

Removal of Heavy Metals by TiO₂ Coated Microfiltration Membranes



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**This thesis is dedicated to our parents for their
undivided love and support**

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Abstract

Water is essential for our economy and our environment. The harsh reality is that water is limited and depleting at a fast rate. According to Water Aid, in Pakistan over 15 million people have no choice but to collect dirty water from unsafe sources, and as a result over 40,000 children die every year from diarrhea. Pakistan ranks at number **80** among **122** nations regarding drinking water quality. Human activities like improper disposal of municipal and industrial effluents are the main culprits for this deterioration (Khattak et al., 2011). Hence it is imperative to conserve, treat, reuse and protect our water resources.

Innovative combination of membrane and nanotechnology was applied to achieve the removal of heavy metals (Lead and Chromium) from water using a microfiltration membrane; which is not possible using simple Membrane Technology. Such membranes reduce the energy demand, cost and use of chemicals for membrane cleaning.

The aim of the study was to engineer the architecture and chemistry of membrane surface by successfully coating the TiO₂ nanoparticles onto commercial (Millipore) Polyvinylidene Fluoride (PVDF) membranes by sol gel synthesis. Low Temperature Hydrothermal method (LTH) was adopted to achieve anatase phase at low temperatures.

Heavy metal rejection studies were carried out onto a designed hybrid flow filtration system prototype at different concentration and different flow rates. The TiO₂-coated membranes showed significant heavy metal removal. The optimum removal of 80-94% was found using the membranes for Lead. The membranes showed best results for lower induced concentration of the pollutants.

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Chapter 1: Introduction

1.1. Background

Weary of the problems arising from shortage of water, the world has begun to realize the importance of reclamation, conservation, and reuse. To achieve this goal we have to overcome economic hurdles by utilizing out of the box ideas. As Sir Winston Churchill said "The era of procrastination, of half-measures, of soothing and baffling expedients, of delays, is coming to a close. In its place we are entering a period of consequences."

Water degradation has threatened fresh water to become endangered. A commodity which was once free has now become priceless which few can afford. As Pakistan is a water stressed country, this gives rise to many issues and challenges which Pakistan can't ignore. The misconception of thinking water as a never ending and cheap source has blinded people from considering the stress placed on natural ecosystems by increasing human demand (State Of Environment Report, 2005).

Increased industrialization is one of the major culprits of water contamination by releasing chemical pollutants and hazardous substances (which are toxic in nature) in water sources. (Tahir, 2000). Heavy metals, out of all the pollutants have significant importance because of its nature of being harmful not only to environment, but having adverse and unseemly effects on human health as well. (Hua *et al.*, 2012).

1.2 Scope of the Study

Heavy metals are mutagenic, carcinogenic and bio accumulative. Greenwood and Earnshaw (1986) found that heavy metals are responsible for impairing neurological function and altering metabolic processes.

With only 8% waste water being treated and annual loss to Arabian Sea, annual per capita water availability has decreased from 5000 in 1940 to just 1000 litres today(world bank,2005).

Contamination of both surface and groundwater resources has severely affected both quality and quantity of water. Only one fourth of the population have access to safe, drinkable water. (Farooq et al., 2008).

Estimated Annual Economic loss of 0.6-1.44% in Gross Domestic Product is faced by Pakistan because of waster related diseases and its treatment (Hashmi et al., 2009).

1.3 Treatment technologies

Water treatment has gained popularity and numerous technologies now exists which include ion exchange process, chemical precipitation , adsorption onto activated carbon electrolytic methods, organic-based ligand precipitation and membrane reverse osmosis processes (Winfield 1979).

For removal of heavy metals adsorption method have proven the most promising. Shukla and Roshan (2005) studied many adsorbents including, respiring biomass (Yan and Viraraghavan 2003) and agricultural by-products. Waste sludge generation, low rate of adsorption and narrow capacity for pollutant concentration have given rise to use of nanomaterial (NMs) as good adsorbents. They have proven to be efficient, eco-friendly and cost effective (Dimitrov, 2006; Dastjerdi and Montazer, 2010).

1.4 Present Research

Membrane technology is the most sought after technology because of its effective methods and limited dependency on chemicals. By incorporating nanotechnology into membrane technology, we achieve the advantages of both, hence improving our systems and tapping into the possibility of making it more economical.

This study is aims to investigate heavy metals rejection by using the immobilized TiO₂ nanoparticles coated on commercial Millipore PVDF microfiltration membranes using sol gel technique. Objectives of the study are as follows:

- Synthesis and characterization of nanoparticles and Sol
- Surface coating of membranes by sol gel technique.
- Application of modified membranes for heavy metal removal.

The modified nanocoated membranes were characterized using XRD. Rejection studies were carried out for Chromium and Lead at different induced concentration using Hybrid flow filtration. This study aimed at saving cost and energy by the rejection of heavy metals by using microfiltration membranes as opposed to nanofiltration membranes.

Chapter 2: Literature Review

2.1 Water pollution in Pakistan and its impact on public health

Water pollution is one of the major threats to public health in Pakistan. Pakistan is ranked 80 among 122 nations with respect to the drinking water quality. Surface and groundwater water is frequently contaminated with microorganisms, metals, organic and inorganic contaminants and pesticides. WHO water quality standards are not met (Khattak et al., 2011). Lack of proper disposal of domestic, agricultural and industrial wastes is the main element that contributes to the degradation of water quality (Khattak et al., 2011).

2.2 Heavy Metals

Heavy metals are simply defined as those elements that are toxic even at very low concentrations. Cadmium (Cd), mercury (Hg), lead (Pb), chromium (Cr) and arsenic (As) are the main examples. Heavy metals are considered dangerous due to their ability of bioaccumulation.

Heavy metals are contaminating aquatic ecosystems round the globe in the recent few years. These are one of the most common pollutants which have severely deteriorated the aquatic ecosystems (Ali et al., 2013). Their release in aquatic ecosystem is triggered by both natural and anthropogenic processes (Zhang et al., 2009). Increase in concentration of toxic metals beyond toxic limits results in loss of water quality making water unfit for drinking, irrigation, aquaculture and recreational purposes (Zhang et al., 2009).

2.3 Nano Particles

There is intense research going on in the field of nanoparticles, because of their ample applications in the fields of biomedicine, optics, and electronics.

Nanoparticles have distinctive properties due to their small size, robust activities and large surface areas. It has also been found that the membrane performance is improved by the presence of diffused inorganic particles in the polymer matrix (Cao et al., 2006).

2.4 Titanium dioxide

TiO₂ is the fourth most easily available element that is present in the earth's crust and has powerful oxidizing properties. TiO₂ has three main forms; rutile, anatase and brookite (Venurini and Bacchi, 2009).

TiO₂ used as nanoparticles has a great specific surface and smaller diameter particles i.e. less than 100 nm. Anatase is the most suitable TiO₂ type due to its high photochemical reactivity and stability in aqueous systems. It is obtained by heating the amorphous form of TiO₂ until 300 °C (Venurini and Bacchi, 2009).

2.5 Membrane Technology

There is significant rise in the number of membrane installations in water treatment plants throughout the world due to the declining water quality. The application of nanocomposite membranes is one of the fastest-growing areas of membrane technology and application. There is a phenomenal rise in the number of research papers published in this area of science which shows a huge amount of time and effort devoted by researchers during last few years as can be seen in the figure below (Chaharmahali, 2012).

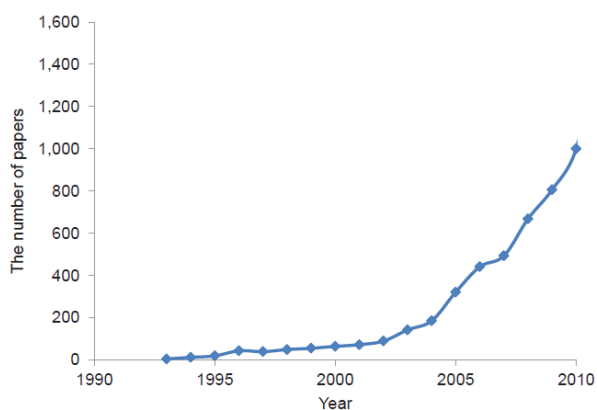


Figure 1: Number of published papers vs. year on nanocomposite membranes (Chaharmahali, 2012).

This significant attention is because the new developed nanocomposite membranes often promise new properties such as antifouling performance, mechanical, thermal and chemical resistance. Such properties are not presented when individual elements are used.

The new characteristics can not only be altered by changing the individual components used but also by changing the morphology and surface chemistry. (Chaharmahali, 2012).

2.6 PVDF composite membranes with nano sized TiO₂ particles

The comparison was made between simple PVDF membranes and PVDF membranes that are coated with TiO₂ nanoparticles. The nanometer size affected the membranes remarkably; as a result, the antifouling property of membranes was enhanced. Experiments further showed that smaller the Titania nanoparticles, the stronger the effect they had upon crystallization of PVDF molecules. TiO₂ nanoparticles improve the membrane properties such as the hydrophilicity of PVDF membranes which further enhances the flux and antibacterial potential of the membranes. Apart from that, the TiO₂/PVDF membrane can notably increase the rate at which few herbicides degrade (Cao et al., 2005).

2.7 Comparison between TiO₂ coated and TiO₂ incorporated membranes

TiO₂ nanoparticles can be either incorporated into the membranes through mixing them into the membranes or coated by depositing them onto the surface of the membranes. Both methods have their own limitations. The first method has the disadvantage of difficulty in attaining a reasonable level of particles dispersion and limit in the loading of inorganic particles. The latter approach, on the other hand, suffers from the drawback of instability in coating layer and it may result in the non-uniform distribution of nanoparticles on the membrane surface. Therefore, it is critical to modify the current methods or develop new

techniques for the fabrication of nanocomposite membranes (Chaharmahali, 2012).

2.8 Sol Gel Technology

The sol gel technique of the preparation of TiO₂ thin film has been proved to be a better method than other techniques like chemical vapor deposition (CVD), plasma spraying, anodization etc. mainly due to the following reasons: (1) simple apparatus, (2) uniform film is achieved easily, (3) film's phase structure can be easily controlled (4) films formed can be distinguished by a gel structure having large specific area. (Manh Tuan et al, 2009)

Chapter 3: Materials and Methods

3.1 Membrane Specifications

Micro porous membranes containing polymer has been used extensively in various treatment systems. Among various polymeric membranes Polyvinylidene Difluoride (PVDF) membranes are most commonly used for ultrafiltration, microfiltration and other filtration processes because of their properties of thermal stability, high flow rates and chemical resistance (C. Su, 2004). We selected commercial Hydrophilic PVDF membranes from Millipore to test the effect on commercial membranes whose parameters are already tested and perfected. Specifications of membrane used are given below:

Membranes	Durapore Membrane, PVDF
Pore Size (μm)	0.22
Water Flow Rate, mL/min x cm^2	>1
Refractive Index	1.42
Wettability	Hydrophilic
Filter Diameter (mm)	90
Maximum Operating Temperature, $^{\circ}\text{C}$	85
Porosity %	70

Table 1: Membrane specifications.

The blending of polymeric membranes with inorganic particles has been in focus for many years. Among these particles, TiO_2 nanoparticles have been frequently used in such practices due to their properties of stability and use in various water treatment technologies. These particles are also easily available. When TiO_2 is coated on these membranes their hydrophilicity increases as water has greater affinity for metal oxides (Rahul A. Damodara).

3.2 Preparation of TiO_2 by sol-gel Method

Sol gel is a best emerging method for the preparation of nanoparticles by changing the reaction conditions. It can be prepared at normal temperature and pressure. This process consists of solution of particles of very small size called sol. This sol acts as a precursor for an integrated network of isolated particles which is called “gel” (Chaharmahali, 2012).

For the preparation of TiO_2 sol Titanium isopropoxide, 2-methoxyethanol and Ethanolamine were taken in a three necked flask in molar ratio of 1:4:0.5 and refluxed for 1 hour to thoroughly mix all these reagents. It was then stirred at room temperature for 1 hr. at 80°C and then at 110°C for further 2 hours (C. Su, 2004). This experimental procedure is shown schematically as:

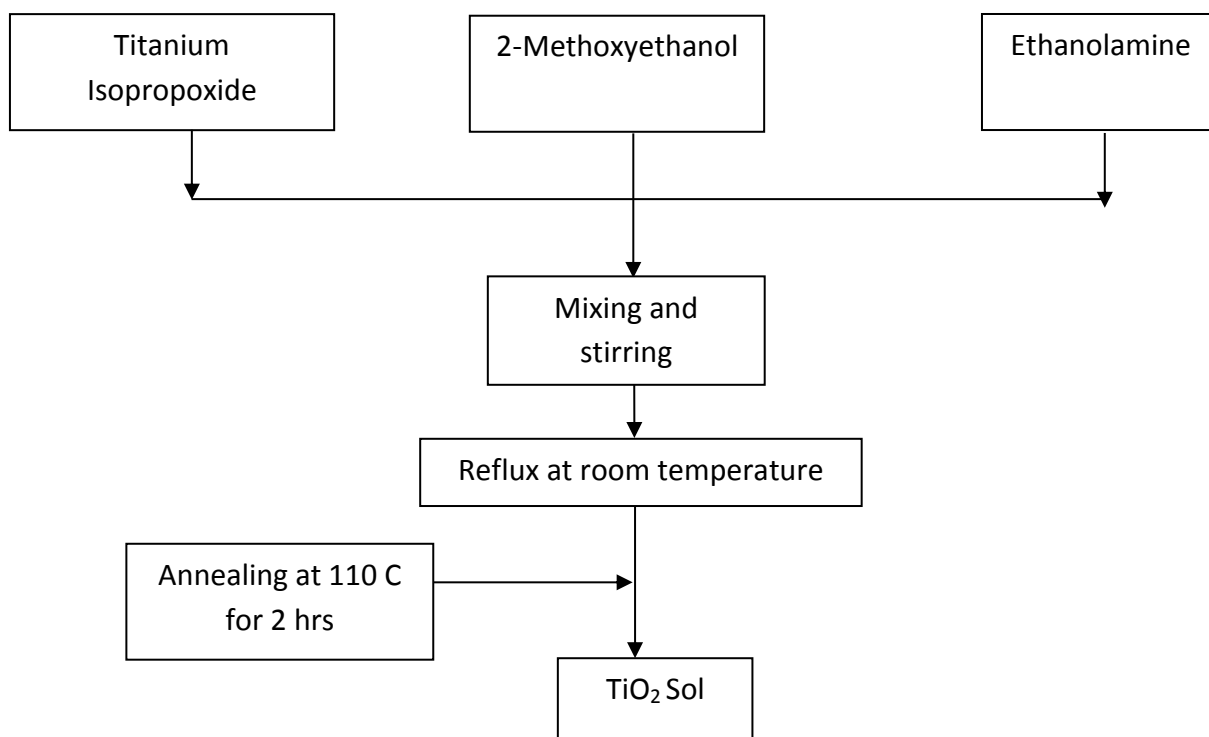


Figure 2: Preparation of TiO_2 Sol.

The resultant sol which was obtained is shown in the figure below.



Figure 3: TiO_2 sol

3.3.1 Dip Coating of Membranes by Sol

After the sol was prepared membranes were coated using different methods to check which method gives the best results. Firstly, sol was added until it completely covered the membranes and membranes were dipped for 8 seconds. It was observed that coating was not homogenous; it was too thick and membrane started to crack.



Figure 4: Membrane dipped into pure sol.

3.3.2 Mixing Sol with Ethanol

As effective coating was not achieved using sol alone, ethanol was added to sol in the ratio 1:2 (5ml of sol was dropped into 10ml of ethanol). The appearance of the sol-ethanol solution changed to a curd like mixture and sol-ethanol solution was not desirable.

3.3.3 Mixing of Sol by Methanol

In sol-ethanol mixture, it was observed that the sol made a cloudy solution with ethanol; therefore methanol was used instead of ethanol in same molar ratio. A homogenous solution was obtained and it was selected to coat the membranes

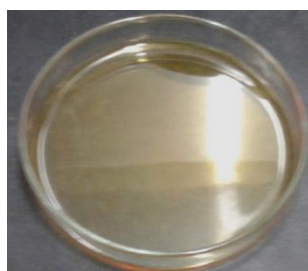


Figure 5: Sol and methanol solution

3.3.4 Low Temperature Hydrothermal Process

The low temperature hydrothermal process was used to achieve anatase phase at low temperature as maximum operating temperature of membrane is 85 °C. The membranes were dip coated in sol and methanol solution using a dip coater with coating speed was about 0.2mm/s and the holding time was about 8 seconds. Each membrane was dip coated thrice to ensure effective coating. Then the coated membranes were placed into a vacuum oven for 24 hours at 80 °C and then placed in water bath having pure water set at 80°C for 24 hours for the thermal treatment of membranes. Then these membranes were washed thrice with distilled water and irradiated by placing under UV lamp for 24 hours to remove any organic impurity left from the coating process (Chaharmahali, 2012).The figure below shows the TiO₂ coated membrane.



Figure 6: TiO₂ coated membrane.

3.5 Preparation of Solutions of Chromium and Lead

The TiO₂-coated membranes were tested for the removal of Lead (Pb) and Chromium (Cr). Different concentrations of lead and Chromium aqueous solutions (1mg/L, 3mg/L and 5mg/L) were prepared using lead acetate (Pb(CH₃COO)₂) and chromium nitrate 9 hydrate (CrNO₃) salts of analytical grade. Hybrid flow filtration cell was designed to carry out the water flux and the rejection studies. Ion metal rejection percentage was determined from the Atomic Absorption Spectroscopy (AAS).

3.6 Hybrid Flow Filtration

3.6.1 Design feature of Hybrid Flow System

Hybrid flow filtration cell (combination of cross flow and dead end flow system) was designed. Dimensions of the prototype are 14cmx14cm x 5 cm and is made by acrylic glass. There are steel inlets and outlets from where the filtrate enters and the permeate leaves the system as effluent respectively. The total height of the filtration system is 5cm and it is divided into two halves; upper and lower. These halves are held together with the help of eight evenly placed screws which keep the membrane in place and ensure that system is water tight. On the upper and lower half there is a depression of 1mm having diameter of 8.3cm from the centre. Grooves are craved on the upper and lower half and they are super imposed. This design feature is added to provide a pathway for water. The grooves are in the form of square waves 1cm apart. The membrane which was placed in between the two halves is about 8cm in diameter and is surrounded by a 3mm thick gas kit. The side view, cross view of upper and lower are given below.

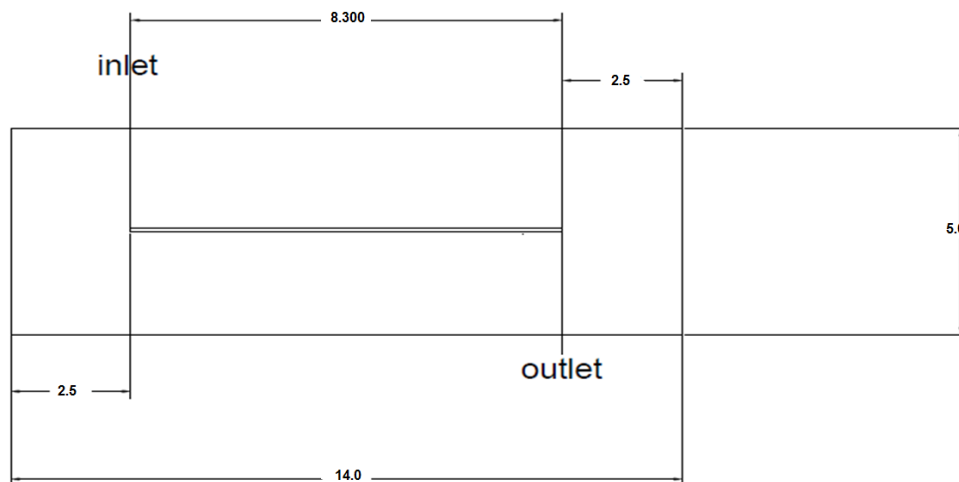


Figure 7: Side view of design of hybrid flow system.

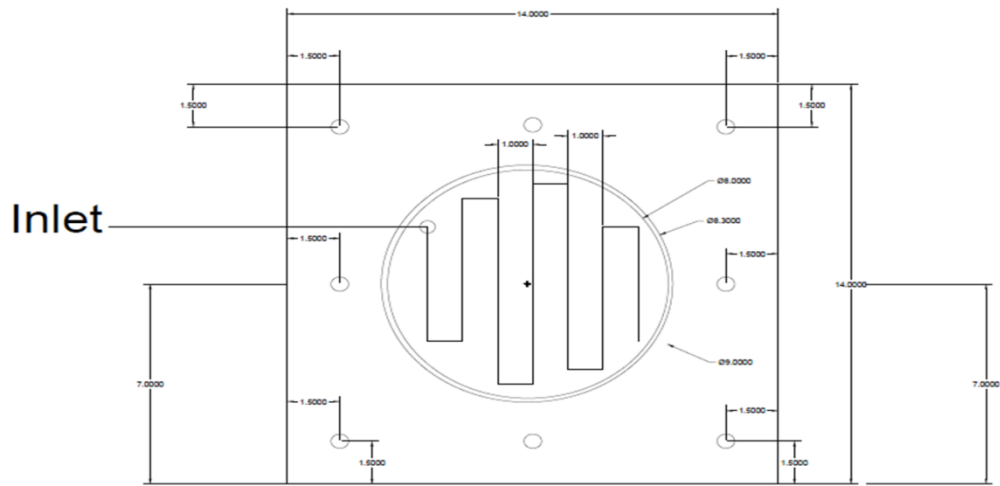


Figure 8: Cross view of upper half of design of hybrid flow system.

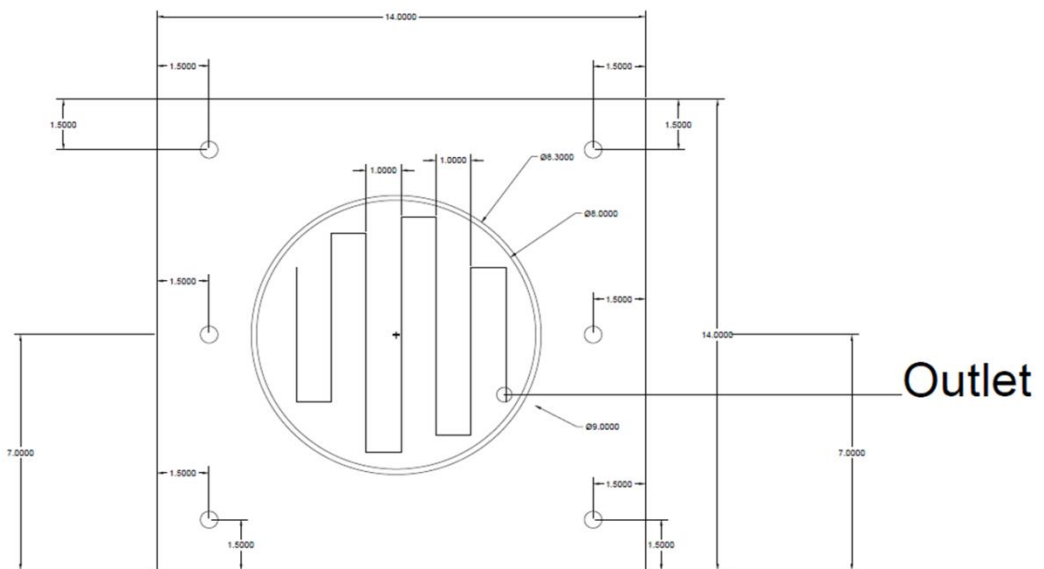


Figure 9: Cross view of lower half of design of hybrid flow system.

The below figures show the 3-D View of the prototype

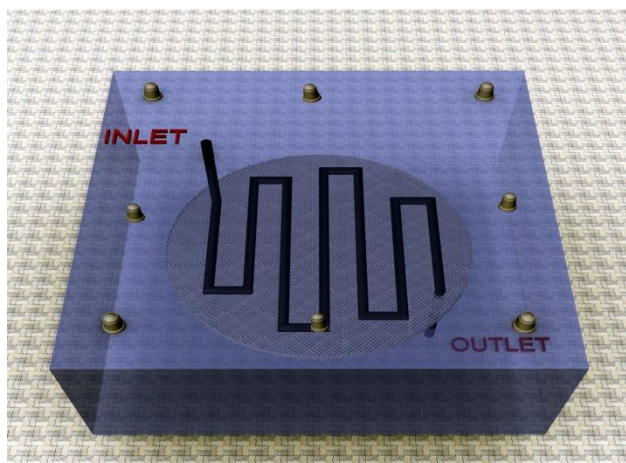


Figure 10: 3-D Top View of prototype

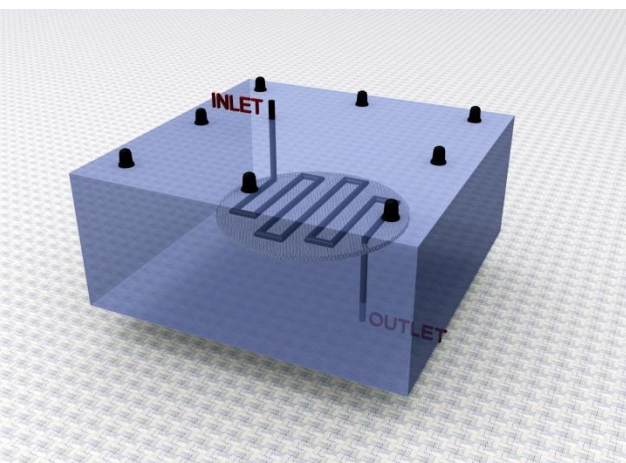


Figure 11: 3-D Side View of Prototype

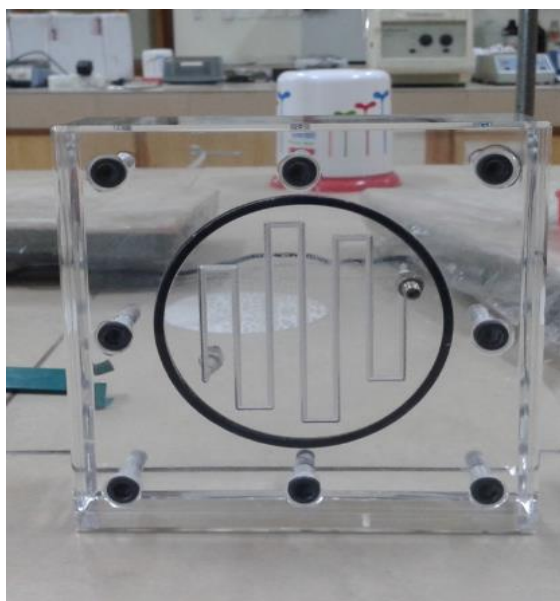


Figure 12: Hybrid Filtration Cell Prototype

3.6.2 Function of Hybrid Flow System

The water enters through the inlet and passes through the grooves on the upper half, and then it passes over the membrane surface that is present between the upper and lower halves of the cell. After passing through the membrane it starts to move out of it and passes through the grooves over the lower half from where it then moves out through the outlet. Hybrid flow system as mentioned above is the combination of cross flow and dead end

systems. At certain point during its operation it acts like a dead end system and after that it acts as a cross flow system. In case of dead end system the membrane is perpendicular to the flow of water whereas in cross flow it is parallel to the water flow. When water is passed through the hybrid system it first works on principle. These two stages of filtration are;

I. Production Phase

In the first phase of filtration i.e. production phase, water strikes the membrane having closed tubes on one side and in this way it acts as dead end filtration system.

II. Flushing Phase

In the second phase of filtration, i.e. flushing phase, the water that did not pass through the membrane is removed from the open tubes as happens in case of cross flow filtration. This is done for cleaning the membrane surface (Hashsham, 2006).

3.7 Experimental Set Up

The experimental setup consisted of the following;

I. Beakers

Beakers containing the solution of lead and chromium were placed in the set up.

II. Hybrid Flow System

Peristaltic pump (longer pump BT 300-2J) was connected with the designed hybrid flow filtration prototype to provide the drive force. 50mL/min, 100mL/min and 150 ml/min Flow rates were used to test the membranes.

III. TiO₂ Coated Membrane

The prepared membrane was placed in the prototype and water containing lead and chromium heavy metals was passed through these membranes.

IV. Stop Watch

The time in which permeate was collected was measured with the help of stop watch for each flow rate. The Experimental setup is shown in the figure 13.

Sample size of 250 mL of the solutions of lead and chromium is allowed to enter the hybrid cell at different flow rates of 50,100 and 150 mL/min, which are set by the peristaltic pump. The filtrate enters the system through the inlet and passes through the grooves; from here it passes through the membrane and moves out through outlet by passing through the grooves on the lower half of the system. The permeate is collected in the beaker. The time taken for the collection of the permeate is noted for every flow rate.

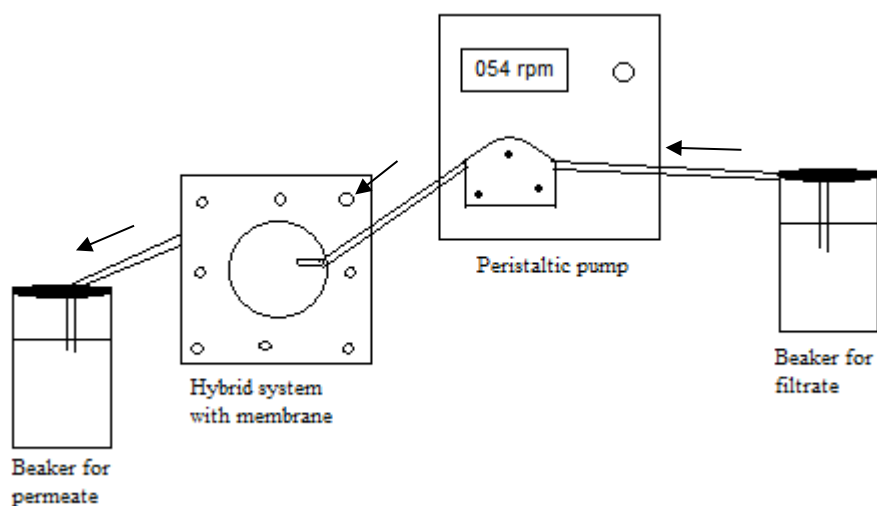


Figure 13: Schematic diagram of hybrid filtration system.



Figure 14: Experimental set up of hybrid filtration system.

3.8 Metal Rejection Studies

Metal rejection studies are carried out to determine the percentage removal of heavy metals. These studies involve measuring the concentration of heavy metals in filtrate and permeate. Filtrate concentration of heavy metals is known i.e. 1, 3, 5ppm for both lead and chromium respectively. For the permeate concentration atomic absorption spectroscopy was used. In the present study, Atomic absorption spectroscopy (AAS Biotech Phoenix 986-UK) was used to analyse the rejection percentage of the metals Pb and Cr. Permeate of the experiment was run on the instrument to determine the concentration of metals rejected after passing through the membrane.

3.8.1 Atomic Absorption Spectroscopy

Atomic absorption is an analytical technique which is used to measure the concentration of any sample. It is most commonly used for finding the concentrations of heavy metals in water. The basic principle of AAS is based on the principle of Lambert Beer

Law. It makes use of the wavelengths of light which is absorbed by the element because atoms of different elements have different types of wavelengths which they absorb.

Lambert-Beer Law is mathematically represented as;

$$A = abc$$

Where A= Absorbance, a = Absorptivity, b = path length, c = concentration of absorbing species. The absorbance of the incident light (I_0) and that of transmitted light (I_t) are measured.

The different components of AAS are shown in figure below.

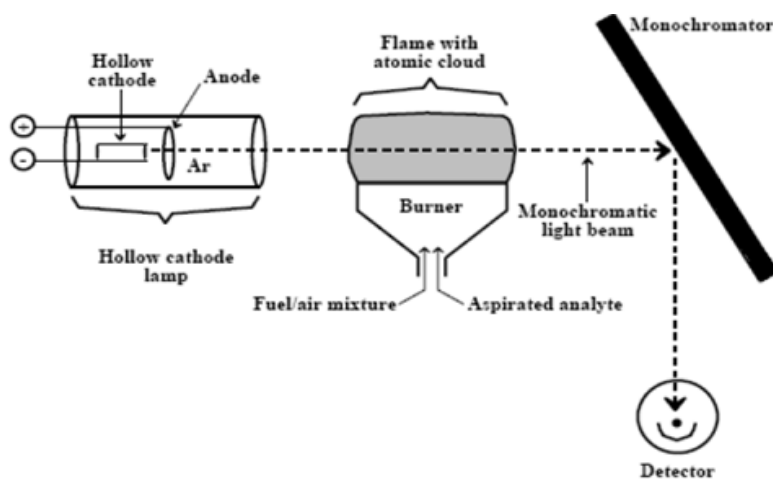


Figure 15: Parts of atomic absorption spectroscopy



Figure 16: Atomic Absorption Spectroscopy in Waste Water Lab IESE, NUST.

I. Hollow Cathode Lamp

First component of AAS is a hollow cathode lamp which is the light source different for different elements because each element has a characteristic wavelength. The metal of the cathode material must be the same as present in the test sample, which in our case is lead and chromium.

II. Atomizer-Burner

The metal present in sample solution is converted into free atoms in acetylene air flame which is used as a burner.

III. Monochromator-Prism and a Slit

The light passing through the sample is dispersed in the monochromator into its component wavelengths. The slit allows the absorbed light to pass through it only and filter out the others.

IV. Detector-Photo Cell

It detects and amplifies the selected light. Also measures the amount of liquid absorbed by the atomized metal atoms in the flame.

V. Computer

The sample runs in the AAS and computer gives all the data about it in the form of excel sheet.

From AAS, permeate concentrations were known for lead and chromium in solutions of different concentration. From these concentrations rejection percent was determined by the following equation:

$$R(\%) = \frac{c_f - c_p}{c_f} \times 100$$

In this equation, C_f is the initial concentration of filtrate and C_p is the final concentration of permeate.

3.6 Water Flux Studies

From the flow rates and the area water flux studies are done.

$$J_w = \frac{Q}{A} = \frac{V}{A\Delta t} \text{ (Shankararaman Chellam, 2001)}$$

Here J_w = water flux in $\text{Lm}^{-2} \text{h}^{-1}$

Chapter 4: Results and Discussion

The objective of the research was to study heavy metals using commercial grade nanoparticles coated microfiltration membranes. The research is divided into three parts:

- Synthesis of Sol Gel.
- Engineering the architecture and chemistry of membrane surface via coating the TiO₂ nanoparticles.
- Water flux and heavy metal rejection studies of the modified commercial microfiltration membrane at different flow rates.

4.1 Characterization of Sol

X-Ray Diffraction (XRD) was used to characterize the prepared Sol. The XRD image indicated that Sol was in the required 'Anatase' phase.

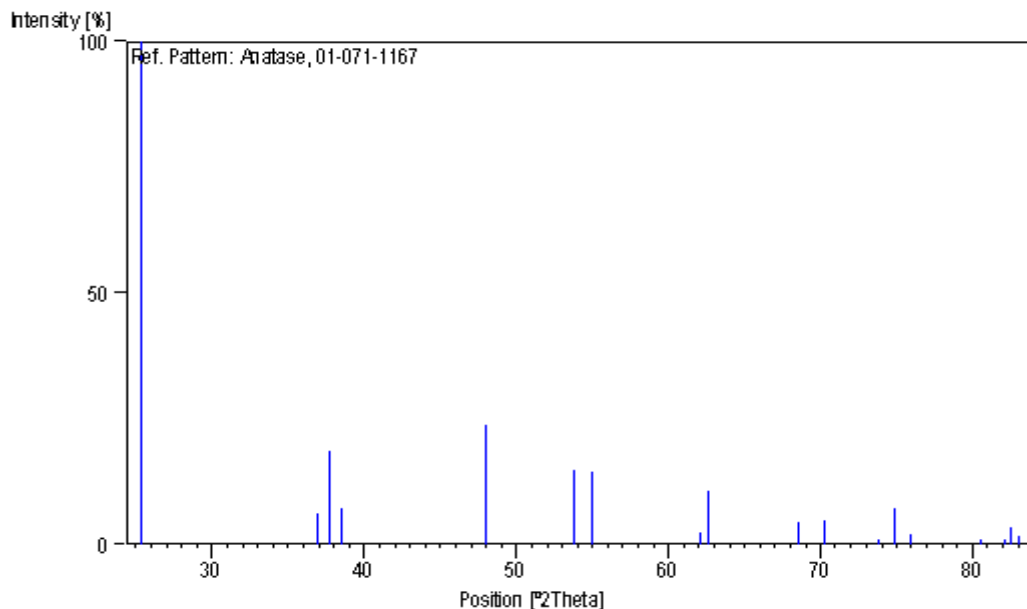


Figure 17: X-ray Diffraction of Sol

4.2 Characterization of surface coated membranes

Commercial PVDF membranes that were coated using Sol gel method were also characterized by X-Ray Diffraction (XRD). It confirmed that anatase phase was achieved using LTH method.

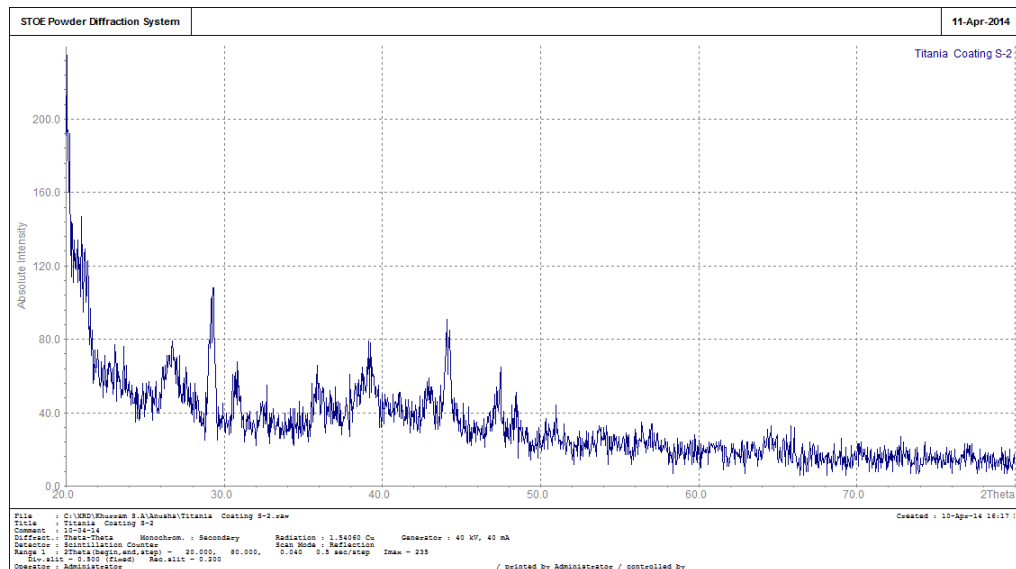


Figure 18: X-ray Diffraction of TiO₂ coated membranes

4.3 Water flux study

$$J_w = \frac{V}{A\Delta t}$$

Volume of the filtrate was taken as 250 mL. The effective area of the membrane was 50.6 cm². A separate TiO₂ nanoparticle coated membrane was used for each flow rate. The figure 4.3 and 4.4 shows the relationship between flow rate (mL/min) and time (min) for Chromium and lead respectively. The graphs (figures 19 and 20) show that as flow rate increases time taken decreases for specific concentration. It also indicates that for a particular flow rate time taken increases as concentration is increased from 1 mg/L to 5mg/L as membrane is becoming exhausted.

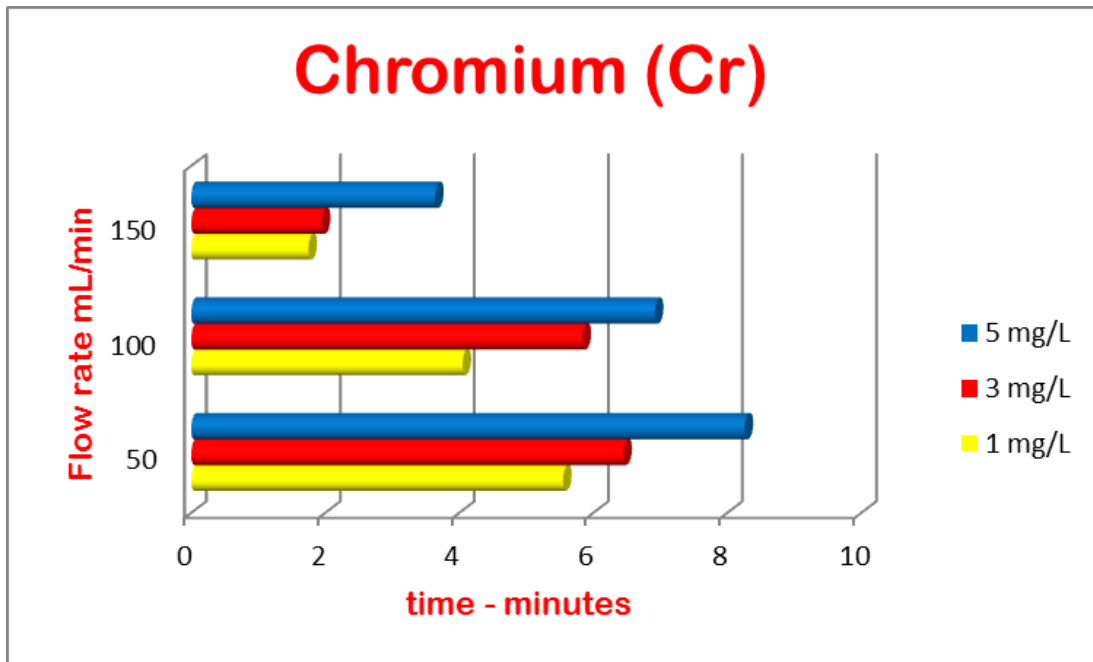


Figure 19: Flowrate with respect to Time for Chromium (Cr)

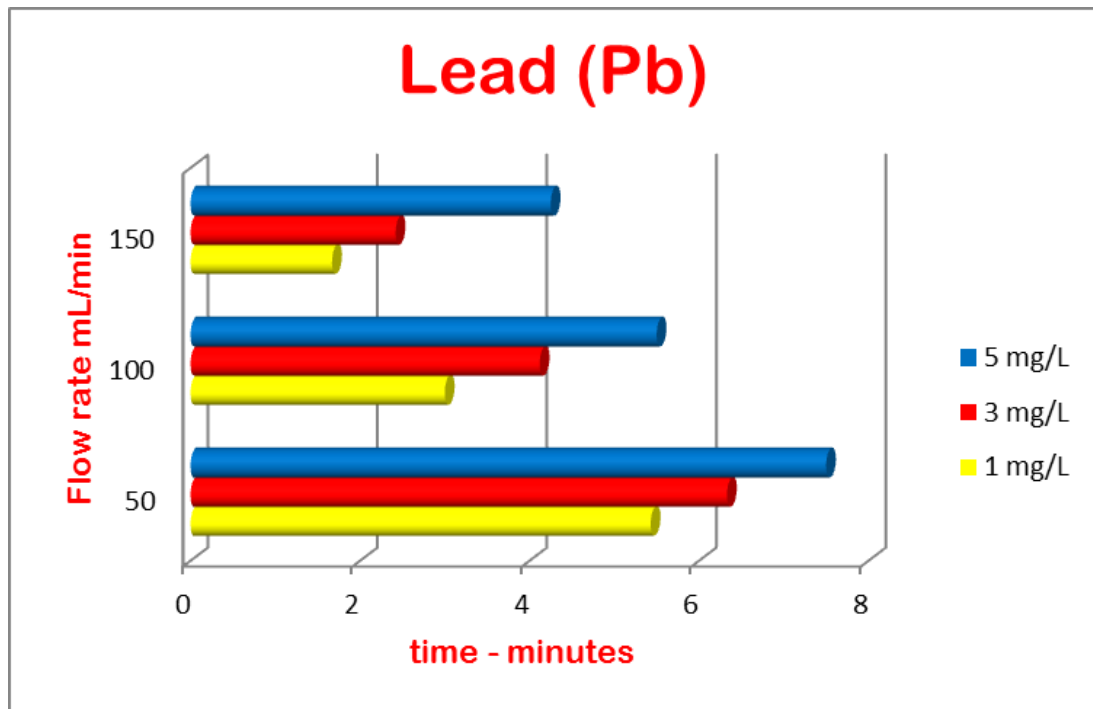


Figure 20: Flowrate with respect to Time for Lead (Pb)

Figures 21 and 22 shows the graphs between water flux (mL/cm²min) and flowrate(mL/min) for Chromium and Lead. The graphs indicate that for each flow rate, water flux

decreases as concentration is increased. It also presents a direct relationship between water flux and flow rate for a specific concentration.

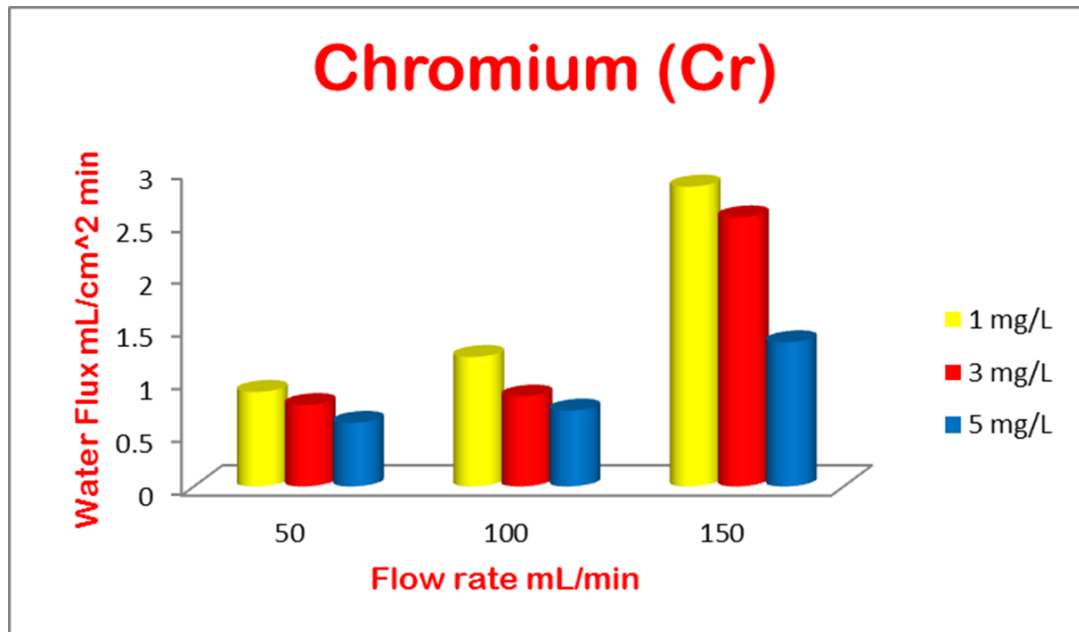


Figure 21: Water flux vs flow rate for Chromium (Cr)

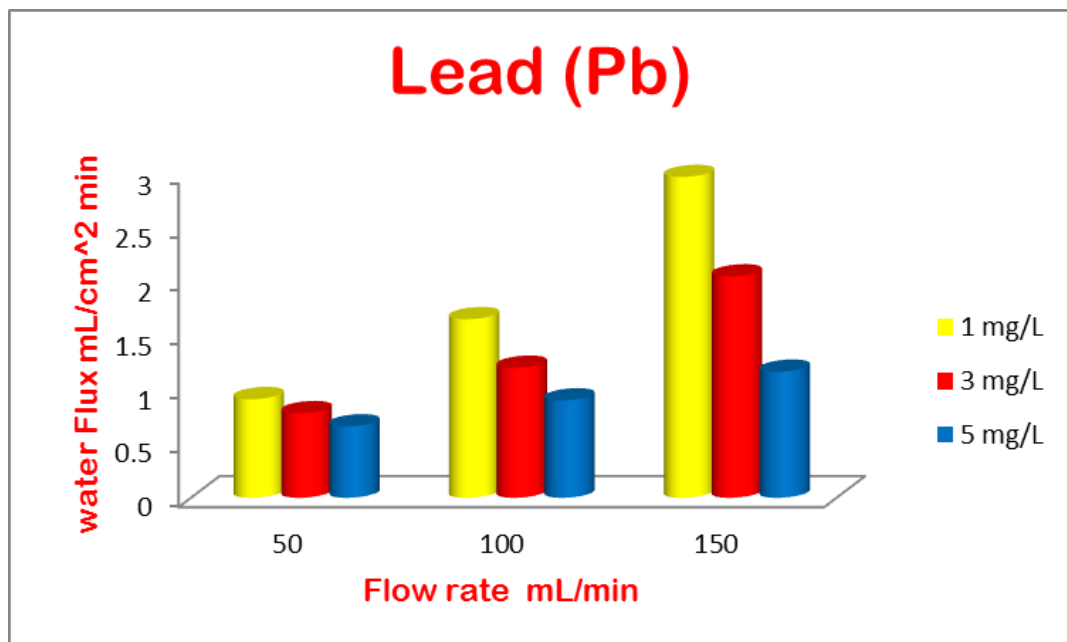


Figure 22: Water flux vs flow rate for Lead (Pb)

4.4 Heavy metal rejection study

Membrane performance in terms of Lead and Chromium metal rejection was experimented in hybrid flow filtration prototype. 250 mL of filtrate was passed through the hybrid cell at different flow rates by the help of peristaltic pump (longer pump BT 300-2J). Different solution of known concentration of lead and chromium were prepared using standard method and the permeate concentration was determined by Atomic Adsorption Spectroscopy.

4.4.1 Heavy metal rejection by PVDF membranes

Figure 23 and 24 shows the percentage rejections in relation to different concentration. Nanoparticles have proved a good adsorbent for heavy metals. As Indicated by the graphs the rejection capacity was higher for Lead (Pb) as compared to Chromium (Cr). 90-80 % rejection of Lead as compared to 36-20 % for chromium .This is because Lead has a higher electronegativity (2.33) as compared to Chromium (1.66). (Seung-Mok *et al.*, 2012)

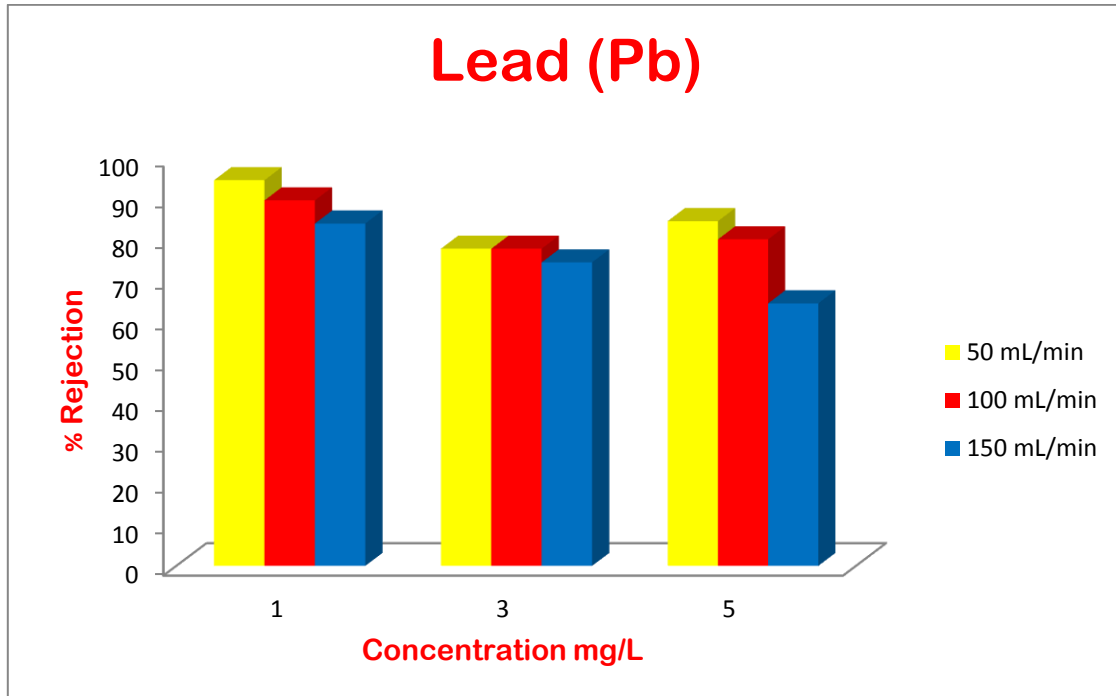


Figure 23: % Rejection vs Concentration (mg/L) of Lead (Pb)

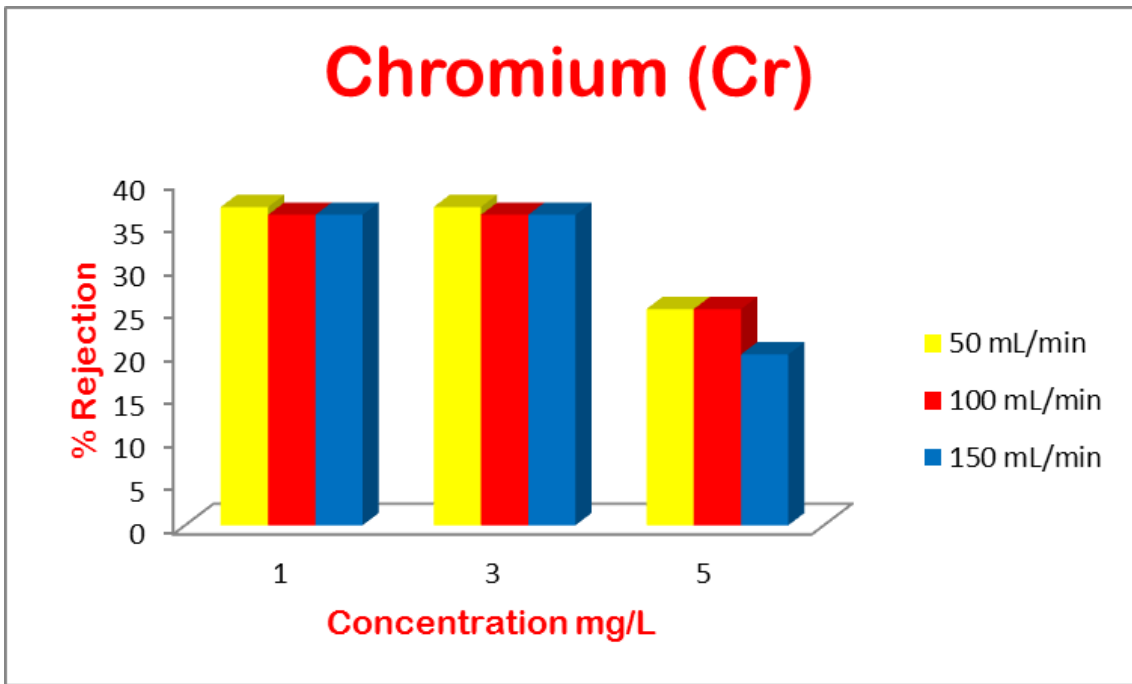


Figure 24: % Rejection vs Concentration (mg/L) of Chromium (Cr)

Chapter 5: Conclusion and Recommendations

This research is comprised of synthesis of Sol gel and TiO₂ nanoparticle coating on the surface of PVDF membrane. The objective of the research was to investigate the potential of the membranes for heavy metal rejection; mainly Lead and Chromium. For rejection studies hybrid flow filtration cell was designed.

5.1 Conclusion

Following conclusion can be drawn from the research:

- ✓ Sol gel synthesis proved to be an effective method for coating of membrane and Successful in achieving anatase phase at low temperature TiO₂.
- ✓ The Titania coated membranes showed good heavy metal removal.
- ✓ Titania coating made it possible to remove heavy metals by Microfiltration membrane.
- ✓ The optimum rejection of 80-94% was found using the membranes for lead (Pb).
- ✓ The membranes worked best in the lower induced concentration of the pollutants.
- ✓ Able to remove heavy metals by Microfiltration membrane. MF membranes have half the pressure demand that of nanofiltration membrane. This help reduce energy demand and operation cost.

5.2 Recommendation for future work

- ✓ Use of other coating techniques such as
 - Chemical Vapour Deposition (CVD)
 - Physical Vapour Deposition (PVD)
 - Plasma Spraying
- ✓ Testing with other nanoparticles.
- ✓ Testing for antibacterial properties.
- ✓ Use of doped nanoparticles and nanotubes.

References

- I. A. R. Chaharmahali, A. Resosudarmo, R. L. Holmes , H. Li, J. Mansouri, V. Chen. (2012) The effect of Modified TiO₂ nanoparticles on the PES ultrafiltration hollow fiber membranes, *Desalination*, Volume 287, Pages 271-280
- II. A. R. Chaharmahali, E. Arifin, G. Dong, J. Mansouri and V. Chen. (2012) Superhydrophobic modification of TiO₂ nanocomposite PVDF membranes for the application in membrane distillation, *Journal of Membrane Science*, Volume 415–416, Pages 850-863
- III. Romanos, G. E., Athanasekou, C. P., Katsaros, F. K., Kanellopoulos, N. K., Dionysiou, D. D., Likodimos, V., & Falaras, P. (2012) Double-side active TiO₂-modified nanofiltration membranes in continuous flow photocatalytic reactors for effective water purification. *Journal of Hazardous Materials*, Volume 304–16, Pages 211-212.
- IV. A.R. Chaharmahali, J. Mansouri, V. Chen. (2012) The effects of mechanical and chemical modification of TiO₂ nanoparticles on the surface chemistry, structure and fouling performance of PES ultrafiltration membranes. *Journal of Membrane Science*, Volume 378, Issues 1-2, Pages 73-84
- V. A. R. Chaharmahali, J. Mansouri, V. Chen. (2011) Titania nanocomposite polyethersulfone ultrafiltration membranes fabricated using a low temperature hydrothermal coating process. *Journal of Membrane Science*, Volume 380, Issues 1-2, Pages 98-113
- VI. Damodar, R. a, You, S.-J., & Chou, H.-H. (2009). Study the self cleaning, antibacterial and photocatalytic properties of TiO₂ entrapped PVDF membranes. *Journal of Hazardous Materials*, 172(2-3), 1321–8.
- VII. Hua, M., Zhang, S., Pan, B., Zhang, W., and Zhang, Q. (2012). Heavy metal removal from water/wastewater by Nanosized metal oxides: A review. *J Hazard Mater.* 211-212:317-331

- VIII. L.-Y. Yu, Z.-L. Xu, H.-M. Shen, H. Yang, Preparation and characterization of PVDF-SiO₂ composite hollow fiber UF membrane by sol-gel method, *Journal of Membrane Science*, 337 (2009)257-265.
- IX. A. Rahimpour, S.S. Madaeni, A.H. Taheri, Y. Mansourpanah.(2008) .Coupling TiO₂ nanoparticles with UV irradiation for modification of polyethersulfone ultrafiltration membranes, *Journal of Membrane Science*, 313 ,158-169
- X. G. Wu, S. Gan, L. Cui, Y. Xu. (2008) Preparation and characterization of PES/TiO₂ composite membranes, *Applied Surface Science*, 254 ,7080-7086.
- XI. Azizullah, A., Khattak, M. N. K., Richter, P., & Häder, D.-P. (2011). Water pollution in Pakistan and its impact on public health--a review. *Environment International*, 37(2), 479–97.
- XII. Hashmi. I., Farooq, S. and Qaiser, S. (2009). Chlorination and water quality monitoring within a public drinking water supply in Rawalpindi Cantt (Westridge and Tench) area, Pakistan. *Environmental Monitoring and Assessment*. 158: 393-403.
- XIII. Farooq, S., Qazi, I., Qaiser, S. and Rasheed, S. (2008). Monitoring of Coliforms and chlorine residual in water distribution network of Rawalpindi, Pakistan. *Environmental Monitoring and Assessment*. 140:339-347.
- XIV. Seung-Mok, L. and Laldawngliana, D. (2012). Iron oxide nano-particles-immobilized-sand material in the treatment of Cu (II), Cd (II) and Pb (II) contaminated waste waters *J. Chemical Engineering*, 195:103–111.
- XV. Seung-Jun, L., Jong-Ryul, J., Sung-Chul, S., Jin-Chul, K. Jong-Duk, K. (2004). Synthesis and characterization of superparamagnetic maghemite nanoparticles prepared by co-precipitation method. *J. Magnetism and Magnetic Materials*, 282:147–150.
- XVI. Cao, X., Ma, J., Shi, X. and Ren, Z. (2006). Effect of TiO₂ nanoparticle size on the performance of PVDF membrane, *Applied Surface Science* 253 (4):2003–2010.

- XVII. Vasanthavigar, M., Srinivasamoorthy, K. and Prasanna, M. (2011). Evaluation of ground water suitability for domestic, irrigational, and industrial purposes: a case study from Thirumanimuttar river basin, Tamilnadu, India. *J. Environmental Monitoring Assessment*, 184: 405-420.
- XVIII. T.-H. Bae, T.-M. Tak, Effect of TiO₂ nanoparticles on fouling mitigation of ultrafiltration membranes for activated sludge filtration, *Journal of Membrane Science*, 249 (2005) 1-8.
- XIX. U. Diebold, The surface science of titanium dioxide, *Surface Science Reports*, 48 (2003) 53-229.
- XX. C. Su, B.-Y. H.-M. (2004). Sol-gel preparation and photocatalysis of titanium dioxide. *Elsevier*, 96 (3), 119-126.
- XXI. Chaharmahali, A. R. (2012). The Effect of TiO₂ Nanoparticles on the Surface Chemistry, Structure and Fouling Performance. *Scientia*, 67.
- XXII. D.Z.Chen, J. Z. (2010). Adsorption of methyl tert-butyl ether using granular activated carbon:Equilibrium and kinetic analysis. 235-242.
- XXIII. Langmuir, I. (1918). The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. *Journal of American Chemical Society* (40), 1361-1403.
- XXIV. Shankararaman Chellam, J. S. (2001). Simplified analysis of contaminant rejection during ground and surface water nanofiltration under the information collection rule. *Water Resources*, 35 (10), 2460-2474.