Synthesising novel adsorbent and membranes using Graphene oxide (GO) for removing lead ions from aqueous solutions

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

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Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

Harish Ravishankar
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List of peer refereed book chapter and journal papers


3. Harish Ravishankar, Felicity Roddick and Veeriah Jegatheesan. “Preparation, characterisation and critical flux determination of Graphene oxide blended polysulfone (PSf) membranes in an MBR system” (Under submission)


Peer-reviewed conference paper


Conference Posters

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<tr>
<td>A2O</td>
<td>Anaerobic-Anoxic-Oxic</td>
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<td>AAm-AMPSNa</td>
<td>Acrylamide-2-Acrylamido- 2-MethylPropane Sulfonic acid Sodium salt</td>
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<tr>
<td>AAS</td>
<td>Atomic Absorption Spectroscopy</td>
</tr>
<tr>
<td>ACC</td>
<td>Activated Carbon Cloth</td>
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<td>ACF</td>
<td>Activated Carbon Fibrous</td>
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<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<td>APTS</td>
<td>Aminopyrene Trisulfonic Acid</td>
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<td>ATR-FTIR</td>
<td>Attenuated Total Reflection Fourier Transform Infra-Red</td>
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<td>PAO</td>
<td>Phosphate Accumulating Organisms</td>
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<td>Polyethylenimine</td>
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<td>SWCNTs</td>
<td>Single Walled Carbon Nano-Tubes</td>
</tr>
<tr>
<td>TMP</td>
<td>Trans Membrane Pressure</td>
</tr>
<tr>
<td>TN</td>
<td>Total Nitrogen</td>
</tr>
<tr>
<td>TP</td>
<td>Total Phosphorus</td>
</tr>
<tr>
<td>UF</td>
<td>Ultrafiltration</td>
</tr>
<tr>
<td>US EPA</td>
<td>U.S. Environmental Protection Agency</td>
</tr>
<tr>
<td>WHO</td>
<td>World Health Organisation</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>Zn</td>
<td>Zinc</td>
</tr>
</tbody>
</table>
Summary

Since the industrial revolution, there have been profound changes in agriculture, mining and manufacturing sectors, which have in turn laid a tremendous burden on the available water resources. In developing countries, almost 70% of industrial wastes are dumped into the main water streams thereby increasing the levels of toxic elements, such as heavy metals. The continuing growth in industrialization and urbanization has necessitated the re-use of water from different sources to fulfil the demands of the future.

Lead is a heavy metal which has been extensively used for various application and often ends up in waste streams. Remediation of lead from wastewater is done through different techniques which include precipitation, adsorption, ion-exchange, membrane processes and biological treatment. Recently, carbon based nano-materials such as graphite/graphene-oxide, fullerene and carbon nanotubes have been reported as effective sorbents for heavy metals due to their high surface area and specificity. Despite such properties, drawbacks of nano-material aggregation and separation of heavy metals from nano-materials, hinders their widespread application. Membrane filtration processes can also be effective in removal of heavy metals. However, long term operation can result in membrane fouling and thus requiring frequent cleaning or replacement of membranes.

Membrane bioreactor (MBR) is a treatment technology which couples both biological treatment and membrane separation processes for the treatment of wastewaters. MBRs are actively employed for municipal and industrial wastewater treatment around the world. The major shortcoming of the MBR system is membrane bio-fouling, which becomes its foremost obstacle for its successful operation. Very limited studies are available on heavy metal treatment using MBR systems.

The present study investigated the application of Graphene-oxide (GO) for treatment of lead through three treatment technologies, namely, adsorption, membrane separation process and MBR.

In the current study, a graphene oxide (GO) based magnetic nano-sorbent was synthesised. This was done by assembling the GO nano-sheets on top of Fe₃O₄ (magnetite) nanoparticles which were coated on the surface of polystyrene nano-beads (denoted as PS@Fe₃O₄@GO). Application of external magnetic field was demonstrated to separate the lead ion attached nano-
sorbent from the solution, which would overcome the issues of aggregation and separation after heavy metal adsorption. Preliminary lead removal studies were performed and upon successful results, parameters such as pH, temperature and contact time were optimised for effective removal. The kinetics and isotherm for lead adsorption were studied and found to follow pseudo first order kinetics and Langmuir adsorption isotherm model. A maximum lead removal of 94% was demonstrated and the mechanism of adsorption was attributed to electrostatic attraction followed by chelation of lead ions onto the carboxyl and hydroxyl groups of GO. This confirmed the role of GO in removal of lead ions. The re-usability of the nano-sorbent was also investigated and it was found to be stable for four consecutive adsorption-desorption cycles.

Membrane fouling/bio-fouling are caused due to the hydrophobic nature of the membrane. Studies have proven that improving the hydrophilicity of membranes can improve the anti-fouling properties. In the present study, GO was explored as a hydrophilic additive by preparing GO blended Polysulfone (PSf) microfiltration (MF) and ultrafiltration (UF) membranes through non-solvent induced phase separation process. UF membranes were studied for lead removal using a cross flow filtration setup. MF membranes were studied for their application in an Anaerobic-Anoxic-Oxic (A2O) MBR system for removal of lead ions and other nutrients.

The effect of different concentrations of GO and PSf on surface morphology, hydrophilicity and mechanical properties were investigated. The porosity and pure water flux were also examined. It was observed that increase in concentration of GO improved the hydrophilicity, porosity and flux of the membranes. The mechanical property i.e., Young’s modulus increased with polymer concentration. Scanning Electron Microscopy (SEM) analysis revealed the presence of circular pores and asymmetric structure of membranes with bigger macro voids for membranes having GO. The pore size for MF and UF membranes were in the range of 179-250 nm and 18-24 nm, respectively. The UF membrane comprised of 15% PSf - 1% GO under cross flow showed a maximum Pb rejection of 98%. The operating pressure played a role in rejection, which decreased with increase in pressure.

The MBR system with virgin PSf and GO blended PSf microfiltration membranes was operated and monitored for treatment of nutrients and lead. The system demonstrated complete removal of COD and ammonia. Phosphorus removal reached a maximum of 52%. Lead removal reached a maximum of 98% with majority of it accumulated in the anaerobic tank due to high MLSS (~5 g/L). GO blended PSf membranes were examined for their ability to mitigate fouling
(under two operational modes, i.e., intermittent with backwash and continuous) through critical flux study. Membranes with higher GO concentrations showed increased critical flux ($J_c$), signifying the antifouling property of the membranes. The long term trans-membrane pressure (TMP) profile of the GO blended membrane lasted longer than the membrane devoid of GO, indicating a longer operation time and needing less frequent cleaning. SEM-EDS results on the fouled membranes showed the presence of Pb peaks indicating the association of lead ions with foulants present on the membrane. The permeate water obtained had a turbidity 0.25 NTU, indicating a good filtration performance by both the MF membranes.

The results indicate the promising role of GO in lead ion removal through nano-sorbent and UF membrane systems. In the MBR system, GO based MF membranes demonstrated fouling mitigation and longer operation for the treatment of lead. However, the feasibility of the treatment systems should be assessed with real wastewater to justify their commercial application.
Chapter 1

Introduction

1.1 Introduction

Since the industrial revolution, there has been profound changes in agriculture, mining and manufacturing sectors, which led to a tremendous burden on the available water resources. Almost 71% of the earth’s surface is made up of water of which only 2.5% is fresh water; 30% of the fresh water is stored underground as groundwater and 0.3% of freshwater is present in lakes and rivers. Of the 2.5% of the total fresh water available, less than 1% is available for human consumption (Jenerette and Larsen, 2006). A continuing growth in industrialisation and urbanisation has led to a considerable increase in the pollution of water. In majority of the developing countries, most of the industrial wastes are dumped into the main water streams thereby increasing the levels of toxic elements, such as heavy metals (Paul Walakira, 2011).

Heavy metals can be defined as a set of elements which have high atomic weight, atomic number and specific gravity greater than 5 kg/m³ (Srivastava and Majumder, 2008). Unlike organic chemicals, heavy metals cannot be broken down to less harmful components (Fu and Wang, 2011). Industrial effluents and residual domestic water are the main sources of heavy metal pollution in water streams (Akpor and Muchie, 2010). In general, industrial wastes contain heavy metals such as arsenic, cadmium, copper, lead, zinc, chromium, nickel, manganese and mercury. Thus, bulk of the groundwater is contaminated by these heavy metals (Hashim et al., 2011). This has created a widespread concern to the global water community. Some of the common heavy metals are listed in Table 1.1.

Heavy metals present in the environment go through different stages and ultimately end up as waste. A generalised flow of heavy metal (life cycle) to waste has been shown in Figure 1.1. However, the concentration and distributions of the heavy metals may vary when they are present at different stages. Approximately, 20% of heavy metals can be removed during the waste treatment process and end up in the residual sludge. Heavy metal removal efficiency can vary depending on the metal solubility (European Commission, 2001).

Various studies have been conducted in analysing the impact of the heavy metal contamination in water bodies. Heavy metal toxicity can result in renal impairment, skin blisters, pustules, anaemia,
haemolysis, tissue edema, liver dysfunction, neuronal cell injury and various other consequences (European Commission, 2002). Therefore, remediation of heavy metals present in water becomes vital and their removal becomes a necessity for water sustainability.

1.1 Treatment

Numerous technologies have been employed in remediation of heavy metals in water. These technologies can be broadly classified into three processes namely: a) physio-chemical, b) biological and c) membrane processes. A combination of these processes is also used to improve the treatment efficiency.

1.1.1 Physio-chemical processes

Adsorption is one such physio-chemical process which has been widely used for the remediation of heavy metals. It involves usage of clays, natural substances, industrial by-products, hydrophobic polymers and carbon-based materials on selective removal of heavy metals from wastewater have been recorded in literature (Fu and Wang 2011; Lee et al.1997; Vimonses et al. 2009 and Monser and Adhoum 2002). Chemical precipitation is quite a popular technique employed in industries for remediation of heavy metals. This is largely attributed to its simplicity in application and low cost (Ku and Jung, 2001). A typical chemical precipitation process includes sulphide or hydroxide precipitation. In addition, use of chelating precipitants such as Trimercaptotriazine, Potassium/Sodiumthiocarbonate and Sodium dimethyldithiocarbamate are gaining popularity (Matlock et al., 2002a). Ion-exchange resins are used for the exchange of cations for heavy metals present in wastewater. These resins can be either synthetic or natural solids with a high removal efficiency (Kang et al., 2004). Moreover, addition of coagulants and flocculants have been reported for heavy metal removal from wastewater (El Samarani et al., 2008 and Fu and Wang et al. 2011). The above physio-chemical processes have several disadvantages despite their wide-spread application. Some of them are (a) generation of large volumes of sludge (b) additional waste disposal costs (c) release of new toxic compounds of different size and (d) high operating costs (Fu and Wang et al. 2011).
Table 1.1 List of common heavy metals.

<table>
<thead>
<tr>
<th>Heavy Metal</th>
<th>Atomic Weight</th>
<th>Atomic Number</th>
<th>Occurrences</th>
<th>Forms</th>
<th>Maximum Contaminant Level (MCL)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>51.99</td>
<td>24</td>
<td>Found as chromite in chrome-iron ore (FeCr₂O₄)</td>
<td>Trivalent forms – Cr(OH)³⁺, Cr(OH)²⁺ and Cr (OH)⁻; Hexavalent forms- CrO₄²⁻ and Cr₂O₇²⁻</td>
<td>1 x 10⁻⁴ g/l</td>
<td>Lenore S Clesceri et al., 1999 and US EPA</td>
</tr>
<tr>
<td>Nickel</td>
<td>58.69</td>
<td>28</td>
<td>Pyrrhotite and Garnierite</td>
<td>The most common aqueous species is Ni²⁺.</td>
<td>1 x 10⁻⁴ g/l</td>
<td>Lenore S Clesceri et al., 1999 and US EPA</td>
</tr>
<tr>
<td>Copper</td>
<td>63.54</td>
<td>29</td>
<td>Chalcopyrite, Chalcocite, Cuprite, Malachite, Azurite and Bornite</td>
<td>Common aqueous species are Cu²⁺, Cu(OH)²⁺, and CuHCO₃⁺</td>
<td>13 x 10⁻⁴ g/l</td>
<td>Lenore S Clesceri et al., 1999 and US EPA</td>
</tr>
<tr>
<td>Zinc</td>
<td>65.38</td>
<td>30</td>
<td>Sulphite sphalerite,</td>
<td>Common aqueous species ZnOH⁺ and Zn²⁺</td>
<td>5 x 10⁻³ g/l</td>
<td>Lenore S Clesceri et al., 1999 and US EPA</td>
</tr>
<tr>
<td>Arsenic</td>
<td>74.92</td>
<td>33</td>
<td>Arsenopyrites, Realgar, Loellingite, Orpiment, Enargite and Arsenic Oxide</td>
<td>pH 3-7; H₂AsO₄⁺; pH 7-11; HAsO₄²⁻; pH &lt; 3; H₃AsO₃</td>
<td>1 x 10⁻⁵ g/l</td>
<td>Lenore S Clesceri et al., 1999 and US EPA</td>
</tr>
<tr>
<td>Element</td>
<td>Atomic Mass</td>
<td>Z</td>
<td>Source of Occurrence</td>
<td>Common Aquous Species</td>
<td>Concentration</td>
<td>Source(s)</td>
</tr>
<tr>
<td>----------</td>
<td>-------------</td>
<td>----</td>
<td>--------------------------------------------------------------------------------------</td>
<td>---------------------------------------------</td>
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</tr>
<tr>
<td>Selenium</td>
<td>78.96</td>
<td>34</td>
<td>Present as Selenate ion (SeO$_4^{2-}$), obtained as by-product of copper refining.</td>
<td>Common aqueous species include Se$^{2-}$, HSe$^{-}$ and Se$^{0}$.</td>
<td>$5 \times 10^{-5}$ g/l</td>
<td>Lenore S Clesceri et al., 1999 and US EPA</td>
</tr>
<tr>
<td>Cadmium</td>
<td>112.41</td>
<td>48</td>
<td>Occurs in sulphide minerals of the zinc ores such as sphalerite.</td>
<td>Common aqueous species is Cd$^{2+}$.</td>
<td>$5 \times 10^{-6}$ g/l</td>
<td>Lenore S Clesceri et al., 1999 and US EPA</td>
</tr>
<tr>
<td>Mercury</td>
<td>200.59</td>
<td>80</td>
<td>Cinnabar</td>
<td>Common aqueous species are Hg$^{2+}$. Hg(OH)$_2$. and Hg$^{0}$.</td>
<td>$2 \times 10^{-6}$ g/l</td>
<td>Lenore S Clesceri et al., 1999 and US EPA</td>
</tr>
<tr>
<td>Lead</td>
<td>207.19</td>
<td>82</td>
<td>Galena, Anglesite and Cerussite</td>
<td>Common aqueous species are Pb$^{2+}$ and hydroxide and carbonate complexes.</td>
<td>$1.5 \times 10^{-5}$ g/l</td>
<td>Lenore S Clesceri et al., 1999 and US EPA</td>
</tr>
</tbody>
</table>
Figure 1.1 Generalised flow of heavy metals to waste.
1.1.1.2 Biological processes

Biological processes involve a biological treatment of the wastewater containing heavy metals. Different bio-removal techniques such as bio-sorption, bio-stimulation, bio-augmentation, phytoremediation and vermicomposting have been employed for heavy metal remediation. These techniques are cost effective, non-invasive and efficient in treatment (Akpor and Muchie, 2010).

1.1.1.3 Membrane Technology

In recent years, membrane technology has received increased attention because of its ability to treat a wide range of effluents. The membrane process works by treating contaminated water by concentrating heavy metals without any addition of chemicals. Different membranes such as nanofiltration (NF), reverse osmosis (RO) and electrodialysis (ED) are used to recover heavy metals from wastewater. Most of the membranes that are currently used are hydrophobic in nature. The hydrophobic property of the membrane makes them more susceptible to fouling, thereby reducing the water flux and decreasing the overall performance. This problem can be eliminated by improving the hydrophilicity of the membrane through chemical grafting, surface modification or physical blending. Physical blending of the membranes with organic materials increase the hydrophilic nature of the membrane. This also improves the thermal and mechanical properties, adsorption capability, and antifouling ability of the membranes (Wang et al., 2012; Zhao et al., 2013; Prachi and Shah 2013 and Mariana et al., 2014).

1.1.1.4 Membrane bioreactor (MBR)

Membrane bioreactor (MBR) is a system, which couples both biological treatment and membrane separation process for the treatment of wastewaters. MBRs are actively employed for municipal and wastewater treatment around the world. MBRs generally allow high concentrations of mixed liquor suspended solids (MLSS), low production
of sludge, high removal efficiency of chemical oxygen demand (COD) and water reclamation (Lin et al., 2012). However, the major drawback of the MBR system is membrane fouling, which deters its widespread application. Development of anti-fouling membrane modules for MBR can reduce the capital costs and offer a smarter solution towards water sustainability.

1.1.1.5 Nanocomposites

Nanocomposites are a new class of adsorbents which are prepared to attain a particular property of the material. A variety of nanocomposites, specifically designed for treatment of heavy metals have been developed and studied. Polymer based nanocomposites, magnetic nanocomposites, nanofiber mats and composite hydrogels with enhanced properties have been reported for their application in treatment of different heavy metals (Liu et al., 2009; Kampilanonwat and Pitt (2010) and Kaşgöz et al., 2008).

1.1.1.6 Carbon based nano-materials

Carbon based nano-materials such as graphite, fullerene and carbon nanotubes are effective sorbents for heavy metals (Kabbashi et al., 2009 and Machida et al., 2006). Graphene, the latest member of the carbon family is believed to be the most interesting material of this century (Sreeprasad et al., 2011). Graphene is a carbon layer with only one atom thickness. It is composed of sp² hybridised carbon, which gives a unique 2D structure. Graphene has excellent physiochemical properties, such as high electronic and thermal conductivity, good mechanical strength, ultralight weight, and a high surface area of 2620 m²/g (Lian et al., 2010). A chemical modification of graphene can enhance their physio-chemical properties, thereby leading to an increased usage in a variety of technological applications. Several studies have shown the application of graphene based materials in environmental clean-up activities (Madadrang et al., 2012; Chandra et al., 2011; Sreeprasad et al., 2011 and Liu et al., 2011).
Graphene oxide (GO) is an oxidised form of graphite which has its basal plane modified with epoxide and hydroxyl groups in addition to carbonyl and carboxyl groups located at the edges. GO based nano-sorbents are developed for better functionalities and performance in different applications, e.g., environmental remediation (Xu and Shi 2011; Gao et al., 2011 and He at al., 2010). The removal of different heavy metals from water using carbon nanotubes has also been reviewed (Abbas et al., 2016).

The present study investigated the application of GO for treatment of lead ions through three treatment technologies, namely, adsorption, membrane separation process and MBR.

### 1.2 Research Aim and Objectives

The current study aims to synthesise a graphene oxide based novel adsorbent and membrane, followed by evaluating their performance for lead ions (Pb (II)) removal from aqueous solution. The following objectives are addressed through the aim:

- To synthesise and characterise a magnetic nano-sorbent and evaluate its efficiency in the removal of lead ions.

- To synthesise and characterise Graphene-oxide (GO) blended Polysulfone (PSf) ultrafiltration and microfiltration membranes. Also, to evaluate their operational performance on lead ions removal through
  - Cross-flow filtration using the prepared ultrafiltration membranes
  - An MBR system using the prepared microfiltration membranes
1.3 Thesis Outline

This thesis comprises of seven chapters. Chapter 2 covers a literature review and discusses the occurrence, usage and impacts of lead contaminated water. It also outlines the available knowledge on the different technologies used for treatment of heavy metal contaminated water. Part of this literature review was published as a book chapter entitled ‘Application of green and physio-chemical technologies in treating water polluted by heavy metals’ in the book “Green technology for sustainable water management”, ASCE, 2016. Chapter 3 describes the different materials and methods used in the current study. Chapter 4 to 6 discusses the findings from the experiments performed based on the research objectives. Chapter 4 gives a detailed understanding on the kinetics, thermodynamics and mechanism of lead ions adsorption on the synthesised nano-sorbent i.e. PS@Fe₃O₄@GO. The findings from this chapter was published in Process Safety and Environmental Protection as a research paper entitled “Removal of Pb (II) ions using polymer based graphene oxide magnetic nano-sorbent” (Process Safety and Environmental Protection, 104, 472-480). In Chapter 5, the preparation and physio-chemical characterisation of PSf-GO ultrafiltration membrane and preliminary lead rejection were examined. Chapter 6 explains the Membrane Bio-reactor (MBR) system for treatment of lead (Pb) contaminated wastewater and establishment of different processes involved in individual treatment units with the PSf/PSf-GO microfiltration membranes. Chapter 7 gives the overall conclusion of this research and the recommendations. Figure 1.2 shows the outline of the thesis.
Figure 1.2 Outline of thesis.
Chapter 2

Review of Literature

2.1 Introduction

Elevated levels of heavy metal contamination have been reported in both soil and water streams (Wuana and Okieimen, 2011 and Reza and Singh, 2010). Lead is one such common heavy metal, known for its wide applications in the field of engineering and science. Recent studies have shown the presence of lead across different water bodies (Shen and Boyle, 1987; Hao et al., 2008 and Kestin et al., 2007). Environmental and health impact of lead toxicity has also been extensively noted (Lars Jarup, 2003 and Spurgeon et al., 1994). Given the toxic concerns of lead, studies on its remediation from different water bodies has become significant.

Numerous technologies have been developed to treat lead wastes depending on the type of water body. Adsorption and membrane separation are some of the widely-used techniques for treatment of lead contaminated wastewater. With recent advancements, nanotechnology and nano based treatment techniques are being well adopted for the treatment of contaminated water. However, the knowledge on the treatment mechanism and functionalities of such new techniques are still limited.

The use of Membrane bioreactors (MBR) is a widely accepted treatment technology for municipal wastewater. Numerous studies are available on the application of MBR treatment on effluents (Chan et al., 2009 and Lin et al., 2012). The treatment efficiency of such system and its mechanism on organic contaminants removal are well reported. However, the fate of inorganics, heavy metals present in waste streams and their removal is less studied and needs to be comprehensively investigated.

This chapter discusses in detail the occurrence of lead and their effect on society (i.e., environment and health). Current remediation strategies and mechanisms involved in the treatment of lead are described in detail. A comprehensive review on MBR
treatment technology have also been provided. A detailed discussion on the advantages and drawbacks of different treatment systems are also presented.

2.2 Occurrences, usage, regulation and disposal of lead

Lead (Pb) is the fifth element in Group 14 of the periodic table. It has an atomic number of 82, atomic weight of 207.2 and its common oxidation states are +2 and +4. The average concentration of Pb in earth’s crust is 13 ppm (parts per million), around 2.6 to 25 ppm is present in the soil and less than 0.1 ppm in ground water. Lead is found in nature as PbO$_2$ as brown or black mineral plattnerite. Lead is commercially produced from trilead tetroxide by oxidation with chlorine. Lead is used in batteries, ammunition, solder, piping, pigments, insecticides, alloys and in gasoline as anti-knocking agent. The US-Environmental Protection Agency (USEPA, 2004) has set the Maximum Contaminant Level Goal (MCLG) to be 0 for drinking water. The Maximum contamination limit (MCL) should be lower than 15 x10$^{-4}$ g/L.

The global consumption of lead in 1998 was estimated to be ~ 6 million tonnes (European Commission, 2002). Almost, 75 % of which was from lead batteries. Lead compounds and extruded lead accounted for 9 % and 6 % respectively. Ammunition and alloys were 3% (European Commission, 2002). Australia is the second largest producer of lead in the world (Australian Government: Geoscience Australia, 2016). Lead recycling is also being extensively done in Australia accounting for almost half of the lead consumption. Domestic lead waste is mainly contributed by old lead pipes, laundry and kitchen wastes. In Italy, around 6x10$^{-3}$ g/L of lead was found in the effluent from ceramics production and its derivatives (European Commission, 2001). The metal and electrical industry wastes in Greece was estimated to have 5x10$^{-4}$ g/L of lead waste in their effluent (European Commission, 2001).

Lead removal from wastewater is mainly done by coagulation, ion exchange and sand filtration. Additionally, activated carbon, media filtration and reverse osmosis methods can also be applied. Organo-metallic compounds of lead are difficult to treat, as the
lead is not free to precipitate. Generally, organo-metallic compounds are oxidised to separate the lead and then adsorbed onto carbon to remove as organic complex.

2.3 Forms of lead in different water bodies

The Pourbaix diagram also known as Eh-pH diagram maps out the possible stable form of an element in an aqueous electrochemical system. The reduction potential of the environment and pH are necessary to identify the speciation of a given element in natural water systems. This diagram assists in identifying a stable thermodynamic form for a given element for a given E (volts) and pH. Figure 2.1 shows the different species of the element lead in different water bodies.

![Pourbaix diagram of heavy metal lead in different water bodies.](image)

**Figure 2.1** Pourbaix diagram of heavy metal lead in different water bodies.

From the Pourbaix diagram, the divalent form Pb$^{2+}$ is stable over most of the region. The oxidised form PbO$_2$, which is in +4 charge is stable in a highly oxidising environment. For a clean lake, the surface water is well aerated and the dissolved
oxygen concentrations are high. This results in higher potential which is close to the $E^o$ of oxygen. Conditions may approach anaerobic (actively reducing) for a highly polluted lake with organic reducing agents or at the bottom layer of a thermally stratified swamp.

2.4 Effects of lead pollution

2.4.1 Environmental impact

Soils become contaminated by accumulation of heavy metals released by anthropogenic activities (Wuana et al., 2011). The continual process of lead discharge increases the risk of groundwater pollution with an augmented toxic metal mobility in plant and contamination in the food chain. In soil, metal mobility depends on two main factors (1) water transfer through the soil and (2) physical/chemical interaction of metal with the particles present in the soil. Acidic soil conditions provide high potential for metal mobilisation as they reduce the chance of mechanisms like hydrolysis and precipitation (Martinez and Motto, 2000).

Long term accumulation of heavy metals in the soil will impair plant growth as the concentration of heavy metals in plant tissues reaches above the threshold value. For example, a high concentration of lead is known to inhibit seed germination of barley plants (Mahmood et al., 2007). Also, lead toxicity leads to an altered mineral nutrition, change in membrane permeability, inhibition of enzyme activity and water imbalance in plants (Sharma et al., 2005). Several studies have been carried out to investigate soil microbial activities near industries, which discharge heavy metals (Garcia et al., 2013; Amin et al., 2015 and Wang et al., 2007). Studies have confirmed that elevated lead levels in the soil interfere with litter breakdown rates through metal toxicity (Doelman and Haanstra, 1979a and Doelman and Haanstra, 1979b). The binding of metal ions to the sulfhydryl groups of the enzymes for the biodegradation of the contaminants are also affected (Tchounwou et al., 2012). Soils co-contaminated with organics and heavy
metals are considered difficult to remediate because of the mixed nature of contaminants (Olaniran et al., 2013).

A report by Tyler (1989) clearly suggests that a low degree of heavy metal pollution is sufficient to bring about measurable disturbances which ultimately reduce the productivity of the eco-system. Jackson et al. (1978) reported that an increased heavy metal concentration affected the soil nutrient pool cycling of forest eco-system. There was also an increase in the essential elements of soil leachate because of heavy metal impaction. In addition, heavy metals in soil are known to have adverse effect on the mineralisation of essential nutrients required by the plants.

2.4.2 Health impact

Heavy metals belong to a class of globally distributed pollutants due to their extensive use in industries. They are known for their wide dispersion and accumulates as toxic wastes in the living tissues of human body (Tchounwou et al., 2012). There are few essential metals (i.e., micro nutrients) which are required for normal functioning of the human body. However, these micronutrients can become toxic on high exposure levels. The Agency for Toxic Substances and Disease Registry (ATSDR) of U.S. Department of Health and Human Services has listed the heavy metals Arsenic, Chromium, Lead and Mercury as most toxic and hazardous (Hu, 2002).

Exposure to these heavy metals can occur through a variety of ways. They can be inhaled as dust or fumes or can be ingested involuntarily through food or water and by direct physical contact. Once they are digested or absorbed they get distributed to tissues and organs (Hu, 2002). In general, excretion of metals occurs through kidneys and the digestive tract, but metals tend to accumulate in specific storage sites such as skeleton, kidneys and liver for years or decades (Tchounwou et al., 2012).

Lead exposure can occur via air and food roughly in equal proportions. Lead mining, use of lead in plumbing equipment, food cans, paint and ceramic ware have resulted in a marked rise in the exposure of lead to humans (Lars Jarup, 2003 and Tchounwou et al., 2012). Earlier, lead in food originated from utensils used for cooking and storage,
and lead acetate was previously used to sweeten port wine (Lars Jarup, 2003). Anti-knock agents (i.e., lead organic compounds) in fuel has been the dominant source of lead emissions to ambient air. However, there has been a decrease in lead emissions in developed countries due to the use of unleaded petrol resulting in low blood lead levels in the general population (Lars Jarup, 2003). The annual worldwide lead production in the year 2002 was approximately 5.4 million tons (McCally, 2002). The major occupational exposure to inorganic lead occurs in mines and smelters, as well as welding of lead painted metal and in battery plants. Airborne lead can be deposited in the soil, which can further concentrate in root vegetables (e.g., onion), leafy green vegetables (e.g., spinach) and thus reaching humans via the food chain (Lars Jarup, 2003).

Almost, 50% of the inorganic lead inhaled is absorbed in the lungs. Adults take up to 10-15% of lead from food, whereas children may absorb up to 50% via gastrointestinal tract (Lars Jarup, 2003). Lead is mainly bound to the erythrocytes in blood and its elimination is slow and principally via urine. Lead also gets stored in the skeleton of the human body (Lars Jarup, 2003). The half-life of lead in blood and skeleton is approximately 1 month and 20-30 years, respectively. In adults, blood does not penetrate the blood-brain barrier, due to well-developed blood-brain barrier (Lars Jarup, 2003). In children, the chance of lead entering the blood-brain barrier is quite high with an under developed brain, making them more susceptible to lead exposure and brain damage (Lars Jarup, 2003). Tetramethyl and tetraethyl lead which are used as anti-knock compounds in petrol can penetrate the skin easily. They also can cross the blood-brain barrier in adults, which can further result in lead encephalopathy (i.e., acute lead poisoning by organic lead compounds). Lead encephalopathy is characterised by sleeplessness and restlessness. Other symptoms of acute lead poisoning include headache, irritability, abdominal pain and various symptoms (Lars Jarup, 2003). Long term low level exposure of lead in children can also result in diminished intellectual capacity. Acute exposure of lead can cause proximal renal tubular damage. Studies also report that certain genetic and environmental factors can increase the detrimental effects of lead on neural development (Winneke and Kraemer 1997; Finkelstein et al., 1998; Lidsky and Schneider, 2003).
2.5 Current remediation strategies for lead

Soil and water are the major sinks for lead release into the environment by anthropogenic activities. Lead persists in the natural environment for an extended period, as it is not biodegradable. Moreover, they also can accumulate in successive levels of the biological chain, thereby causing acute and chronic diseases. With the enactment of several water legislations and guidelines worldwide, lead has been listed as an environmental priority pollutant (U.S-EPA, 2014). Many methods are being currently employed for its removal. The remediation techniques that are currently in practice are discussed below.

2.5.1 Chemical Precipitation

Chemical precipitation is the most commonly used process in the industry because of its simple mode of operation and lower operating costs than other treatment processes. In a precipitation process, the chemicals react with the heavy metal ions to form insoluble precipitates which are separated by sedimentation or filtration. The treated water can then be discharged or re-used. A conventional precipitation process is performed by using a hydroxide or sulphide or chelating precipitants (Fu and Wang, 2011).

2.5.1.1 Hydroxide precipitation

Hydroxide precipitation is known for its simplicity, low cost and ease of pH control. The solubilities of different metal hydroxides are minimised in the pH range of 8.0-11.0 (Figure 2.2). The metal-hydroxide complex can be removed by flocculation and sedimentation. Slaked lime or calcium hydroxide, Ca (OH)₂ is the most commonly used industrial hydroxide precipitant. Sometimes the addition of coagulants like alum, iron salts and organic polymers enhance the removal of heavy metals from wastewater (Fu and Wang, 2011). In a study conducted by Chen et al. (2009), calcium oxide, CaO, was
used as a precipitant for lead with an initial concentration of 100 mg/L at pH 7-11. Sodium hydroxide, NaOH, was studied in the removal of Cu (II) and Cr (VI) from wastewater by Mirbagheri and Hossein (2005). Despite the wide use of hydroxide precipitation in industries, there are a few limitations in this process. Firstly, hydroxide precipitation generates a large volume of sludge resulting in dewatering and disposal problems. Secondly, some metal hydroxides are amphoteric, and when the wastes contain mixed metals, using hydroxide precipitation can be a problem as the ideal pH of one metal can set another metal back into the solution. Thirdly, when complexing agents are present in the wastewater, they will inhibit metal-hydroxide precipitation (Fu and Wang, 2011).

**Figure 2.2** Solubility of metal hydroxides at different pH (Adopted from US-EPA, 2003).
2.5.1.2 Sulphide Precipitation

Sulphide precipitation is also an effective process for the treatment of toxic heavy metals. One of the main advantages of sulphide precipitation is that the solubility of metal-sulphide is dramatically lower than hydroxide precipitate. Also, sulphide precipitates are not amphoteric as compared to hydroxide precipitates (Figure 2.3). The metal-sulphide sludge also shows better thickening and dewatering characteristics than the corresponding hydroxide sludge. A major disadvantage of using the sulphide precipitation process is the generation of hydrogen sulphide, H₂S, fumes in acidic conditions. So, it is essential to perform the precipitation process in a neutral or basic medium. Also, the metal sulphide precipitation tends to form colloidal precipitates that can cause separation problems in either settling or filtration processes. In a study conducted by Alvarez et al. (2007), 92% of Pb (II) was precipitated using biogenic hydrogen sulphide produced by sulphate reducing bacteria at pH 3. Cu (II) and Zn (II) also showed a precipitation greater than 94% under the same conditions. Pyrite and synthetic iron sulphide was also investigated for the removal of Cu²⁺, Cd²⁺ and Pb²⁺ (Özverdi and Erdem, 2006). The mechanism governing the metal removal processes was determined as chemical precipitation at low pH (<3) due to hydrogen sulphide (H₂S) generation.
2.5.1.3 Precipitation by chelation

Trimercaptotriazine, Potassium/Sodium thiocarbonate and Sodium dimethyldithiocarbamate are the most commonly used heavy metal precipitants (Matlock et al., 2002a). Apart from these commonly used precipitants, specific precipitants for a given heavy metal are being developed. For example, a thiol based precipitant 1, 3-benzenediamidoethanethiol (BDET²) was designed and synthesised (Matlock et al., 2002 b, c) for precipitating lead and mercury. The results indicated a removal greater than 99% for both mercury and lead. Potassium ethyl xanthate was employed to remove copper ions from wastewater (Chang et al., 2002). Similarly, dipropyl dithiophosphate was used to remove lead, cadmium, copper and mercury (Xu and Zhang, 2006).
2.5.2 Ion exchange

Ion exchange resins work on the principle of exchanging cations with the metals in the wastewater. Their major advantages include high treatment capacity, high removal efficiency and fast kinetics. Among the materials used in ion-exchange process, synthetic resins are most effective. Most common cation exchangers are either strongly acidic with sulfonic acid groups (-SO$_3$H) or weakly acidic with carboxylic acid groups (-COOH). The general process of the ion-exchange when the wastewater passes through the resin can be understood by these simple equations (Fu and Wang, 2011)

\[
nR\text{-SO}_3\text{H} + M^{n+} \rightarrow (R\text{-SO}_3^\cdot)_nM^{n+} + nH^+ \text{ (Resins with -SO}_3\text{H group)}
\] (2.1)

\[
nR\text{-COOH} + M^{n+} \rightarrow (R\text{-COO}^\cdot)_nM^{n+} + nH^+ \text{ (Resins with -COOH group)}
\] (2.2)

where M represents the metal.

Natural zeolite, clinoptilolite ion-exchange resin was studied and modelled for exchange of Pb$^{2+}$ ions under different conditions (Inglezakis and Grigoropoulou, 2003 and Berber-Mendoza et al., 2006). A maximum Pb (II) removal efficiency of 55 % was reported by Inglezakis et al. (2007) for clinoptilolite ion-exchange resin. The uptake of heavy metals depends on certain variables like pH, temperature, initial metal concentration and contact time. Low cost naturally occurring silicate minerals are also widely used to remove heavy metals (Karnib et al., 2014).

2.5.3 Adsorption

Adsorption is the most widely used process for heavy metal contaminated wastewater treatment (Hegazi, 2013). It is an effective and economical treatment process, which offers flexibility in design and operation. Since, in most cases adsorption is reversible,
the adsorbents used can be regenerated by a suitable desorption process. The different types of adsorbents that are currently used are discussed below.

2.5.3.1 Carbon based adsorbents

Activated carbon adsorbents are predominantly used because of their large micropore and mesopore volumes resulting in high surface areas. Extensive research is being done on the use of activated carbon in removing heavy metals (Table 2.1). However, with a depleting coal resource, the cost of preparing coal based activated carbon has increased considerably (Fu and Wang, 2011). Therefore, development of activated carbon composites is being considered as an alternative. Additives like alginate, tannic acid, magnesium and surfactants are being used to develop activated carbon composite adsorbents for heavy metals (Fu and Wang, 2011). The use of activated carbon from eucalyptus bark and from poultry litter was also explored (Kongsuwan et al., 2009 and Guo et al., 2010).

Carbon nanotubes (CNTs) have been widely studied for their excellent physico-chemical/mechanical properties and applications. They are highly effective in removing heavy metals like lead, cadmium, chromium, copper and nickel from wastewater (Fu and Wang, 2011). Various studies were performed using raw CNTs for the removal of different heavy metals. Kabbashi et al. (2009) conducted experiments with raw CNTs and reported a maximum of 96% lead removal. In a different study, sorption capacities of divalent metal ions by raw CNTs were analysed and was reported to follow the order: Pb$^{2+}$>Ni$^{2+}$>Zn$^{2+}$>Cu$^{2+}$>Cd$^{2+}$ (Rao et al., 2007). The sorption capacities were significantly increased after oxidation by HNO$_3$, NaClO and KMnO$_4$ (Rao et al., 2007). The results of these studies have made CNTs as a promising candidate for adsorption of heavy metals.

CNTs can be broadly classified into two types 1.) Single-walled CNTs (SWCNTs) and 2.) Multi-walled CNTs (MWCNTs). These can further be functionalised with addition of necessary functional groups. In one such functionalised study, acidified MWCNTs were investigated for Pb (II) removal. It was noted that the oxygenous
Table 2.1 List of various activated carbon adsorbents used for adsorbing different heavy metals.

<table>
<thead>
<tr>
<th>Heavy Metal</th>
<th>Type of Adsorbent</th>
<th>Optimum pH</th>
<th>Adsorption Capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg (II)</td>
<td>PAC-Nuchar SA</td>
<td>4-5</td>
<td>40.12</td>
<td>Huang and Blankenship (1984)</td>
</tr>
<tr>
<td>Hg (II)</td>
<td>ACC</td>
<td>2.5-5.5</td>
<td>65</td>
<td>Babic et al. (2002)</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>GAC</td>
<td>N.A.</td>
<td>6.84</td>
<td>Monser et al. (2002)</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>GAC - Filtrasorb</td>
<td>2.5</td>
<td>145</td>
<td>Shanna and Forester (1996)</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>GAC - Filtrasorb</td>
<td>2</td>
<td>53.19</td>
<td>Dantas et al. (2001)</td>
</tr>
<tr>
<td>Cr (III)</td>
<td>GAC - Filtrasorb</td>
<td>&gt;4.5</td>
<td>30</td>
<td>Park et al. (2001)</td>
</tr>
<tr>
<td>Pb (II)</td>
<td>GAC- HD400</td>
<td>6</td>
<td>30</td>
<td>Reed and Arunachalam (1994)</td>
</tr>
<tr>
<td>Zn (II)</td>
<td>GAC-C</td>
<td>7</td>
<td>18</td>
<td>Leyva-Ramos et al. (2002)</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>ACF</td>
<td>6</td>
<td>146</td>
<td>Rangel-Mendez et al. (2002)</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>Oxidised ACF</td>
<td>3.5 – 4</td>
<td>10</td>
<td>Shim et al. (2001)</td>
</tr>
<tr>
<td>Cu (II)</td>
<td>GAC</td>
<td>N.A.</td>
<td>38</td>
<td>Monser et al. (2002)</td>
</tr>
</tbody>
</table>

GAC - Granular Activated Carbon  PAC – Powdered Activated Carbon

ACC - Activated Carbon Cloth  ACF – Activated Carbon Fibrous
functional groups of MWCNTs play an important role in the adsorption of lead ions. The adsorption of heavy metals is generally attributed to the electrostatic attraction, sorption-precipitation and chemical interaction between the metal ions and the surface functional groups of CNTs (Rao et al., 2007).

Extensive use of CNTs can cause a serious risk to humans as they are eventually discharged to water environment. To resolve this, efforts are being made to develop an environmental friendly adsorbent. For example, CNTs immobilised by calcium alginate were prepared and tested on the removal of copper (Li et al., 2010).

Graphene and graphene based composites have also been used for the treatment of different pollutants. A study conducted by Sreeprasad et al. (2013) showed the successful removal of rhodamine-6G (a dye) and chlorpyrifos (a pesticide) by graphene sand composite. The role of graphene oxide nano-sheets for heavy metal ions removal (Cd (II) and Co (II)) was also elucidated by Zhao et al. (2011). Pb (II) removal using a polymer based graphene oxide nanocomposite was successfully shown by Musico et al. (2013). Reduced graphene oxide metal/metal oxide composites were also tested for Hg (II) removal by Sreeprasad et al. (2011).

2.5.3.1.1 Mechanism of heavy metal adsorption onto carbon based adsorbents

Activated carbon is obtained from coir piths, coal, wood, peat and coconut shells. Different forms of activated carbon have been studied for heavy metal removal. Kadirvelu et al. (2000) demonstrated the adsorption of three divalent metal ions (Cu\(^{2+}\), Ni\(^{2+}\)and Pb\(^{2+}\)) using activated carbon cloth. The mechanism of its removal was studied using the pH changes before and after adsorption. Based on the pH changes, the adsorption mechanism was proposed to be ion-exchange. The role of metal precipitation was also discussed.

Goel et al. (2005) studied the adsorption of Pb (II) using treated granular activated carbon. The granular activated carbon (GAC) obtained from coconut shell was surface modified with sulphur. The adsorbents were studied for their adsorption mechanism and it was proposed to be ion exchange and surface complexation. Surfactant modified
GAC was prepared and examined for cationic heavy metal removal from aqueous solutions (Ahn et al., 2009). Three surfactants namely sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS) and dioctyl sulfosuccinate sodium (DSS) were employed. The mechanism of the surfactant modified GAC was examined and it was proposed that the anionic hydrophilic head of the modified GAC had a negative surface charge, and favoured Cd (II) adsorption. Adsorption of mercury using activated carbon from fertilizer waste was investigated by Mohan et al. (2001). It was concluded that the adsorption followed film diffusion mechanism at low concentrations, whereas it was particle diffusion at higher concentrations of mercury.

The mechanism of adsorption of heavy metals ions onto CNTs are complicated and different hypothesis have been proposed in literature. Some of the predominant mechanism that are electrostatic attraction, sorption precipitation and chemical interaction between the metal ions and the surface functional groups of CNTs. Figure 2.4 shows the generalised mechanism of heavy metal ion attachment onto the functionalised CNTs (Rao et al., 2007).

![Figure 2.4 Mechanism of heavy metal ion attachment onto functionalised CNTs](Reproduced from Rao et al., 2007).
Electrostatic attraction was reported as the mechanism behind adsorption on Zn (II) ions onto purified SWCNTs and MWCNTs (Lu et al., 2006). Li et al. (2003) studied single and competitive adsorption of Pb\(^{2+}\), Cu\(^{2+}\) and Cd\(^{2+}\) on MWCNTs. It was found that sorption-precipitation and electrostatic attraction were the main adsorption mechanisms involved that were involved during the process.

The presence of strong functional groups on the GO surface makes GO a potential adsorbent for metal ion complexation through electrostatic and coordinate approaches. Most of the heavy metal ions are of cationic forms, but some metals such as Cr (VI) are in anionic forms (CrO\(_4^{2-}\) and Cr\(_2\)O\(_7^{2-}\)). After modification of GO with organics or metal oxides, GO composites are used for anionic metal removal because of their functionalisation. Ma et al. (2012) showed that the ethylenediamine-reduced GO (ED-RGO) sheets can be used for an effective removal of chromium. The predicted mechanism for the Cr (VI) removal from aqueous solution was by indirect reduction on the carbocyclic six membered ring of ED-RGO. This has been illustrated in the Figure 2.5.

![Figure 2.5](image_url)

**Figure 2.5** Proposed mechanism of Cr (VI) removal by ED-RGO (Reproduced from Ma et al., 2012).
Agglomeration and uncontrollable precipitation of nano-sheets were seen during the interaction of GO nano-sheets with cationic divalent metal ions. This may be due to the cross-linking of the graphene oxide sheets by the divalent cations. Park et al. (2008) undertook an in-depth analysis on graphene oxide interaction with divalent ions mainly Mg$^{2+}$/Ca$^{2+}$. XRD investigations on metal interacted with GO showed an increased layer to layer distance in comparison with that of an unmodified graphene oxide. Based on the functionalities that are present in the GO sheets, two modes of interaction of cations with GO sheets were proposed 1) bridging the edges of the sheets through carboxylate chelates to the metal and 2) intercalating between the basal planes through either weak alkoxide or dative bonds from carbonyl and hydroxyl group. The former bond was found to be stronger than the latter. A schematic model of the reaction between GO and metal (M= Mg$^{2+}$/Ca$^{2+}$) is shown in Figure 2.6.

**Figure 2.6** Schematic model of the reaction between GO and metal (M= Mg$^{2+}$/Ca$^{2+}$) (Reproduced from Park et al., 2008).
Sun et al. (2013) studied the ion penetration through GO membranes. This study demonstrated the selective divalent cation (Mn$^{2+}$, Cd$^{2+}$ and Cu$^{2+}$) penetration and usage of GO for water purification applications. The oxygen containing functional groups of GO tend to cluster together leaving the other non-oxidised regions to form a two-dimensional network of graphene nano-capillaries. The penetration abilities of heavy metal salts primarily depend on the coordination between the heavy metal-ions and functional groups decorated on the GO sheets. Among, the three studied heavy metals, Cu$^{2+}$ ions favour square planar geometry, Cd$^{2+}$ ions favour tetrahedral coordination and Mn$^{2+}$ favoured trigonal bipyramidal geometry. The oxygen-containing functional groups can easily substitute water molecules from the hydrated complex because the water molecules do not contain the functional groups needed to strengthen the bond to a metal ion. Also, the interaction energies of negatively charged functional groups are significantly greater than those of neutral functional groups. In the case of Cu$^{2+}$ and Cd$^{2+}$ ions, the Cu$^{2+}$ is a d$^{9}$ ion, and its complexes possess a doublet ground state, whereas, the Cd$^{2+}$ is a d$^{10}$ ion, whose complexes possess a singlet ground state. With respect to the coordination of ions with oxygen-containing functional groups (e.g., carboxylate groups), the Cu$^{2+}$ ions tend to bind in asyn conformation, whereas, Cd$^{2+}$ ions are more likely to bind in a direct conformation, where they share two carboxylate oxygen atoms equally. These differences in coordination conformation result in a smaller average distance between Cu$^{2+}$ ions and carboxylate groups than that of Cd$^{2+}$ ions, indicating a larger binding energy of Cu$^{2+}$-O than that of Cd$^{2+}$-O. In contrast with Cu$^{2+}$ ions, the Mn$^{2+}$ ions are more likely to bind with carboxylate groups in an anti-conformation, which is less stable than the syn conformation. This difference leads to a larger average distance of Mn$^{2+}$-O bonds than that of Cu$^{2+}$-O bonds, indicating a smaller binding strength of Mn$^{2+}$-O compared to the Cu$^{2+}$–O bonds. Figure 2.7 explains the schematic coordination of different divalent cations with the GO nano-sheets. The above discussed interactions of heavy metals with GO gives us a basic understanding of the mechanisms of heavy metal ion adsorption on GO nano-sheets.
2.5.3.2 Low-cost adsorbents

As the name suggests, these are cost-effective adsorbents used for heavy metal remediation. Materials which are available in large quantities or waste products are the ideal candidates for low-cost adsorbents. Agricultural wastes, natural substances, industrial by-products and wastes are the most commonly used low cost adsorbents (Refer Table 2.2). Numerous studies have been conducted on development of low-cost adsorbents. The use of kaolinite and montmorillonite have been reported successfully in heavy metal removal (Bhattacharyya and Gupta, 2008). Industrial by-products like lignin, diatomite, clino-pyrrhotite, lignite, aragonite shells, natural zeolites, clay and peat have also been reported to have good adsorption capacity for heavy metals (Fu
and Wang, 2011). In a specific study, the use of kaolinite clay obtained from Longyan, China could remove heavy metal ions like Pb (II), Cd (II), Ni (II) and Cu (II) from wastewater. The kaolinite clay could bring down the Pb (II) concentration from 0.160 g/L to 0.008 g/L (Jiang et al., 2010). Due to low costs, the adsorbents can be disposed directly without any regeneration step.
Table 2.2 List of low cost adsorbents used for adsorbing different heavy metals.

<table>
<thead>
<tr>
<th>Heavy Metal</th>
<th>Type of Adsorbent</th>
<th>Optimum pH</th>
<th>Adsorption Capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd (II)</td>
<td>Cocoa Shell</td>
<td>2.0</td>
<td>4.94</td>
<td>Meunier et al. (2003)</td>
</tr>
<tr>
<td>Cr (III)</td>
<td>Cocoa Shell</td>
<td>2.0</td>
<td>2.52</td>
<td>Meunier et al. (2003)</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>Cocoa Shell</td>
<td>2.0</td>
<td>2.63</td>
<td>Meunier et al. (2003)</td>
</tr>
<tr>
<td>Zn (II)</td>
<td>Cocoa Shell</td>
<td>2.0</td>
<td>2.92</td>
<td>Meunier et al. (2003)</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>Cocoa Shell</td>
<td>2.0</td>
<td>2.87</td>
<td>Meunier et al. (2003)</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>Orange Peel</td>
<td>6-8</td>
<td>6.01</td>
<td>Annadurai et al. (2003)</td>
</tr>
<tr>
<td>Cu (II)</td>
<td>Orange Peel</td>
<td>6-8</td>
<td>3.65</td>
<td>Annadurai et al. (2003)</td>
</tr>
<tr>
<td>Zn (II)</td>
<td>Orange Peel</td>
<td>6-8</td>
<td>5.25</td>
<td>Annadurai et al. (2003)</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>Sawdust</td>
<td>2.0</td>
<td>15.82</td>
<td>Dakiky et al. (2002)</td>
</tr>
<tr>
<td>Element</td>
<td>Source</td>
<td>Release (mg/kg)</td>
<td>Ads (mg/kg)</td>
<td>Ref.</td>
</tr>
<tr>
<td>----------</td>
<td>-------------------------</td>
<td>-----------------</td>
<td>-------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>Maple Sawdust</td>
<td>5.0</td>
<td>5.1</td>
<td>Yu et al. (2003)</td>
</tr>
<tr>
<td>Cu (II)</td>
<td>Banana Peel</td>
<td>6-8</td>
<td>4.75</td>
<td>Annadurai et al. (2002)</td>
</tr>
<tr>
<td>Zn (II)</td>
<td>Banana Peel</td>
<td>6-8</td>
<td>5.80</td>
<td>Annadurai et al. (2002)</td>
</tr>
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<td>Ni (II)</td>
<td>Banana Peel</td>
<td>6-8</td>
<td>6.88</td>
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<tr>
<td>Ni (II)</td>
<td>Hazelnut Shell</td>
<td>3.0</td>
<td>10.11</td>
<td>Demirbas et al. (2002)</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>Hazelnut Shell</td>
<td>1.0</td>
<td>170</td>
<td>Kobya et al. (2004)</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>Activated alumina</td>
<td>4.0</td>
<td>1.6</td>
<td>Bishnoi et al. (2003)</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>Rice Husk</td>
<td>2.0</td>
<td>0.79</td>
<td>Bishnoi et al. (2003)</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>Almond Shell</td>
<td>2.0</td>
<td>10.62</td>
<td>Dakiky et al. (2002)</td>
</tr>
<tr>
<td>Cu (II)</td>
<td>Coir Pith</td>
<td>4-5</td>
<td>10.22</td>
<td>Kadirvelu et al. (2001a)</td>
</tr>
<tr>
<td>Ni (II)</td>
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<td>91.63</td>
<td>Kadirvelu et al. (2001a)</td>
</tr>
<tr>
<td>Element (II)</td>
<td>Material</td>
<td>Value</td>
<td>Percent</td>
<td>Reference</td>
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<tr>
<td>-------------</td>
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<tr>
<td>Ni (II)</td>
<td>Coir Pith</td>
<td>5</td>
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<tr>
<td>Cd (II)</td>
<td>Sugar-cane pith</td>
<td>6.0</td>
<td>24.70</td>
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<tr>
<td>Cd (II)</td>
<td>Cassava waste</td>
<td>4-5</td>
<td>18.05</td>
<td>Abia et al. (2003)</td>
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<tr>
<td>Cu (II)</td>
<td>Cassava waste</td>
<td>4-5</td>
<td>56.82</td>
<td>Abia et al. (2003)</td>
</tr>
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<td>Zn (II)</td>
<td>Cassava waste</td>
<td>4-5</td>
<td>11.06</td>
<td>Abia et al. (2003)</td>
</tr>
<tr>
<td>Cu (II)</td>
<td>Peanut Hulls</td>
<td>4-5</td>
<td>53.65</td>
<td>Periasamy and Namasivayam (1996)</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>Maize Cob</td>
<td>9</td>
<td>57.5</td>
<td>Selvakumari et al. (2002)</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>Jackfruit</td>
<td>5</td>
<td>52.08</td>
<td>Inbaraj and Sulochana (2004)</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>Fly Ash Type</td>
<td>8.0</td>
<td>0.99</td>
<td>Bayat (2002)</td>
</tr>
<tr>
<td>Pb (II)</td>
<td>Iron slags</td>
<td>3.5-8.5</td>
<td>95.24</td>
<td>Feng et al. (2004)</td>
</tr>
<tr>
<td>Pb (II)</td>
<td>Steel slags</td>
<td>5.2-8.5</td>
<td>32.26</td>
<td>Feng et al. (2004)</td>
</tr>
<tr>
<td>Element</td>
<td>Material</td>
<td>Concentration</td>
<td>Load</td>
<td>Reference</td>
</tr>
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<tr>
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<td>88.50</td>
<td>Feng et al. (2004)</td>
</tr>
<tr>
<td>Cu (II)</td>
<td>Steel slags</td>
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<td>16.21</td>
<td>Feng et al. (2004)</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>Bagasse</td>
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<td>0.03</td>
<td>Rao et al. (2002)</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>Fly Ash</td>
<td>6.0</td>
<td>0.01</td>
<td>Rao et al. (2002)</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>Rice Husk Ash</td>
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<td>25.64</td>
<td>Bhattacharya et al. (2008)</td>
</tr>
<tr>
<td>Zn (II)</td>
<td>Green Sands</td>
<td>5.5-6.0</td>
<td>32.46</td>
<td>Lee et al. (2004)</td>
</tr>
<tr>
<td>Zn (II)</td>
<td>Rice Husk Ash</td>
<td>5.0</td>
<td>14.30</td>
<td>Bhattacharya et al. (2006)</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>Fly Ash Zeolite</td>
<td>5.0</td>
<td>95.6</td>
<td>Ayala et al. (1998)</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>Fly Ash</td>
<td>7.2</td>
<td>198.2</td>
<td>Apak et al. (1998)</td>
</tr>
<tr>
<td>Hg (II)</td>
<td>Fly Ash</td>
<td>3.5-4.5</td>
<td>2.82</td>
<td>Sen and De. (1987)</td>
</tr>
<tr>
<td>Hg (II)</td>
<td>Treated Rice Husk</td>
<td>5.6-5.8</td>
<td>9.32</td>
<td>Feng et al. (2004)</td>
</tr>
<tr>
<td>As (III)</td>
<td>Fly Ash Coal-char</td>
<td>2.2-3.9, 2.2-3.1</td>
<td>3.7-89.2</td>
<td>Pattanayak et al. (2000)</td>
</tr>
<tr>
<td>As (V)</td>
<td>Material</td>
<td>pH</td>
<td>DO (mg/L)</td>
<td>Reference</td>
</tr>
<tr>
<td>-------------</td>
<td>--------------------------</td>
<td>------</td>
<td>-----------</td>
<td>-------------------------------------</td>
</tr>
<tr>
<td></td>
<td>Fly Ash</td>
<td>4.0</td>
<td>7.7-27.8</td>
<td>Diamadopoulos et al. (1993)</td>
</tr>
<tr>
<td></td>
<td>Fly Ash Coal-char</td>
<td>7.3-9.3, 2.2-3.0</td>
<td>0.02-34.5</td>
<td>Pattanayak et al. (2000)</td>
</tr>
</tbody>
</table>
2.5.4 Membrane-based separation

Membrane filtration technology employs different types of membranes for removal of heavy metal ions with high efficiency, ease of operation and a small footprint. Different membrane processes are used to recover heavy metals from wastewater. The most commonly used ones are ultrafiltration, reverse osmosis and nanofiltration.

2.5.4.1 Ultrafiltration membranes

Ultrafiltration (UF) is a membrane technique that utilises low transmembrane pressure for removing the dissolved and colloidal materials. The molecular weight cut off (MWCO) for ultrafiltration membrane follows in the range of $10^3$-$10^6$ Da. With a large pore size, the dissolved heavy metal ions in the form of hydrated ions or low molecular complexes can pass easily through the UF membrane pores. To obtain high removal efficiency of heavy metal ions, the micellar enhanced ultrafiltration (MEUF) was developed by Dunn et al. (1985).

MEUF is a technique where surfactants are introduced into wastewater to form micelles. These micelles can bind with the metal ions to form large metal-surfactant structures. Micelles containing the metal ions are retained by the UF membrane. In order to obtain a good retention of heavy metal ions, surfactant of electric charge opposite to that of the heavy metal ions needs to be introduced. Sodium dodecyl sulphate (SDS) is the most commonly used anionic surfactant for the removal of heavy metal ions in MEUF. Metal removal efficiency by MEUF depends on the concentration of the metal and surfactants, solution pH, ionic strength and parameters related to membrane operation. For a good rejection, the surfactant to metal molar ratio (S/M) should be above 5. Numerous studies have been conducted using synthetic wastewater and rejection coefficients up to 99% were obtained by maintaining this S/M ratio (Landaburu-Aguirre et al., 2009). Surfactant accounts for a large percentage of operating costs in MEUF systems. Recovery of surfactants is done by using either acid or alkali treatment of the retentate. Li et al. (2009) reported that the SDS micelles along with the heavy metals were separated by using EDTA. They could recover about 65% of the SDS after the treatment. A similar recovery study using H$_2$SO$_4$ was performed and 58% of SDS was recovered.

PEUF is a technique, where a water-soluble polymer is employed to complex metallic ions, thereby forming macromolecules having a higher molecular weight cut-off than that of the membrane. The retentate having the macromolecules are treated to recover the metallic ions.
The polymeric agent obtained after recovery process can then be re-used. Polymeric agents such as polyacrylic acid (PAA), polyethyleneimine (PEI) diethyleneimine cellulose and humic acid (Fu and Wang, 2011) are known for their selective separation and recovery of heavy metals with low energy requirements. Some important parameters which affect PEUF performance are type of the metal and polymer used, the ratio of metal to polymer, pH and presence of other metal ions in the solution. The major advantages of using PEUF includes high removal efficiency, high binding selectivity and a highly concentrated metal complex for its reuse.

Recently, a class of ultrafiltration composite membranes was developed and studied for heavy metal removal. Mbareck et al. (2009) prepared composite ultrafiltration membranes by phase inversion process having blends of polysulfone and polyacrylic acids and studied for their effectiveness in heavy metal removal. The prepared membranes had semi-interpenetrating polymer networks which increased the hydrophilicity, decreased the porosity and permeability of the membrane. The pore size of the outer-surface pores, sub-structure open pores and fine pores inner the sub-structure were estimated to be 680 nm, 136 nm and 25 nm, respectively. PSf/PAA membranes showed a high rejection (100%) for lead, cadmium and chromium at pH above 5.7 and a low rejection at low pH. The feed concentration and applied pressure was also studied for their influence on the heavy metal rejection. The high metal removal was attributed to the role of carboxylic groups in ion exchange or complexation.

Kaminski and Modrzejewska (1997) examined the application of chitosan ultrafiltration membranes for the removal of transition metal ions Cr(VI), Mn(II), Fe(III), Ni(II), Cu(II), Zn(II), and Cd(II). The separation ability was investigated for individual and mixture of ions. A complete separation of metal ions Cu(II), Cd(II), Co(II), Zn(II), and Ni(II) was observed. The mechanism for separation was ascribed to complexation of metal ions onto the chitosan membranes.

### 2.5.4.2 Nanofiltration membranes

Nanofiltration (NF) is a promising technology for removal of heavy metals from water sources (Huang and Koseoglu, 1993). The benefits of using nanofiltration include ease of operation, reliability and comparatively low energy consumption as well as high efficiency of heavy metal pollutant removal (Hilal et al., 2004).
Al-Rashdi et al. (2013) investigated the rejection of heavy metal ions using a commercial nanofiltration membrane (NF270). The role of pH, initial metal ion concentration and pressure were analysed on removal of Cd(II), As(III), Cu(II), Mn(II) and Pb(II). It was observed that when the pH was less than the isoelectric point of the NF membrane, the rejection was higher due to electrostatic repulsion and/or adsorption/deposition of metal onto the membrane. Cu (II) showed 100 % removal at all pH and pressure applied. As (III) failed to be rejected showing the membrane’s unsuitability for this species. The membrane showed a removal of 99%, 89% and 74% for cadmium, manganese and lead respectively, at pH 1.50 and 4 bar pressure.

Other commercially available NF90 and N30F membranes have shown a lot of promise in heavy metal removal. Basaran et al. (2016) studied the removal of Ni (II) and Cr (VI) ions using NF 90 membrane and NF 270 membranes. Under optimal conditions, NF 90 membrane performed better with a rejection of 99.2 and 96.5% as opposed to 98.7 and 95.7% by NF 270 for Ni (II) and Cr (VI) respectively. The removal of pentavalent arsenic from synthetic wastewater by N30F membrane was reported by Figoli et al. (2009). Operating parameters such as feed concentration, pH, pressure and temperature on arsenic rejection was investigated. It was observed that an increase in pH and a decrease of operating temperature and arsenic feed concentration determined a higher efficiency of arsenic removal. NF membranes were also used for treating mine wastewater. In one study, NF membrane was investigated for the recovery of silver from mining wastewater after the silver was taken into the solution as AgCN employing re-cyanidation and subsequent sedimentation and pre-filtration of wastewater (Koseoglu and Kitis, 2009). Silver recovered after hybrid cyanidation and membrane separation was found to be 29%-59%.

Composite NF membranes prepared by phase inversion have also been studied for heavy metal removal. A thin film composite polyamide NF membrane developed by Murthy and Chaudhari (2008) was shown to have a rejection of 98% and 92% of Ni for initial concentrations of 5 and 250 x10^{-3} g/L. Shah and Murthy (2013) prepared amide, azide and oxide functionalised MWCNT composite membranes and studied for the removal of different heavy metal ions. The prepared membranes showed enhanced properties and different removal rates for heavy metal ions. Azide functionalised MWCNT membranes showed better removal of 94.8, 93.9, 90.8, 79.1 and 80.8% for Cr (VI), Cu (II), Pb (II), Cd (II) and As (III), respectively. Boricha and Murthy (2008) also studied the removal of nickel ions using N, O-carboxymethyl chitosan-polyether sulfone composite nanofiltration membrane. Different concentrations of nickel in feed were investigated for their removal. A maximum removal of 80 and 62% for 5 ppm, 78
and 59% for 10 ppm; and 74 and 57% for 50 ppm feed concentration of nickel sulfate-water and nickel chloride-water systems, respectively.

### 2.5.4.3 Reverse Osmosis

Reverse Osmosis (RO) which uses a semi-permeable membrane allowing the fluid to be purified to pass through while rejecting the contaminants. RO is an increasingly popular wastewater treatment technique used in chemical and environmental engineering. Appropriate RO systems need to be employed to remove specific heavy metals. Ozaki et al. (2002) studied the performance of an aromatic polyamide (ES 20) ultra-low pressure reverse osmosis membrane (ULPROM) for separating divalent (Cu$^{2+}$, Ni$^{2+}$) and hexavalent (Cr$^{6+}$) ions from synthetic and real wastewater from heavy metal industry and reported. Rejection greater than 95% was reported. Ujang and Anderson (1996) worked on Zn$^{2+}$ and Cu$^{2+}$ removal using low pressure sulfonated polysulfone RO composite membrane after EDTA complexation. A removal of 99% was achieved at optimal conditions. Sometimes RO systems are used in combination with other removal techniques to obtain higher efficiency. In a study by Dialynas and Diamadopoulos (2009) a pilot scale MBR system was coupled with RO. The designed system showed 89% and 49% removal of Cr and Cu respectively, and complete removal of Pb and Ni. The combination of these two processes resulted in good quality effluent devoid of heavy metals and low organic content. The major drawbacks of RO systems are high power consumption due to the pumping pressures, and membrane restoration.

### 2.5.4.4 Electrodialysis

Electrodialysis (ED) is a process for the separation of ions across charged membranes from one solution to another using an electric field as driving force. In most of electrodialysis processes, ion exchange membranes either cation (-SO$_3^-$, -COO$^-$, -PO$_3^{2-}$ and -PO3H$^-$) or anion (-NH$_3^+$, -NRH$_2^+$ -NR$_3^+$ and -SR$_2^+$) exchange are used. Treatment of hexavalent chromium was performed using an ED pilot plant with a set of ion-exchange membranes (Nataraj et al., 2007). The results obtained were satisfactory in meeting the maximum contamination level of 1 x10$^{-4}$ g/L of chromium. A similar study was performed on the separation of Cu and Fe in solutions from electrowinning operations (Cifuentes et al., 2009). In summary, electrodialysis was proven to be effective in the removal of Cu and Fe from the working solution.
2.5.4.5 Mechanisms involved to improve membrane properties

Most membranes used for membrane separation processes suffer from membrane fouling due to the hydrophobicity of the membrane. Consequently, considerable efforts are being devoted to improve the hydrophilicity, porosity, mechanical strength and fouling resistant properties of the membrane. Chemical modification of the surface and bulk membrane preparation by blending compounds with the polymer before casting are the common ways for preparation of composite membranes with enhanced properties.

Shi et al. (2013) worked on developing a hydrophilic membrane by tethering a glycopolymer poly (2-gluconamidoethyl methacrylate) onto polysulfone membrane surface via surface initiated atom transfer radical polymerisation (ATRP). The ATR-FTIR results confirmed the successful anchoring of PNMG polymer chains on the membrane surface via blending. The composition of the membrane surface was determined using an XPS analysis. The analysis revealed an increase in oxygen content and the oxygen/sulfur ratio was also high due to the multi-hydroxy group nature of NMP group. Also, the presence of COO- group in the spectrum of PSF-g-PNMG3 membrane attributed to the ester group from PNMG chains confirmed the anchoring of the NMG groups at the membrane surface. This decreased the water contact angle which improved the hydrophilicity of the membrane. The pore size and porosity notably increased with the blend.

In a related study by Crock et al. (2013) different nanocomposite membranes were prepared with exfoliated graphene with and without gold nanoparticles. The cast membranes were characterised and the presence of Au nanoparticles was checked for catalytic activity. The conceptual illustration of hierarchical nanofillers as building blocks for multifunctional nanocomposite membranes is shown in Figure 2.8.
Figure 2.8 Schematic illustration of hierarchical nanofillers as building blocks for multifunctional nanocomposite membranes (Reproduced from Crock et al., 2013).

Introduction of exfoliated graphene showed a 22-fold increase in the permeability of the membrane. The selectivity was also improved (by 40%). The tensile strength and elongation at break, however, decreased with graphene loading.

Xu et al. (2014) prepared organosilane functionalised graphene oxide PVDF membranes to improve the anti-fouling characteristics of the membrane. FT-IR spectra of the functionalised membrane showed the presence of carboxylic group incorporated onto the nascent PVDF membrane by the GO and f-GO blending. Also, the stretching vibration of Si–O–C, –CH₂, and N–H groups confirmed the incorporation of APTS monomer into the GO via the functionalisation process. The resistance in series model was applied to study the fouling mechanism on the developed membrane. Membrane fouling was found to increase with a greater roughness due to the protein (test sample) being accumulated in the membrane. The functionalised GO membrane created a smooth layer as compared to GO blended membrane thereby improving the anti-fouling property in comparison with that of a native GO blended membrane. A schematic illustration of the doped membranes with the additives and the relationship between surface morphology and fouling behaviour is shown in Figure 2.9.
In another study, GO blended membrane (i.e., polysulfone blended with GO) was prepared and cast by Lee et al. (2013). The presence of GO in the sub surface layer of the membrane was confirmed by EDS (energy dispersive spectroscopy). The Raman spectrum of PSF/GO showed the structural imperfections generated by epoxide and hydroxyl groups of the carbon basal plane which assured the presence of GO in the nanocomposite, however, the exact mechanism of GO interaction with the polymer was not clear.

**2.5.4.6 Mechanism of heavy metal attachment onto the modified membranes**

Min et al. (2012) prepared micro-nano structure PES/PEI nanofibrous membranes by electrospinning. These membranes were further characterised and used for adsorption of heavy metals (Pb (II), Cu (II) and Cd (II)). XPS analysis was done on the heavy metal interacted membrane samples. Characteristic peaks were observed at the binding energy of 941.1 eV, 137.9 eV and 404.8 eV, which were attributed to the Cu 2p orbital, Pb 4f orbital and Cd 3d orbital respectively. Also, the change in BE peak of N 1s at 398.9 eV to two different BE peaks at 397.4 eV and 404.0 eV indicated the bond formation between the heavy metal and the lone pair of electrons of nitrogen in amine and imino group on the membrane. A schematic diagram of the proposed mechanism is shown in Figure 2.10.
Liu et al. (2006) conducted a study on copper ion removal using a highly porous chitosan/cellulose hollow fibre membrane. XPS analysis of the Cu interacted membrane samples revealed that there was no clear evidence to prove the role of hydroxyl group in the chemical adsorption of copper ions onto the hollow fibre membranes. However, the increase in binding energies of the N 1s provides an evidence of N atoms in the –NH$_2$ and/or the – NH and the –NH$_3^+$ were involved in the adsorption of copper ions, this might surface complex with the lone pair of electrons from the N atoms.

Hong et al. (2014) prepared a surface modified PSF/PAN membranes with dopamine and was studied for adsorption of Lanthanum (II) ions. XPS analysis was performed to understand the possible adsorption mechanism of the lanthanum onto the novel polydopamine complex hollow membranes. The BE peak at 832 eV indicated the adsorption of lanthanum onto the hollow membrane. The change in the BE peak of O 1s after interaction showed the coordination bond O-La indicating that there was a chemical bond between O atom and La atom. The possible mechanism of La adsorption onto the PDA membrane was also predicted (as shown in Figure 2.11).
2.5.5 Coagulation and Flocculation

Coagulants or flocculants are used to either coagulate or flocculate heavy metals present in wastewater. This is followed by sedimentation and membrane filtration to separate the heavy metals. Addition of coagulant generally destabilises the colloids by neutralizing the forces that keep them apart. The commonly used coagulants for wastewater treatment are ammonium, ferrous sulphate, ferric chloride and polyaluminium chloride (PAC). A combination of coagulants has also been studied for heavy metal elimination. El Samrani et al. (2008) studied the use of commercial coagulants (ferric chloride and polyaluminium chloride) in heavy metal removal of combined sewer overflow. Both coagulants provided effective clarification and excellent heavy metal elimination was achieved at around optimum coagulant concentrations.

A different type of coagulant was developed (Chang and Wang, 2007) by grafting a sodium xanthogenate group with polyethyleneimine. This was done to remove both the soluble heavy metal and insoluble substances as the existing coagulants were specific in action for the hydrophobic colloids and suspended particles. This newly developed coagulant was an amphoteric polyelectrolyte, which coagulated the negatively charged species at low pH.

Flocculation is the action of polymers in forming the bridges between the flocs and binds the particles into large aggregates or clumps. Once the aggregates are formed, they are removed or separated by filtration. Although flocculants like PAC, polyferric sulphate (PFS) and polyacrylamide (PAM) are widely used in treatment of wastewater, these commercially available flocculants are not effective in removing the heavy metals. Macromolecular heavy metal flocculants are used as an alternative to polymeric flocculants in treating wastewater having heavy metal contaminants. Chang et al. (2009) prepared a macromolecular heavy metal flocculant mercaptoacetyl chitosan by reacting chitosan with mercaptoacetic acid. This coagulant could remove turbidity and heavy metals present in the wastewater. Different macromolecule flocculants like Konjac-graft-poly (acrylamide)-co-sodium xanthate and poly-
ampholyte chitosan derivatives – N- carboxyethylated chitosans were also developed and studied for heavy metal removal. Konjac-graft-poly (acrylamide)-co-sodium xanthate (Duan et al., 2010) was investigated for floculating Cu\(^{2+}\) ions under different anions and cations concentrations in the medium. The presence of cations in the medium favoured the Cu\(^{2+}\) ions removal. Poly-ampholyte chitosan derivatives – N- carboxyethylated chitosans (Bratskaya et al., 2009) was investigated for removal of Cu\(^{2+}\), Zn\(^{2+}\) and Ni\(^{2+}\) ions. The flocculation performance decreased in the in the row Cu\(^{2+}\) > Zn\(^{2+}\) > Ni\(^{2+}\)corresponding to the row of the hydroxocomplex stability for these metals.

Flocculation of humic acid (HA) bound heavy metal is also being currently investigated. Enhanced removal of heavy metal ions like Pb\(^{2+}\) and Zn\(^{2+}\) has been studied after binding the ions to HA and then coagulating with the cationic polyelectrolyte polydiallyldimethylammonium chloride (Poly-DADMAC). The removal of the bound ions was found to increase with the extent of coagulation-flocculation of the HA by Poly-DADMC. Generally, the metal-HA complexes are removed by polyelectrolyte flocculation, followed by filtration. Recently a new flocculation technique was proposed using thermosensitive polymers for removing the undesirable heavy metals and humic acid (Tokuyama et al., 2010). A new tannin based flocculant has also been commercially developed and investigated for removal of Zn\(^{2+}\), Ni\(^{2+}\) and Cu\(^{2+}\) (Heredia and Martín, 2009). Different flocculant concentrations (20, 50, 100 and 150 mg/L) were considered for the removal study. All metals showed a minimum of 75% removal at an optimised flocculant dosage and pH. Generally, coagulation-flocculation technique cannot completely treat the heavy metal from wastewater, therefore they are followed by another treatment technique.

### 2.5.6 Bio-based technologies in heavy metal remediation

Bioremediation is the process which offers a green technology solution for heavy metal contamination. There are different techniques to biologically treat the wastewater containing heavy metals. These techniques are cost effective, non-invasive and efficient in treatment. Here, primary bio-removal techniques that are currently employed for heavy metal removal will be discussed below.
2.5.6.1 Bio-sorption

Bio-sorption is the adsorption of metal onto the cell surface by physiochemical mechanisms. The dead cell and metabolically inactive biomass concentrate the heavy metals present in the environment. This property can be attributed to the cell wall structure of the biomass. Recently the role of exopolysaccharides (EPS) in sequestration of heavy metals has been clearly explained (Harish et al., 2012). Although not all bio-sorbents have been systematically examined, a substantial amount of evidence has been collected which identified that ion exchange is the principal mechanism of metal bio-sorption. Bio-sorption can be divided into metabolism dependent and non-metabolism dependent. Bio-sorption can also be classified based on the location, where the metal removed is found, sites being extra cellular accumulation/precipitation, cell surface sorption/precipitation and intracellular accumulation. pH plays a very important role in bio-sorption process, as it determines the protonation and de-protonation of the binding sites thereby influencing the availability of the site to the adsorbate. By lowering the pH, the metal ions adsorbed can be released from the binding site. This property is used to recover the metal adsorbed and so regenerate the bio-sorbent.

2.5.6.2 Bio-stimulation

Bio-stimulation is a technique popularly used to promote the growth of indigenous microorganisms present in a contaminated site. This is done by supplementing the microorganisms with the necessary nutrients, which ultimately enhances the activities of heavy metal removal (Abioye, 2011). Along with supplements, the necessary environmental conditions must be provided for efficient bio-removal.

2.5.6.3 Bio-augmentation

Bio-augmentation is another approach where microorganisms capable of remediating the heavy metals are introduced into the contaminated environment to assist the indigenous microbes with the removal process. This normally involves introduction of microbial isolate or microbial consortium best suited for remediation in the contaminated site (Abioye, 2011). Sometimes, genetically modified organisms are introduced for treatment of contaminated site. A list of different types of biosorbents used for adsorbing heavy metal ions has been given in the Table 2.3.
2.5.6.4 Bio-leaching

Bio-leaching is the process of extracting heavy metals through excretion of organic acids or methylation reactions by the microorganisms (Olson et al., 2003). It can also be defined as the mobilisation of metal cations from insoluble ores by biological oxidation or complexation processes (Rohwerder et al., 2003). Two major mechanisms, namely contact and non-contact, have been reported for bioleaching. In the contact mechanism, the cells attach to the surface of sulfide mineral ores. The electrochemical process for the dissolution of sulfide minerals takes place at the interface between the cell wall and the mineral sulfide surface. The non-contact mechanism is generally exerted by phytoplanktonic bacteria which oxidise the Fe (II) ions in solution (Rohwerder et al., 2003). The resulting Fe (III) ions are reduced back to Fe (II) ions on contact with the mineral surface and enter the cycle again.

Mulligan et al. (2004) conducted a study on heavy metal leaching from low-grade mining ore using the fungal strain *Aspergillus niger*. In this study, the fungal strain *Aspergillus niger* was added to the ore along with different substrates. The different organic acids produced, were analysed along with their ability to solubilise metals. Maximum solubilisation of 68%, 46% and 34% for copper, zinc and nickel respectively, were reported to have been achieved. Bio-leaching using *Penicillium chrysogenum* strain F1 from heavy metal contaminated soil was conducted through one and two-step process (Deng et al., 2012). The two-step process had higher removals of 63% Cd, 56% Cu, 14% Pb and 54% Zn as compared to 50%, 35%, 9% and 40% of Cd, Cu, Pb and Zn, respectively. This was attributed to the increased organic acids production which further declined the pH value during the two-step process. The mass ratio of soil to culture medium was maintained at 5% (w/v) for this study. The effect of pure and mixed cultures of *Acidithiobacillus* spp was studied by Akinci and Guven (2011). In their work, single and mixed cultures of *A. thiooxidans* and *A. ferrooxidans* were examined for their metal solubilisation abilities. It was observed that *A. thiooxidans* was found to be the most effective bacteria in comparison to *A. ferrooxidans* and the mixed culture had the ability to oxidise sulfur rapidly, and grow sufficient cell concentrations in the bioleaching medium. Solubilisation efficiencies for heavy metals Cr, Cu, and Zn were 80% and 63% for Pb with *A. thiooxidans*.

Bioleaching has been commercially used due to its applicability for recovering metal from concentrates that are difficult to treat. This is most suitable for treating low concentrations of heavy metals and can be very cheap compared to other physio-chemical techniques.
Table 2.3 Biosorbents used for adsorbing heavy metals (Adopted from Wang and Chen., 2009).

<table>
<thead>
<tr>
<th>Heavy Metal Ions</th>
<th>Bacterial species</th>
<th>Biosorption Capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>Bacillus sp.</td>
<td>92.3</td>
</tr>
<tr>
<td>Pb</td>
<td>Corynebacterium glutamicum</td>
<td>567.7</td>
</tr>
<tr>
<td>Pb</td>
<td>Enterobacter sp.</td>
<td>50.9</td>
</tr>
<tr>
<td>Pb</td>
<td>Pseudomonas putida</td>
<td>56.2</td>
</tr>
<tr>
<td>Zn</td>
<td>Aphanothece halophytica</td>
<td>133</td>
</tr>
<tr>
<td>Zn</td>
<td>Streptomyces rimousus</td>
<td>80.0</td>
</tr>
<tr>
<td>Zn</td>
<td>Thiobacillus ferrooxidans</td>
<td>172.4</td>
</tr>
<tr>
<td>Zn</td>
<td>Pseudomonas putida</td>
<td>17.7</td>
</tr>
<tr>
<td>Cu</td>
<td>Bacillus sp.</td>
<td>16.3</td>
</tr>
<tr>
<td>Cu</td>
<td>Pseudomonas putida</td>
<td>96.9</td>
</tr>
<tr>
<td>Cu</td>
<td>Enterobacter sp.</td>
<td>32.5</td>
</tr>
<tr>
<td>Cu</td>
<td>Micrococcus luteus</td>
<td>33.5</td>
</tr>
<tr>
<td></td>
<td>Species</td>
<td>Value</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------</td>
<td>-------</td>
</tr>
<tr>
<td>Cd</td>
<td><em>Aeromonas caviae</em></td>
<td>155.3</td>
</tr>
<tr>
<td>Cd</td>
<td><em>Psedumonas sp.</em></td>
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</tr>
<tr>
<td>Cd</td>
<td><em>Staphylococcus xylosus</em></td>
<td>250.0</td>
</tr>
<tr>
<td>Cd</td>
<td><em>Streptomyces rimosus</em></td>
<td>64.9</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td><em>Aeromonas caviae</em></td>
<td>284.4</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td><em>Staphylococcus xylosus</em></td>
<td>143.0</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td><em>Psedumonas sp.</em></td>
<td>95.0</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td><em>Bacillus thuringiensis</em></td>
<td>83.3</td>
</tr>
<tr>
<td>U</td>
<td><em>Arthrobacter nicotianae</em></td>
<td>68.8</td>
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<tr>
<td>U</td>
<td><em>Nocardia erythropolis</em></td>
<td>51.2</td>
</tr>
<tr>
<td>U</td>
<td><em>Bacillus subtilis</em></td>
<td>52.4</td>
</tr>
<tr>
<td>U</td>
<td><em>Bacillus licheniformis</em></td>
<td>45.9</td>
</tr>
<tr>
<td>Th</td>
<td><em>Bacillus megaterium</em></td>
<td>74.0</td>
</tr>
<tr>
<td>Th</td>
<td><em>Micrococcus luteus</em></td>
<td>77.0</td>
</tr>
</tbody>
</table>
2.5.6.5 Bio-surfactants

Surfactants are compounds which can lower the surface tension of the liquid in which they are dissolved by their hydrophilic and hydrophobic groups. A decrease in the surface tension of water makes the heavy metals more available for remediation (Hashim et al., 2011). Bio-surfactants are obtained from biological sources. Biologically produced surfactants like surfactin, rhamnolipids and sophorolipids were tested for removal of heavy metals such as Cu, Zn, Cd and Ni from contaminated sites. Rhamnolipid was studied for its metal removal capacity both in liquid and foam forms (Hashim et al., 2011). Rhamnolipid type I and type II with surface tensions of 29mNm$^{-1}$ were found to be suitable for heavy metal removal. Glycolipids or lipopeptides are the best examples of low-molecular weight biosurfactants. The metals form complexes with the surfactants due to low interfacial tension and hence associate with surfactant micelles. Cd showed a removal percentage of 73.2 and Ni showed 68.1 with the pH adjusted to 10. A similar study was performed by Aşçı et al. (2010) using rhamnolipids for extracting Cd (II) and Zn (II) from quartz. An average of 66.5% and 30.3% of Zn (II) and Cd (II) respectively, was removed at high saturation metal ion loadings of quartz. Pb (II) removal from contaminated soil and water was investigated using biosurfactant, anionic, and non-ionic surfactants in continuously stirred batch reactors by Kim and Vipulanandan (2006). The removal of lead from water was dependent on the surfactant type, concentration, and its concentration in the solution. A maximum removal of 75% was achieved by bio-surfactant produced from vegetable oil at critical micelle concentration (CMC) of 10. In a different batch study by Nielson et al. (2003) 15.3% Pb removal was reported using 10 mM of rhamnolipid bio-surfactant.

2.5.6.6 Bio-precipitation

In-situ bio-precipitation (ISBP) is a process where the heavy metals are immobilised in ground water as precipitates (mainly sulphides) in the solid phase (Hashim et al., 2011). Carbon sources such as molasses, lactate, acetate and compost are injected into the aquifer where they undergo fermentation and trap the metal ions in the organic matrix. In-situ bio-precipitation is a strategy employed mainly to treat groundwater. Heavy metal ions like Mn, Cd, Ni, Co and Zn were tested for treatment using in-situ bio-precipitation (Vanbroekhoven et al., 2007). From the column tests, Ni and Co showed > 99% removal. Janssen and Temminghoff (2004) assessed in-situ bio-precipitation of Zn plume with bacterial sulphate reduction (BSR) having molasses
as carbon source in an aquifer. The pilot experiments demonstrated a Zn removal of 99.9% (from around 40 mg/L to less than 0.01 mg/L). Satyawali et al. (2010) investigated the stability of Zn and Co precipitates formed after ISBP in an artificial (made of artificial sand, artificial groundwater and carbon source) and natural solid matrix (made of natural aquifer and groundwater samples). In the artificial matrix, the Zn precipitates were not affected by the redox changes, but 58% was mobilised with sequential pH change. In natural matrix, the stability of the metal precipitates of Zn and Co was largely affected by the carbon source used. A lead resistant *Providencia alcalifaciens* 2EA strain was reported to bio-precipitate lead as lead phosphate by Naik et al. (2013). Liang et al. (2016) also examined bio-precipitation of lead using yeasts with organic phosphorus-containing substrate as the primary phosphorus source. The test results demonstrated that yeasts were capable of mediating precipitation of lead through cellular phosphatase activity.

### 2.5.6.7 Vermicomposting

Vermicomposting is the process of composting using earthworms that are present in the soil. Earthworms play an indispensable role in improving soil quality; by their burrowing, feeding, excreting and metabolic redox material, both the soil texture and nutrition content are improved. Chemical groups such as –COOH and –CO that are generated and exuded by their activity, help in acidifying the soil, thereby activating the heavy metal (Wu et al., 2010). The excretions of the earthworms facilitate the complexation and chelation of metal ions. Due to a relatively low specific surface area and small concentration, such improvements are neither notable nor stable. The effectiveness and efficiency of composting depend on environmental conditions such as temperature, pH and moisture content (de Bertoldi et al., 1983). The three conditions mentioned had a positive effect on the presence and diffusion of actinomycetes, which are particularly necessary during last stages of decomposition (de Bertoldi et al., 1983). Therefore, right conditions must prevail for effective removal of heavy metals.

### 2.5.6.8 Phytoremediation

Phytoremediation is a process that utilises plants to partially or substantially remediate the contaminated soil, groundwater or wastewater. It is also referred as green remediation, botanoremediation, agro-remediation or vegetative remediation (Wuana and Okieimen., 2011).
The advantages of phytoremediation compared with classical remediation are that it is economically viable, it is less disruptive, does not require new plant communities to recolonise the site and disposal sites are not needed. In other words, this process is more likely to be accepted as it aesthetically pleasing. It also avoids transportation of the polluted media thus reducing contamination, and has the potential to treat a site having more than one type of pollutant. Depending on the type of contaminant and underlying process, phytoremediation is broadly classified as phytodegradation, phytoextraction, phytostimulation, phytovolatilisation, and phytostabilisation (Akpor and Muchie., 2011).

Phytodegradation is the breakdown of organic contaminants by the internal and external metabolic processes of the plant. Plants generally absorb the contaminant, store and then metabolically degrade the contaminants within the tissue (Akpor and Muchie., 2011). The plants can also release exudates that help to degrade the pollutants via co-metabolism.

Phytoextraction is a type of phytodegradation whereby plants absorb, translocate, and store contaminants along with nutrients and water. This is primarily used for wastes containing metals. The process of phytoextraction is known to occur either continuously (natural) using hyperaccumulators or induced through the addition of chelates to increase bioavailability (Akpor and Muchie., 2011). Different plants have varying abilities to uptake and withstand high levels of pollutants (Akpor and Muchie., 2011).

Phytostimulation is a process where the plants release natural substances through their roots, thereby supplying nutrients to microorganisms, which in turn enhance biological degradation (Akpor and Muchie., 2011). It is a symbiotic relationship between plants and microorganisms for the degradation of contaminants. During phytostimulation, the release of organic substances and oxygen by plant roots increases the microbial activity in the rhizosphere compared to bulk soils (Akpor and Muchie., 2011). This leads to increased microbial activity, which in turn results in the stimulation of natural degradation of organic contaminants.

Phytovolatilisation makes use of the ability of a plant to take up the contaminants from the growth matrix and subsequently transform and volatilise them into the atmosphere through its leaves (Akpor and Muchie., 2011). The contaminant can be modified while it travels through the plant’s vascular system and get vaporised from the leaves. Some of the contaminants can pass through the plants to the leaves and volatilise into the atmosphere via the stomata at comparatively low concentrations. For the contaminant to enter the plant roots, they must be soluble to get adsorbed and pass through the system.
Phytostabilisation is an in-place inactivation process where the contaminants are adsorbed or accumulated onto the roots, thereby limiting their mobility and hence reducing their availability in the food chain (Akpor and Muchie., 2011). Even if the plants remove little or no contaminants, they are useful as phytostabilisation agents if they tolerate and grow under contaminated conditions. Plants used for phytostabilisation should be able to decrease the amount of water percolating through the soil matrix that may result in the formation of a hazardous leachate, and act as barrier to prevent direct contact with the contaminated soil, soil erosion and distribution of toxic metals to other areas (Akpor and Muchie., 2011).

2.6 Membrane Bioreactor Technology (MBR)

2.6.1 MBR technology

The Membrane bioreactor (MBR) process is an advanced wastewater treatment technology which uses both a biological stage and a membrane module for treatment. The bioreactor and membrane module each have a specific function: a.) biological degradation of organic pollutant by adapted microorganism and b.) separation of microorganisms from the treated water by the membrane module. The membrane module acts as a physical barrier for all suspended solids and therefore enable not only recycling of the activated sludge to the bioreactor, but also enables the production of permeate free of suspended matter, bacteria and viruses. MBR technology has proven to be quite effective in removing organic and inorganic contaminants as well as microorganisms, and so has gained popularity due to the stringent environmental regulations and growing water reuse initiatives.

2.6.2 Configurations of MBR technology

MBRs are generally available in two main configurations, external/side-stream configurations and submerged/immersed configurations. Apart from these two conventional configurations, there are other hybrid MBR systems like airlift configuration. The design of MBR systems is mainly based on the type of effluent to be treated. Figure 2.12 shows the different membrane bioreactor configuration.
Figure 2.12 Membrane Bioreactor Configurations: (a.) external configuration, (b.) submerged configuration and (c.) airlift configuration (Reproduced from Lin et al., 2012).

The external configuration involves the recirculation of mixed liquor through a membrane module that is outside the bioreactor, and usually employs high cross-flow velocity (CFV) along the membrane surface to provide the membrane driving force and to control membrane fouling (Lin et al., 2012). This configuration provides more direct hydrodynamic control of membrane fouling. Furthermore, it offers the advantages of easy membrane replacement and high flux, but at the expense of frequent cleaning and high energy consumption (Lin et al., 2012). For submerged configuration, membrane modules are directly placed in the mixed liquor. The driving force across the membrane is achieved by pressurizing the bioreactor or creating negative pressure on the permeate side. Several distinct advantages of submerged MBRs are their much lower energy consumption and less rigorous cleaning procedures. The side-stream air-lift MBR is an evolution from the previous types, which is more robust and reliable, while incorporating all the advantages of low energy-consuming submerged systems (Lin et al., 2012).
2.6.3 MBR technology for heavy metal removal

Considerable research has been conducted on treatment of heavy metal contaminated water using MBR systems. Apart from the overall heavy metal removal performance, the toxicity to the biological system by heavy metals and their contribution in fouling of membranes were also studied. Moslehi et al. (2008) studied the performance of chromium, zinc and lead removal from semi synthetic wastewater using MBR system. The toxicity of heavy metals and relative effect on COD removal was also analysed. For the heavy metals investigated, it was noticed that with an increase their concentration, the removal decreased. Chromium showed a removal efficiency greater than 95% for concentrations less than 50 mg/L. COD removal was found to be higher than 92%. Zinc removal decreased from 86 % to 76 % when its concentration increased from 10 to 50 mg/L. The MLSS concentration decreased with increase in zinc concentration, showing the impact of its toxicity on the microorganisms. Lead removal was almost 100 % for 10 mg/L concentration. However, it decreased to 60% when the concentration was increased to 50 mg/L. This had very little effect on the MLSS of the system, indicating no toxic effects of lead even at high concentrations.

Amiri et al. (2010) investigated the effects of chloride and sulphate salts of heavy metals on sludge characteristics, permeability and fouling of MBR. They reported that low concentration increase of heavy metals had a positive effect on permeability. Beyond 0.2 g/L, a negative impact on the permeability was observed, as the concentration was toxic to the sludge properties such as exopolysaccharides (EPS). Sulphate salts of Mn and Ni showed better permeability than the chloride salts, which could be due to toxicity of chloride ions to the sludge. The loosely bound EPS production increased when the concentration of heavy metals was increased from 0.1 to 0.4 g/L. For concentrations below 0.1 g/L, the loosely bound EPS concentration is lower, leading to a reduction in fouling and an increase in the membrane permeability.

Arevalo et al. (2013) investigated the heavy metal removal performance of two MBR systems having microfiltration and ultrafiltration systems working under real operating conditions. Eighteen heavy metal elements were studied and their removal performances were high, regardless of whether microfiltration or ultrafiltration membrane was used. The influence of activated sludge concentration on heavy metal removal was also analysed by having four comparison groups (< 5, 5-10,10-15 and 15-20 g/L). High removal was obtained for Cr, Ni,
Sb, Cr and Zn with an increased activated sludge concentration. For activated sludge concentrations above 10 g/L, most of the heavy metals showed removal close to 100%.

2.6.4 Challenges in MBR operation

The major drawback of MBR systems is membrane fouling. Membrane fouling is a challenging task and has been so since the inception of MBRs for wastewater treatment. Membrane fouling is caused by plugging/clogging by colloidal particles and adsorption of soluble compounds on the membrane. This results in formation of a cake layer and spatial and temporal changes in the foulant composition during long-term operation. Parameters like the feed characteristics, biomass characteristics, membrane characteristics and operational conditions play a major role in membrane fouling.

Currently most of the research on MBRs is on mitigating membrane fouling. Common fouling control strategies include gas sparging, sustainable flux operation, sludge retention time (SRT) control, activated carbon/coagulant/flocculant addition, membrane modification, backwashing and physical/chemical cleaning. These measures help to improve operational performance of the MBR systems.

Membrane modification with GO nano-platelets was studied for anti-fouling and hydrophilic properties for waste water treatment by Lee et al. (2013). The prepared membrane was also tested in an MBR system. The modified membranes had better anti-fouling property, superior mechanical strength and better water permeability.

2.7 Summary of literature review

Lead is a widely used heavy metal and is released into different water bodies by anthropogenic and natural activities. Due to its toxic effects on environment and health, it has been listed as an environmental priority pollutant (US-EPA, 2014). Remediation of lead contaminated water bodies is performed by a variety of wastewater treatment techniques to enable safe disposal and re-use.

Several treatment techniques that are currently in use include chemical precipitation, ion-exchange, adsorption, membrane and biological processes. Chemical precipitation has been traditionally carried out due to its simplicity and low cost. The major drawbacks of this
technique are the use of corrosive chemicals and generation of large volumes of wastes (US-EPA, 2000). Ion exchange resins are used to treat contaminated water with low metal ion concentration. The resins can be regenerated by cleaning with chemical reagents, which can in turn lead to a source of secondary pollution.

Adsorption is a widely-used method for treatment of heavy metal contaminated water. Many low-cost adsorbents have been developed and studied for heavy metal removal (Babel and Kurniawan, 2003). Recently, a class of carbon based nano-sorbents was developed and studied for treating pollutants in waste streams (Rao et al., 2007 and Park et al., 2008). CNTs and graphene composites were reported to show high specificity towards different heavy metals (Li et al., 2010 and Ma et al., 2012). However, the aggregation of the nano-sorbents and their separation after adsorption of the heavy metal were the major challenges encountered. Additional research on reaction parameters such as pH, contact time, temperature and stability of nano-sorbents is required.

Membrane technology (i.e., nanofiltration and reverse osmosis) can remove heavy metal ions with high efficiency. The ease of operation and the comparatively low cost, makes it an excellent choice for treatment (Hilal et al., 2004). In general, membranes suffer from fouling, leading to lower flux and reduction in their life. The fouling and low permeability are a direct result of low surface hydrophilicity and porosity (Ganesh et al., 2013). Research on improving the hydrophilicity, porosity and mechanical strength needs greater attention.

Bio-sorption is a biological treatment process where heavy metals are adsorbed onto naturally available biological materials such as seaweeds, plant materials, industrial and agricultural wastes and natural residue (Fomina and Gadd, 2014). This technique is non-invasive and has proven to remove wide variety of heavy metals from wastewater with limitation being its ability to treat only low concentrations of heavy metals.

Over the last two decades, the use of MBRs, an advanced wastewater treatment technology, well known for removing organics, inorganics and microorganisms has gained popularity. This technology offers advantages like excellent effluent quality, good disinfection capability and reduced footprint and sludge production. Majority of the studies conducted on MBR systems focussed on treatment on municipal and industrial wastes with high organic loading (Lin et al., 2012). To date, very limited studies on treatment of inorganic wastes are available, especially of heavy metals.
Graphene oxide (GO), the oxidised form of graphite, has oxygenated functional groups which makes them easily dispersable in organic solvents, water, and different matrices. This is a major benefit as it can combine with different matrices and enhance their physio-chemical and mechanical properties. GO can be functionalised with specific functional groups, targeting them for a defined application.

Nano-sorbent systems are highly specific and requires less reaction time for pollutant removal. Due to easy dispersability and functionalising ability of GO, application of GO based nano-system for treatment of lead in aqueous solution would be an ideal approach to improve their treatment capability. Membrane processes are effective treatment technology, that can be enhanced further with longer membrane life and better antifouling properties. Addition of GO can enhance the hydrophilicity, mechanical and physio-chemical properties of the membrane. MBR system is known to treat high strength wastewater by coupling biological and membrane processes. Biological process assist in degradation of organics and promotes adsorption of non-biodegradable pollutants. The membrane section helps in separation of microorganisms and provide good quality effluent. Application of GO based membranes can mitigate bio-fouling tendency, thereby increasing the life of membranes and reducing the operational costs of the system.

In the present study, graphene oxide (GO) based nano-sorbent and membrane systems was investigated for the treatment of lead ions. This study also examined the performance of the MBR system for lead ions removal.
Chapter 3

Materials and methods

This chapter explains the different materials and methods used in this thesis. The protocol for preparation, assembly and experimental procedure for adsorption of lead by GO based magnetic nano-sorbent is discussed in section 3.1. Section 3.2 describes the preparation procedure and characterisation techniques used for GO blended MF and UF membranes. Lead rejection experiments using UF membranes by cross-flow filtration is described in section 3.3. Section 3.4 describes the analytical techniques, operating conditions and experimental procedures used for lead removal using MBR with the MF membranes.

3.1 GO based magnetic nano-sorbent

This section describes the materials used, preparation protocol, characterisation techniques and experimental studies performed on the nano-sorbent PS@Fe₃O₄@GO. More detailed information is provided in subsequent result chapter wherever necessary.

3.1.1 Materials

Potassium persulfate (K₂S₂O₈ or KPS), Styrene (St) and acrylic acid (AA) and graphite were obtained from Sigma–Aldrich. Prior to experiments, St and AA were purified by distillation under reduced pressure. Ferric chloride hexahydrate, ferrous chloride tetrahydrate, sodium bicarbonate (NaHCO₃), ammonium hydroxide (NH₄OH), sodium hydroxide (NaOH) and potassium permanganate were purchased from Chem-supply Pty Ltd (Gillman, Australia). Sodium nitrate (NaNO₃), sulphuric acid (H₂SO₄) and hydrogen peroxide (H₂O₂) were purchased from Merck, Australia.

3.1.2 Synthesis of nano-components

The different components of the magnetic nano-sorbent including polystyrene (PS) nanobeads, magnetite nanoparticles (Fe₃O₄) and GO were synthesised individually.
PS nanobeads were synthesised by soap free emulsion polymerisation of styrene with acrylic acid (Wang et al., 2012). Styrene (5mL), 0.12 g NaHCO₃ and 0.5 mL acrylic acid were added to a three-necked condenser flask containing 100 mL de-ionised water and continuously stirred. KPS was used as an initiator for polymerisation. The reaction was carried out at 70˚C under N₂ atmosphere and after 12 h the resulting latex was centrifuged at 3000 rpm for 10 min and re-dispersed in de-ionised (D.I.) water.

Fe₃O₄ nanoparticles were prepared by Massart’s method (Wang et al., 2012), where 20 mL of freshly made ferric chloride hexahydrate (2.70 mM) and ferric chloride tetrahydrate (1.35 mM) were added to ammonia solution (1.5M) under N₂ atmosphere. After 30 min, magnetic decantation was performed and Fe₃O₄ nanoparticles were washed with D.I. water.

GO nano-sheets were prepared by modified Hummer’s method (Wang et al., 2012). Graphite flakes of 10 g and 7.5 g of sodium nitrate were added to 300 mL of sulphuric acid (98%). 40 g of potassium permanganate was added at a slow rate to the mixture. The container was stirred at room temperature for 3 days. A litre of hydrogen peroxide (1% in water) was added to the reaction mixture followed by filtering and washing with D.I water until the pH became 7. The dark brown mixture obtained was further dialysed against D.I. water for a week. The resulting brown suspension was dried at 40˚C and then redispersed by sonication. The redispersed GO was centrifuged at 3000 rpm for 30 min to remove the un-exfoliated GO. The resultant brown dispersion was used for the assembly of nano-sorbent.

3.1.3 Assembly of nano-sorbent

PS latex of 1 mL was added to a 5-mL dispersion of Fe₃O₄ under vigorous stirring at pH 3. After 6h, the hetero-aggregates were separated by centrifugation and washed with acidic solution (pH 3, adjusted with HCl) to remove the non-adsorbed Fe₃O₄. The resulting concentrate was re-dispersed into fresh D.I water (pH 7).

GO (20 mL) was added to the dispersed PS@Fe₃O₄ and was shaken gently for 6 h. The final product was separated using a magnet and washed three times with D.I water to remove the non-adsorbed GO nano-sheets.
3.1.4. Characterisation of the nano-sorbent

The morphologies and the structure of nano-components were studied under scanning electron microscopy (SEM) (Supra, SEM 55VP), atomic force microscopy (AFM) (Bruker, Nanoscope) and transmission electron microscopy (TEM) (JEOL-2100 microscope operated at 200kV). Optical absorption spectra were measured using Merck Spectroquant Pharo 300. The curves of magnetisation versus applied magnetic field (M–H) were measured at room temperature using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design Inc). The Fourier transform infrared (FT-IR) spectra were measured using Bruker Vertex 70 FT-IR spectrophotometer using the KBr pellet method. X-ray photoelectron spectroscopy (XPS) analysis was performed on the Pb (II) interacted and un-interacted nano-sorbent using Thermo ESCALAB 250 spectrometer with Mg Kα (1253.6eV) achromatic X-ray source. Zeta potentials of the nano-components and the sorbent were measured using a Malvern Zetasizer Nano-ZS. The Pb (II) concentrations were measured by atomic absorption spectroscopy (AAS) using Varian AA140 at 217 nm.

3.1.5. Adsorption test

Adsorption experiments were designed to evaluate the effect of contact time, pH and temperature on Pb (II) removal. Lead solution (10 mg/L) was prepared by using stock lead nitrate solution (100 mg/L). Prepared lead solution of 23 mL at pH 4.3 was reacted with 2 mL of PS@Fe₃O₄@GO (0.002 g/mL). To estimate the equilibration time, samples were collected at 2, 4, 6, 8, 12, 16 and 24 h after interaction. With an optimised contact time (8 h), the effect of pH on adsorption was studied by varying the pH from 3 to 7 with nitric acid (HNO₃) and sodium hydroxide (NaOH). The effect of temperature on adsorption was studied at 20, 25, 30 and 35 °C at an optimised pH (pH 6) and contact time. After each adsorption experiment, samples were subjected to an external magnetic field to separate the Pb (II) loaded sorbent PS@Fe₃O₄@GO from the solution. The residual lead concentration in the supernatant was then measured using AAS. Lead samples was acidified using 40% nitric acid prior to estimation using AAS.
3.1.6. Adsorption kinetics study

Kinetic experiments were performed by adding 2 mL of 0.002 g/mL of the synthesised PS@Fe₃O₄@GO to the prepared 10 mg/L of lead concentration at different pH ranging from 3 to 7, stirring at 150 rpm and temperature maintained at 35°C (optimised temperature). Samples were withdrawn at specified time intervals. After magnetic separation, the residual lead concentration was measured and the sorption quantity at a given time was calculated using the formula:

\[ q_t = \frac{(C_0 - C_t) V}{m} \]  (3.1)

Where \( q_t \) is sorption quantity (mg/g), \( C_0 \) and \( C_t \) (mg/L) are the concentrations of lead initially and at time \( t \), \( V \) (L) is the total volume of the interaction medium and \( m \) is the mass (g) of the PS@Fe₃O₄@GO nano-sorbent.

3.1.7. Adsorption isotherm and thermodynamic study

Adsorption isotherms were determined by adding 2 mL of 0.002 g/mL of the synthesised PS@Fe₃O₄@GO into 23 mL of lead solution with concentrations of 2.5, 5, 7.5 and 10 mg/L at 20, 25, 30 and 35°C respectively. The pH was maintained at 6 for all the experiments. The amount of adsorption at equilibrium (\( q_e \)) was calculated by

\[ q_e = \frac{(C_0 - C_e) V}{m} \]  (3.2)

Where \( q_e \) is sorption quantity (mg/g) at equilibrium, \( C_e \) (mg/L) is the concentrations of Pb (II) at equilibrium, \( V \) (L) is the total volume of the interaction medium and \( m \) is the mass (g) of PS@Fe₃O₄@GO nano-sorbent. The obtained data was modelled with different isotherms and was further utilised to determine the spontaneity of the adsorption process.

3.1.8. Recoverable lead removal capacity of PS@Fe₃O₄@GO

The lead recoverable from the adsorbent was determined by adding 2 mL of 0.002 g/mL of the synthesised PS@Fe₃O₄@GO to the prepared 10 mg/L of lead concentration at pH 6, stirring at 150 rpm at 35°C. Following the adsorption, the PS@Fe₃O₄@GO nano-sorbent was separated
using a magnet and was gently washed with 10% nitric acid (HNO₃) to desorb the lead ions for 24 h. The nano-sorbent was separated and then reacted with fresh lead solution (10 mg/L) for re-adsorption. The reusability of the prepared adsorbent was studied for four consecutive cycles. Lead concentrations after adsorption and desorption were measured using AAS.

De-ionised (D.I.) water was used throughout the whole synthesis and experimental processes and was produced by a Milli-Q system (Millipore) with a resistivity of 18 MΩ/cm. Each batch of the synthesised individual components were characterised before assembly for quality control. After each successful assembly, the nano-sorbent was once again characterised and compared prior to the adsorption experiments. Each set of experiments were carried out in triplicate. Experiments were repeated separately to ensure reproducibility.

### 3.2 GO blended PSf microfiltration and ultrafiltration membranes

This section describes the materials used, preparation protocol and characterisation techniques of GO blended PSf microfiltration and ultrafiltration membrane. Further details are given in result chapter five and six wherever necessary.

#### 3.2.1 Materials

Polysulfone (average Molecular Weight ~35,000) (PSf) and Graphene oxide powder (GO) were purchased from Sigma Aldrich. 1-Methyl-2-pyrrolidone EMPLURA (NMP) was purchased from Merck.

#### 3.2.2 Preparation of GO blended PSf membranes

The PSf was held in an oven at 100°C overnight to remove any moisture, and then cooled to room temperature in a desiccator. The desired amount of PSf (15, 18 and 20 %) was then added to NMP (making the total to 100 wt%) and mixed at 50°C, shaking at 300 rpm overnight. For the GO blended PSf membranes, different amounts of GO (0.125, 0.25 and 1 %) were added to NMP (making it to 100 wt % with PSf) and sonicated (1-3 hrs) prior to the addition of PSf. After overnight mixing of polymer and solvent (with/without GO), sonication was performed for an hour to remove any trapped air bubbles. The solution was cooled to room temperature and then cast on a glass plate using a casting knife (Elcometer, 3580). After casting, the glass plate was transferred to a bath maintained at 20-30°C and allowed to cure (Appendix A-1).
After 10 min, the membrane formed was transferred to a fresh tray of de-ionised water for storage.

In the case of ultrafiltration membranes, three blends namely 15% PSf, 15% PSf - 0.25% GO and 15% PSf - 1% GO were chosen and cast. The membranes were cured in a de-ionised water bath with 5% ethanol prior to storage (Appendix A-2).

3.2.3 Characterisation of the prepared membranes

a) Hydrophilicity- Water Contact angle

The hydrophilicity of the membrane was measured using a water contact angle goniometer (contact angle and surface energy system, OCA). A small droplet was placed on the membrane surface using a micro syringe and the contact angle was measured after 30 seconds (Appendix A-3). To ensure repeatability, a minimum of five contact angle readings were taken on different sections of the prepared membranes and an average value was calculated.

b) Tensile strength test

Membrane samples of 15 mm wide and 100 mm long were cut and placed in between the clamps of Instron 4467 tensile testing instrument. The distance between the two clamps was set as 75 mm, to ensure sufficient length of sample was available. The average thickness of the sample was calculated using a digital thickness gauge and fed into the operating software. Tensile strength tests were performed at room temperature with a strain rate of 2 mm/min. Young’s modulus and elongation at break were calculated from an average of five tests for each sample (Appendix A-4).

c) Scanning Electron Microscopy

The surface and cross sectional morphology of the prepared membranes were analysed using a FEI Quanta Scanning Electron Microscope. The samples for SEM were prepared by cutting small pieces of the membrane (surface and thin areas of cross sections), adhering them to carbon tape on an aluminium sample stub and coating with platinum (3 nm) using a precision etching and coating system (PECS).
d) Membrane permeation - Pure water flux

Pure water flux for the membranes was determined using a cross flow filtration rig (Figure 3.1 & Appendix A-5) with a membrane area of 0.0075 m². The permeation tests were conducted at 20 °C and at 1, 2 and 3 bar pressure for half an hour until a steady flux was obtained. The pure water flux of the membranes was calculated using equation 3.3:

\[ J_w = \frac{V}{St} \]  

(3.3)

where, \( J_w \) is the pure water flux, \( V \) is the volume of permeate collected (L), \( S \) is the surface area of the membrane (m²) and \( t \) is the time (h) for which the experiments were performed.

Figure 3.1 Schematic of cross flow membrane filtration equipment.
e) Porosity

The porosity of the membrane was calculated by the dry-wet weight method (Zhao et al., 2013). Membrane samples of 50 mm x 50 mm were cut and placed in water overnight. The wet membranes were weighed using an analytical balance that was capable of measuring to five decimals. The samples were then dried at room temperature overnight and weighed. The thickness of the membranes was measured using Vernier caliper. Based on the wet and dry weight, the porosity was calculated by equation 3.4:

\[ P_r = \frac{(m_w - m_d)}{\rho_S l} \]  

(3.4)

where, \( P_r \) is the porosity, \( m_w \) and \( m_d \) are the wet and dry weight (g), \( \rho \) is the density of water (0.998 g/mL) at 20 °C, \( S \) is the membrane area (m\(^2\)) and \( l \) is the thickness (m).

f) Pore size

The average pore size (\( r_m \)) of the membranes was calculated using the Guerout-Elford-Ferry equation. Results from the permeation tests, i.e., flow rate, membrane thickness, membrane surface area, operational pressure and porosity values obtained from the dry-wet weight tests were used to calculate the pore size using equation 3.5

\[ r_m = \sqrt{\frac{(2.9-1.75\varepsilon)\times 8\eta lQ}{\varepsilon A \Delta P}} \]  

(3.5)

where, \( r_m \) is the mean pore radius, \( \varepsilon \) is the porosity, \( \eta \) is the viscosity of the water at 25 °C (8.9 x 10\(^{-4}\) Pa.s), \( l \) is the membrane thickness (m), \( Q \) is the flow rate of water (m\(^3\)/s), \( A \) is the membrane area and \( \Delta P \) is the operational pressure (Pa).
3.3 Lead ions removal using ultrafiltration membranes

The prepared PSf and PSf-GO ultrafiltration membranes were tested for lead rejection using cross flow filtration setup. This section describes the experimental setup, operational condition and rejection calculations used in chapter six of this thesis.

3.3.1 Cross flow filtration rig setup and operating conditions

Figure 3.1 gives the schematic of the cross-flow rig setup used for the lead rejection experiments. The rig consisted of stainless steel membrane housing with a surface area of 0.0075 m². The retentate stream was sent back to the feed stream thereby concentrating it. The feed flow pump frequency was set at 30 Hz. This was maintained constant during the experiment.

3.3.2 Lead rejection

Lead rejection experiments were performed at 3 different pressures, i.e., 1, 2 and 3 bar at 20 °C. Initial lead concentration of 50 mg/L was prepared from 1000 mg/L lead nitrate stock. The feed solution was maintained around pH 6 using NaOH and HNO₃. The permeate samples were collected after 30 min and analysed for lead concentration by Atomic Absorption spectroscopy (AAS) Varian AA140 at 283 nm. The pure water flux was estimated using equation 3.3. The rejection was calculated using the following equation:

\[ R = 1 - \frac{C_p}{C_f} \]  

(3.6)

where, \( C_p \) and \( C_f \) are the concentration of lead in permeate and feed respectively.
3.4 Membrane Bioreactor system with microfiltration membranes for lead ions removal

This section describes the MBR setup, materials, analytical techniques, operating conditions, experimental protocol and mass balance equations for lead used in chapter seven of this thesis.

3.4.1 A2O MBR system

Figure 3.2 shows a schematic of the MBR system (Appendix A-6). The hydraulic capacities of the anaerobic, anoxic and oxic (aerobic) tanks were 3, 5 and 10 litres, respectively. The MBR was initially seeded with activated sludge (Table 3.1) from Anglesea Wastewater Reclamation Plant situated near Geelong, Australia, and acclimatised to the synthetic feed for four weeks.

In order to increase the microbial population by increasing the surface area for attachment, 20 and 30 polypropylene bio-balls (40 mm ø and 450 m²/m³ of surface area) were added to the anaerobic and anoxic tanks, respectively. Flat sheet PSf membranes with or without GO (having a surface area of 0.0196 m² and pore size of 0.2-0.3 µm) were attached to the membrane module and immersed in the oxic tank. Air was supplied to the oxic tank through a central compressed air system via air flow meter and air stones. The dissolved oxygen in the oxic tank was maintained at 7 mg/L by controlling the air flow to 0.2 m³/h. In order to maintain anaerobic conditions, nitrogen gas was sparged to the anaerobic tank.

Synthetic feed having the composition similar to that of wastewater (given in Table 3.2) was fed at 3 L/day (Rondon et al., 2015). The hydraulic retention times of the anaerobic, anoxic and the oxic tanks were 0.5, 0.8 and 1.6 days, respectively. Mixed liquor recirculation was provided between the oxic and the anoxic tanks at the rate of 6 L/day. A peristaltic pump was used for transferring the feed to the anaerobic tank. The overflow from the anaerobic tank reached the oxic tank through the anoxic tank and a second peristaltic pump was used for recirculation from the oxic to the anoxic tank. Finally, a third peristaltic pump was used as a suction pump, to draw the permeate from the oxic tank through the flat sheet membrane. The third peristaltic pump was connected to an electronically controlled timer to enable suction on/off period of 8.5 min/1.5 min. During the off period, air was supplied to the module to backwash the membrane. The TMP was monitored using a vacuum pressure gauge fitted between the membrane module and the suction pump.
The permeate obtained from the oxic tank through the membrane was passed through a UV disinfection unit (254 nm, 6.602 Wsec/cm²; 20.3 W) before reaching the permeate tank (Figure A-11).

Table 3.1 Characteristics of activated sludge.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.9</td>
</tr>
<tr>
<td>Conductivity (µS/cm)</td>
<td>1667.5</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>1067.5</td>
</tr>
<tr>
<td>Temperature (ºC)</td>
<td>18.5</td>
</tr>
<tr>
<td>D.O. (mg/L)</td>
<td>0.44</td>
</tr>
<tr>
<td>ORP (mV)</td>
<td>-220.4</td>
</tr>
</tbody>
</table>

Figure 3.2 Schematic of MBR system.
**Table 3.2** Synthetic feed composition.

<table>
<thead>
<tr>
<th>Constituent Salt</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose (C₆H₁₂O₆)</td>
<td>710 mg/L</td>
</tr>
<tr>
<td>Ammonium acetate (CH₃COONH₄)</td>
<td>200 mg/L</td>
</tr>
<tr>
<td>Sodium hydrogen carbonate (NaHCO₃)</td>
<td>750 mg/L</td>
</tr>
<tr>
<td>Ammonium chloride (NH₄Cl)</td>
<td>30 mg/L</td>
</tr>
<tr>
<td>Potassium dihydrogen phosphate (KH₂PO₄)</td>
<td>30 mg/L</td>
</tr>
<tr>
<td>Potassium hydrogen phosphate (K₂HPO₄)</td>
<td>60 mg/L</td>
</tr>
<tr>
<td>Magnesium sulphate (MgSO₄.7H₂O)</td>
<td>50 mg/L</td>
</tr>
<tr>
<td>Calcium chloride (CaCl₂.2H₂O)</td>
<td>30 mg/L</td>
</tr>
<tr>
<td>Sodium chloride (NaCl)</td>
<td>30 mg/L</td>
</tr>
<tr>
<td>Lead Nitrate (PbNO₃)</td>
<td>5 mg/L</td>
</tr>
</tbody>
</table>

### 3.4.2 Operational conditions of the MBR

The constructed MBR was operated for over a period of 1 year and its operational performance was monitored. **Table 3.3** gives the chronological sequence for different quarters of MBR operation.

In the first quarter, the A2O MBR system was seeded with activated sludge and the biological performance acclimatised to the conditions mentioned in **Table 3.3**. The membrane module having virgin PSf membrane was installed in the aerobic tank. Minor tweaks on the feed flow
rate, recirculation rate, pump and timer settings of the MBR system was also carried out during this quarter. In the second quarter, lead ions were introduced at a concentration of 5 mg/L along with an increased glucose concentration. This was done to overcome the impact of the addition of lead into the system. The overall nutrient and Pb removal performance of the MBR system was also being monitored from this quarter.

3.4.3 Short term critical flux experiments

Several short term critical flux experiments were performed for the chosen membranes namely 15 % PSf, 15 % PSf - 0.25 % GO, 15 % PSf - 1 % GO and 20 % PSf - 1 % GO, using the common flux step method. The flux step method involves step-wise increments of flux for a set duration. During the increments, the transmembrane pressure (TMP) is monitored. The tests were performed either by continuous or intermittent permeate suction with or without backwash. The flux step duration was 30 min. The flux step height and the starting flux of different membranes are listed in the Table 3.4.

The flux step increments were calculated based on the suction pump flow rate indicated on the motor. The suction pressure increments were performed at a rate of 2.5 mL/min (from 2.5 to 10 mL/min) over the four step increments. Virgin membranes used for each experiment were run until it reached a maximum TMP of 45 kPa.
Table 3.3 Operational characteristics of the MBR.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Quarter 1 (0-90 days)</th>
<th>Quarter 2 (90-180 days)</th>
<th>Quarter 3 (180-270 days)</th>
<th>Quarter 4 (270-365 days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent feed flow rate, Q (L/d)</td>
<td>5</td>
<td>5</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Glucose in Feed solution (mg/L)</td>
<td>710</td>
<td>2500</td>
<td>2500</td>
<td>710</td>
</tr>
<tr>
<td>Flux (L/m²h)</td>
<td>10.62</td>
<td>10.62</td>
<td>6.37</td>
<td>6.37</td>
</tr>
<tr>
<td>Hydraulic retention time (HRT), h</td>
<td>86.4</td>
<td>86.4</td>
<td>144</td>
<td>144</td>
</tr>
<tr>
<td>Solid Retention time (SRT), days</td>
<td>Infinite</td>
<td>Infinite</td>
<td>Infinite</td>
<td>Infinite</td>
</tr>
<tr>
<td>Recirculation rate (L/d)</td>
<td>10</td>
<td>10</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Influent COD/TP ratio</td>
<td>52.6</td>
<td>64.6</td>
<td>64.6</td>
<td>46.8</td>
</tr>
<tr>
<td>Influent COD/TN ratio</td>
<td>24.1</td>
<td>44.2</td>
<td>44.2</td>
<td>20.2</td>
</tr>
<tr>
<td>Influent COD/TN/TP ratio</td>
<td>51.6/2.2/1</td>
<td>64.6/1.52/1</td>
<td>64.6/1.52/1</td>
<td>47/1.73/1</td>
</tr>
<tr>
<td>Lead (Pb(II)) ions concentration (mg/L)</td>
<td>-</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Events carried out</td>
<td>Day 14 – PSf membrane was introduced</td>
<td>Day 109 – Pb (II) ions were introduced in the form of lead nitrate</td>
<td>Day 210 – Short term critical flux experiments were carried out</td>
<td>Day 301 – GO-PSf membrane was introduced</td>
</tr>
</tbody>
</table>
Table 3.4 Short term critical flux test conditions. (Note: Higher starting flux for 15 PSf -1 GO and 20 PSf – 1 GO was due to higher hydrophilicity and porosity of the membranes).

<table>
<thead>
<tr>
<th>Membrane Composition</th>
<th>Flux step height (L/m²h)</th>
<th>Starting Flux (L/m²h)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Continuous Mode</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 PSf</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>15 PSf - 0.25 GO</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>15 PSf - 1 GO</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>20 PSf - 1 GO</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td><strong>Intermittent Mode</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 PSf</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>15 PSf -0.25 GO</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>15 PSf - 1 GO</td>
<td>2</td>
<td>11</td>
</tr>
<tr>
<td>20 PSf - 1 GO</td>
<td>2</td>
<td>6</td>
</tr>
</tbody>
</table>

3.4.4 Long term TMP of MBR

The MBR was operated with 15 % PSf membrane for the first two quarters at a flux of 10.62 L/m²h. During the fourth quarter, 15 % PSf membrane and 15 % PSf - 1% GO membrane were used for MBR operation at a flux of 6.37 L/m²h which was below their critical flux value. The TMP during the period of operation was constantly monitored using the installed pressure gauge.

3.4.5 Mass balance for lead

To understand the mechanism of Pb ions removal process, a mass balance for lead was performed. This was done by using a simple equation

\[
\text{Mass (Pb}_{\text{in}}) = \text{Mass (Pb}_{\text{accumulated}} + \text{Mass (Pb}_{\text{out}}) \quad (3.7)
\]

where \( \text{Mass (Pb}_{\text{in}} \) is amount of lead entering the system (mg/day), \( \text{Mass (Pb}_{\text{accumulated}} \) is the amount of lead accumulated in the system (mg/day) and \( \text{Mass (Pb}_{\text{out}} \) is amount of lead coming
out of the system (mg/day). Figure 3.3 shows the schematic of the mass balance for Pb in the MBR system.

**Figure 3.3** Schematic of mass balance equation for lead.

Samples were collected at the different sampling points (shown in Figure 3.3) based on the individual tank retention times (0, 24, 40, 80 and 80 h for feed, anaerobic, anoxic, aerobic recirculation and permeate tanks, respectively). For mass balance calculations, it was assumed that all tanks had reached a steady state conditions. The concentration of lead (Pb) in these samples was averaged from three samples and was used in the mass balance equations as listed below.

\[ Q_0 C_0 = Q_0 C_1 + E \]  

\[ Q_0 C_1 + Q_1 C_4 = (Q_0+Q_1) C_2 + F \]  

\[ (Q_0+Q_1) C_2 = Q_1 C_4 + Q_0 C_3 + G \]

where \( Q_0 C_0 \) is the mass of lead entering from feed tank to anaerobic tank (mg/d), \( Q_0 C_1 \) mass of lead entering to anoxic tank from anaerobic tank (mg/d), \( Q_1 C_4 \) mass of lead recirculated from aerobic tank to anoxic tank, \( (Q_0+Q_1) C_2 \) mass of lead entering from anoxic tank to aerobic
tank, $Q_0C_3$ mass of lead coming out from the membrane as permeate, $E$ is the mass of lead accumulated in anaerobic tank, $F$ is the mass of lead accumulated in anoxic tank and $G$ is the mass of lead accumulated in aerobic tank.

### 3.4.6 Scanning Electron Microscopy-Energy Dispersive X-ray spectroscopy (SEM-EDS)

In order to study the membrane surface morphology and its composition, SEM-EDS analysis were performed using FEI Quanta Scanning Electron Microscopy. The samples for SEM were prepared by cutting small pieces of the membrane (surface and thin areas of cross sections) and coating with carbon using standard technique. The sample composition was characterised using Aztec Energy EDS microanalysis software.

### 3.4.7 Analytical techniques

The parameters of pH, conductivity, total dissolved solids, temperature, dissolved oxygen (D.O.) and oxidation reduction potential (O.R.P.) of the MBR were monitored using Hach probe (MM150 Portable Multi Meter). Turbidity of the permeate was measured using the Hach (2100N) turbidimeter. MLSS was measured using the standard method 2540 (APHA,1985).

COD was measured by the reactor digestion method (Method 8000) using Hach high range COD test kits. Total Nitrogen (TN) and total phosphorus (TP) were estimated using persulfate digestion (method 10072) and molybdovanadate (method 10127) method using high range Hach kits. Ammonia (NH$_3$-N) was estimated using high range Hach kit by salicylate method (method 10031). Nitrate (NO$_3$-N) and nitrite (NO$_2$-) were estimated using cadmium reduction (method 8171) and ferrous sulfate method (method 8153), respectively. All samples were centrifuged for 5 minutes at 3000 rpm and the supernatant was used for analysis. Lead in the samples was estimated after filtering them using Atomic Absorption spectroscopy (AAS) Varian AA140 at 217 nm.
3.5 Summary

This chapter summarises the experimental procedures used to achieve the set objectives of the study. GO based nano-sorbent and membranes were prepared and characterised. Three systems namely nano-sorbent, membrane and MBR were studied for the removal of lead ion from aqueous solution. Relevant experimental protocols and analytical methods were also discussed. The role of GO on lead removal through these three systems were systematically analysed and discussed in the subsequent chapters.
Chapter 4

Removal of Pb (II) ions using polymer based graphene oxide magnetic nano-sorbent

4.1 Introduction

Water pollution is considered to be the world’s biggest threat and is expected to cause severe health risk. With widespread awareness on the water woes, enforcement of stringent regulations is being imposed to efficiently use water resource by treating the contaminated water and re-using it.

Lead (Pb) is a common heavy metal pollutant which is quite prevalent in industrial wastewater. It is non-biodegradable and can accumulate in living organisms causing serious disorders such as renal impairment, anaemia, haemolysis, liver dysfunction and neuronal cell injury (Järup, 2003 and Musico et al., 2013). Consequently, World Health Organisation (WHO) has set the permissible limit of lead in drinking water to be 0.01 ppm (Bhattacharjee et al., 2003). Technologies such as membrane separation (Van der Bruggen et al., 2003), adsorption, ion-exchange, coagulation, precipitation and bio-sorption are being currently used for treating lead contaminated water (Fu and Wang, 2011). Among these technologies, adsorption is the most widely preferred choice due to its simplicity of use and low cost (Monser and Adhoum, 2002). Carbon based adsorbents are extensively used for treating wide variety of pollutants in wastewater (Pham et al., 2013). Recent advancements in nanotechnology has contributed to generation of carbon based nanomaterials like graphene (Huang et al., 2011), fullerenes (Cheng et al., 2004) and carbon nano-tubes (Stafiej and Pyrzynska, 2007) with increased surface area, higher adsorption capacity and fast kinetics (Cheng et al., 2004). Graphene oxide (GO), an oxidised form of graphene, can readily participate in chemical reactions (Dreyer et al., 2010) with a wide range of pollutants and has been extensively studied for heavy metal removal application. However, the application of GO is limited by the difficulty in its separation after adsorption and possible agglomeration and restacking due to the π-π interactions between the GO nano-sheets (Zhang et al., 2013). The addition of magnetic nanoparticles can prevent the restacking of GO nano-sheets and provide an easy way for the separation of GO after adsorption.
Magnetic nano-composites have successfully established themselves as effective heavy metal adsorbents due to several attributes including high loading capacity and easy manipulation by external magnetic field. Magnetic nano-composites are generally composed of magnetic elements like iron, cobalt, nickel or their oxides such as haematite (Fe₂O₃), magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃), nickel ferrite (NiFe₂O₄) and cobalt ferrite (CoFe₂O₄) with a “chelator” coating, with functional groups like amino, imines and thiols which help in creating a strong affinity towards heavy metal ions (Gómez-Pastora et al., 2014). High accuracy and super-paramagnetic behaviour help them to overcome the problems of separation and regeneration.

In this chapter, a spherical magnetic nano-composite which has a polystyrene latex carrier loaded with Fe₃O₄ nanoparticles and GO on the outside shell (denoted as PS@Fe₃O₄@GO) was synthesised and investigated for Pb (II) ions removal. The parameters including pH, temperature and contact time were optimised for Pb (II) ions removal and the obtained data was modelled for adsorption kinetics, adsorption isotherms and thermodynamics. The possible mechanism of Pb (II) adsorption onto the nano-sorbent was also proposed according to the FT-IR and XPS results. The regeneration and reuse of the nano-sorbent was also investigated using HNO₃ to desorb the lead.

4.2 Characterisation of the synthesised nano-component and preliminary lead removal study

4.2.1 Characterisation of the synthesised nano-components and the assembled nano-sorbent

PS@Fe₃O₄@GO was prepared according to a self-assembly based on electrostatic interaction (Wang et al., 2012). In this method, PS nanobeads, Fe₃O₄ nanoparticles and GO nano-sheets were synthesised separately. Typical morphologies of each component are shown in Figure 4.1. PS nano-beads were found to be around 400 nm (Figure 4.1a), and the magnetite (Fe₃O₄) nanoparticles were found to be ~10 nm (Figure 4.1b).

GO nano-sheets were synthesised according to modified Hummer’s method. Figure 4.1c shows the AFM image of the GO nano-sheets having a thickness of 1-2 nm. The synthesised GO nano-sheets were observed to be thicker compared to the pristine graphene sheets (usually are
about 0.34 nm). This may either be due to the transformation of the sp2 hybridised planar form of carbon in graphene sheets to distorted sp3 hybridised geometry of carbon in graphene oxide, or due to the multi layering of nano-sheets in the sample observed (Stankovich et al., 2007). The UV-Vis spectrum of the synthesised GO shows the characteristic absorption peak at 224 nm and a shoulder peak at 261 nm (Li et al., 2012) (Figure 4.1d). The zeta potential of PS, Fe₃O₄ and GO was found to be -44.9, +16.9 and -47.9 mV.

Fe₃O₄ nanoparticles and GO nano-sheets were consecutively deposited on the PS nano-beads to construct the PS@Fe₃O₄@GO composite. Electrostatic interaction was utilised as the driving force to self-assemble the components. After mixing the positively charged Fe₃O₄ with the negatively PS, the PS@Fe₃O₄ obtained was found to be positively charged with a zeta potential of +34.5 mV, which is close to that of Fe₃O₄. GO is negatively charged due to the presence of carboxyl, hydroxyl and epoxy groups. Hence the self-assembly of GO on the PS@Fe₃O₄ surface can readily take place through electrostatic interactions. The assembled PS@Fe₃O₄@GO composite had a zeta potential of -16 mV and its isoelectric point was found to be 2.5. The surface area of the assembled PS@Fe₃O₄@GO nano-sorbent was estimated to be 28.15 m²/g.
Figure 4.1. (a.) SEM image of Polystyrene (PS) nano-beads, (b.) TEM image of magnetite (Fe₃O₄) nanoparticles, (c.) AFM image of the synthesised GO and (d.) UV-Vis spectra of synthesised GO.

Figure 4.2a shows a typical morphology of the prepared PS@Fe₃O₄@GO. The PS@Fe₃O₄@GO composite maintained its spherical morphology after assembly. Fe₃O₄ and GO dispersed densely and evenly on the surface of the PS nano-beads. The size of the synthesised PS@Fe₃O₄@GO composite was found to be in the range of 410-420 nm. These results were well corroborated with the TEM findings (Figure 4.2b). The TEM image clearly shows the core shell structure of the synthesised nano-composite. The dark spots on the PS nano-beads reveals the presence of Fe₃O₄ nanoparticles layered on them.
The magnetisation curve of PS@Fe₃O₄@GO was measured at room temperature (Figure 4.2c). The saturation magnetisation of PS@Fe₃O₄@GO was found to be 7.8 emu/g, which was lesser than that of the Fe₃O₄ nanoparticles (33.93 emu/g). The decrease in saturation magnetisation of the nano-sorbent may be attributed to the lower amount of Fe₃O₄ in the nano-sorbent. The magnetic remnant was nearly zero, indicating no remaining magnetisation upon removal of the external magnetic field. This super paramagnetic property of the assembled nano-sorbent enables its ready separation in aqueous solution using a conventional magnet.

4.2.2 Removal of Pb (II) ions by the nano-sorbent (PS@Fe₃O₄@GO)

A preliminary lead adsorption and separation study was performed by interacting lead solution (10 mg/L) with 2 mL of nano-sorbent (0.002 g/mL) at pH 4. Figure 4.3 shows the magnetic separation of the PS@Fe₃O₄@GO from the host liquid. The colour of the initial PS@Fe₃O₄@GO was brownish, after application of the external magnetic field, the PS@Fe₃O₄@GO was concentrated to the side of magnet. Lead (Pb (II)) of 4.7 mg/L was found in the supernatant after adsorption.
4.3 Optimisation of parameters, adsorption- kinetics, isotherm and mechanism

4.3.1 Effect of contact time on lead adsorption

Figure 4.4a shows the removal percentage as a function of contact time ranging from 2 to 24 h. The adsorption process of Pb (II) ions was rapid and reached equilibrium in 4 h. This quick adsorption process maybe attributed to the two dimensional flat structure of GO which promotes adsorption, as it exposes the active sites sufficiently to facilitate interaction with the Pb (II) ions in the medium. Similar equilibration times have been reported by Musico et al. (2013) and Yang et al. (2014) for lead adsorption by a polymer based graphene oxide nano-composite and poly (O-phenylenediamine)/reduced graphene sheets respectively.
4.3.2 Effect of pH on lead adsorption

pH has a critical effect on the surface charge of adsorbents, degree of ionisation and speciation of the adsorbate. Figure 4.4b shows the effect of pH on the adsorption of Pb (II) ions. It shows that the Pb (II) removal efficiency increased with increase of pH from 3 to 7. The free \(-\text{COO}^-\) and \(-\text{O}^-\) sites on the GO are protonated at low pH, resulting in decreased adsorption of the Pb (II) ions. With increasing pH, more sites are available for adsorption of Pb (II) ions, and 93.5\% of Pb (II) ions were removed from the solution at pH 6. The removal efficiency increased to 98\% when the pH increased to 7. Since Pb (II) may precipitate as Pb (OH)$_2$ at pH 7 (Liu and Liu, 2003), pH 6 was chosen as the optimal pH for carrying out the adsorption studies.

4.3.3 Effect of temperature on lead adsorption

The effect of temperature on Pb (II) adsorption was investigated at 20, 25, 30 and 35 °C. Figure 4.4c shows the removal percentage of Pb (II) at different temperatures. The removal efficiency of Pb (II) ions increased from 68.56 \% at 20° C to 88.81\% at 35° C, indicating that the adsorption process was favourable at higher temperature. With the increase of temperature, the movement of Pb cations in the solution increases thereby increasing the chances of adsorption onto the GO present in the nano-sorbent. Similar results were reported by Ganesan et al. (2013) on adsorption of nitrate ions by graphene in aqueous solutions.
Figure 4.4 (a.) Effect of contact time on lead removal (Operating conditions: Pb (II) concentration = 10 mg/L and pH = 4.3), (b.) Effect of pH on lead removal efficiency (Operating conditions: Pb (II) concentration = 10 mg/L and contact time = 8 h) and (c.) Effect of temperature on lead removal (Operating conditions: Pb (II) concentration = 10 mg/L, contact time = 8 h and pH = 6). Data expressed in Mean ± 3 S.D.

4.3.4 Adsorption kinetics study

To understand the adsorption behaviour of Pb (II) ions onto the synthesised nano-sorbent, adsorption kinetics study was carried out. The data was modelled with pseudo first and pseudo second order kinetic models. Pseudo first order model is represented by the following equation:

\[
\log (q_e - q_t) = \log q_e - \left( \frac{k_1}{2.303} \right) t \quad (4.1)
\]
where, $q_e$ and $q_t$ are adsorption capacities at equilibrium and time $t$, $k_1$ is the rate constant of the reaction. The slope and intercept of the plots of $\log (q_e - q_t)$ versus $t$ is used to determine the rate constant for pseudo-first-order.

Pseudo second order kinetics model is represented by the equation:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2t \quad (4.2)$$

where, $k_2$ is the rate constant of the reaction. The slope and intercept of the plots of $1/(q_e - q_t)$ versus $t$ is used to determine the pseudo-second-order rate constant.

It was observed that adsorption of Pb (II) onto PS@Fe$_3$O$_4$@GO nano-sorbent followed pseudo first order kinetics model. The pseudo first order kinetic is shown in Figure 4.5a. The correlation coefficients of pseudo first order kinetics model suggest adsorption of Pb (II) onto the nano-sorbent is based purely on the number of active sites present on the adsorbent.

**Table 4.1.** Pseudo first order kinetics parameter at different pH (Operating conditions: Pb (II) concentration = 10 mg/L, temperature = 35º C and contact time =8 h).

<table>
<thead>
<tr>
<th>pH (Experimental)</th>
<th>$q_e$ (mg/g)</th>
<th>$k_1$ (min$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>14.75</td>
<td>0.00783</td>
<td>0.9873</td>
</tr>
<tr>
<td>4</td>
<td>32.81</td>
<td>0.005297</td>
<td>0.9749</td>
</tr>
<tr>
<td>5</td>
<td>42.56</td>
<td>0.003385</td>
<td>0.913</td>
</tr>
<tr>
<td>6</td>
<td>38.68</td>
<td>0.005067</td>
<td>0.9371</td>
</tr>
<tr>
<td>7</td>
<td>29.43</td>
<td>0.0076</td>
<td>0.9529</td>
</tr>
</tbody>
</table>
Figure 4.5 (a.) Pseudo first order kinetic model plots for the adsorption of lead onto the nano-sorbent (PS@Fe₃O₄@GO) at different pH (Operating conditions: Pb (II) concentration = 10 mg/L, temperature = 35º C and contact time = 8 h) and (b.) Langmuir plot $C_e$ vs $C_e/q_e$ for adsorption of lead onto the nano-sorbent (PS@Fe₃O₄@GO) at different temperatures (Operating conditions: Pb (II) concentration = 10 mg/L, pH=6 and contact time = 8 h).
4.3.5 Adsorption isotherm study

Adsorption isotherms give a clear understanding of the interaction between the adsorbate and adsorbent which is critical for optimising the use of adsorbents. To optimise the adsorption system, it is important to draw suitable conclusions from the equilibrium diagram. Herein the equilibrium data was modelled for Langmuir and Freundlich adsorption isotherms.

4.3.5.1 Langmuir adsorption isotherm

The Langmuir adsorption isotherm model is one of the common adsorption models which have been widely applied to study adsorption of pollutants onto different adsorbents. It is primarily based on a few assumptions such as monolayer adsorption, binding of the adsorbate onto the surface of adsorbent occurs primarily through a chemical reaction, and all sites have equal affinity for the adsorbate. The Langmuir equation is given by

\[
\frac{C_e}{q_e} = \frac{1}{q_{max} \cdot K_l} + \frac{C_e}{q_{max}}
\]  

(4.3)

where \( q_{max} \) (mg/g) is the maximal adsorbed amount of particles, \( C_e \) is the equilibrium concentration of lead and \( K_l \) is the Langmuir adsorption constant.

Table 4.2 shows the Langmuir adsorption parameters at different temperatures. The Langmuir adsorption plot between \( C_e/Q_e \) and \( C_e \) at different temperatures is shown in Figure 4.5 b. The Langmuir adsorption isotherm model fitted well for the adsorption of Pb (II) onto the prepared nano-sorbent. This confirms that the adsorption was monolayer and the adsorption of each molecule had equal activation energy. Table 4.2 shows that the \( q_{max} \) for Pb (II) ion adsorption was 73.52 mg/g. This was comparable with a similar water dispersible magnetic chitosan/GO composite which was studied for lead removal (76.94 mg/g) (Fan et al., 2013). However, the present result of 73.52 mg/g was higher than the results from studies using exfoliated graphene nano-sheets (35.46 mg/g) (Huang et al., 2011), activated carbon from cow bone (47.619 mg/g) (Cechinel et al., 2014) and magnetic (Fe₃O₄) nano-sorbent (36 mg/g) (Nassar, 2010). A detailed
list of magnetic nano-composites previously used for Pb (II) removal is summarised in Table 4.3.

The monolayer adsorption also supplements well with the pseudo first order kinetics results as the adsorption was based on the number of active sites present on the adsorbent. The active sites are the hydroxyl and carboxyl groups present on the GO which act as Lewis base to form the electron donor-acceptor complexes with the metal ions. Strong surface complexation between metal ions and GO occurs through this Lewis acid-base interaction which also contributes to the metal ion adsorption (Monser and Adhoum, 2002).

Table 4.2. Langmuir and Freundlich adsorption isotherm and thermodynamic parameters at different temperatures (Operating conditions: Pb (II) concentration = 10 mg/L, pH=6 and contact time =8 h).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>q_{max} (mg/g)</th>
<th>K_f (l/mg)</th>
<th>R^2</th>
<th>ΔG (kJ/mol)</th>
<th>K_f (l/mg)</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>27.427</td>
<td>2.641</td>
<td>0.9968</td>
<td>-7970.37</td>
<td>3.694</td>
<td>0.9858</td>
</tr>
<tr>
<td>298</td>
<td>53.475</td>
<td>1.231</td>
<td>0.995</td>
<td>-529.776</td>
<td>5.210</td>
<td>0.9203</td>
</tr>
<tr>
<td>303</td>
<td>73.529</td>
<td>1.062</td>
<td>0.9847</td>
<td>-152.722</td>
<td>7.068</td>
<td>0.9943</td>
</tr>
<tr>
<td>308</td>
<td>60.240</td>
<td>1.865</td>
<td>0.9229</td>
<td>-7492.48</td>
<td>7.747</td>
<td>0.8916</td>
</tr>
</tbody>
</table>
Table 4.3. List of magnetic nano-adsorbents reported in literature for Pb (II) removal.

<table>
<thead>
<tr>
<th>Magnetic Nano-adsorbent</th>
<th>Magnetism type</th>
<th>Working Conditions (Metal ion concentration; pH)</th>
<th>Adsorption Capacity (mg/g)</th>
<th>Removal efficiency (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃O₄@Chitosan</td>
<td>Ferromagnetic</td>
<td>10mg/L; 4</td>
<td>31.6</td>
<td>94.8</td>
<td>Liu et al. (2008)</td>
</tr>
<tr>
<td>Fe₃O₄@Gum kondagogu</td>
<td>Ferromagnetic</td>
<td>100mg/L; 5</td>
<td>56.6</td>
<td>78.4</td>
<td>Saravanan et al. (2012)</td>
</tr>
<tr>
<td>Fe₃O₄ @ SiO₂-NH₂</td>
<td>Super-paramagnetic</td>
<td>26.8-49.7 mg/L; 5.5</td>
<td>128.21</td>
<td>16.55</td>
<td>Tang et al. (2013)</td>
</tr>
<tr>
<td>Fe₃O₄ –NH₂</td>
<td>Super-paramagnetic</td>
<td>5mg/L; 7</td>
<td>369</td>
<td>98%</td>
<td>Tan et al. (2012)</td>
</tr>
<tr>
<td>Fe₃O₄@SiO₂-SH</td>
<td>Super-paramagnetic</td>
<td>1mg/L; 6.5</td>
<td>91.5</td>
<td>90-100% in synthetic water and 54.8-99.1% in tap, river, lake and ground water</td>
<td>Li et al. (2011)</td>
</tr>
<tr>
<td>PAA@GO@Fe₃O₄</td>
<td>Super-paramagnetic</td>
<td>10mg/L; 8</td>
<td>-</td>
<td>95%</td>
<td>Zhang et al. (2013)</td>
</tr>
<tr>
<td>PS@ Fe₃O₄@GO</td>
<td>Super-paramagnetic</td>
<td>10mg/L; 6</td>
<td>73.52</td>
<td>93.78</td>
<td>This study</td>
</tr>
</tbody>
</table>


4.3.5.2 Freundlich adsorption isotherm

The Freundlich adsorption isotherm is an empirical model allowing multi-layer adsorption on the surface. The linearised logarithmic form of the equation is given below

\[ \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \] (4.4)

where, \( K_f \) is the Freundlich constant related to adsorption capacity and \( n \) is the energy or intensity of adsorption. Even though the data followed Freundlich isotherm model at 30° C, the adsorption data had a better fit to Langmuir model at other temperatures as shown in Table 4.2 (\( R^2 \) was closer to 1 showing the better fit).

4.3.6 Thermodynamics of adsorption

The spontaneity of the adsorption process was evaluated by calculating the thermodynamic parameter, i.e., Gibbs free energy (\( \Delta G \)) using the formula

\[ \Delta G = -RT \ln K_l \] (4.5)

where \( R \) is the gas constant (J/ mol K), \( T \) is the temperature (K) and \( K_l \) is the Langmuir equilibrium constant. The \( \Delta G \) values calculated (Table 4.2) were found to be negative, indicating that the adsorption process was spontaneous.

4.3.7 Mechanism of adsorption

To understand the exact mechanism of lead ion adsorption onto the synthesised nano-sorbent, FT-IR and XPS analysis of the nano-sorbent before and after its interaction with lead ions were carried out and the results are shown in figures 4.6 and 4.7. The two major peaks observed at 1064 cm\(^{-1}\) and 1699 cm\(^{-1}\) in the FT-IR spectra of pure nano-sorbent correspond to the C-O and C=O stretching vibrations, respectively, of the GO present on the nano-sorbent (Zhao et al., 2011) (Figure 4.6). After interaction with the Pb (II) ions, the C-O stretching frequency shifted
to 1066 cm$^{-1}$ with a decrease in intensity, and the C=O stretching frequency observed at 1699 cm$^{-1}$ also showed significant decrease in the intensity indicating that the interaction of lead ions occurs via C-O and C=O functional groups present in the GO as also observed by Zhao et al. (2011).

**Figure 4.6.** FT-IR spectra of nano-sorbent before and after adsorption of Pb (II) ions.

XPS survey spectra of pure nano-sorbent and after its interaction with the lead ions are shown in Figure 4.7. The high resolution individual C1s spectra of the pure nano-sorbent and after its interaction with lead ions is shown in figure 4.8a and b. The C1s core level spectrum de-convoluted into three different carbon species and their Binding Energy (BE) observed at 284.6, 286.4 and 289 eV (Figure 4.8a), wherein last two component BEs were assigned to the different oxygen containing functional groups of the GO such as carbonyl and the carboxylic group respectively (Sitko et al., 2013). After inter-action with Pb (II) ions (Figure 4.8b), the C1s core level BE that corresponds to the carbonyl group shifted from 284.6 eV to 286.6 eV (0.2 eV shift) and the carboxylic group shifted from 289 eV to 288.7 eV, along with a decrease
in the intensity. This was due to the adsorption of lead ions onto the electronegative oxygen of the GO present in the nano-sorbent. The increase in the BE of the carbonyl components on the GO confirms the adsorption and electrostatic interaction between the O atom and the Pb (II) ions. The BE of lead nitrate having lead in +2 oxidation state is generally observed between 139 and 139.5 eV (Moulder et al., 1992). The BE that corresponds to the Pb 4f core level was observed at 138.85 eV in the case of Pb (II) interacted nano-sorbent material (Figure 4.8c), which is characteristic of the Pb–O interaction (Moulder et al., 1992). This result confirms that there was no change in the oxidation state of lead (+2) even after adsorption. Also, it was noted that the synthesised nano-sorbent had a zeta potential of −16 mV and that of the Pb (II) solution was 0.73 mV at pH 6. This confirms that the adsorption of lead ions on the surface of GO was initiated by the electrostatic interaction between the negatively charged nano-sorbent and lead cations, which was followed by the chelation of lead ions on the surface of GO (Fan et al., 2013). The electrostatic attraction and chelation further affirms that the removal of Pb (II) ions was mainly a physisorption process.

**Figure 4.7.** XPS spectra of the (a.) un-interacted sample and (b.) Pb (II) interacted sample.
4.3.8 Desorption and reuse

The reusability of an adsorbent is an important property required for industrial applications. Since adsorption of Pb (II) ions was primarily through physisorption, the recycling performance of nano-sorbent was investigated by performing several cycles of lead adsorption followed by desorption with 10% HNO$_3$. In each cycle, after incubation in lead solution, the nano-sorbent was removed with the aid of an external magnet and washed with de-ionised water until neutralised. As shown in Figure 4.9, after the first cycle of adsorption, 93.8% of removal efficiency was achieved. After 4 adsorption-desorption cycles, the lead removal efficiency decreased to 41%. The decrease of the adsorption capacity may be due the incomplete desorption of the adsorbed sites of the nano-sorbent.

To achieve a sustainable treatment process, the management of spent regeneration solutions and the spent nano-sorbent must be properly addressed. In the case of spent regeneration
solution, the lead ions can be recovered by different technologies like precipitation, ion flotation, electro-deposition and electro-dialysis. Electro-deposition has been reported to be an efficient method for recovery of metals like lead, zinc and manganese with current efficiency as high as 90% (Gómez-Pastora et al., 2014). While these technologies have not been extensively used for recovery of valuable substances from desorption solutions, they are attractive alternatives for management of the spent wastes, as they not only generate a marketable product by resource recovery but also help in resolving the disposal issues. Better regeneration processes should also be developed whereby greater removal of lead attached onto the nano-sorbent is obtained. Management of the spent nano-sorbents has been scarcely studied and very little information is available on handling them. At present the spent nano-sorbents are either being stored or destroyed by irreversible aggregation or dissolution from which the constituent materials can further be recovered or processed by conventional methods (Gómez-Pastora et al., 2014).

![Figure 4.9. Lead removal after successive adsorption-desorption cycles. Data expressed in Mean ± 3 S.D.](image)
4.4 Conclusion

In this chapter, a polymer based GO magnetic nano-sorbent (PS@Fe₃O₄@GO) was synthesised and applied for removing low concentrations of lead from aqueous solutions. The effect of contact time, pH and temperature on adsorption was investigated and the most suitable condition for effective adsorption was determined. The adsorption of Pb (II) ions was found to follow pseudo first order kinetics. The Langmuir isotherm for lead adsorption was shown to be best fir for the data. The adsorption capacity of the nano-sorbent was determined to be 73.52 mg/g. The Gibbs free energy was calculated and found that adsorption process was spontaneous. The mechanism of adsorption was further studied using FT-IR and XPS, which revealed the probable bond formation between the O atoms of the GO and the Pb (II) ions. The re-generation of the nano-sorbent after adsorption was demonstrated using 10% HNO₃ as eluent. Further investigation on regeneration conditions would be required before the nano-sorbent could be used in practice.
Chapter 5

Characterisation and application of GO-PSf ultrafiltration membranes for lead ions rejection

5.1 Introduction

Membrane technology has been successfully used for multiple applications across various industries, from potable water purification to treatment of wastewater before being discharged into a larger water body; and to maintain the high-quality standards required by beverage companies (Gao et al., 2011; Bruggen et al., 2003 and Girard et al., 2000). The ease of operation, combined with smaller foot print and lower energy consumption, have made them the preferred treatment choice (Buonomenna, 2013). With such widespread applications and advantages, newer concepts are being explored with regard to synthesising membranes with better properties.

Graphene oxide (GO), the oxidised form of graphene has various oxygenated functionalities (hydroxy, epoxy on the basal plane and carbonyl, carboxylic acid at the edges) making them versatile for various applications. The ability of GO to adsorb lead ions by electrostatic attraction and chelation was elucidated in Chapter 4. Although the prepared nano-sorbent system showed high removal efficiency, the possibility of GO to leach into the aqueous system is a concern.

To overcome this shortcoming, preparation of hybrid membrane by blending GO with PSf would be a suitable alternative. The prepared membrane would require less GO, could prevent leaching of GO and can also be regenerated and reused. Along with these advantages, the hybrid membranes can also bring in desired functionality regarding membrane pore size, hydrophilicity, porosity and mechanical strength.

In this chapter, hybrid ultrafiltration membranes were prepared by blending different concentrations of GO with PSf. A minimum of 0.2 wt % GO was reported to have improved the physical and morphological properties of GO blended PVDF membranes (Wang et al., 2012). In this study 15 wt % PSf was blended with GO having concentrations 0, 0.25 and 1 wt %. The membranes were characterised for their properties such as flux, porosity, pore size, hydrophilicity and mechanical strength. The surface morphology was studied using SEM. The
prepared membranes were further investigated for lead rejection using cross flow filtration setup at different operating pressures.

5.2. Characterisation of the prepared membranes

5.2.1 Hydrophilicity – Water contact angle

The water contact angle or the hydrophilicity reflects the wettability of the membrane. Figure 5.1. shows the water contact angle of the prepared membranes. The water contact angle decreased with addition of GO, showing increase in hydrophilicity of the membrane. The water contact angle was lowest (34.2˚) for the membrane blend with 1 wt % GO. Polysulfone is a high strength material with negligible interaction capability with metal ions, hence the addition of GO with its carboxyl, hydroxyl and carbonyl groups, enhances its ability to interact with metal ions through ion-exchange and complexation is enhanced (Zhao et al., 2011).

![Figure 5.1 Water contact angle of different membranes.](image-url)
5.2.2 Tensile strength test

The mechanical properties of the membranes were evaluated using the tensile strength test. From the stress-strain results, the Young’s modulus and elongation at break were estimated (Table 5.1). The results indicate that the Young’s modulus significantly increased for the membrane with 0.25 wt % GO but it decreased for the membrane with 1 wt % GO. The improvement for the membrane with 0.25 wt % GO concentration could be explained by the positive reinforcement brought by GO over the PSf crystallinity (Ionita et al., 2014). At higher concentrations of GO (1 wt %), the Young’s modulus decreased probably due to poor dispersion of GO and formation of clusters in the membrane (Lee et al., 2013). In regards to the elongation of the membranes, the PSf had a shorter elongation length at break than the membranes with GO. However, the increment in elongation length was not substantial among the three membranes compared.

Table 5.1 Characteristics of prepared ultrafiltration membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Young’s Modulus (MPa) (Mean ± 3 S.D.)</th>
<th>Elongation at break (mm) (Mean ± 3 S.D.)</th>
<th>Pore Size (nm) (Mean ± 3 S.D.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 % PSf</td>
<td>130.73 ± 15.84</td>
<td>10.23 ± 4.36</td>
<td>17.36 ± 5.4</td>
</tr>
<tr>
<td>15 % PSf - 0.25 % GO</td>
<td>188.13 ± 15.36</td>
<td>14.83 ± 3.75</td>
<td>23.72 ± 6.9</td>
</tr>
<tr>
<td>15 % PSf - 1% GO</td>
<td>79.46 ± 28.57</td>
<td>12.48 ± 6.5</td>
<td>22.73 ± 9.6</td>
</tr>
</tbody>
</table>

5.2.3 Porosity and pore size of membranes

The pore size of the membranes prepared were calculated (Table 5.1) and ranged from 18 nm – 24 nm, confirming the prepared membranes were of ultrafiltration grade. The porosity of membranes increased with GO concentration (Figure 5.2). The hydrophilicity effect of GO, expedited the exchange of solvent/non-solvent during the phase inversion process which led to higher porosity in membranes. Similar observation was reported by Wang et al. (2012) with PVDF membranes blended with GO.
5.2.4 Scanning Electron Microscopy (SEM)

Figure 5.3 shows the SEM images of the surface and cross sectional views of the prepared ultrafiltration membranes. The SEM of the surface shows the pores present on the membranes. The SEM of the cross-section shows that the membranes are asymmetrical, which was consistent with other studies that focused on morphology (Ganesh et al., 2013). A dense top layer which was supported by a porous layer was observed for all the membranes. The dense top layer formed is a characteristic of membranes prepared using non-solvent induced phase separation process (Ganesh et al., 2013). The porous layer varied significantly with the addition of graphene oxide from tighter and void-free pores to big macro-voids observed for the 1% GO membrane (Fig 5.3f). The addition of GO increased the porosity of the membrane as it increased the macro-voids and reduced the thickness of the walls, thus increasing the permeability of the membrane as observed in section 5.2.5. It was also noted that the hydrophilic nature of GO helped in formation of larger longer pores and macro-voids (Rezaee, et al., 2015).
Figure 5.3 SEM images of surface (a - mag 16,000x, c - mag 12,000x and e - mag 12,000x) and cross sections (b – 800x, d – 1,200x and f – 1,200x) of membranes having compositions 15 % PSf (a, b.), 15 % PSf - 0.25 % GO (c, d.) and 15 % PSf - 1 % GO (e, f.) respectively.
5.2.5 Membrane permeation - pure water flux and permeability

The pure water flux of the prepared membranes at different pressures is shown in Figure 5.4. The flux increased with GO concentration in the membrane, the pure water flux was highest (163.71 L/m²h) for 1 % GO at 3 bar. At 1 bar, 1 % GO had a lower flux than the 0.25% GO. This may be due to the higher concentration of GO constricting the water from passing through at the low pressure. However, at higher pressures this was not the case. The permeability also showed an increase (Figure 5.4) and was estimated as 25.7, 45.5 and 52.1 L/m²hbar for 15 % PSf, 15 % PSf - 0.25 % GO and 15 % PSf - 1 % GO, respectively. Increase in flux with GO concentrations for PVDF ultrafiltration membranes have also been reported by Wang et al. (2012).

Figure 5.4 Pure water flux and permeability of membranes at different pressures.

5.3 Lead ions rejection

Heavy metal ion rejection through membranes can predominantly be achieved through size exclusion, charge exclusion and metal deposition (Al Rashdi et al., 2013). Here the approach was to improve the rejection by enhancing the charge exclusion phenomenon by addition of GO. Figure 5.5 shows the lead ion rejection at different pressures by different membranes. From the figure, it can be noted that higher rejection was achieved with the 1 % GO membrane.
at 1 bar of pressure. All membranes demonstrated a decrease in rejection with increase in pressure which can be attributed to increase in water permeation rate with pressure.

A minimum rejection of 93% was obtained for membrane devoid of GO at 3 bar. This high rejection by pristine PSf membrane could be due to presence of smaller pores. Further investigation will add more insights on the high removal. The influence of GO could be seen with the increase in rejection, which was not very high but definite. The membrane having 1 % GO showed a maximum rejection of 98% at 1 bar pressure.

![Graph showing lead rejection of the membranes at different pressures](image)

**Figure 5.5** Lead rejection of the membranes at different pressures (lead concentration = 50 mg/L and pH = 5.5).

Shah and Murthy (2013) studied the role of functionalised multi-walled carbon nanotube (MWCNT) - PSf composite membrane on rejection of different salts. With the addition of functionalised MWCNTs, the pore size was brought down from 100 nm to 26 nm. Lead reduction of 90 - 91% was achieved using amide and azide functionalised MWCNT/PSf membrane. The effect of pressure, pH and initial metal ion concentration on rejection of different metals by NF270 membrane was studied in detail by Al-Rashdi et al. (2013). Increase in pressure from 3 to 4 bar increased lead rejection which however decreased when the pressure was increased from 4 to 5 bar. Higher rejection was observed for lead at the low pH of 1.5. This was attributed to the positive charge of the membrane which repelled the cations. Lead, cadmium and copper were better rejected at low concentrations. Lead rejection of 80 % was
achieved for 100 mg/L initial concentration at pH 5. In a related study, GO/PSf membranes (25 wt % PSf and 1000 & 2000 mg/L GO) were studied for \( \text{Na}_2\text{SO}_4 \) and NaCl rejection (Ganesh et al., 2013) and it was observed that the solute rejection increased with GO doping. The membrane with the highest GO loading showed maximum rejection of 72% for a concentration of 1000 mg/L of \( \text{Na}_2\text{SO}_4 \) at 4 bar pressure.

5.4 Conclusion

GO blended PSf ultrafiltration membranes were successfully prepared and displayed enhanced hydrophilicity and porosity which improved their overall flux and permeability compared to the GO free membrane. The pore size of ultrafiltration membranes ranged from 18 nm to 24 nm. The addition of 0.25 % GO to 15 % PSf improved Young’s modulus which, however, decreased at 1 % GO concentration (15 % PSf - 1% GO) due to poor dispersion and formation of clusters in the membrane. The positive impact of GO incorporation was observed with increased elongation at break lengths for GO blended membranes. SEM micrographs revealed the presence of bigger macro-voids in GO blended PSf membranes which was consistent with their enhanced flux and permeability. Lead rejection studies were carried out with an initial concentration of 50 mg/L. A maximum rejection of 98% was achieved with 15 % PSf - 1 % GO membrane at 1 bar pressure, which however decreased with increase in pressure and with decrease in GO concentration.

These results are encouraging and should be extended to study the rejection of lead and other metals at higher concentrations. Further longevity, regeneration and re-use studies will give us an understanding on the long-term stability of the composite membranes, which is significant for practical applications.
Chapter 6

Characterisation and application of Graphene-oxide (GO) - PSf micro filtration membrane in MBR system for lead removal

6.1 Introduction

The application of a treatment technique depends on the type of wastewater to be treated. Nanosorbent systems for heavy metal treatment are highly specific and requires less reaction time for removal. However, the downside of such systems is their inability to treat wastewater containing mixed contaminants. Membrane processes are efficient in treating heavy metal contaminated water after pre-treatment. Membrane fouling is a concern for successful application of membrane process as it can result in severe flux decline and affect the quality of water being produced (Xu et al., 2010). MBR system couples both the biological and membrane processes are used for treatment of wastewater of high strengths (Lin et al., 2012). The biological process helps in degradation of organics and promotes adsorption of different non-biodegradable pollutants such as heavy metals, thereby reducing the necessity for pre-treatment (Mack et al., 2004; Shayegan et al., 2008; Amiri et al., 2010; Katsou et al., 2011; Arevalo et al., 2013; Feng et al., 2013). The membrane process separates the microorganisms, solids and the other contaminants thereby producing treated wastewater of good quality (Chang et al., 2002; Tay et al., 2007).

Modification of the membranes have been considered as a potential alternative by researchers to mitigate fouling. It was observed that hydrophilic membranes had better antifouling properties compared to hydrophobic membranes (Yu et al., 2009; Madaeni et al., 2011; Rahimpour et al., 2011; Liu et al., 2011; Liang et al., 2012).

The successful results from the chapter 5 in preparation of hybrid hydrophilic membrane could serve as an apt alternative to study their ability to mitigate fouling and remove lead ions in an MBR system.

In this chapter, graphene-oxide blended polysulfone (PSf) microfiltration membranes with different concentrations of GO and PSf were prepared by phase inversion process. The effect of different concentrations of the PSf (15–20 wt %) and GO (0-1 wt %) on the membrane morphology, surface properties, mechanical strength, porosity and pure water flux was
systematically investigated. Based on the characterisation results, four membranes were chosen for application in an A2O MBR system to study their fouling characteristics by short term critical flux tests. From the short term critical flux results, two membranes were further chosen for long term study. In order to understand the role of the membranes in lead ion separation, the fouled membranes were analysed for their atomic composition using SEM-EDS. The overall performance of the MBR system for lead removal was monitored for over a period of 270 days.

6.2 Characterisation of the prepared membranes

6.2.1 Hydrophilicity – Water Contact Angle

The water contact angle decreased as a result of increase in GO concentration (Table 6.1), making the membranes more hydrophilic. The contact angle was lowest (49.9°) for the blend with 20 % PSf -1 % GO. This can be attributed to the presence of a larger number of oxygen containing functional groups dispersed on the membrane surface during the solvent-non solvent de-mixing phase inversion process. It was also observed that the water contact angle decreased with increase in polymer concentration in the absence of GO, due to the inherently hydrophilic nature of the polysulfone.

6.2.2 Tensile strength test

The Young’s modulus for the membranes increased significantly with increase in both polymer and GO concentration (Table 6.1). This shows the positive reinforcement of GO on the mechanical properties of the membrane. The elongation at break point increased with PSf concentration as expected, and it tended to decrease with increase in GO concentration (Table 6.1). These results indicate that the membrane elasticity tends to decline with increase in the additive (GO) concentration. A similar observation was reported by Wang et al. (2012) for GO blended PVDF membranes.
6. 2.3 Membrane permeation - Pure Water Flux

The pure water flux of the prepared membranes was determined using cross flow filtration setup (Figure 6.1). The pure water flux was highest (168.92 L/m²h) for the composition of 15 % PSf and 1 % GO at 3 bar. There was an increase in flux from 12 to 27 L/m²h for 18 % PSf compared with 15 % PSf membranes without GO at 3 bar, and this trend occurred at 2 and 1 bar as well. The increase in flux correlates well with increase in hydrophilicity of the membranes. Van der Marel et al. (2010) observed a similar increase in flux with PVDF hydrophilic membranes. Although the flux decreased for membranes with 20 % PSf, the composition with the maximum GO content, i.e., 20 % PSf - 1 % GO, had a flux of 55.35 L/m²h at the operating pressure of 3 bar.

6. 2.4 Porosity and Pore Size of membranes

The porosity and pore size of the prepared membranes were calculated and there was an increase in porosity after incorporation of GO in the PSf membrane (Table 6.1). This increase correlated well with increase in flux and decrease in water contact angle. For membranes without GO, the porosity decreased with increase in PSf concentration, and the pore size varied from 192 to 250 nm. The increase in water flux can be directly related to increase in hydrophilicity and porosity of the membranes.
### Table 6.1 Characteristics of the membranes.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Water Contact Angle (°) (Mean ± 3 S.D.)</th>
<th>Porosity (%) (Mean ± 3 S.D.)</th>
<th>Pore Size (nm) (Mean ± 3 S.D.)</th>
<th>Young’s Modulus (MPa) (Mean ± 3 S.D.)</th>
<th>Elongation at break (mm) (Mean ± 3 S.D.)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>15 % PSf with</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No GO</td>
<td>71.0 ± 5.5</td>
<td>73.1 ± 2.3</td>
<td>250 ± 17.1</td>
<td>54.71±11.1</td>
<td>7.83±2.1</td>
</tr>
<tr>
<td>0.125 % GO</td>
<td>68.6 ± 1.3</td>
<td>73.5 ± 1.2</td>
<td>240 ± 23.1</td>
<td>72.41±15.8</td>
<td>6.78±1.9</td>
</tr>
<tr>
<td>0.25 % GO</td>
<td>65.1 ± 2.2</td>
<td>78.4 ± 3.7</td>
<td>230 ± 25.5</td>
<td>81.35±10.8</td>
<td>4.9±1.4</td>
</tr>
<tr>
<td>1 % GO</td>
<td>57.6 ± 1.5</td>
<td>80.2 ± 2.1</td>
<td>200 ± 12.6</td>
<td>100.32±16.4</td>
<td>4.5±1.4</td>
</tr>
<tr>
<td><strong>18 % PSf with</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No GO</td>
<td>68.0 ± 1.5</td>
<td>69.7 ± 2.1</td>
<td>230 ± 14.4</td>
<td>120.87±9.4</td>
<td>10.64±2.2</td>
</tr>
<tr>
<td>0.125 % GO</td>
<td>64.6 ± 1.6</td>
<td>73.1 ± 1.5</td>
<td>214 ± 9.6</td>
<td>120.22±19.3</td>
<td>11.4±1.3</td>
</tr>
<tr>
<td>0.25 % GO</td>
<td>62.3 ± 2.1</td>
<td>77.0 ± 2.5</td>
<td>200 ± 15.0</td>
<td>139.92±15.3</td>
<td>10.7±2.0</td>
</tr>
<tr>
<td><strong>20 % PSf with</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No GO</td>
<td>60.0 ± 0.3</td>
<td>69.0 ± 2.4</td>
<td>192 ± 13.8</td>
<td>125.27±9.9</td>
<td>25.6±4.7</td>
</tr>
<tr>
<td>0.5 % GO</td>
<td>56.1 ± 1.6</td>
<td>70.8 ± 2.5</td>
<td>190 ± 14.2</td>
<td>134±22.5</td>
<td>23.5±5.2</td>
</tr>
<tr>
<td>1 % GO</td>
<td>49.9 ± 1.0</td>
<td>71.6 ± 3.8</td>
<td>179 ± 20.4</td>
<td>153.6±15.3</td>
<td>21.2±4.8</td>
</tr>
</tbody>
</table>
Figure 6.1 Pure water flux of the different membranes ((a.) 15 % PSf and GO, (b.) 18 % PSf and GO and (c.) 20 % PSf and GO) at different pressures (data represented in mean ± percentage error).
6.2.5 Scanning Electron Microscopy (SEM)

The surface morphology of the prepared membranes (Figure 6.2) at different magnifications showed apparently smooth surface of the membranes. The pore size of the membranes observed under the SEM ranged from 200 to 300nm.

The cross-sectional images of the prepared membranes showed a dense top layer above finger-like pore structures forming the porous layer (Figure 6.3 a, b and c). The membranes with GO had a less dense top layer (Figure 6.3 d-j). The narrow finger-like pore channels became noticeably wider with increasing GO concentration (Figure 6.3 c, h and j). Macro-voids were also observed below the porous layer, and larger macro-voids occurred for membranes with higher concentrations of GO at the different PSf compositions. As noted in chapter 5, this is due to instantaneous de-mixing by solvent/nonsolvent in the coagulation bath, further promoted by the presence of GO in the mixture. The bigger-macro voids and the wider pore channels would improve the water flux of the membranes.

Pore size and shape play an important role in membrane fouling. If the particle size is smaller than the pore size, membrane pores can be clogged, which can further reduce the flux. In a study conducted by Fang and Shi (2005), four microfiltration (MF) membranes with pore sizes narrowly ranged between 0.20 and 0.22 µm were tested in parallel for pore fouling. They noted that the membrane which had a uniformly small cylindrical pore configuration was less prone to fouling as it was difficult for foulants to deposit inside the pores, whereas the other three membranes with sponge-like microstructure were more vulnerable to pore fouling due to their porous network. Bromely et al. (2002) also studied the effect of pore shapes on fouling. They observed that there was a five-fold increase in critical flux of membranes with slotted pores than those with circular pores.
Figure 6.2 SEM images of the prepared membranes at different magnifications taken using SEM (a.) 15 % PSf (mag 8000x), (b.) 18 % PSf (mag 8000x), (c.) 20 % PSf (mag 13000x), (d.) 15 % PSf - 0.125 % GO (mag 8000x), (e.) 18 % PSf - 0.125 % GO (mag 6400x), (f.) 15 % PSf - 0.25 % GO (mag 8000x), (g.) 18 % PSf - 0.25 % GO (mag 8000x), (h.) 20 % PSf - 0.5 % GO (mag 15000x), (i.) 15 % PSf - 1 % GO (mag 20000x) and (j.) 20 % PSf - 1 % GO (mag 20000x).
Figure 6.3 SEM images of cross sections of the prepared membranes at different magnifications (a.) 15% PSf (mag 1500x), (b.) 18% PSf (mag 1000x), (c.) 20% PSf (mag 800x), (d.) 15% PSf - 0.125% GO (mag 400x), (e.) 18% PSf - 0.125% GO (mag 800x), (f.) 15% PSf - 0.25% GO (mag 800x), (g.) 18% PSf - 0.25% GO (mag 400x), (h.) 20% PSf - 0.5% GO (mag 1500x), (i.) 15% PSf - 1% GO (mag 400x) and (j.) 20% PSf - 1% GO) (mag 1500x).
6.3 Operational performance of the MBR system – A2O process establishment and other parameters

6.3.1 MBR with A2O process

The MBR system was based on the A2O process (having anaerobic-anoxic and aerobic tanks in sequence) designed to remove nitrogen, phosphorus and other nutrients present in the wastewater (refer section 3.4.1). In this process, phosphorus is released by the phosphate accumulating organisms (PAOs) in the anaerobic zone, which is utilised in the aerobic zone by the microorganisms to multiply (Metcalf and Eddy et al., 2003). Nitrification and denitrification occurs in the aerobic and anoxic zone, respectively (Metcalf and Eddy et al., 2003).

Nitrification is the oxidation of ammonia to nitrite and then to nitrate. The key organisms involved belong to *Nitrosomonas* and *Nitrobacter* species. The reactions are given below (Metcalf and Eddy et al., 2003)

*Nitrosomonas*

\[
2\text{NH}_4^+ + 3\text{O}_2 \rightarrow 2\text{NO}_2^- + 2\text{H}_2\text{O} + 4\text{H}^+ \quad (6.1)
\]

*Nitrobacter*

\[
2\text{NO}_2^- + \text{O}_2 \rightarrow 2\text{NO}_3^- \quad (6.2)
\]

Overall Reaction

\[
\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O} \quad (6.3)
\]

Denitrification is the reduction of nitrate to nitrogen gas by heterotrophic microorganisms present in the anoxic zone. The reaction is given by

\[
\text{C}_{10}\text{H}_{19}\text{O}_3\text{N} + 10\text{NO}_3^- \rightarrow 5\text{N}_2 + 10\text{CO}_2 + 3\text{H}_2\text{O} + \text{NH}_3 + 10\text{OH}^- \quad (6.4)
\]
where \( \text{C}_{10}\text{H}_{19}\text{O}_3\text{N} \) represents the rapidly biodegradable matter molecule (Metcalf and Eddy et al., 2003).

PAO’s in the anaerobic zone work by assimilating fermentation products and converting them into storage products in the form of polyhydroxybutyrate (PHB), along with the concomitant release of phosphorus from stored polyphosphates (Metcalf and Eddy et al., 2003). In the aerobic zone, the stored PHB is oxidised and the energy released is used to form polyphosphate bond by utilising the excess phosphate released in the anaerobic zone (Metcalf and Eddy et al., 2003). During this process, new biomass is formed along with phosphorus removal. This system combines the biological nitrogen and phosphorus removal designs thereby helping to achieve removal of both through a single step process.

This A2O system was operated for a period of 1 year, with four quarters operated under different experimental conditions as explained in section 3.4.3.

### 6.3.2 Temporal variations of essential MBR parameters

MBR health was monitored through key parameters like pH, temperature, dissolved Oxygen (DO), oxidation reduction potential (ORP), conductivity and total dissolved solids (TDS) in all tanks over the period of operation.

**pH:** Figure 6.4 shows the temporal variations of pH in all tanks. The average pH of anaerobic, anoxic, aerobic and permeate tanks were 7.0, 7.6, 8.6 and 8.7, respectively. The initial synthetic feed had a pH value of 7.8 which decreased to 7.0 in the anaerobic tank. The recommended pH for phosphorus removal is above 6.5 (Sedlak, 1991). The optimum pH for nitrification and denitrification are 7-7.2 (Metcalf and Eddy et al., 2003) and 7-8 (Dawson and Murphy, 1972) respectively. Although the pH is expected to decrease due to the release of H\(^+\) ions during nitrification in the aerobic zone, the alkalinity provided by oxidation of PHB and utilisation of orthophosphate in the phosphorus removal process prevents the pH from reducing thereby providing a suitable condition for nitrification (Metcalf and Eddy et al., 2003). Nitrogen removal through ammonia striping will be negligible below pH 9.5, therefore nitrogen removal is chiefly due to nitrification-denitrification process in the present system (Liao et al., 1995).
**Figure 6.4** Temporal variation of pH.

**Temperature**: The average temperatures were around 25°C for the anaerobic and anoxic tanks, and 20°C for aerobic and permeate tank (Figure 6.5). Biological processes are temperature sensitive and their activity tend to increase with temperature until a maximum rate is achieved (Jeyanayagam, 2005), after which inhibition occurs.

In case of nitrification, the inhibition sets in at around 40°C. It is also reported that as a rule of thumb, a 30% decrease of nitrification rate will be observed when the temperature drops from 20°C to 10°C (Jeyanayagam, 2005). With respect to phosphorus removal, temperatures above 30°C appear to decrease the removal rates (Jeyanayagam, 2005). This is due to lower anaerobic Volatile Fatty Acid (VFA) production rate and aerobic phosphorus uptake rate. Also, at higher temperatures, the PAOs face competition for the available VFA in the anaerobic zone with other organisms that do not accumulate PHBs (Jeyanayagam, 2005).
**Figure 6.5** Temporal variation of temperature.

*DO:* Dissolved oxygen (DO) is a crucial parameter in nitrogen and phosphorus removal processes. Figure 6.6 shows the temporal variation of the DO in all tanks. The average DO levels in anaerobic and anoxic tanks were 0.20 and 0.22 mg/L. The aeration tank had a DO of 7.5 mg/L and the permeate DO was 7.7 mg/L. The DO must be just sufficient to meet the carbonaceous and nitrogenous demands (Jeyanayagam, 2005). Over-aeration can result in detrimental effects that include i) secondary phosphorus release due to cell lysis, ii) high DO in the recirculation flow and iii) high operating costs. Phosphorus removal requires a minimum DO of 1 mg/L in the aerobic zone (Jeyanayagam, 2005). Low DO (<0.5 mg/L) can greatly inhibit the nitrification rates (Metcalf and Eddy et al., 2003). In such situations, incomplete nitrification can occur, resulting in increased nitrite levels in the effluent (Metcalf and Eddy et al., 2003).
Dissolved Solids and Conductivity: Figures 6.7 and 6.8 show the conductivity and total dissolved solids (TDS) of all the tanks. TDS is a measurement of inorganic and organic substances dissolved in the solution and conductivity indicates the concentration of dissolved ions present in the solution.

The average TDS and conductivity values for feed were 910 mg/L and 1420 µS/cm. The TDS and conductivity values for anaerobic, anoxic, aerobic and permeate tanks were 825, 788, 745, 735 mg/L and 1285, 1216, 1180 and 1150 µS/cm respectively. From the average TDS values, it can be estimated that 19 % removal of total dissolved ions was observed by the treatment of MBR system.
Figure 6.7 Temporal variation of TDS.

Figure 6.8 Temporal variation of conductivity.

**ORP:** The oxidation-reduction potential (ORP) determines the tendency of chemical species present to be either oxidised or reduced. This key parameter provides an understanding on how the system functions in nitrification/de-nitrification processes. The average ORP of the anaerobic and anoxic tanks were estimated to be -342 mV and -301 mV respectively (Figure 6.9). These strongly negative ORP values clearly indicate anaerobic conditions and possible presence of sulphates/carbonaceous organics as an electron acceptor for de-nitrification. Generally, at low ORP levels, production of organic acids and methane gas can also be observed (Environmental Y.S.I, 2008). The average ORP of the aerobic tank and permeate was
estimated at +63 mV and +78 mV respectively. The value of +63 mV in the aerobic tank clearly exemplifies nitrification conditions with oxygen as an electron acceptor. These conditions also favour organic carbon oxidation and polyphosphate production within cells accounting for phosphorus removal (Environmental Y.S.I, 2008).

Figure 6.9 Temporal variation of ORP.

6.3.3 COD, TP, TN, Ammonia, Nitrite and Nitrate removal

6.3.3.1 COD

Figure 6.10 shows the COD removal in the MBR system operated. It was observed that a stable and high COD removal of 99.14 % was maintained to date, even when the COD concentration was increased from 1100 mg/L to 2400 mg/L. This was done to supplement the microbes while introducing Pb in the feed initially. The average COD removal for each quarter were estimated to be 99.71, 99.77, 99.14 and 99.62 % respectively.

Figure 6.11 gives the representative trend of COD values estimated in different tanks for the four quarters. Most COD removal occurred in the anaerobic tank. The anoxic, aerobic and membrane processes further remove the remaining COD, thereby helping to achieve over 99 % removal. The membrane separation contributed 0.2–1 % to COD removal, indicating the overall removal was predominantly through biological degradation. The UV lamp also showed
a noticeable role in COD removal by contributing 0.1-0.4 %. The effluent from the MBR system had an average COD value of 5 mg/L.

![Figure 6.10 COD concentration in different tanks and overall removal percentage.](image)

**Figure 6.10** COD concentration in different tanks and overall removal percentage.

![Figure 6.11 COD concentration in different tanks during the four quarters.](image)

**Figure 6.11** COD concentration in different tanks during the four quarters.

### 6.3.3.2 Total Phosphorus (TP)

The total phosphorus (TP) concentration in the influent, effluent and in the different tanks is shown in Figure 6.12. It can be seen that the removal percentage increased from 10 % to attain a maximum removal of 52 % in the third quarter. During the first quarter, there was an increase
in phosphorus concentration in the effluent. This could be due to low MLSS in the aerobic tank which would utilise and remove the excess phosphorus released from the anaerobic and anoxic process. The influent COD/TP ratio during this quarter was 52.6. Once the MLSS increased, the phosphorus removal increased to 10 % and 52 % during quarters 2 and 3. The influent COD/TP ratio during these two quarters were 64.6. In the fourth quarter, the phosphorus removal dropped to 38 % which was due to decrease in influent COD/TP ratio to 46.8. For effective phosphorus removal, the influent COD/TP ratio is expected to be around 30-40 for BNR process (You et al., 2001). In a study by Lu et al. (2016) on COD/TP for biological nutrient removal, it was reported that increased COD/TP ratio favoured TP removal. Effluent TP < 0.5 mg/L was obtained when the COD/TP ratio was around 200.

**Figure 6.12** Total phosphorus concentration in different tanks and overall removal percentage.

Figure 6.13 shows the phosphorus concentration in different tanks during the four quarters. It can be noted that the phosphorus concentration decreased in the anaerobic tank and then increased in the anoxic condition. The decrease in the anaerobic tank is a result of utilisation of phosphorus by the heterotrophic organisms (non-PAOs) for their metabolism. The release of phosphorus by the PAOs under anoxic conditions can be observed. The released phosphorus was utilised by microorganisms in the aerobic tank, indicating removal in quarters 2, 3 and 4. It was noted that there was a slight increase in phosphorus concentration in the permeate. This could be due to the release of phosphorus from the cake layer formed on the fouled membrane, as PAOs could release phosphorus under anaerobic conditions (Fu et al., 2009).
6.3.3.3 Total Nitrogen (TN)

Total nitrogen concentration and its removal is shown in Figure 6.14. The total nitrogen removal in the first quarter was estimated to average 83 %. This was stabilised and a minimum removal of 72 % was maintained. The influent TN varied from 34–60 mg/L during the overall operation. The COD/TN ratio during the four quarters were 24.1, 44.2, 44.2 and 20.2 respectively. Theoretically, a ratio of 7-10 is preferred for TN removal (Blackburne et al., 2008). In a study by Yang et al. (2009), total nitrogen and ammonia removal was investigated with a COD/TN ratio of 21 in a moving bed MBR system. They reported an ammonia removal of 93.6 % and total nitrogen removal of 62.3 %. When the COD/TN ratio was decreased to 14.7, the ammonia removal decreased to 84.1 % and total nitrogen removal increased to 76.1 %, signifying a decrease in COD/TN ratio favoured TN removal.
Figure 6.14 Total nitrogen concentration in different tanks and overall removal percentage.

Figure 6.15 shows the concentration of TN in the different tanks during the four quarters. The TN concentration increased in the anaerobic tank from quarter 1 to quarter 4. This is due to lack of recirculation from the aerobic tank to the anaerobic tank. The average total nitrogen concentration in the effluent during the four quarters was estimated to be 8, 12.7, 13.5 and 12.7 mg/L, respectively. The lowest effluent TN limit that can be achieved through municipal wastewater treatment process is about 3 mg/L (Metcalf and Eddy et al., 2003).

Figure 6.15 Total nitrogen concentration in different tanks during the four quarters.
6.3.3.4 Ammonia, Nitrate and Nitrite

To understand the total nitrogen conversion and its removal, ammonia, nitrite and nitrate concentrations were also monitored. Ammonia removal and its concentration in different tanks is shown in Figure 6.16. The ammonia concentration in the influent ranged from 30-50 mg/L. Throughout the year-long operation, a high removal of 99% was maintained. The effluent had an ammonia concentration between 0.1 and 0.2 mg/L. The average concentrations of ammonia during the four quarters is shown in Figure 6.17. It can be observed that ammonia concentration decreases in each tank and is completely removed in the aerobic tank, demonstrating complete nitrification.

Figure 6.16 Ammonia concentration in different tanks and overall removal percentage.

Figure 6.17 Ammonia concentration in different tanks during the four quarters.
The nitrite and nitrate concentrations were also monitored (Figures 6.18 and 6.19). The effluent during the first quarter recorded nitrate and nitrite concentrations of 3 and 0.5 mg/L, respectively. This however stabilised and was maintained at 2 mg/L from the second quarter respectively. The US EPA has a prescribed limit of 2.3 mg NO₃-N/L in drinking water (Fernández-Nava et al., 2008).

![Figure 6.18 Nitrite concentration in different tanks.](image1)

![Figure 6.19 Nitrate concentration in different tanks.](image2)
6.3.4 Mixed Liquor Suspended Solids (MLSS)

Mixed liquor suspended solids (MLSS) refers to the biomass present in the reactor. Figure 6.20 shows the MLSS of the different tanks analysed over the operation period. It can be observed that the MLSS almost stabilised and was ~ 5 g/L in the anaerobic and anoxic tanks. The aerobic tank had an average MLSS of 0.4 g/L. The average MLSS of the MBR system was calculated to be 10.6 g/L. MBRs are generally operated at 2-20 g/L of MLSS. The concentration of MLSS can have a direct impact on biofouling of the membrane. In a study by Damayanti et al. (2011) to treat high concentration organic wastewater, a hybrid MBR system was used to analyse the impact of MLSS on biofouling and critical flux of the membrane. It was reported that the membrane biofouling rate increased with an increasing MLSS concentration (varied from 5-20 g/L). Also, the critical flux of the membrane decreased with increasing MLSS concentration. It is worth noting that in the present study, the membrane module was placed in the aerobic tank which had a markedly lower MLSS than the anaerobic and anoxic tanks, thereby reducing the chance of membrane biofouling and enabling longer membrane operation without compromising much on the removal performance.

![Figure 6.20 MLSS in different tanks.](image)

Figure 6.20 MLSS in different tanks.
6.3.5 Food to microorganism ratio (F/M)

The food to microorganisms (F/M) ratio is an important process control parameter for biological treatment systems. It is the ratio of the incoming food (BOD) to that of microorganisms (MLVSS) present in the system. The F/M ratio helps in maintaining the desired number of microorganisms for the system. A high F/M ratio favours bacterial multiplication and activity. However, with low mean cell residence time, it can lead to poor sludge settling characteristics resulting in a turbid effluent. Low F/M ratio along with high cell residence time can limit the amount of food available for the microorganisms. This can result in endogenous degradation of cells which begin to clump together to form flocs that settles easily (Richard et al., 2003).

Typically, MBR systems run at a third to half of F/M ratio (i.e. 0.05-0.15 g BOD/g MLVSS/day) compared to the conventional activated sludge process (Judd, 2010). In the present A2O system, the F/M ratio was calculated based on cumulative addition of MLVSS present in each tank (i.e., anaerobic, anoxic and aerobic tank). The BOD and MLVSS were calculated based on the rule of thumb conversion ratios i.e. COD/BOD and MLVSS/MLSS as 2.0 and 0.8 (Metcalf and Eddy et al., 2003).

The F/M ratio of the individual tanks and the MBR system for the four quarters was calculated as described by Water Environment Federation (2007) and from Table 6.2 it ranged between 0.06-0.21 g BOD/g MLVSS/day for the operational period.

<table>
<thead>
<tr>
<th>Tanks</th>
<th>F/M (g BOD/g MLVSS/day) ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q1</td>
</tr>
<tr>
<td>Anaerobic Tank</td>
<td>0.150</td>
</tr>
<tr>
<td>Anoxic Tank</td>
<td>0.09</td>
</tr>
<tr>
<td>Aerobic Tank</td>
<td>0.09</td>
</tr>
<tr>
<td>A2O MBR system</td>
<td>0.09</td>
</tr>
</tbody>
</table>
6.3.6 Performance of microfiltration membrane

The prepared and characterised PSf and PSf-GO microfiltration membranes were tested for operational performance through trans-membrane pressure (TMP) profile and turbidity of permeate water. Short term critical flux experiments were performed to analyse the fouling tendency of the membranes. Based on the experiments, one GO blended PSf membrane was selected for comparative lead removal study. SEM-EDS analysis was performed on the fouled membrane samples to check for presence of lead ions. Mass balance of lead was also undertaken to determine the mechanism of lead removal by the MBR system.

6.3.6.1 Turbidity

The turbidity of the permeate was monitored throughout the operational period (shown in Figure 6.21). The average turbidity was calculated to be 0.25 NTU, indicating the good separation efficiency of the prepared membranes (Figure A-13). Commercial MBRs demonstrate good effluent quality with turbidity of < 1 NTU (Frenkel et al., 2006). Turbidity increased beyond 0.3 NTU when the TMP reached 55 kPa; this can be attributed to membrane fouling, signifying the necessity for cleaning or replacement of the membrane. No significant change in turbidity was observed irrespective of the membrane used.

![Figure 6.21 Turbidity of permeate water during operation.](image-url)
6.3.6.2 Critical Flux of the membranes

Critical flux can be defined as a flux below which a decline of flux with time does not occur and above which fouling is observed (Field et al., 1995). Fouling can be a result of build-up of materials that can take place either by adsorption of materials due to attractive interaction between membrane and the particles, deposition of particles resulting in layers (also referred as cake formation), and gel formation due to concentration polarisation. Operating below critical flux range can improve the life and performance of membranes (Zhang et al., 2006).

Critical flux can be determined by different techniques such as a.) direct observation through the membrane, b.) particles mass balances and c.) flux-TMP measurements (Bacchin et al., 2006).

The commonly used short term critical flux determination involves incremental increase of flux for a fixed duration and for each increment, leading to a stable TMP at low flux, but an ever-increasing TMP after the flux crosses its criticality \(J_c\) (Le Clech et al., 2003). This method of evaluation is widely preferred as the convective flow of solute towards the membrane is constant and can be controlled during the run (Le Clech et al., 2003). In the present study, \(J_c\) was evaluated for the chosen membranes during continuous and intermittent modes of operation.

Figure 6.22 a shows the flux profile of the different membranes operated over a period of 120 min with four flux steps, each for 30 min. The 15 % PSf membrane with and without 0.25 % GO had an initial flux of 4 L/m\(^2\)h at suction rate of 2.5 mL/min pump setting. However, the 15 % PSf - 1 % GO and 20 % PSf -1% GO membranes had a higher flux of 12.5 and 8.3 L/m\(^2\)h for the same initial suction rate. This can be attributed to the higher hydrophilicity and porosity of the membranes with higher GO content. Although the 15 % PSf - 0.25 % GO membrane contained some GO, no substantial increase in flux was observed when compared to original PSf membrane.
Figure 6.22 Short term flux step test in continuous mode (a.) Flux variation with time and (b.) TMP variation with time.

In general, all membranes had a steep increase in flux on initial TMP increase before decreasing to attain a constant flux within 2 min. This was due to the solution retained in the tube which increased the initial flux and tapered off when a constant flow across the membrane was achieved.

The TMP profiles of different membranes under continuous operation are shown in Figure 6.22 b. The TMP increased with every flux step increase; the 15 % PSf and 15 % PSf - 0.25 % GO membranes reached a TMP of 35 and 40 kPa during the final flux step increment, indicating the effect of fouling. The 20 % PSf - 1 % GO and 15 % PSf - 1 % GO membranes however
had led to a lower TMP, i.e., 25 and 30 kPa, during the same step, indicating less fouling due to the introduction of GO. The membrane with higher polymer concentration (20% PSf - 1% GO) had lower TMP when compared to 15% PSf - 1% GO which had the same GO content.

A plot of $P_{\text{avg}}$ (average TMP for a particular flux) vs flux showed that the relationship was linear until the flux was 6.7, 7.5, 16.5 and 12.8 L/m$^2$h for the membranes 15% PSf, 15% PSf - 0.25% GO, 15% PSf - 1% GO and 20% PSf - 1% GO, respectively (Figure 6.23). This indicated that the permeability was constant during this period. The fluxes above these values plateaued with an increase in $P_{\text{avg}}$.

The rate of change of TMP (dTMP/dT) with flux showed that dTMP/dT increased differently for different membranes (Figure 6.24). Critical flux can be estimated from a point where the dTMP/dT value increases rapidly and tends to follow an exponential trend beyond that value. It was observed that the rapid increase varied across each membrane. For this study, it was decided that if dTMP/dT > 0.01 kPa/min, the flux at that point was critical. It is worth noting that there is no fixed dTMP/dT value for MBR systems to estimate critical flux, unless it is greater than zero (Le Clech et al., 2003). The advantage of this method is that the threshold is clearly defined which makes it easier to compare or identify the critical fluxes of membranes operated at different conditions.

**Figure 6.23** $P_{\text{avg}}$ - flux for membranes operated in continuous mode.
Figure 6.24 $d\text{TMP}/dT$ variation with flux of different membranes operated in continuous mode.

From the $d\text{TMP}/dT$ results (Figure 6.24), the critical fluxes for the 15 % PSf, 15 % PSf - 0.25 % GO, 15 % PSf - 1 % GO and 20 % PSf - 1 % GO membranes were estimated to be 6.7, 7.5, 16.5 and 12.75 L/m$^2$h respectively. The critical flux increased with increase in GO for 15 % PSf. Zhao et al. (2014) observed a similar increase in flux from 30-33 L/m$^2$h to 48-50 L/m$^2$h for pristine PVDF and PVDF/GO composite membranes and attributed the increase to improved hydrophilicity of the modified membrane.

For the membranes with the same GO concentration, but different polymer concentrations (i.e., 15 and 20 % PSf), the critical flux value decreased. This may be due to decrease in porosity owing to higher packing density caused by the polymer concentration. For membranes with higher porosity the pores are very close to each other, and this can promote steric hindrance between particles and prevent deposition on top of them. This mechanism can even prevail beyond critical flux (Bacchin et al., 2006).

Figures 6.25 (a) and (b) show the flux and TMP profiles of the membranes operated in intermittent mode over 120 mins. The raw flux vs time graph (Figure 6.25 a) shows the intermittent operation (8.5 min on and 1.5 min off) of the system with flux step increments after every 30 min. From the TMP vs time graph (Figure 6.25 b), the influence of residual and cake layer fouling (as observed by Howell et al., 2004) can be noted.
Figure 6.25 (a.) Short term flux step test - Flux variation with time in intermittent mode and (b.) TMP variation with time in intermittent mode.

The relationship between $P_{avg}$ and flux can be observed in Figure 6.26. This graph can also help to predict the critical flux considering the point where there is transition from TMP-dependent to TMP-independent flux.

The dTMP/dT profile of different membranes run during intermittent operation is shown in Figure 6.27. The critical flux values were identified when the dTMP/dT $>$ 0.01 kPa/min and were found to be 7, 6.4, 19 and 15 L/m$^2$h for the 15 % PSf, 15 % PSf - 0.25 % GO, 15 % PSf - 1 % GO and 20 % PSf - 1 % GO membranes, respectively, correlating well with the critical flux values from the relationship between $P_{avg}$ vs flux.
From the results, it was observed that the mode of operation had little influence on critical flux for the 15% PSf and 15% PSf - 0.25% GO membranes. However, for membranes with higher GO concentrations (15% PSf - 1% GO and 20% PSf - 1% GO), the critical flux value increased for intermittent with backwash operation, indicating that operational mode was more appropriate for them. In a related study by Dimuth et al. (2002), it was reported that intermittent mode with membrane relaxation was useful in mitigating fouling and removing foulants from
membrane at lower MLSS concentration. Le Clech et al. (2003) also reported a similar critical flux range (when dTMP/dT>0.01 kPa/min) for an aerobic submerged tubular membrane to be 10-12 L/m²h and 15-19 L/m²h for synthetic and real wastewater respectively. Related studies (refer Table 6.3) also estimated critical flux through dTMP/dT changes. The dTMP/dT values ranged between 0.004 – 0.05 kPa/min and it was entirely dependent on the prevailing operating conditions.
Table 6.3. Summary of related studies on critical flux in MBR.

<table>
<thead>
<tr>
<th>MBR Type</th>
<th>Membrane characteristics</th>
<th>Conditions</th>
<th>J_c (Critical Flux) (L/m²h)</th>
<th>dTMP/dT</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UASB – side stream Bench top</td>
<td>PVDF-MF (0.22µm)</td>
<td>Crossflow with flat plate; Fed with UASB treated effluent</td>
<td>0.3-0.5 g/L; Short-term critical flux: 50; Long-term flux :30</td>
<td>0.004 kPa/min</td>
<td>Cho and Fan (2002)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerobic – side stream</td>
<td>Alumina multi-tube membranes (0.05µm)</td>
<td>Tubular filtration; COD loading rate 3g/L</td>
<td>1.8 g/L; Critical fluxes:30-40</td>
<td>0.03 bar/hr</td>
<td>Oginer et al. (2002, 2004)</td>
</tr>
<tr>
<td></td>
<td>Tubular membranes (0.2 µm)</td>
<td>Tubular filtration; synthetic and real wastewater</td>
<td>4-12 g/L; Critical fluxes: 10-12 for synthetic and 15-19 for real wastewater</td>
<td>0.01 kPa/min</td>
<td>Le Clech et al. (2003)</td>
</tr>
<tr>
<td>Pilot plant with anoxic and aerobic Tanks-Submerged</td>
<td>PVDF-hollow fibre (0.04 µm)</td>
<td>Domestic wastewater with COD loading of 574.6 ± 165.9 mg/L with intermittent mode of operation (540)</td>
<td>10 ± 0.5 g/L; Critical flux: 30-31 when aeration rate was 0.5 Nm³/m²h and 24.9 when aeration rate was 0.3 Nm³/m²h</td>
<td>0.015 kPa/min</td>
<td>Guglielmi et al. (2007)</td>
</tr>
</tbody>
</table>
Aerobic-submerged Lab scale | Hollow fibre PE membrane module (0.4 µm) | Fed with synthetic wastewater with COD loading of 750 mg/L; Continuous and intermittent modes of operation (12 mins on and 3 mins off) | 4-7 g/L Critical fluxes for 4-7 g/L MLSS: 48-51, 36-39 for intermittent cycles and 36-39, 30-33 for continuous cycle of step duration of 20 and 40 mins; 7-10 g/L MLSS: 15-18, 12-15 and 15-18,12-15 for intermittent and continuous cycles with duration of 20 and 40 mins respectively | 0.035 kPa/min | Howell et al. (2004)

| Aerobic-submerged | Flat sheet membranes | Flat sheet filtration; Synthetic wastewater with organic loading 4.8 kg/m³’d | 4-5 g/L Critical fluxes based on visual observation of step-wise flux increment: 30-33 for PVDF membrane and 48-50 for PVDF/GO composite membrane | Notvaluated | Zhao et al. (2014)
6.3.6.3 Long term TMP profiles of the chosen membranes

The long term TMP profile of the MBR is shown in Figure 6.28 a. The first four cycles were operated at 10.62 L/m$^2$h with PSf membrane devoid of GO. Cycle 5 and 6 represent the 15% PSf and 15% PSf -1% GO membranes operated at 6.37 L/m$^2$h. When the TMP reached 55 kPa, the membrane was removed and either cleaned or changed. The membranes were cleaned by soaking them in de-ionised water overnight after removing them from their module. A cycle here represents when a membrane is due for change (when the TMP reaches 55 kPa) after it has been cleaned once. Membranes were changed after each cycle. For cycles 5 and 6, the membranes were run without cleaning for comparative study. From the results, the average number of days for one single cycle was calculated to be 50 days for PSf membrane. In a study by Zhao et al. (2014), a commercial PVDF membrane with an operating flux of 10 L/m$^2$h was reported to have filtration cycle of 65 days with membrane cleaned thrice during its operation.

TMP profiles of 15 % PSf and 15 % PSf – 1 % GO are shown in Figure 6.28 b. Both the membranes were operated at 6.3 L/m$^2$h, below their critical flux values. From the figure, it can be observed that the PSf membrane reached 55 kPa in around 60 days. The GO blended PSf membrane reached a maximum of 30 kPa during the same period and took 85 days to reach 55kPa. This demonstrates the positive effect of GO on filtration time, cleaning frequency and against fouling. Zhao et al. (2014) reported a similar increase in filtration cycle of a GO blended PVDF membrane as 80 days operating at a flux of 10 L/m$^2$h, below its critical flux.
Figure 6.28 (a.) Long term TMP profile of the MBR and (b.) TMP profiles of 15 % PSf and 15 % PSf – 1 % GO blended membranes (Cycle 5 and 6).

6.4 Lead (Pb) removal

Lead concentration of 5 mg/L was introduced into the system from the 109\textsuperscript{th} day. Figure 6.29 shows the lead removal over the three quarters with SRT remaining infinite. The average removal for the second quarter was estimated to be 73 % with a HRT of 86.4 h. When the HRT
was increased to 144 h in the third quarter, the average removal percentage increased to 89% with a maximum removal of 98% during this phase. During the fourth quarter, the glucose concentration was decreased (Table 3.3) which varied the COD/TP and COD/TN ratio. This resulted in a reduction of lead removal to 80% with a maximum removal of 85%. The average effluent lead concentrations during the three quarters were 1.40, 0.6 and 1.1 mg/L.

![Figure 6.29](image.png)

**Figure 6.29** Lead concentration in feed and permeate tanks and its overall removal percentage.

Biological treatment for metal removal is predominantly through adsorption and complexation of the metals with the microorganisms (Metcalf and Eddy et al., 2003). The negatively charged microbial surfaces interact with the positively charged metal ions and adsorb them. Metal ions also form complexes with the carboxyl, hydroxyl, phosphate and sulphate groups present on the lipids, proteins and polysaccharides present on the microbial cell surface (Metcalf and Eddy et al., 2003). Other mechanisms involved in metal removal include bioaccumulation, transformation and chemical precipitation (Gadd, 2004 and Bae et al., 2000). The removal of heavy metals in MBR systems is mainly due to biosorption (Santos and Judd, 2010). Arevalo et al. (2013) looked at removal performance of heavy metals in MBR systems with microfiltration and ultrafiltration membranes. It was reported that Cr, Cd, Cu, Zn, Sn and Pb showed good removal and had a great affinity for attachment to sludge particles. Also, lead removal with MBR having ultrafiltration membrane did not show significant advantage over microfiltration membrane. Statistically significant results were observed in lead removal with
increase in activated sludge MLSS concentrations from < 5 g/L to 20 g/L showing a maximum removal of 99.51 % at maximum MLSS concentration. Moslehi et al. (2008) reported on heavy metal removal from industrial wastewater using a membrane bioreactor. Heavy metal and COD removal were studied with increasing concentration of the metal ion concentration when the COD/N/P ratio was 100/5/1. It was observed that at a concentration greater than 10 mg/L of lead, the removal significantly decreased.

6.5 Mass balance for lead

The accumulation of lead (Pb) ions in different tanks was calculated using the mass balance equations (refer section 3.4.6). The accumulation of lead in the anaerobic (E), anoxic (F) and aerobic (G) tanks was estimated to be 10.65, 1.98 and -0.36 mg/day respectively. It can be noted that the accumulation in aerobic tank had a small negative value. This small imperfection in the balance is undoubtedly due to the error in estimation of lead. Assuming the accumulation in the aerobic tank and on the membrane surface is negligible (i.e., value for G = 0) due to very low MLSS and recirculation, the E and F values would be 10.65 and 1.62 mg/day. Table 6.4 gives the numerical data of lead mass balance equations.
Table 6.4 Numerical data of lead mass balance equations.

<table>
<thead>
<tr>
<th>Tank</th>
<th>Flow rate (L/day)</th>
<th>Mass of lead (mg/day)</th>
<th>Accumulation of lead (mg/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Tank</td>
<td>$Q_0 = 3$L/day</td>
<td>$Q_0 C_{0(Pb \text{ inflow to anaerobic tank})} = 16.17$</td>
<td></td>
</tr>
<tr>
<td>Anaerobic</td>
<td>$Q_0$</td>
<td>$Q_0 C_{1(Pb \text{ inflow to anoxic tank})} = 5.52$</td>
<td>$E = 10.65$</td>
</tr>
<tr>
<td>Anoxic</td>
<td>$Q_0+Q_1 = 9$L/day</td>
<td>$(Q_0+Q_1) C_{2(Pb \text{ inflow to aerobic tank})} = 19.08$</td>
<td>$F = 1.62$</td>
</tr>
<tr>
<td>Aerobic</td>
<td>$Q_1 = 6$L/day</td>
<td>$Q_1 C_{4(Pb \text{ recirculation tank})} = 15.54$</td>
<td>$G = 0$</td>
</tr>
<tr>
<td>Permeate</td>
<td>$Q_0$</td>
<td>$Q_0 C_{3(Pb \text{ outflow as permeate tank})} = 3.9$</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

The accumulation results corroborate well with the MLSS values of different tanks i.e., ~5 g/L in anaerobic and anoxic tank and 0.4 g/L in aerobic tank, suggesting the predominant role of biomass in accumulation of lead. The present results are also in agreement with the study by Arevalo et al. (2013) discussed earlier which highlighted that heavy metal removal was predominantly due to the activated sludge MLSS concentration in an MBR system.

6.6 SEM-EDS of the membranes

The membrane surface composition and its chemistry play a crucial role in interaction between foulants and its surface. SEM-EDS analysis was used for analysing the surface morphology and elemental/chemical composition of the samples.
Figure 6.30 shows the scanning electron micrographs of the membrane samples. The micrographs reveal the fouled portions of the membranes. The 15 % PSf - 1% GO membrane (Figure 6.30 b) had cracks on the fouled surface due to sample drying.

**Figure 6.30** SEM of fouled (a.) 15 % PSf membrane and (b.) 15 % PSf - 1% GO membrane.
The EDS spectra of the membrane samples are shown in Figure 6.31. From the spectra, it can be noted that the fouled PSf membrane showed characteristic Pb X-ray peaks Kα1, Mα1, Lα1, Lβ1 and Lγ1 emitted by the K, M and L energy level shells. The 15 % PSf - 1 % GO membrane had Pb X-ray peaks Mα1, Lα1, Lβ1 and Lγ1 emitted by the M and L energy level shell. Both results confirm the presence of Pb on the fouled membranes.

**Figure 6.31** EDS spectra of fouled (a.) 15 % PSf membrane and (b.) 15 % PSf – 1 % GO membrane.
The composition of the elements deposited on the fouled membranes was estimated (Table 6.5). The elements that were predominantly present were C and O. The amount of C in the 15 % PSf – 1 % GO membrane was higher than in the PSf membrane due to the presence of GO. The element S from the polymer polysulfone was also detected. The concentration of S was higher in the 15 % PSf – 1 % GO fouled membrane. This could be a result of the amplified signal from the un-fouled region of the membrane observed (Figure 6.30 b.). Trace elements such as Si, Cl, K, Cu and Zn were also detected. A small percentage of Pb was also seen on the fouled membranes. This could be the result of Pb associated with foulants present on the membrane being retained.

The elemental composition maps of the membranes are presented in Figure 6.32. From the maps, it can be observed that the Pb was well distributed throughout the membranes. Pb deposits were also found on the un-fouled regions of the 15 % PSf – 1 % GO membrane (Figure 6.32b), indicating the role of the membrane in Pb separation. P, Ca and Fe were predominantly deposited only in the fouled sections of 15 % PSf – 1 % GO membrane, suggesting their interaction with the foulant.
Table 6.5 Elemental composition of fouled membranes.

<table>
<thead>
<tr>
<th>Spectrum Label</th>
<th>Map sum Spectrum of 15 % PSf fouled membrane (%)</th>
<th>Map sum Spectrum of 15 % PSf and 1 % GO fouled membrane (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>55.97</td>
<td>63.99</td>
</tr>
<tr>
<td>O</td>
<td>34.88</td>
<td>25.48</td>
</tr>
<tr>
<td>Na</td>
<td>0.52</td>
<td>0.39</td>
</tr>
<tr>
<td>Mg</td>
<td>0.4</td>
<td>0.21</td>
</tr>
<tr>
<td>Al</td>
<td>0.24</td>
<td>0.1</td>
</tr>
<tr>
<td>Si</td>
<td>0.19</td>
<td>0.1</td>
</tr>
<tr>
<td>P</td>
<td>2.33</td>
<td>1.33</td>
</tr>
<tr>
<td>S</td>
<td>0.88</td>
<td>4.7</td>
</tr>
<tr>
<td>Cl</td>
<td>0.03</td>
<td>0.16</td>
</tr>
<tr>
<td>K</td>
<td>0.31</td>
<td>0.1</td>
</tr>
<tr>
<td>Ca</td>
<td>1.99</td>
<td>1.11</td>
</tr>
<tr>
<td>Fe</td>
<td>1.7</td>
<td>2.01</td>
</tr>
<tr>
<td>Cu</td>
<td>0.11</td>
<td>0.1</td>
</tr>
<tr>
<td>Zn</td>
<td>0.08</td>
<td>0.06</td>
</tr>
<tr>
<td>Pb</td>
<td>0.36</td>
<td>0.15</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
(a.)
Figure 6.32 Elemental composition maps (a.) 15 % PSf membrane and (b.) 15 % -1 % GO membrane.
6.7 Conclusion

The present chapter investigated the role GO and PSf in determining the properties of the prepared microfiltration membranes. The PSf concentration played a positive role in improving the mechanical strength of the membrane, and the addition of GO significantly enhanced the flux, porosity and hydrophilicity of the membranes. The applicability of the microfiltration membranes was studied using an MBR system.

The performance of the GO blended PSf microfiltration membranes in an MBR system was assessed through short term critical flux experiments under two operational modes (continuous and intermittent). The results showed that the mode of operation had little influence on critical flux for membranes having low content of GO (15 % PSf and 15 % PSf - 0.25 % GO). For membranes with higher GO concentrations (15 % PSf - 1 % GO and 20 % PSf - 1 % GO) the critical flux value increased, indicating the positive influence of GO against fouling. The membrane 15 % PSf - 1 % GO with asymmetric morphology and 0.2 µm pore size showed best performance with a critical flux of 16.5 and 19 L/m²h for continuous and intermittent mode, respectively.

A comparative study on long term TMP profile of 15% PSf and 15% PSf - 1% GO membranes was performed at a flux of 6.3L/m²h (below their critical flux). It was found that the GO blended membrane demonstrated longer filtration time and need for lower cleaning frequency, which in turn can reduce the operational costs and improve the ease of operation.

The MBR system with the microfiltration membrane was studied for lead ions removal. Operational parameters such as pH, temperature, DO, ORP, conductivity and TDS were constantly monitored. Synthetic wastewater containing lead ions was fed and its removal performance was assessed. COD removal of 99.14 % was maintained throughout the operation process. Total phosphorus had a maximum removal of 52 % and total nitrogen showed an average minimum removal of 72%. Complete removal of ammonia was achieved. Trace amounts of nitrite and nitrate were present in the permeate water. The MBR was operated with an average MLSS of 10.6 g/L and varying F/M ratio (0.06-0.21). Irrespective of the membranes, the permeate water had an average turbidity of 0.25 NTU, demonstrating good separation efficiency.

A maximum lead removal of 98% was achieved when the HRT was 144 h. For the same HRT, only 85% removal was observed when the influent COD concentration was decreased,
indicating the requirement of COD for its removal. Mass balance for lead revealed that much of its removal was through accumulation by the biomass present in the anaerobic and anoxic tanks. SEM-EDS analysis of the fouled membranes showed Pb peaks on the fouled and un-fouled sections of 15 % PSf and 15 % PSf – 1 %GO membranes indicating the association of Pb with the foulant and the role of membrane in Pb separation.

Figure 6.33. Schematic of MBR’s performance.
Chapter 7
Conclusions and future recommendations

7.1 Conclusions

This thesis examined the application of GO in different treatment systems for Pb (II) ions removal. At first, GO based magnetic nano-sorbent was synthesised, characterised and studied for lead removal. Then, GO blended PSf ultrafiltration membranes were prepared and demonstrated to reject lead. Finally, an MBR system with A2O process was evaluated for lead removal using the synthesised GO blended microfiltration membranes.

The nano-sorbent (PS@Fe3O4@GO) synthesised for lead ion adsorption showed a maximum removal of 93.78%. This was achieved at an operating condition of contact time = 8h, temperature= 35 °C and pH =6. The adsorption followed pseudo first order kinetics and the Langmuir adsorption isotherm model. The adsorption capacity of the nano-sorbent was estimated to be 73.52 mg/g. The role of GO on lead ions removal was confirmed using FT-IR and XPS results, showing the removal was mainly due to electrostatic attraction and chelation of lead ions onto the GO surface. The regeneration and re-usability of the prepared magnetic nano-sorbent was also studied for four adsorption-desorption cycles. Although the removal decreased to 40% at the end of fourth cycle, it was shown that adsorbent had potential for regeneration and thus reuse.

The results from the above study contributed insights on the mechanism of lead adsorption by the nano-sorbent. Knowledge on the specificity of interaction between GO and Pb (II) ions was also gained. The optimised operational parameters and the regeneration/reuse study provided an understanding on the feasibility of practical application of the nano-sorbent. This provided the direction for the next phase where GO was blended membranes were prepared.

Microfiltration and ultrafiltration membranes with enhanced physio-chemical properties were prepared by blending GO with PSf. Increased composition of GO in the blend considerably improved the hydrophilicity, porosity and flux of the membranes. The mechanical property, i.e., Young’s modulus, increased with polymer concentration. Scanning electron micrographs revealed the asymmetric structure of membranes with bigger macro-voids for membranes having GO. The pore size for microfiltration and ultrafiltration membranes were in the range
of 179-250 nm and 18-24 nm respectively. Ultrafiltration membranes were investigated for lead removal using a cross flow filtration set-up. A maximum rejection of 98% was observed for 15 % PSf - 1% GO membrane, which was higher by 1% for membrane devoid of GO. The operating pressure also played a role in rejection, and decreased with increase in pressure.

These results provided insights on membrane preparation with enhanced properties and different pore sizes. Knowledge on the morphological changes after incorporation of GO was gained. The effect of operating pressure and high lead rejection by the prepared GO-PSf ultrafiltration membranes demonstrated the possibility of its practical application. This was a standalone application of GO blended membrane for contaminated liquid streams devoid of organics. For liquid streams contaminated with organics, biological treatment along with membrane process is preferred.

This lead to our next phase of work where an MBR system was examined for removal of Pb ions along with other nutrients. Complete removal of COD and ammonia was reported. Total phosphorus had a removal of 52%. Lead removal reached a maximum of 98% with majority of it accumulation in the anaerobic tank. GO blended microfiltration membranes were investigated for its ability towards fouling mitigation under two operational modes (intermittent with backwash and continuous) through critical flux study. Membranes with higher GO concentrations showed increased critical flux, demonstrating the antifouling property of the membranes. Long term TMP profile also established the positive effect of GO in filtration time and cleaning frequency. Mass balance for lead revealed that majority of lead was accumulated in the anaerobic tank. SEM-EDS indicated the role of membrane in lead separation, with much of lead was present on the foulant.

The above study contributed insights on the application of custom made microfiltration membranes in an MBR system. The role of individual treatment units (biological processes and membrane process) on nutrient and lead removal was established. Knowledge on the fouling mechanism of different GO blended microfiltration membranes were gathered. A year-long operation of the MBR helped in establishing the operational conditions, which can further be extended for real time application.
7.2 Recommendations for future studies

The majority of the environmental applications of magnetic nano-sorbents are targeted towards treatment of a specific pollutant. Treatment of wastewater containing different contaminants using magnetic nano-sorbents has scarcely been studied. Further, insights on the mechanism of treatment of such contaminated wastewaters is still required. Another important issue with the use of magnetic nano-sorbents is its potential toxicity to environment and human beings. This area needs to be duly addressed via toxicity research studies. Such studies would help us to understand and address the issue of disposal of spent nano-sorbents and treated solutions. Economic feasibility studies should also be conducted to compare with other low cost adsorbents, to check for viable commercial application.

Advancements in nanotechnology have led to new knowledge in the development of composite membranes for different applications. These membranes are known to provide specific functionalities in addressing different issues. However, there is a lack of reports on the robustness and operational life of such membranes. Also, a better understanding is needed of the fouling mechanisms of composite membranes. Eco-toxicity studies of composite membranes should also be performed as the nano-components used may be released into the environment over their operational life.

MBRs are an effective treatment system used to predominantly treat municipal and industrial sludge with high organic loading. Relatively few studies have been reported on treatment of inorganic and heavy metals using MBR systems. Such studies can further enhance our understanding of the applicability of MBRs for the treatment of non-biodegradable substances. The fate of heavy metals and inorganics accumulated in the sludge should be investigated, as this would provide a better knowledge on disposal techniques that could be adopted. The role of the membrane in separation of contaminants and microorganism removal can be studied by decreasing the HRT, as this would provide insights on the suitability of membranes for the MBR treatment process. Data on the microbial flora of MBRs can also help in selection of specific microbial strains for a designated treatment process, thereby overcoming the problems of acclimatisation and toxicity caused by the waste. Further research on energy reduction through better designs is also encouraged. Information on operational and capital costs would give us better understanding on the scale up of such system for commercial application.
References


Appendices

Appendix A-1 Membrane casting process.

Appendix A-2 Membranes after casting (L-R: 15 % PSf membrane, with 0.25 % GO and 1 % GO).
Appendix A-3 Representative image of water contact angle (Result of 15 % PSf membrane).

Appendix A-4 Representative graph of tensile strength test (Result of 18% PSf membrane).
Appendix A-5 Cross-flow membrane filtration rig.

Appendix A-6 Membrane Bioreactor (MBR) system used for the study.
Appendix A-7 Standard curve of lead used for research chapter 4.

Appendix A-8 SEM image of assembled nano-sorbent (PS@Fe₃O₄@GO).
Appendix A-9 SEM cross sections of the pore channels.

Appendix A-10 Standard curve of lead used for research chapter 5.
Appendix A-11 Standard curve of lead used for research chapter 6.

Appendix A-12 Custom made membrane module with 15 % PSf membrane.
Appendix A-13 Permeate water after MBR treatment process.