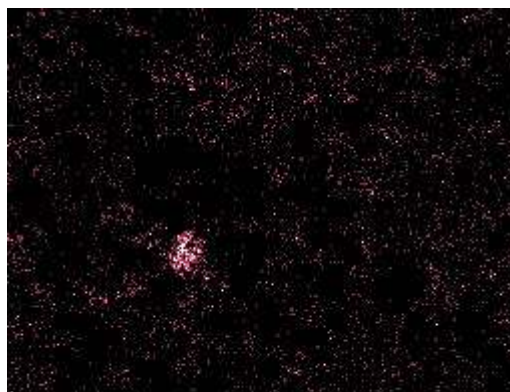
### 4.1. Morphology

The Scanning Electron Microscope with elemental analysis and EDS mapping of both samples 1 and 2 are given in the following figures as follows.

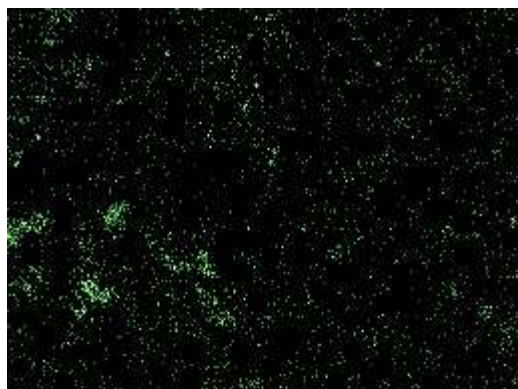
# Sample 1



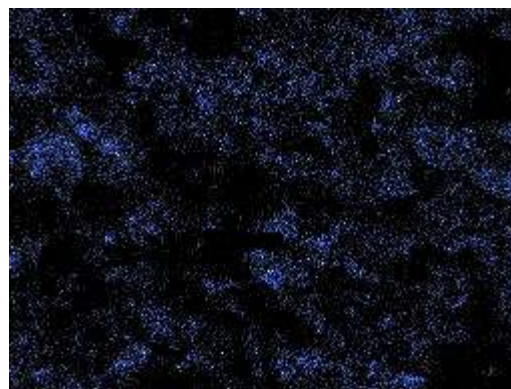
A) O Ka1



B) C Ka1\_2



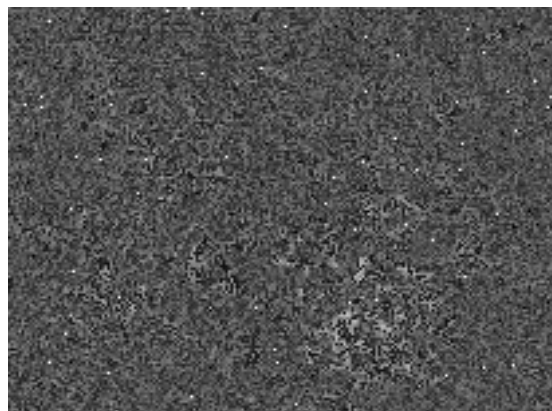
C) Ti Ka1



D) Si Ka1



E) Al Ka1



F) Ca Ka1



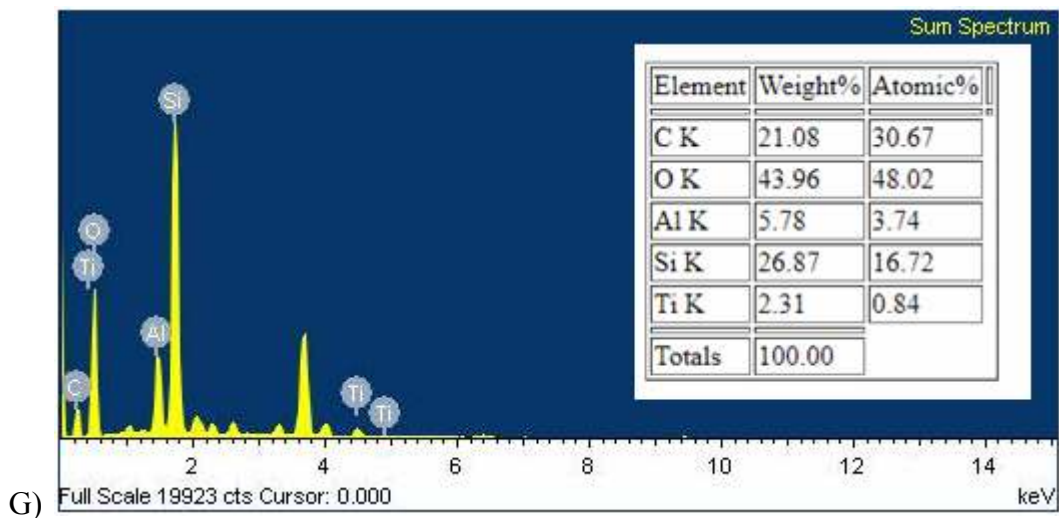
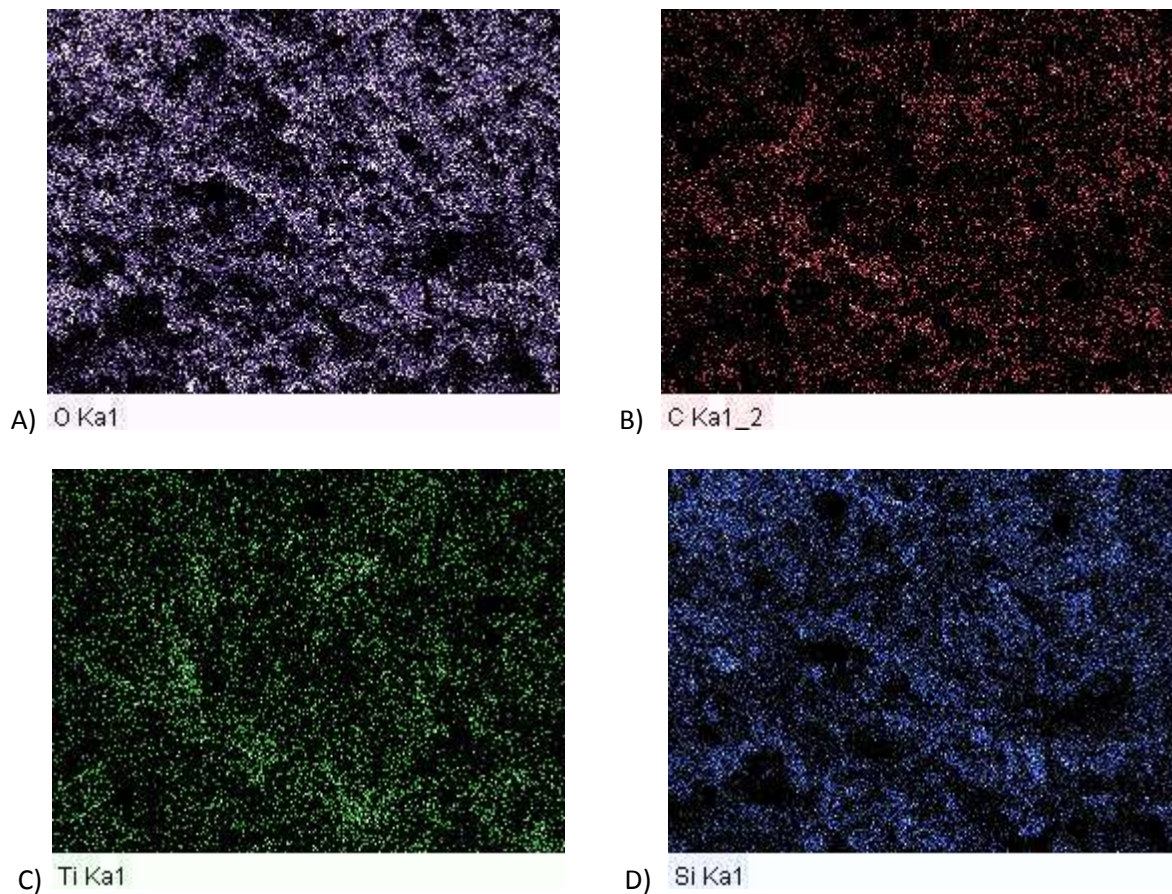


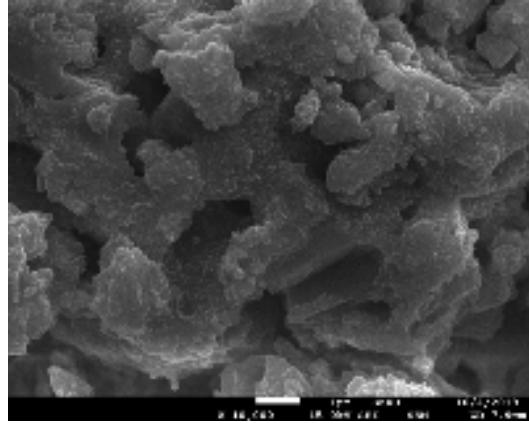
Figure 9. Characteristic images of modified ceramic membranes, (A- E) EDS Mapping of individual compounds, (F) Sample SEM image (G) EDS Chart result with amounts for sample 1.

### Sample 2

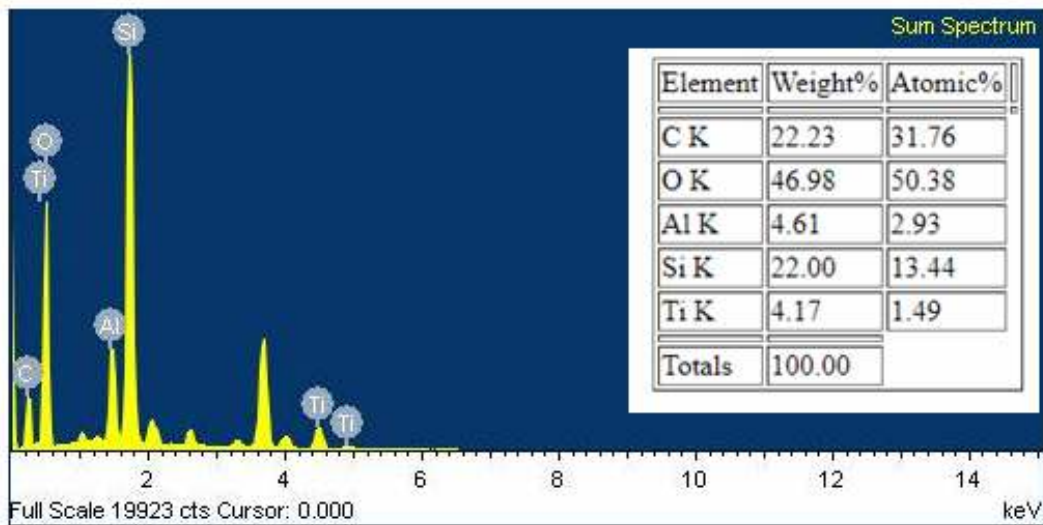




E) Al Ka1



F)



G)

Figure 10. Characteristic images of modified ceramic membranes, (A- E) EDS Mapping of individual compounds, (F) Sample SEM image (G) EDS Chart result with amounts for sample 2.

As noted above while SEM shows us a broad image of a sample showing its morphology and physical structure, EDS gives us the complete mapping/distribution patterns of individual elements with respective amounts. From the SEM image above one can see the pore distribution and surface arrangement some particles on the ceramic structure. Upon closer inspection, one can see that the porous structures are indeed tortuous as well as particles distributed on these pores and surfaces.

Further mapping confirms that there are indeed  $\text{TiO}_2$  particles as well as a significant amount of carbon confirming the presence of CTAC. Mapping of sample 1 clearly shows a rough/poor distribution of Ti, O, and C confirming that the coating was done poorly. It shows that while in sol-gel preparation, to get an adequate coating, one must wait until the sol is properly formed and coating should be done carefully. On the contrary we have an improved good coating in sample 2. This can be attributed to the method of solution preparation (Acid-  $\text{TiO}_2$  solution) and the ease of which  $\text{TiO}_2$  solution can flow through the ceramic surface as opposed to the Sol sample. I.e. compared to sample 1 the mobility of the solution (less viscous nature) of sample 2 is believed to have greatly contributed to the uniform coating of the surface and a more dispersed and covered coating in Ti, C and O shows as that this indeed is a good method to achieve our objective. In both cases, we have the distribution given as well as individual weight percents of each element. While in both cases the amount is similar in carbon and oxygen, the samples have a definite difference in the amount of Ti. Sample 1 has about 2.31 weight % while sample 2 has 4.17 weight % showing that sample 2 has indeed a better distribution that arises due to the better preparation method and the ease of coating involved.

#### **4.2. Phase Identification**

In this study, data regarding composition and the nature of materials manufactured was obtained using a powdered x-ray diffraction method. The obtained raw data was used to draw the corresponding chart in order to match the experimental data with the reference data found in international databases. As seen in fig 13 below the initial membrane without any modification as well as the subsequent modifications incurred are shown in the XRD pattern. Furthermore, the major peaks were identified and labeled according to the materials found in the samples.

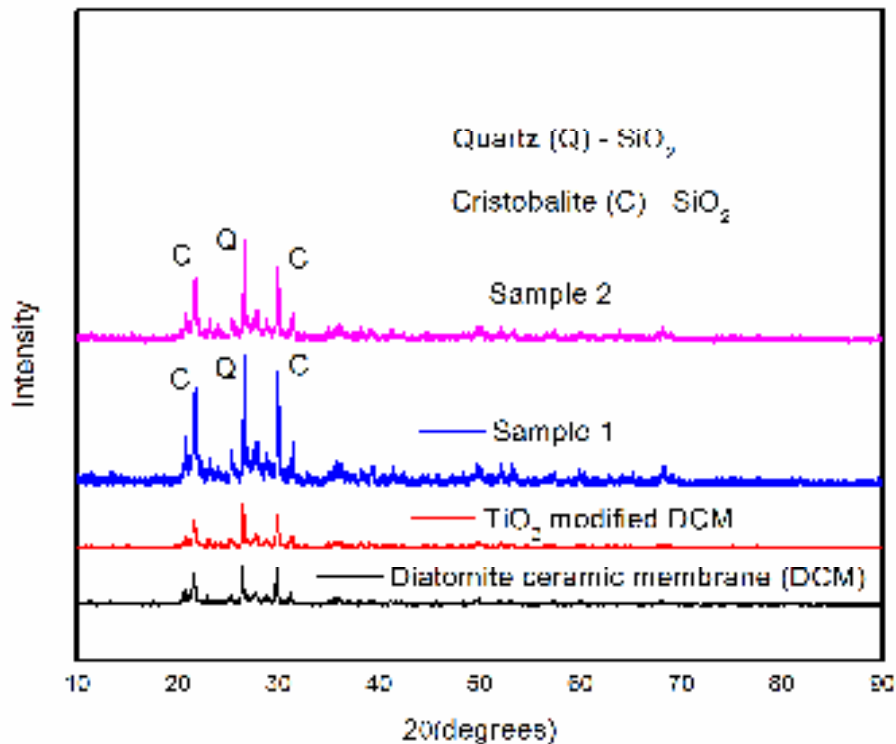


Figure 11: XRD Diffraction pattern of unmodified Diatomite ceramic membrane and modified membranes

As can be seen in Figure 13, the individual XRD Diffraction patterns of the processed samples are given. Attributed to the nature of diatomite material being around 80% silicon, the major peaks are expected to be dominated by some form of silicon dioxide materials due to the different processing carried out in manufacturing the membrane. As expected the major peaks are made up of Quartz and Cristobalite which support the assumption of having silicon dominated pattern. The main goal of the phase identification test was to find out whether or not  $\text{TiO}_2$  was indeed found on the sample as CTAC being organic material doesn't show up. Unfortunately due to the amount of  $\text{TiO}_2$  being very small the XRD peaks were not clearly identified and shown on the XRD pattern. As can be seen in the above graph the only noticeable difference one sees is the sharp increment of the major identified peaks. The reasons for  $\text{TiO}_2$  peaks not being correctly identified lies in the processing steps used in XRD and the amount of  $\text{TiO}_2$  used in the material. In the processing steps, it is believed that due to unforeseen human errors correct XRD analysis was not done properly and that the sample used



for XRD was either contaminated or not properly prepared. Besides unforeseen errors, a small amount of  $\text{TiO}_2$  was used in the experiment resulting in nanoscale particles attached to the membrane. Due to their amount when compared to the crushed powder of the diatomite membrane it is believed that  $\text{TiO}_2$  particles were small enough to be covered by the Diatomite powder thus resulting in not being picked up by the XRD machine. As a result, it has been quite difficult to distinguish the XRD peaks of  $\text{TiO}_2$  in the samples. Thus to meet expectations and to achieve the objectives desired SEM and EDS mapping were done giving the necessary proof that is required.

### **4.3. Sample Performance and Permeate Characteristics**

Sample performance tests involve the use of various methods to determine the capabilities/limits of any manufactured sample membranes. The tests involve rigorous use of sample materials in determining the quality as well as the efficiency of said materials. Some of the tests include:- membrane integrity tests, cleaning tests, as well as filtration/retention tests. Unfortunately, due to circumstances and limitations beyond capacity, the integrity and cleaning tests could not be completed. The reason for this lies in the unavailability of the required chemicals and laboratory pieces of equipment. Despite the setbacks, filtration/retention tests were conducted to determine percent retention.

The prepared stock solution as per the directives was filtered using three samples. The first filtration was done with an unmodified ceramic membrane, the second filtration with just  $\text{TiO}_2$  modified membrane and the third being the complete  $\text{TiO}_2$  with CTAC modified sample used for filtration. Using Nanodrop 2000 spectrophotometer, the Calibration curve was conducted from samples prepared from the stock solution in the range of  $1\ \mu\text{g}/\text{ml}$  -  $6\ \mu\text{g}/\text{ml}$ . Average Data values of absorbance vs. concentration and the Calibration curve with the line equation are displayed in appendix A.

As seen in the figure 14 (Appendix A) the calibration curve was plotted and found to be within the acceptable range of  $R^2$  value of greater than 95% thus operating within the acceptable error range. The need for this calibration curve is to determine the relationship between absorbance measured and concentration in the form of equation which incidentally is:-

$$Y = 0.001x + 0.001 \quad (\text{Eq. 1})$$

where : Y is Average absorbance value

X is concentration in  $\mu\text{gm/ml}$

Using this equation, one can determine the chromium concentration of the measured absorbance values of the three samples that can be found. All absorbance values shown henceforth are average values of multiple iterations. Based on the resulting data efficiency pertaining to the three samples was conducted. The Calculation to determine concentration and efficiency is shown as follows.

#### 4.3.1. Results of Sample 1 (Filtration test using commercially available membrane)

Filtration using an unmodified membrane was conducted and the resulting solution was tested using the Nanodrop spectrophotometer. The average absorbance value of the stock solution was tested and found to be 0.0697 while the average absorbance value of sample 1 is 0.0195. Taking these values and using Eq.1 the calculation is:-

$$Y = 0.001x + 0.001$$

$$X = \frac{Y - 0.001}{0.001}$$

$$0.001$$

Concentration of stock solution     $X = \frac{0.0697 - 0.001}{0.001}$

$$0.001$$

$$X = 68.7 \mu\text{gm/ml}$$

$$\text{Concentration of sample 1 solution } X = \frac{0.0195 - 0.001}{0.001}$$

$$0.001$$

$$X = 18.5 \mu\text{g/ml}$$

$$\text{Efficiency (\% Retention) } = \frac{(\text{sample concentration} - \text{stock concentration}) * 100 \%}{\text{stock concentration}}$$

$$\text{stock concentration}$$

$$= (18.5 \mu\text{g/ml} - 68.7 \mu\text{g/ml}) * 100 / 68.7 \mu\text{g/ml}$$

$$\% \text{ Retention} = 73.01 \%$$

From this one can conclude that a substantial amount of chromium metal has been removed due to the use of commercially available ceramic membranes. The reason for this can be attributed to the very fine pore sizes of the filtration membrane as well as the tortuous path the water must follow. As seen in the SEM images the pores are not situated in a straight line manner, thus travel of water from one side to the other could be significantly slowed down giving the chance for impurities to stuck in the pores. Heavy metals that stuck in the paths thus have not been able to pass through with water making it a somewhat effective filtration.

#### **4.3.2. Results of Sample 2 (Filtration test using TiO<sub>2</sub> modified membrane)**

the average absorbance value of sample 2 is 0.0147. Taking these values and using Eq.1 the calculation is:-

$$X = \frac{Y - 0.001}{0.001}$$

$$0.001$$

$$\text{Concentration of sample 1 solution } X = \frac{0.0147 - 0.001}{0.001}$$

$$0.001$$

$$X = 13.7 \mu\text{gm/ml}$$

$$\text{Efficiency (\% Retention)} = \frac{(\text{sample concentration} - \text{stock concentration}) * 100 \%}{\text{stock concentration}}$$

$$= (13.7 \mu\text{gm/ml} - 68.7 \mu\text{gm/ml}) * 100 / 68.7 \mu\text{gm/ml}$$

$$\% \text{ Retention} = 80.05 \%$$

As expected the efficiency has been increased from the basis by the application of photocatalytic TiO<sub>2</sub> nanoparticles. Here one can see that, just like discussed in the previous works of some researchers, the addition of a TiO<sub>2</sub> greatly improves the removal of chromium ions. The reason for this lies in the fact that chromium (VI) ions found in the wastewater have a general tendency to be anionic (i.e. they are negatively charged). Due to its photocatalytic nature, TiO<sub>2</sub> becomes positively charged when exposed to UV rays and thus attracting and reducing the chromium (VI) to chromium (III) is able to increase the efficiency of the filter media.

#### **4.3.3. Results of Sample 3 (Filtration test using CTAC and TiO<sub>2</sub> modified membrane)**

The average absorbance value of sample 3 is 0.011. Taking these values and using Eq.1 the calculation is:-

$$Y = 0.001x + 0.001$$

$$X = \frac{Y - 0.001}{0.001}$$

$$0.001$$

$$\text{Concentration of sample 1 solution} \quad X = \frac{0.011 - 0.001}{0.001}$$

$$0.001$$

$$X = 10 \mu\text{gm/ml}$$

$$\text{Efficiency (\% Retention)} = \frac{(\text{sample concentration} - \text{stock concentration}) * 100 \%}{\text{stock concentration}}$$

$$= (10 \mu\text{gm/ml} - 68.7 \mu\text{gm/ml}) * 100 / 68.7 \mu\text{gm/ml}$$

$$\% \text{ Retention} = 85.44 \%$$

Finally as seen above the application of CTAC as a coating to the nanomaterials modified ceramic membrane has improved efficiency by about 5.4 %. This increment of efficiency could be attributed to two reasons. The first being, the nature of CTAC being a cationic surfactant is believed to have reduced the anionic chromium ion to its stable form just like  $\text{TiO}_2$ . Cationic surfactants having positively charged surfaces can be responsible for the reduction of chromium ions. One of the reasons CTAC has been selected for this study was due to this very nature. Ref has shown in his study that CTAC has a vast advantage over the reduction capabilities of anionic heavy metal (particularly chromium) when compared with other surfactants. It shows that the introduction of CTAC has indeed improved the system. Another reason could also be attributed to the nature of CTAC. CTAC has been found to have improved the photocatalytic property of photocatalytic materials by inhibiting the formation of agglomerate materials. Thus one can argue that the addition of CTAC to the system might even have improved the reducing capability of  $\text{TiO}_2$  in the membrane. Therefore, attributed to both reasons it can be safely said that the application of CTAC has benefited the removal process and has improved the functionality of the ceramic membrane.

# CHAPTER V

## Conclusion and Recommendation

In conclusion, this study has tried to manufacture ceramic membranes modified by nanomaterials (TiO<sub>2</sub>) and CTAC coated surface. What makes it unique than other nanomaterials modified emerging ceramic membranes is the use of cationic surfactants as coating additives. The Results look promising in the field and functionality of the ceramic membrane modification. Initial advancement in synthesizing nanoparticles with the sol-gel process has made the manufacture of better quality membranes possible. In this study, the characterization, filtration tests, calibration tests, and spectrophotometer analysis have shown the improvement in regards to commercial membranes as well as modified membranes by the application of cost-effective additives.

Even though filtration tests were carried out, a full compressive analysis was not done regarding the membrane integrity, operating time, fouling rate and capacity. The reason for these setbacks can be attributed to the unavailability of most cleaning and testing chemicals as well as the poor laboratory working conditions. Thus the scope of the study was limited to manufacturing and simple available tests which despite being hindered delivered excellent results in the proof of the hypothesis. Further studies are being done with the aim of making environmentally safe effective membranes and the addition of surfactants could yield yet another promising results. Membrane technologies are not only the ones who could benefit from the incorporation of surfactants as an extra system booster and that I believe studies regarding this should be done as an alternative simpler way of modification rather than designing of whole processes.

# CHAPTER VI

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# Appendix

## Appendix - A

Concentration ( $\mu\text{g}/\text{ml}$ )	0	1	2	3	4	5	6
Absorbance	0.001	0.003	0.004	0.005	0.0055	0.0068	0.0073

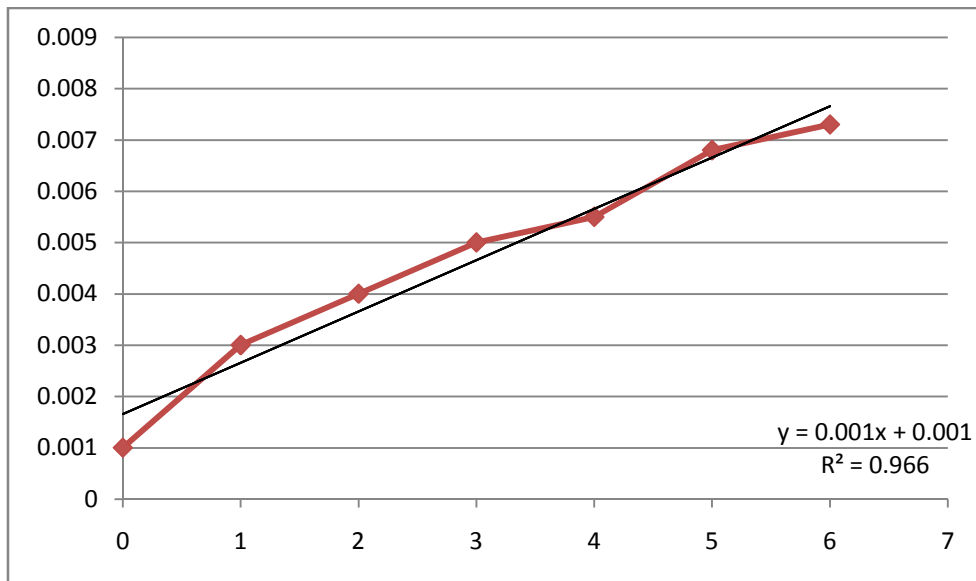


Figure 12: Absorbance vs. Concentration data and chart with characteristic equations