APPLICATION OF CERAMIC MEMBRANE IN WATER AND WASTEWATER TREATMENT

A thesis submitted in partial fulfillment of the requirement for the award of the degree of

MASTER OF ENGINERING
in
WATER RESOURCES AND HYDRAULIC ENGINEERING

Submitted by

SWACHCHHA MAJUMDAR
(EXAMINATION ROLL NO M6WRP22004)

Under the Guidance of

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Faculty of Engineering and Technology, Jadavpur University
Kolkata – 700 032, India
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CERTIFICATE OF RECOMMENDATION

This is to certify that the thesis entitled "Application of Ceramic Membrane in Water and Wastewater Treatment" is a bonafide work carried out by Mr. Swachchha Majumdar under our supervision and guidance for partial fulfilment of the requirement for the Post Graduate Degree of Master of Engineering in Water Resources and Hydraulic Engineering during the academic session 2021-2022.

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This forgoing thesis is hereby approved as a credible study of an engineering subject carried out and presented in a manner satisfactorily to warranty its acceptance as a prerequisite to the Degree for which it has been submitted. It is understood that by this approval, the undersigned does not endorse or approve any statement made or opinion expressed or conclusion drawn therein but approves the thesis only for the purpose for which it has been submitted.

Committee of the final examination

For the evaluation of the thesis

[**] Only in case of the thesis is approved

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Swachchha Majumdar

Date: August, 2022

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DECLARATION OF ORIGINALITY AND COMPLIANCE OF ACADEMIC ETHICS

I hereby declare that this thesis contains a literature survey and original research by the undersigned candidate as part of the Master of Engineering in Water Resources and Hydraulic Engineering in the Faculty of Interdisciplinary Studies, Jadavpur University during the academic session 2019-2022.
All information in this document has been obtained and presented in accordance with academic rules and ethical conduct.

I also declare that, as required by these rules and conduct, I have fully cited the references of all materials that are not original to this work.

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Abstract

The report presents some basic details of membranes processes and particularly ceramic membranes, methods of characterisation of ceramic membranes. In the experimental part, feasibility of ceramic membrane based processes for river water purification, tannery wastewater treatment and Oxidation of Iron (II) and Arsenic (III) to Iron (III) and Arsenic(IV)through Ceramic membrane contactor has been investigated.

In the recent years, membrane technology including ceramic membrane is being widely applied in different separation and purification application. This is due to the fact that with the threshold limits of water quality parameters and various discharge norms of the treated wastewater are getting stringent day by day and many of the conventional treatment systems are not being able to meet many of these norms. But with the incorporation of membrane based systems, meeting such norms have become possible.

As the structural and operational advantages of modular ceramic membranes, the basic laboratory investigation with saline river water has established the potential of using ceramic membrane for turbidity removal after primary sedimentation. For tannery wastewater, the investigation has shown promising result in terms of removal of certain pollutant parameter.

In another investigation, the porous morphological structure has been used not as a separation device, but it was used for surface contacting device for gas-liquid interphase for better oxidation of Iron(II) and Arsenic (III). In addition, field application of ceramic membranes for removal of arsenic from contaminated groundwater has been discussed.

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CHAPTER 1

INTRODUCTION

1.1 Membrane and Membrane Filtration

A membrane can be having homogeneous or heterogeneous structures through which passive or active transport can take place. Pressure, concentration or temperature difference is the driving force of passive transport. Usually the natural membranes are biological in nature. Synthetic membranes are those which can be synthesised artificially. Membranes can be of organic and inorganic in nature. Membranes can be classified based on the morphology or structure. Based on the structure and morphology, membranes can be isotropic and anisotropic in nature. Isotropic membranes have a homogenous composition where their structure is made up of a single material and have symmetric pore structure over the cross section. Isotropic membranes are further divided into macro porous membranes, nonporous dense films, and electrically charged membranes.

Anisotropic membranes are heterogeneous, have thin porous or nonporous selective barrier which is supported upon a much thicker porous substructure. Anisotropic membranes can be phase-separation membranes and composite membranes based on their structures. Phase separation membranes have layered or graded structure, having different pore size, porosity and thickness across graded structure. Composite membranes have a heterogeneous chemical composition of at least two different materials and structures. Thin film membranes consist of a thin layer on top having a selective membrane material and a thick porous support.

Based on the above, in general membranes can be of following types:

a) natural and synthetic membranes
b) gas phase and liquid phase membranes
c) porous and non-porous membranes
d) adsorptive and diffusive membranes
e) others like ion exchange membranes, osmotic membranes, inert membranes etc.

1.2 Membrane, its classification

Membrane separation is an important technology used in many industrial purification applications. A membrane is a thin, film-like structure capable of separates two fluids. A membrane separation system separates an influent stream into two effluent streams known as permeate and concentrate. Permeate is the portion of the fluid that has passed through the semi-permeable membrane whereas the concentrate stream contains the constituents that have been rejected by the membrane. Membrane layer is permselective barrier between two phases and which is selectively impermeable to specific particles, molecules, or substances under specific driving force. Membranes can be of various thicknesses with homogeneous or heterogeneous structure. Membrane are also classified based on pore diameter. According to IUPAC, there are three different types of pore size classifications:

- Micro-porous (dp< 2 nm),
- Meso-porous (2 nm <dp< 50 nm) and
- Macro-porous (dp> 50 nm)

Membranes can also be classified by pore size into Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and reverse osmosis (RO) as per the following table:

Table 1.1 Types membrane based on pore sizes

Membrane type	Average pore sizes	Pressure Difference	Application
Microfiltration	0.1 –10 µm	0.5 –2 bars	Separation of suspended particles
Ultrafiltration	1-100 nm	1-10 bars	Separation of macromolecules e.g. proteins & virus
Nanofiltration	0.5 – 5 nm	10-70 bars	Separation of dyes; Water softening
Reverse Osmosis	< 1 nm	10-100 bars	Desalination

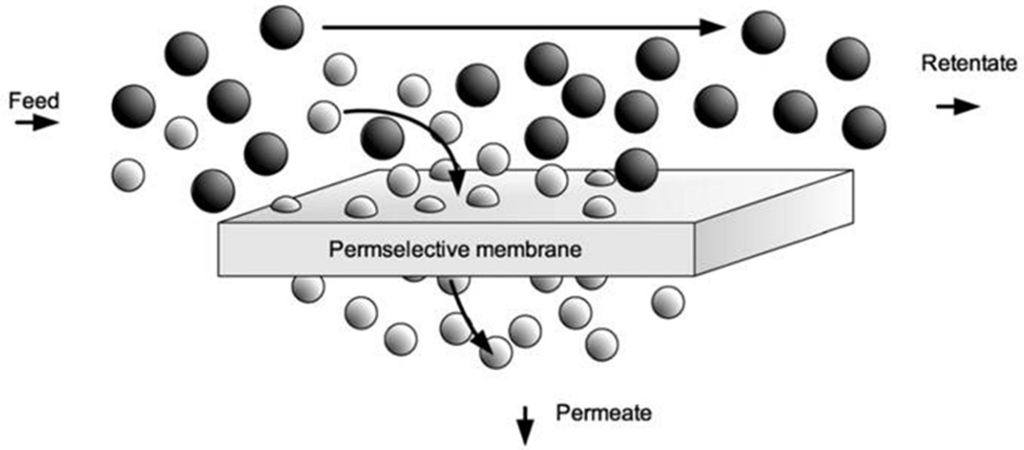


Fig. 1.1 Schematic of membrane process

On the basis of material of constructions, membranes can be organic e.g. polymeric or inorganic e.g. Metal or ceramic substances. **Organic Membranes** are widely used as these have good flexibility with respect to rejection characteristics. Cellulose acetate, polyamide and polysulfone etc. are extensively used for organic membrane manufacturing.[1] **Inorganic membranes** are having several advantages over polymeric membranes as their material property and operational ruggedness are suitable in many applications. The downside is their high cost which explains their application currently is limited to aggressive/high temperature fluids treatment. Materials most commonly used for inorganic membranes are oxides of Alumina, Zirconium, Titanium and Silica. These and other inorganic materials can also be mixed in proportion for making inorganic membranes.

Asymmetric ceramic membranes comprises of membrane layers, of nano and micro pores, adhering to the substrate of macro porosity. Primarily the substrate pore sizes are in the range of 3-5 microns and total porosity will be over 45%. Membrane layers are deposited by slurry/sol gel techniques. Intermediate layer typically contains pore sizes in the 100-200nm range and is obtained by the deposition of alumina slurry with binders on substrates followed by heat treatment. The ultrafiltration layer normally comprises of pores in the 10-20nm range and is deposited using sol gel precursors of respective metal oxides A typical cross section is shown below:

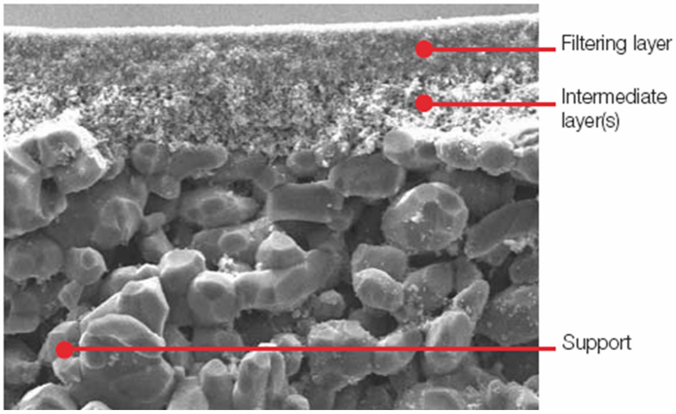


Fig. 1.2 Schematic of membrane process

Filtration is separation of two or more components from a fluid stream primarily based on size differences. Membrane filtration extends this application not only for separation of immiscible particles from a liquid stream but also to separation of dissolved solutes in liquid streams and for separating gas mixtures.

A membrane can be thought of as a selective barrier that allows the passage of certain components while restricting others. A membrane unit splits the feed stream into two parts—

1. Permeate--components which are small enough to pass through membrane

2. Retentate--large components retained by the membrane

The pressure across the membrane separation unit is termed as Trans Membrane Pressure (TMP). While suspended particles can be retained by MF (TMP: 0.1 – 4 bar), macromolecules like proteins can be retained by UF(TMP: 5-10 bar), sugars, dissociated acids, divalent salts can be retained by a NF(TMP: 10-30 bar) while RO, with smallest pore size and operating at a very high TMP(35-100 bar) can retain undissociated acids, monovalent salts etc.

According to the mode of operation, membrane filtration can be classified as a Dead- end filtration unit or a Crossflow filtration. The feed is sent perpendicular to the membrane during dead end filtration, which leads to quick clogging of pores while in Crossflow mode, the feed is sent tangentially across the membrane leading to auto cleaning of the pores. The impurities present on the pores are scrubbed off by the next layer of water and thus the tendency of clogging of membranes is much less in this case compared to dead end filtration. Dead-end mode is considered as the most basic form of filtration. It could be a practical technique for concentrating compounds.[2]

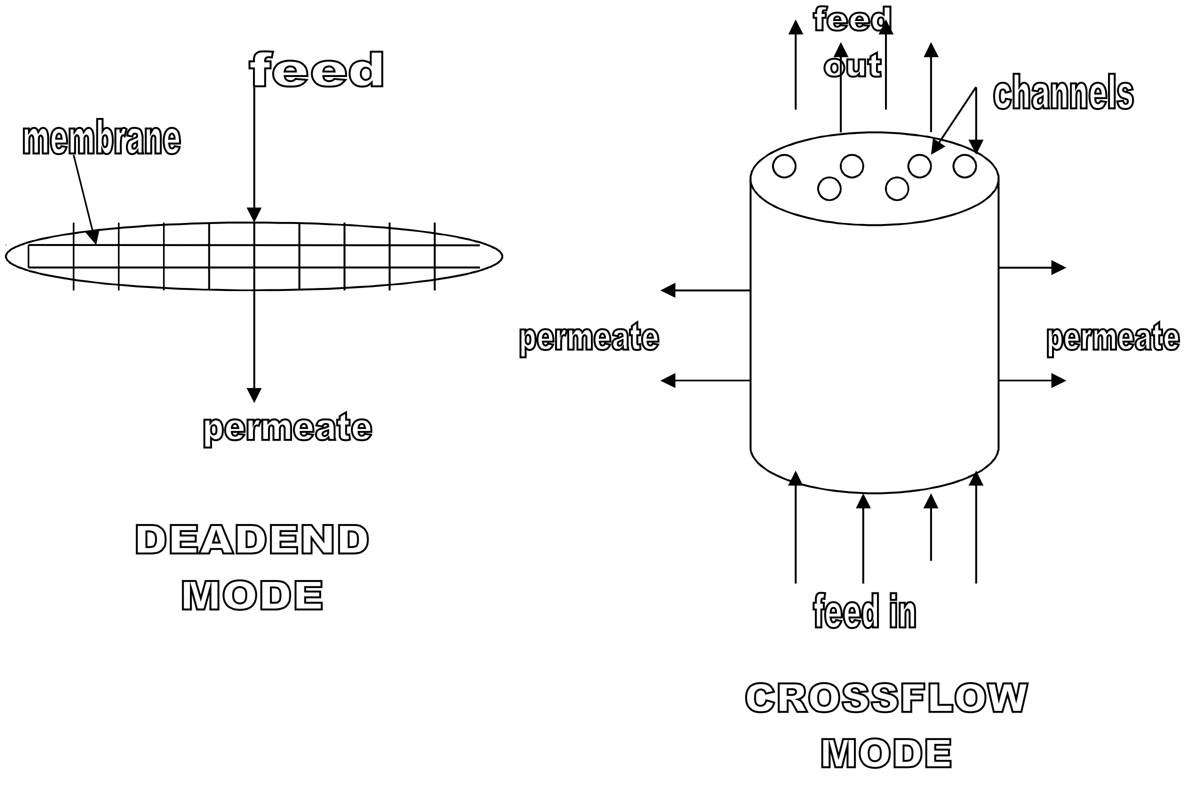


Fig. 1.3 Different modes of Operation

1.3 Ceramic Membranes and their advantages

Ceramic membranes are inorganic membranes which are generally tubular in shape. Each tube may have a number of smaller tubes (lumens) through which the feed flows parallel to the tube axis and the permeate flows out from the sides perpendicularly. The supports for the membranes are usually made of alumina, silica etc. with open pores. These materials provide a high degree of mechanical stability and also are highly permeable. A membrane layer of few microns/nanometres thick are applied by coating techniques to the inner surface of the channels. The membrane material may be made of Alumina, Titania, and Zirconia etc. Before applying the active microporous top layer, a mesoporous intermediate layer is often applied over the macroporous support to reduce surface roughness.

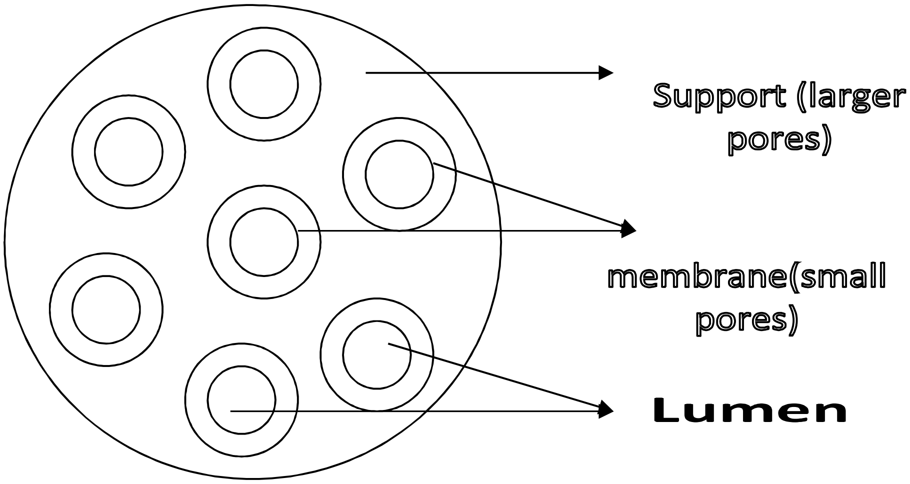


Fig. 1.4 Cross section of a Ceramic Membrane

The advantages of ceramic membrane are manifold.

1. It is inert to common chemicals and solvents and can tolerate a Chlorine dosage of upto 2000 ppm.
2. It can operate within wide temperature and pressure (10 bar) limits and tolerates wide pH limits (1-13).
3. It supports backflushing excellently and can be cleaned easily.
4. It has got an extended lifetime of 5-7 years.

Major disadvantages of ceramic membrane are high initial cost of fabrication and brittleness. Mostly, ceramic membranes operate in the MF and UF range and there are very few Ceramic nanofiltration membrane manufacturers in the world. Ceramic Membranes are also being developed in configurations like hollow fiber and catalytic membranes. However in the MF regime, the ceramic membrane is a very good investment in spite of the high initial installation cost because of its long life, wide operating ranges, less cleaning and savings in labour costs.

1.4 Applications of Ceramic Membranes

Ceramic Membranes are being successfully used nowadays in not only in water or wastewater treatment but also in a) Oil-water separation b) Biomass Separation c) Purification of proteins d) Fermentation e) Fruit Juice clarification f) Effluent concentration.

Ceramic Membranes also find application in industrial sectors like, Cosmetics, Dairy, Brewery, Oil & gas, Pharmaceutical, Water Treatment etc.

1.5 Water Quality

Water quality (in terms of treated effluent) is defined by some physical like Turbidity, pH, Total Dissolved Solids (TDS), Conductivity, Chemical Oxygen Demand (COD), Dissolved Oxygen (DO), Biological oxygen demand (BOD) etc. and chemical parameters like elemental components as well as some compounds like chlorides, sulphates etc.

1.5.1 Turbidity

Water is said to be turbid when particles suspended in it restrict the transmission of light and give a cloudy/muddy appearance. Turbidity is the amount of particulate matter that is suspended in water. Turbidity measures the scattering effect that suspended solids have on light: higher the intensity of the scattered light, higher is the turbidity. Materials causing the water to appear turbid include clay, silt, finely divided organic and inorganic matter, plankton and microscopic organisms. Turbidity makes water cloudy/opaque and in measured by shining a light through water and reported in nephelometric turbidity units (NTU).

1.5.2 pH

pH is a measure of the acidity or basicity of a solution. The full form of pH is Power of Hydrogen. It is defined as the cologarithm of the activity of dissolved hydrogen ions (H+). Hydrogen ion activity coefficients cannot be measured experimentally, so they are based on theoretical calculations. The pH scale is not an absolute scale; it is relative to a set of standard solutions whose pH is established by international agreement. Pure water is said to be neutral. The pH for pure water at 25 °C (77 °F) is close to 7.0. Solutions with a pH less than 7 are said to be acidic and solutions with a pH greater than 7 are said to be basic or alkaline. pH is defined as minus of the decimal logarithm of the hydrogen ion activity in an aqueous solution. By virtue of its logarithmic nature, pH is a dimensionless quantity, where aH is the (dimensionless) activity of hydrogen ions.

1.5.3 Total Dissolved Solids (TDS)

Total Dissolved Solids represents combined content of all inorganic and organic substances in a liquid which are present in a molecular, ionized or micro-granular (colloidal sol) suspended form. Dissolved solids must be of that size so that these pass through filtration device having a sieve size of two micrometres. Total dissolved solids are normally only discussed for freshwater systems, since salinity comprises some of the ions constituting the definition of TDS. TDS is not considered as a primary pollutant but aesthetic characteristics of drinking water are related to TDS. It is measured in grams of dissolved solids per litre of water.

1.5.4 Conductivity

It is a measure of the ability of an aqueous solution to carry electric current. This ability depends on the presence of ions; their total concentration, mobility and valence. It also depends on the temperature of measurement .The conductivity of river water is its ability to conduct electricity.

When an electrical potential difference is placed across a conductor, its movable charges flow, giving rise to an electric current. The conductivity σ is defined as the ratio of the current density J to the electric field strength E:

$$\mathbf{J} = \sigma \mathbf{E}$$

Conductivity is the reciprocal (inverse) of electrical resistivity, ρ, and has the SI units of siemens per metre ($S.m^{-1}$):

$$\sigma = \frac{1}{\rho}.$$

Conductivity measurement is similar to TDS measurements. The measurement is made with an electronic sensor in micro/milli Siemens per cm or ppm. Conductivity gives a good approximation to TDS measurement using the conversion factor **1ppm=2µS/cm.** Conductivity is temperature sensitive and is standardized to 25°c.

1.5.5 Chemical Oxygen Demand (COD)

COD is the capacity of water to consume oxygen during the decomposition of organic matter and inorganic chemicals like ammonia and nitrite. It is an indirect measure of the amount of Oxygen used by organic and inorganic matter in water. The oxidizing agents used are potassium dichromate and sulphuric acid. Though various methods are available for COD determination the method adopted in the study is the open-reflux method of COD determination.

1.5.6 Biological Oxygen Demand (BOD)

BOD is a measure of the oxygen used by microorganisms to decompose the organic waste present in water. If there is high organic waste in water, the BOD level will be high as well. When BOD is high, the DO levels decrease quickly. To measure BOD, an instrument called BOD TRAK developed by M/s HACH Company, USA was used in the study which measures BOD on the basis of partial pressure drop.

1.5.7 Dissolved Oxygen

Dissolved oxygen analysis measures the amount of gaseous oxygen (O_2) dissolved in an aqueous solution. Oxygen gets into water by diffusion from the surrounding air, by aeration (rapid movement), and as a waste product of photosynthesis. Adequate dissolved oxygen is necessary for good water quality. Oxygen is a necessary element to all forms of life. Natural stream purification processes require adequate oxygen levels in order to provide for aerobic life forms. As dissolved oxygen levels in water drop below 5.0 mg/l, aquatic life is put under stress. Lower the concentration, greater is the stress. Oxygen levels that remain below 1-2 mg/l for a few hours can result in large fish kills.

1.5.8 Salinity

Salinity is the saltiness or dissolved salt content of a body of water. It is a general term used to describe the levels of different salts such as sodium chloride, magnesium and calcium sulphates and bicarbonates etc. It is measured as percentage of salt present in the water. Direct methods to measure the salinity are time consuming and do not generally yield precise results. Hence generally indirect methods are used to measure the salinity of water.

1.5.9 Total Suspended Solids

TSS are solid materials, including organic and inorganic, that are suspended in the water. These would include silt, plankton and industrial wastes. It is listed as a conventional pollutant in the U.S. Clean Water Act. This parameter was at one time called non-filterable residue (NFR), a term that refers to the identical measurement: the dry-weight of particles trapped by a filter, typically of a specified pore size. However, the term "non-filterable" suffered from an odd (for science) condition of usage: in some circles (Oceanography, for example) "filterable" meant the material retained on a filter, so non-filterable would be the water and particulates that passed through the filter. In other disciplines (Chemistry and Microbiology for examples) and dictionary definitions, "filterable" means just the opposite: the material passed by a filter, usually called "Total dissolved solids" or TDS. Thus in chemistry the non-filterable solids are the retained material called the residue.

1.6 Objective

The objective of this work is to assess the feasibility of using ceramic membrane in water purification like river water purification, enhancing the conversion of Arsenite to Arsenate using ceramic membrane contactor, presenting the case study of Ceramic membrane based arsenic removal plant and also to explore the feasibility of application of ceramic membranes for wastewater treatment from tannery.

CHAPTER 2

LITERATURE REVIEW

The continuous growth of human population will further challenge the fresh water supply required for drinking consumption and the food production. Thus, it will lead to more municipal wastes and ground water contaminated with pesticides and fertilizers that shall be treated for its re-use and to be discharged. There is another major source of water contamination that relates with the increased consumption of different types of goods including electronic devices as a result of increase of middle-class population and the life quality. The production of these goods triggers more intensive discovery of carbon- and minerals-based natural resources from the underground depositions. It is worth to notice that it will continuously shift the balance of chemical elements since all these carbon- and mineral-based compounds will be finally introduced to the environment in the polluted streams generated during each stage of the whole life cycle of the products. In the future, biobased economy might ideally close the carbon loop and substitute the fossil fuels, but it is rather impossible to expect the renewable mass-production of minerals resources, first of all, precious metals. The increasing demand in these metals for production of the electronic devices, batteries and solar panels will lead to faster depletion of known deposits. Therefore, the sustainable development would require not only the shortage of excess consumption of products, but also seeking for the alternative sources of raw materials. By this means, the contaminated water shall be considered as a source of the diversity of different valuable components, where the clean water will be one among other components. Nowadays, any type of polluted water can be separated to gain the products with the desired quality by using the conventional processes as distillation, crystallization, membrane separation, adsorption, chemical and biological treatment, if the cost and energy intensity of such treatment are not subject of interest. Water is a basic need for any living organism on earth. Water contributes heavily in different economic activities like agriculture, industry and commerce. It is a fundamental part of the ecological system, sustaining and being sustained by it. It is a means of transportation, a public good and an important part of our social and cultural life[3]. Annual renewable water resources (ARWR) of at least 2000 m3 /capita is required. If the ARWR is in the range of 1000–2000 m3 /capita there may be infrequent and localized water shortages.

Physical methods such as sedimentation and filtration (membranes, media filtration) are widely used for wastewater and water treatment. As far as chemical methods are concerned, coagulation, pH adjustments, addition of anti-scalants and acids etc. are very common.[4,5]

Irrespective of the sources, wastewater generated poses a serious environmental threat. Therefore effective treatment for its safe discharge within the regulatory norms is a prerequisite. Wastewater in many situations contains hazardous chemicals like metals (e.g., As, Pb, Cr, Cd and Zn), toxic compounds like endocrine disruptors, dyes and pigments, and if the organic matters are present, produces pungent smell. Ground water may be contaminated either by naturally occurring materials or due to human activities which generates pollutants. Heavy metals, such as mercury, copper and lead can cause serious health problems in excessive amounts, including reduced growth and development, autoimmune diseases, cancer, organ damage, nervous system damage and in extreme cases, death.[6]

In recent years, integrated membrane systems for treatment have gained popularity due the process reliability, availability, modularity, relative insensitivity in case of raw water processing and lower operating costs. Integrated membrane systems are also gaining importance proposed as the most suitable solution for decentralized wastewater treatment.[7,8]

High output both in terms of product recovery as well as pollutants removal can be obtained in membrane based processes. It can be envisaged as a low operational cost technology in comparison with other competing technologies, because there is no water phase change and the process employs minimal or no use of chemical additives.[9]

Ceramic membranes are more and more employed in the drinking water and wastewater treatment industries when compared with organic and polymeric counterparts due to their resistance to extreme operating conditions and numerous available and sustainable cleaning protocols.[10] This allows longer service lifetime and highly efficient filtration performance. Tubular membranes modules provide a modest surface area to volume ratio, and thus the highest cost per unit area of all cylindrical membrane geometries, but also provide potentially the greatest turbulence promotion and the best access to the membrane surface.[11]

The advantage of membrane separation over conventional clarification techniques is reduction of the flocculation time to a great extent, therefore the footprint of integrated plant can substantially be reduced. [12] Water having high organic matter can be effectively treated by combined coagulation -microfiltration. In such integrated process, the organic matter content in water and its turbidity can be reduced to a great extent. [13] When Microfiltration process is used for removal of humic acids from water, a tight cake layer can quickly on the membrane surface, thus can cause severe fouling on the membrane surface.[14] However, if it is used in combination with coagulation, the coagulants binds with humic acid particles to form larger aggregates which are larger than the pore size of the microfiltration membranes and therefore chance of clogging is reduced to a great extent.[15] Studies indicated considerable increases in steady state flux when coagulation was combined with MF using cationic polyelectrolytes. Considerable improvement also occurred in effluent quality, in terms of COD removals and turbidity, when MF was integrated with coagulation. COD removal was improved up to 60% and turbidity removal by

75% when MF was coupled with coagulation, which showed much better performance than when MF was used alone.[16]

Arsenic is naturally occurring element that is found in groundwater enclosed in aquifers and these elements are brought into water by various natural phenomena like tectonic movement, weathering of minerals etc.[17]. This metal has many uses for production of glass, agricultural pesticides, textile dyes, doping agents for semi conductors etc.[18,19] Although the element has many applications it is potentially harmful to human system. Arsenic poisoning causes cancer, cardiovascular complications, Black Foot disease, diabetes, neurological problems, hyperkeratosis, gastrointestinal problems etc, [20,21,22] The problems of arsenic contamination are being faced by large Part of India particularly the state of West Bengal & Bihar and also the adjoining country like Bangladesh, Nepal. Arsenic contamination is there in United States of America also.[23] World Health Organization (WHO) has set a limit of 10µg/L of arsenic in drinking water[24]. Arsenic typically occurs in trivalent and pentavalent oxidation states. Trivalent state of arsenic is more toxic than pentavalent state. Therefore it is necessary to convert trivalent arsenic to pentavalent arsenic by oxidation. For these reasons it is necessary to remove arsenic from drinking water system. Various treatment methods has been adopted from arsenic removal like ion-exchange, adsorption, ultrafiltration, reverse-osmosis, and adsorption–co-precipitation by metals (predominately ferric chloride) followed by coagulation. Among these methods, the most common technique used is based on chemical treatment or adsorption. Oxidation of arsenite to arsenate increased in presence of manganese oxide and iron oxide[25]. Conventional oxidation agents are manganese dioxide, chlorine, and ozone, potassium permanganate.

Arsenic is a natural component of the earth's crust and is widely distributed throughout the environment in the air, water and land. It is highly toxic in its inorganic form. Arsenic contamination of groundwater is widespread and there are a number of regions where arsenic contamination of drinking-water is significant. It is now recognized that at least 140 million people in 50 countries have been drinking water containing arsenic at levels above the WHO provisional guideline value of 10µg/L[26]. The greatest threat to public health from arsenic originates from contaminated groundwater. Inorganic arsenic is naturally present at high levels in the groundwater of a number of countries, including Argentina, Bangladesh, Chile, China, India, Mexico, and the United States of America. in 2012 approximately 19 million people were exposed to drinking water containing arsenic level above 50 µg/L and 39 million people were exposed to drinking water with levels of arsenic levels of above 10 µg/L[27]. In 2012, annual total of nearly 43000 deaths (~5.6% of all death) was due to chronic arsenic exposure for all districts of Bangladesh.

The consumption of arsenic contaminated water has long term health hazards. The immediate symptoms of arsenic poisoning are vomiting, abdominal pain, diarrhoea, muscle cramping and in extreme case death can also occur. The long term consumption of arsenic through drinking water can cause skin lesion, pigmentation, hard patches on palm and soles which finally causes the cancer. According the research, inorganic arsenic is one of the precursors of cancer in humans due to long term consumption of arsenic contaminated drinking water.

Arsenic is a naturally occurring metalloid and abundantly distributed in the Earth's crust generally as arsenic sulphide or as metal arsenates and arsenite.[28, 29] It is introduced into soil and ground water during weathering of minerals and rocks by leaching and runoff and anthropogenic sources such as poorly managed discharge from metallurgical and mining industries, and application of Arsenic containing pesticides.[30, 31] Arsenic mobilization from the earth crust to ground water triggered by specific biogeochemical trigger. Arsenic is released from the sulphide minerals in the shallow aquifer due to oxidation and desorption or dissolution of arsenic from iron oxides distributed arsenic in water.[32] According to report, especially the Ganga-Meghna-Brahmaputra (GMB) Plain of India and Bangladesh in the Asian continent are the worst arsenic affected area. In the year 1983, arsenic contamination in ground water first reported from 33 affected villages in four districts in west Bengal. In the year 2008, the arsenic menace spreads to 3417 vilages in 111 blocks in nine districts.[33] In Kolkata, municipal corporation area, 262 water samples from all 144 wards was studied and reported that 51 wards have arsenic level above 50 µg/L. It was also found that 49 wards have arsenic level between 11 to 50 µg/L and only 44 wards have been found below 10 µg/L[34]. According to Peters et al.[35] the presence of arsenic was in the range of <0.0003-180 µg/L from 992 drinking water samples from the randomly selected households of New Hampshire, USA. In this report, it was shown that domestic drilled bedrock wells contained higher level of arsenic than municipal sources. The groundwater arsenic contamination was found to be average of 159 µg/L from the city of Hanoi and around 1-3050 µg/L from the surrounding rural districts of the Red River alluvial tract[35]. It was reported that private water supplies in Cornwall of South West England exceeded the arsenic contamination above 10 µg/L.[36]

Tannery effluent is very hazardous in nature. Tannery wastewater contains heavy metals, toxic chemicals, chloride, lime with high dissolved and suspended salts and other pollutants. Tanneries generate wastewater in the range of 30 - 35 L/kg skin / hide processed with variable pH and high concentrations of suspended solids, BOD, COD, tannins including chromium.[37]

Tannery industry also consumes huge quantity of water. The high chemical oxygen demand

(COD) and suspended solids (SS) loading are serious economic problem in tannery operatrions. For tannery wastewater treatment, Various physico-chemical techniques have been studied for their applicability to the treatment of tannery wastewater[38, 39] Coagulation, flocculation, ozonation, reverse osmosis, ion exchange and activated carbon adsorption have been attempted for tannery wastewater treatment. [40] It has been demonstrated in laboratory that coagulation with aluminium sulphate and ferric chloride is an effective method to clarify tannery wastewater by reducing the COD, SS and chromium content of the wastewaters. [41] Ceramic microfiltration studies have been attempted for treatment of Beam house operation which is a unit operation of tanning process.[42] Polymeric nanofiltration have been studied in pickling and tanning process.[43]

CHAPTER 3

River water purification using Ceramic membranes

2.1 Purpose of River water treatment

River water is the most common source of municipal supplies. Because of the universal pollution of ground water, natural surface water is considered to be safe for use as public water supply after proper treatment. So it is desirable for river water to be subjected to a preliminary treatment before passing to the main treatment plant. Hence the river water is treated in various ways to make it suitable for different purposes. Traditional treatment processes involving coagulation, settling, sand filtration and chlorination are conventionally used widely. However, contaminants like heavy metals, virus, bacteria, and disinfection by-products in the source water strongly affect the quality of drinking water[44, 45]. Therefore, to address these concerns, membrane technology is finding a promising place in water treatment industries. Membrane technologies such as ultrafiltration (UF) and microfiltration (MF) are used to purify river water. Polymeric UF or MF membrane are being widely used in water treatment[46]. The combination of coagulation and ceramic membrane microfiltration process was studied as the pretreatment of pre-biochemical coking wastewater and the removal rates of turbidity, colour Degree, oil content, and COD were 95%, 80%, 90%, and 81%, respectively[47]. Ceramic membranes have good tolerance toward oxidative disinfectants like as chlorine and ozone. Dosing of oxidants such as ozone before ceramic membranes are used in drinking water treatment due to which higher removal rates of natural organic matter (NOM) is observed.[48]

2.2 Sedimentation and Settling

Sedimentation

Sedimentation is the tendency for particles in suspension or molecules in solution to settle out of the fluid in which they are entrained, and come to rest against a wall. This is due to their motion through the fluid in response to the forces acting on them: these forces can be due to gravity, centrifugal acceleration or electromagnetism. The term is typically used in geology, to describe the deposition of sediment which results in the formation of sedimentary rock, and in various chemical and environmental fields to describe the motions of often-smaller particles and molecules.

Settling

Settling is the process by which particulates settle to the bottom of a liquid and form the sediments. Particles that experience a force, either due to gravity or due to centrifugal motion will tend to move in a uniform manner in the direction exerted by that force. For gravity settling, this means that the particles will tend to fall to the bottom of the vessel, forming slurry at the vessel base.

2.3 Coagulation and coagulating agents

Chemical coagulation in the water treatment is the process of bringing suspended matter in untreated water together for the purpose of settling and for the preparation of the water for filtration. Coagulation involves three specific steps, which are: Coagulation, Flocculation, and Sedimentation. It is a process for increasing the tendency of small particles in aqueous suspension to attach to one another and to attach to the surface such as the grains in a filter bed. It is also used to effect the removal of certain soluble materials by absorption or precipitation. Coagulation typically includes promoting the interaction of particles to form aggregates or clumps called flocs. Coagulating agents (or coagulants), are chemicals which are used to initially destabilize a suspension to enhance coagulation and they are typically added in rapid-mix process. They neutralize the repulsive electrical charges (typically negative) surrounding particles allowing them to "stick together" creating clumps or flocs.

Examples-Alum, Ferrous Sulphate,Lime, Aluminium Sulphate etc.

2.4 Flocculation and Flocculating Agents

Flocculation is a gentle mixing stage and it increases the particle size from submicroscopic microfloc to visible suspended particles. The microflocs are brought into contact with each other through the process of slow mixing. Collisions of the microfloc particles cause them to bond to produce larger, visible flocs called pinflocs. Once the floc has reached it optimum size and strength, the water is ready for the sedimentation process. Here a solute coles out of the solution in the form of larger flocs. It differs from precipitation in that the solute coming out of the solution does so at a concentration generally below its solubility limit in the liquid. Basically it is a physical process of producing inter particle contacts.

Flocculating agents (or flocculants), are chemicals that promote flocculation by causing colloids and other suspended particles in liquids to aggregate, forming a floc. Flocculants are used in water treatment processes to improve the sedimentation or filterability of small particles. They facilitate the agglomeration or aggregation of the coagulated particles to form larger floccules and thereby hasten gravitational settling. In most cases they are added after the addition of the coagulant; its purpose is to enhance floc formation and to increase strength of the floc structure. Sometimes it is called a ‘coagulant aid’. Depending on how and where it is used and at what dosage, a coagulant is sometimes used as a flocculant and vice versa.

Examples- Activated Silica, Magnesium, Certain Colloidal Clays (such as Bentonite), Alum etc.

2.5 Methodology

In the present study, Ichamati River water at low tide was collected from the Katakhal area of Taki, North 24 Parganas, West Bengal. The normal settling studies and coagulant assisted settling studies were conducted. Subsequently, a ceramic microfiltration membrane was used for direct filtration of the supernatant of the coagulation assisted settling experiment for a particular coagulant. The collected river water sample has the following physical parameters:

Table 2.1: Physical properties of the river water

Turbidity (NTU)	pH	Conductivity (mS/cm)	Salinity (%)	TDS (gm/l)	TSS (mg/l)
842	7.20	17.66	10.3	8.82	1635

2.6 Sedimentation study for 24 hours (without adding any coagulant or flocculants)

Experiment:-

100ml of the river water sample was taken from the Jerry can after shaking the can vigorously using a graduated measuring cylinder and was allowed to settle for 24 hours. After that the supernatant was collected and the following physical parameters were measured with it.

Table 2.2: Physical properties of the supernatant after sedimentation

Turbidity (NTU)	pH	Conductivity (mS/cm)	Salinity (%)	TDS (gm/l)	TSS (mg/l)
4.02	7.96	17.42	10.3	8.71	350

2.7 Sedimentation study with coagulants

Batch sedimentation experiments were performed with four different coagulants. They are:

a) Ferric Chloride, $FeCl_3$

b) Ferrous Sulphate, $FeSO_4$

c) Calcium Carbonate, $CaCO_3$

d) Aluminium Sulphate, $Al_2(SO_4)_3$

2.7.1 Batch study

50ml of river water each was taken in four measuring cylinders. Then 0.025 g of each coagulant was weighed and $FeCl_3$ was added to the first measuring cylinder, $FeSO_4$ to the second measuring cylinder, $CaCO_3$ to the third one and $Al_2(SO_4)_3$ to the fourth one(all at the same time). These were allowed to settle for three hours after stirring those with the help of magnetic stirrers for 2 minutes at 8 rpm. Then the supernatants from each cylinder were collected. The $FeCl_3$ and $FeSO_4$ supernatants were visually yellow (shades were different). The other two appeared colourless. They were named as SN_1, SN_2, SN_3 and SN_4 respectively. The following physical parameters were measured with the four types of supernatants.

Table 2.3 : Physical parameter of supernatants after coagulation

Supernatants	Coagulant used	Turbidity (NTU)	pH	Conductivity (mS/cm)	Salinity (%)	TDS (gm/l)	TSS (mg/l)
SN_1	$FeCl_3$	47.1	2.64	17.9	10.5	8.95	840
SN_2	$FeSO_4$	27.8	6.29	17.66	10.6	8.42	200
SN_3	$CaCO_3$	39.1	7.81	17.34	10.2	8.69	700
SN_4	$Al_2(SO_4)_3$	24.4	4.68	17.14	10.1	8.58	550

Table 2.4 : Comparative Study of the Supernatants of the four different Coagulants

Parameters	$FeCl_3$	$FeSO_4$	$CaCO_3$	$Al_2(SO_4)_3$
Turbidity(NTU)	47.1	27.8	39.1	24.4
pH	2.64	6.29	7.81	4.68
Conductivity (mS/cm)	17.9	17.66	17.34	17.14
Salinity(%)	10.5	10.6	10.2	10.1
TDS(gm/l)	8.95	8.42	8.69	8.58
TSS(mg/l)	840	200	700	550
Metal dosage(mg metal / litre of river water)	172.31	184.21	200.00	78.95

It is observed that

a) Turbidity of supernatant was of least value among the four coagulants used when river water was allowed to settle with $Al_2(SO_4)_3$ as coagulant.

b) The supernatant of $Al_2(SO_4)_3$ was colourless. Hence no effort had to be given to remove the colour from the solution. Whereas when iron based coagulants were used, the supernatants were yellowish.

c) Sludge residues obtained from the four measuring cylinders were filtered using four filter papers. The filter papers with the sediments on them were dried in the oven at 110°C for one hour and then put in the dessicator for 30 minutes. Then they were weighed in the balance and the following data was obtained:

Table 2.5 : Weight measurement of different sediments obtained

Samples	Weight of dry filter paper without sediments (mg)	Weight of wet filter paper with sediments (mg)	Weight of dry filter paper with sediments (mg)	Weight of wet sediments (mg)	Weight of dry sediments (mg)
$FeCl_3$	94.2	2344.6	1024.4	1440.4	120.2
$FeSO_4$	94.2	2292.5	1019.8	1388.3	115.6
$CaCO_3$	94.2	2439.0	1031.1	1538.8	126.9
$Al_2(SO_4)_3$	94.2	2444.5	1013.3	1540.3	109.1

Subsequently, 10 litres of river water was mixed with 5 gm of $Al_2(SO_4)_3$ coagulant and 4 gm hydrated silica flocculant. It was allowed to settle for one hour after being stirred magnetically for 2 minutes at 8 rpm.

Supernatant was collected after one hour of settling and the following parameters were measured.

Table 2.6 : Physical properties of supernatant after $Al_2(SO_4)_3$ and hydrated silica addition

Turbidity (NTU)	pH	Conductivity (mS/cm)	Salinity (%)	TDS (gm/l)	TSS (mg/l)
21	4.22	18.00	10.6	9.01	760

Then 7 litre of supernatant was collected from the above experiment and the membrane study was performed using the 7 litre of supernatant. The membrane study was carried out in a cross flow microfiltration laboratory set up in which a 200 mm long 19-channel circular ceramic membrane was fitted. The experiments were carried out in two modes. In one mode, the transmembrane pressure (TMP) was varied from 0.4 bar to 1.2 bar. In other mode, the filtration behaviour was observed by maintaining the constant pressure of 1.2 bar. In the first mode, permeate was collected at transmembrane pressures of 0.4 bar, 0.6 bar, 0.8 bar, 1.0 bar and 1.2 bar at intervals of 15 minutes each. The characteristics of those samples collected were measured.

Table 2.7 : Physical properties of Ceramic membrane treated river water after coagulation at different transmembrane pressure

Pressure(TMP) (Kg/cm^2)	**Flux(l/hr)**	**Turbidity (NTU)**	**pH**	**Conductivity (mS/cm)**	**Salinity (%)**	**TDS (gm/l)**	**TSS (mg/l)**
0.4	9.57	3.71	4.75	17.56	10.3	8.81	400
0.6	15.6	2.04	5.05	17.66	10.4	8.83	365
0.8	18	2.01	5.23	17.91	10.5	8.95	335
1.0	22.56	1.98	5.42	17.79	10.4	8.87	20
1.2	22.8	1.95	6.36	17.55	10.3	8.77	280

In the second mode which was performed at a constant pressure, samples of water coming out of the membrane were collected each at 15 mins interval at a steady pressure of 1.2 TMP. They were T_0 , T_{15} , T_{30} , T_{45} and T_{60} . Then two samples were collected each at an interval of one hour. These are T_{120} and T_{180} .

Table 2.8 : Physical properties of Ceramic membrane treated river water after coagulation at constant transmembrane pressure

Time (minutes)	Flux(l/hr)	Turbidity (NTU)	pH	Conductivity (mS/cm)	Salinity (%)	TDS (gm/l)	TSS (mg/l)
T_0(0)	22.8	1.95	6.36	17.55	10.3	8.77	280
T_{15}(15)	23.1	1.92	6.38	17.56	10.3	8.76	245
T_{30}(30)	23.4	1.9	6.4	17.96	10.6	8.76	210
T_{45}(45)	22.8	1.87	6.43	18.08	10.6	8.71	180
T_{60}(60)	22.2	1.85	6.47	18.02	10.6	8.82	145
T_{120}(120)	21.6	1.82	6.62	18.15	10.5	8.85	130
T_{180}(180)	19.2	1.80	6.78	18.08	10.7	8.83	125

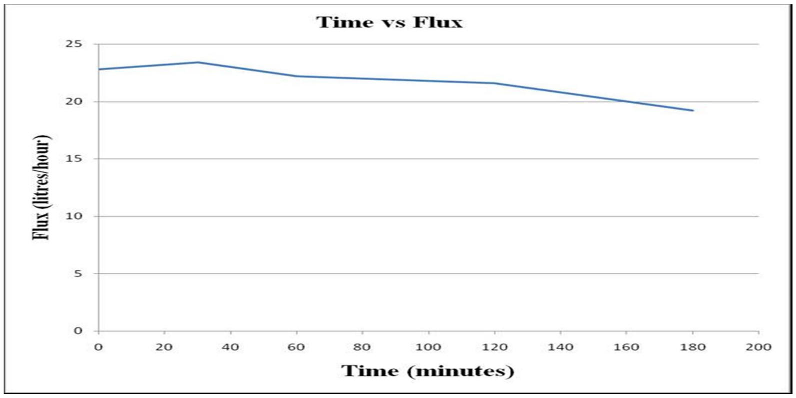


Fig. 2.1 Flux in LPH vs time of operation

2.8 Conclusion

The purpose of the above experiment was mainly to decrease the turbidity of river water so that it could be used for different purposes. Three types of sedimentation studies were performed before passing the supernatant through the ceramic membrane:

a) 24 hour study without adding any coagulant or flocculant.
b) 3 hour study by adding a coagulant.
c) 1 hour study by adding a coagulant and a flocculant.

From the results obtained we see that the most beneficial was the 1 hour process as it decreased the turbidity to a large extent in a very short time. If it is desired to perform a large scale experiment it is going to be very efficient and also a continuous process. Hence it will be profitable too. So the third process was selected, the supernatant collected and passed through the ceramic membrane. The turbidity was decreased to 1.8 NTU after the last experiment was performed.

CHAPTER 3

Tannery Wastewater Treatment using Ceramic Membrane

3.1 Wastewater treatment

Wastewater treatment is the process of removing the contaminants from sewage and wastewater to produce liquid and solid (sludge) suitable for discharge to the environment or for reuse. It is a form of waste management. Wastewater treatment is classified as primary, secondary, or tertiary, depending on the degree to which the effluent is purified. Primary treatment is removal of floating and suspended solids. Secondary treatment uses biological methods such as digestion. Complete, or tertiary, treatment removes all but a negligible portion of bacterial and organic matter. Industrial wastes are treated by a number of methods, depending on the specific nature of the waste. Increasingly, governments are forcing industries to process effluents either chemically or mechanically, or both ways, so that harmful substances are removed.

Wastewater treatment, however, can also be organized or categorized by the nature of the treatment process operation being used; for example, **physical, chemical or biological.** A complete treatment system may consist of the application of a number of physical, chemical and biological processes to the wastewater.

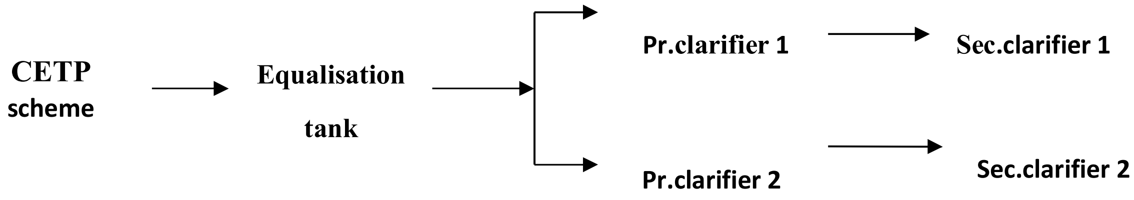
Table 3.1: Types of wastewater treatment

Physical	***Chemical***	***Biological***
➢ Sedimentation (Clarification) ➢ Screening ➢ Aeration ➢ Filtration ➢ Flotation and Skimming ➢ Degasification ➢ Equalization	➢ Chlorination ➢ Ozonation ➢ Neutralization ➢ Coagulation ➢ Adsorption ➢ Ion Exchange	***Aerobic*** ➢ Activated Sludge Treatment Methods ➢ Trickling Filtration ➢ Oxidation Ponds ➢ Lagoons ➢ Aerobic Digestion ***Anaerobic*** ➢ Anaerobic Digestion ➢ Septic Tanks ➢ Lagoons

3.2 Microfiltration study of secondary clarifier wastewater

Experimental procedure:

The schematic of common effluent treatment is shown below in brief



3.2.1 Methodology

Effluent was collected from CETP Bantala, Secondary Clarifier (Module – 1) and was characterised. Thereafter it was subjected to direct filtration through ceramic membranes and the permeate samples were characterised to see the removal efficiency under ceramic membrane filtration. In another study, raw composite effluent was collected from CETP, Bantala and direct microfiltration using ceramic membrane was conducted. The permeate sample was characterised and then further subjected to reverse osmosis membrane treatment to evaluate the product water characteristics.

Fig. 3.1 A typical secondary clarifier in CETP plant

3.2.2 Permeability study of secondary clarifier water in microfiltration

Direct microfiltration study was conducted using the effluent. Ceramic membrane having properties as shown in Table 3.3 was used. Figure 3.5 shows the schematics of the set up used. It has a storage tank(10 L). The stainless steel module for fitting the membrane has an outer diameter of 60 mm and length 200 mm. The membrane module was horizontally fitted in the setup. Feed is pumped under transmembrane pressure and permeate samples are collected through a bottom outlet. 8 l of feed solution was used at varying transmembrane pressure of 4-1.2 kg/cm^2. Effect of time was observed by operating the experiment at a constant pressure of 1 TMP for 2 hours. The permeate flux was measured at different intervals and characterization of permeate samples were done for pH, turbidity, conductivity, COD, BOD, TSS etc. Deionised water is used for cleaning before each run and after the experiment was over the tube was cleaned with with 0.1 (N) of nitric acid solution, 0.1 (N) of sodium hydroxide solution and finally with deionized water.

Two types of effluent were collected from CETP of CLC Tanners' Association located at Bantala. These two types of effluent were treated in the ceramic membrane based experimental set up in the CGCRI laboratory. The results of the study are described below.

Fig. 3.2 Settling tank for raw composite effluent

Fig. 3.3 Primary clarifier for raw composite effluent

Fig. 3.4 Aeration tank for biological treatment unit at CETP, Bantala

Initial characterisation of the effluents was conducted immediately after sample collection which is shown in Table 3.2 The raw effluent collected from inlet point to CETP is denoted as Effluent 1 and the finally treated effluent collected from discharge point (after secondary clarifier) of CETP is denoted as Effluent 2. Particle size distribution of the effluents are given in Fig. 3.5 and Fig. 3.6.

Table 3.2 : Characteristics of Raw composite Tannery effluent collected from CETP, Bantala

Sample	pH	TDS (g/l)	Conductivity (ms/cm)	Salinity (%)	Turbidity (NTU)	COD (mg/l)	BOD (mg/l)	TSS (mg/l)
Effluent 1 (raw composite effluent)	8.62	6.435	56.8	6.5	285	5680	759	1690
Effluent 2 (collected from secondary clarifier)	5.92	5.35	10.76	6.1	8.47	887.04	88	88

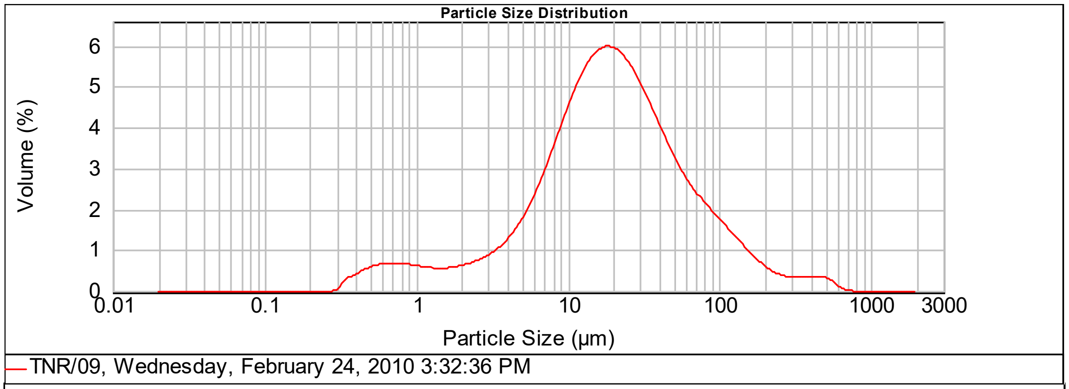


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Fig. 3.5 Particle size distribution of Effluent 1 (Raw composite effluent)

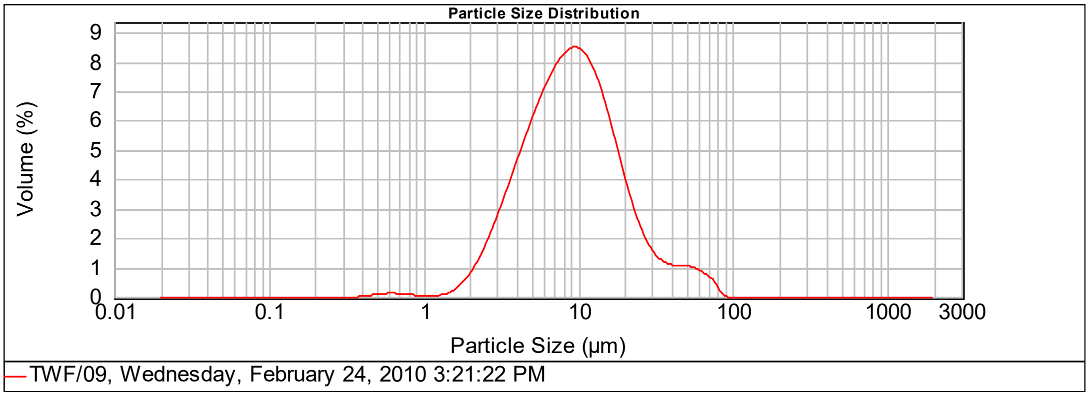

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Fig. 3.6 Particle size distribution of Effluent 2 (collected from secondary clarifier)

Membrane filtration of the effluent 2 was conducted. A 200 mm long ceramic microfiltration membrane was used. This 200 mm piece was cut form a 1002 mm long standard porous ceramic membrane, the physical dimensions and physical characteristics of which is given in table 3.3. A schematic of the experimental setup is shown in Fig. 1.6. The feed quantity taken was 8 litres. Experiments were conducted at different transmembrane pressures. In addition, experiment was continued for 2 hours maintaining a fixed pressure of 1.0 kg/cm^2. The permeate samples were collected at regular intervals and COD, turbidity, BOD, pH, conductivity, TDS and TSS were measured. Similar study was conducted with effluent collected from secondary clarifier which was subjected to direct membrane filtration.

Table 3.3: Properties of standard ceramic membrane used in the experiment

Membrane length	1002 mm
Outer Diameter	35.73 mm
Inner Diameter	4.73 mm
channel inner diameter	4.75 mm
Outer volume	1009.48 cm^3
Each channel volume	17.90 cm^3
Total channel volume	340.15 cm^3
Actual tube volume	664.33 cm^3
Weight	1592.1 gm
Calculated density	2.40 g/cc

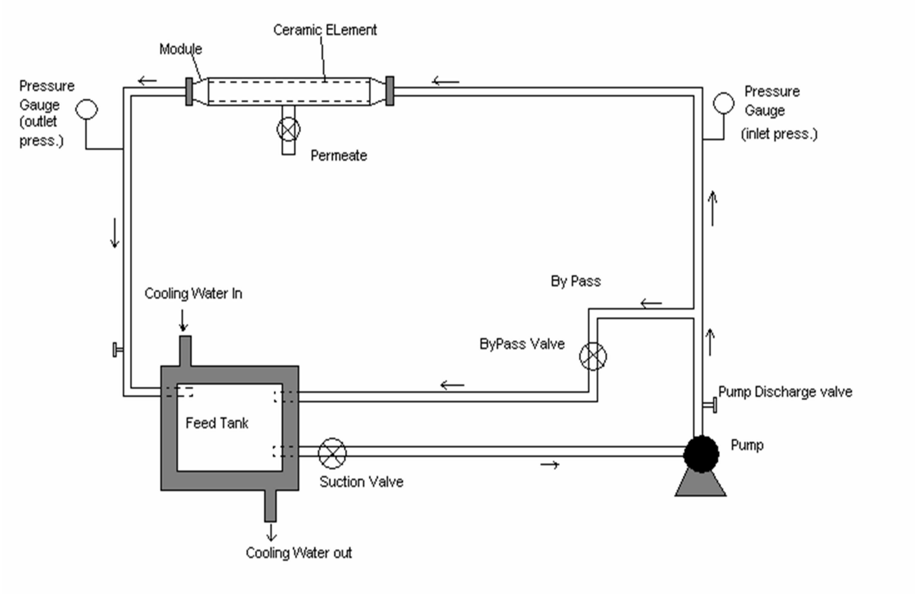


Fig. 3.7 Schematic of the experimental set up of crossflow microfiltration study

3.3 Results and Discussions

The performance of ceramic membrane in terms of removal of some parameters is shown in the following table:

Table 3.4: Properties membrane treated effluent at different time intervals with constant transmembrane pressure of 1 bar

Time	pH	TDS (g/l)	Conductivity (ms/cm)	Salinity (%)	Turbidity (NTU)	COD (mg/l)	BOD (mg/l)	TSS (mg/l)	Flux (LMH)
T_0	5.92	5.35	10.76	6.1	8.47	887.04	88	88	
T_{15}	7.42	5.03	9.93	5.6	0.904	210.8	49.3	44	45.5
T_{30}	7.43	4.96	9.93	5.6	0.721	215.7	48.8	43.2	40.72
T_{45}	7.44	4.96	9.93	5.6	0.622	201.8	48.1	44.1	41.91
T_{60}	7.51	4.96	9.94	5.6	0.446	198.7	47.1	44	41.91
T_{90}	7.57	4.97	9.96	5.6	0.428	196.1	46.8	43.8	43.11
T_{120}	7.53	4.98	9.95	5.6	0.408	192.3	45.9	43.6	43.11

In this study, the feed solutions of 8 litre was taken. A fixed transmembrane pressure of 1 kg/cm^2 was maintained. The samples from the permeate outlet was collected at intervals of 15, 30, 45, 60, 90 and 120 minutes. Reduction in the Turbidity, COD, BOD and TSS is shown in table 3.5.

Table 3.5: Properties membrane treated effluent at different time intervals with constant transmembrane pressure of 1 bar

TMP (bar)	pH	TDS (g/l)	Conductivity (ms/cm)	Salinity (%)	Turbidity (NTU)	COD (mg/l)	BOD (mg/l)	TSS (mg/l)	Flux (LMH)
0.4	7.6	5	10.02	5.6	0.804	210.8	48.4	42.1	23.95
0.6	7.6	4.96	9.93	5.6	0.821	212.9	48.1	43.2	30
0.8	7.7	4.96	9.93	5.6	0.832	200.1	48	43.8	34.7
1.0	7.6	4.95	9.92	5.6	0.408	200.9	47.8	44.3	43.5
1.2T	7.6	4.96	9.93	5.6	0.500	197.8	48.4	44	48

In the above study, effluent 2 was subjected to ceramic membrane based treatment under varying transmembrane pressure. The effect of higher pressure leads to higher flux or permeate output but the values of COD, BOD, Turbidity, TSS etc. varied very little and the changes were insignificant.

3.4 Treatment of raw tannery wastewater by combined Ceramic Microfiltration and Reverse osmosis membrane

Wastewater characterisation:

Parameters characterised are shown in table 3.5.

3.4.1 Microfiltration study

8 liters of feed was taken in the feed tank. The feed was thoroughly mixed. After applying transmembrane pressure, the permeate was collected through a sample collecting port. While operation, as the permeate used to be collected continuously, the make up feed also was given continuously. The tests were conducted under varying transmembrane pressure. At 1.0 bar pressure the set up was operated for 8 hours per day for 15 days i.e. about 120 hours so that sufficient permeate is generated in total to undertake Reverse osmosis experiment.

3.4.2 Reverse osmosis experiments

Feed for RO experiments was the permeate water collected from MF study. One spiral wound RO membrane (4040) was used. In this experiment, reject water from RO was again fed back to the inlet. After carrying out the RO experiments at varying pressure of 25- 200 psi pressure, at a constant pressure of 100 psi, longer duration studies were conducted.

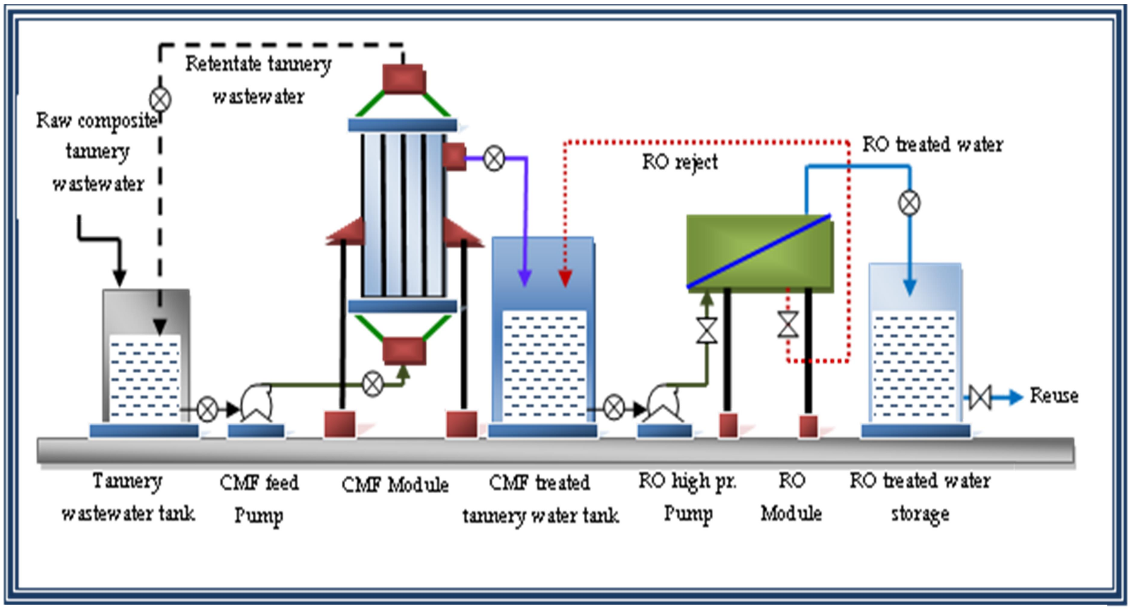


Fig. 3.8 Schematic of the experimental set up of combined crossflow microfiltration and reverse osmosis study

3.4.3 Results and Discussions

The results found during the ceramic microfiltration & RO process are given below in tabular form.

Table 3.6: Characteristics of untreated, permeate & retentate wastewater

Parameters	Raw composite effluent	MF Permeate	MF Retentate	RO permeate	RO retentate
pH	8.62	8.22	8.52	8.1	8.24
COD (mg/L)	5680	520	780	BDL	200
BOD (mg/L)	759	69	519	BDL	33
Turbidity (NTU)	285	0.785	308	0.025	45.2
Conductivity (µS/cm)	1342	1188	1389	649	985
Salinity (ppt)	6.5	6.1	6.9	0.33	4.8
TOC (mg/L)	514	180	579	12.4	490
TKN (mg/L)	2.87	0.98	2.98	BDL	0.7
TSS (mg/L)	1690	64	292	BDL	200
TDS (mg/L)	8500	6224	7250	448	8015
TS (mg/L)	10140	6090	7604	451	8110
Fe (mg/L)	150	11.0	9.4	ND	2.4
Ca (mg/L)	2980	108.1	88.8	3.75	143.5
Mg (mg/L)	677	69.6	60.4	2.75	102.5
Na (mg/L)	17420	2262.8	1947.7	354.02	2949.3
K (mg/L)	191	23.1	18.9	3.34	30.0
Mn (mg/L)	26	0.3	0.3	ND	0.1
P (mg/L)	165	53.4	5.6	0.09	4.5
Cr (mg/L)	521	0.7	1.6	0.24	1.6
Cu (mg/L)	2	0.4	0.7	0.01	0.8
Pb (mg/L)	7	0.6	0.3	0.03	0.7
Zn (mg/L)	19	17.4	1.0	0.06	1.7
S (mg/L)	2860	207.4	106.3	14.37	464.8
Co (mg/L)	1	0.1	ND	ND	ND
Ni (mg/L)	5	0.3	0.4	0.04	0.7

Figure 3.9 (i) MF permeate, (ii) Raw tannery, (iii) MF retentate, (iv) RO permeate

3.4.4 Permeability study of tannery wastewater in microfiltration & RO process

For the both the microfiltration & RO process, flux (LMH) vs. pressure (kg/cm2) graph is plotted from the variable pressure permeability data. It is observed that flux increases with pressure. Similarly, flux (LMH) vs. time (min) graph has been plotted from the time study data for both the process. It can be seen that flux has been declined with time.

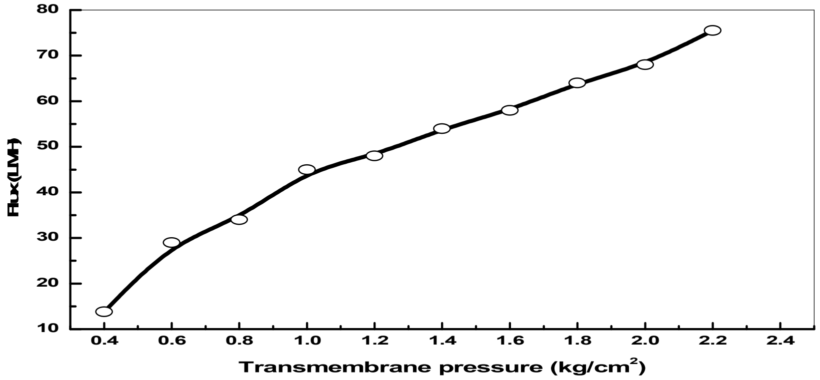


Fig. 3.10 Flux vs. TMP in ceramic microfiltration study

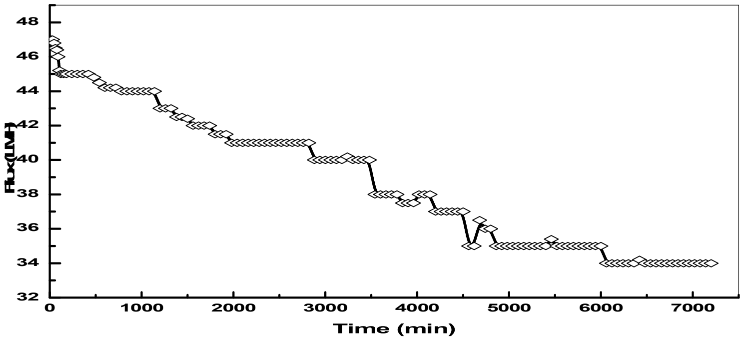


Fig. 3.11 Flux vs. Time result in microfiltration study at 1 kg/cm^2 pressure

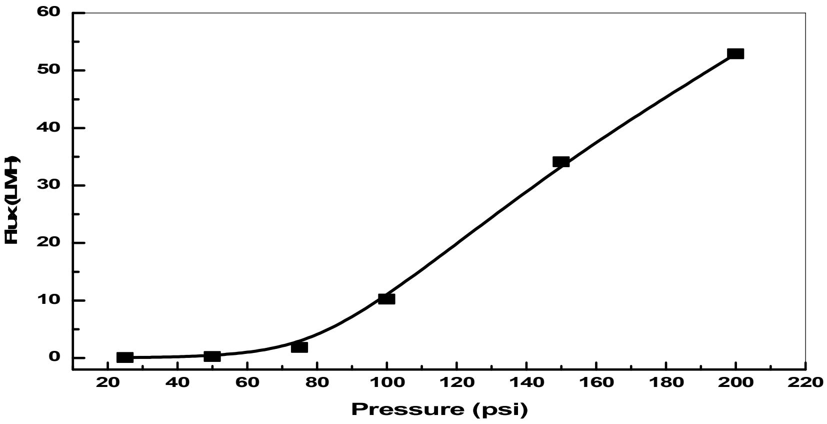


Fig. 3.12 Flux vs. Pressure study during RO process

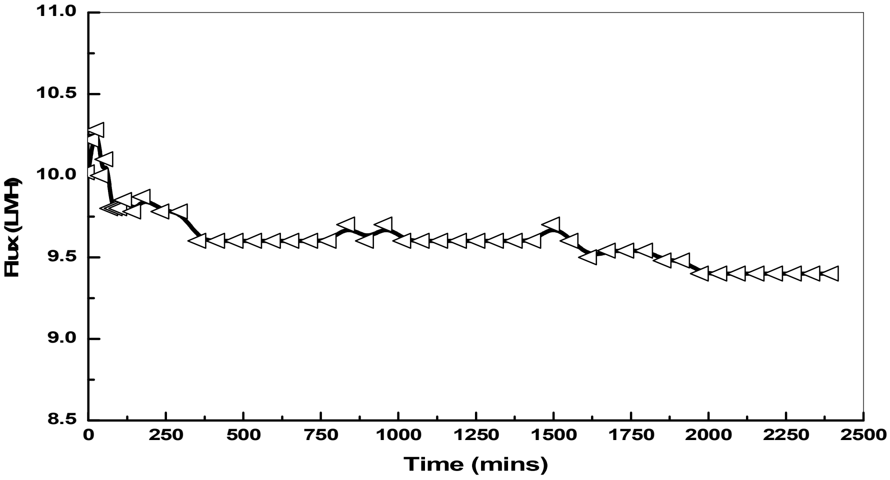


Fig. 3.13 Flux vs. Time during RO process at 100 psi pressure

3.5 Conclusion

Tannery wastewater is highly complex and is characterized by high contents of organic, inorganic and nitrogenous compounds, chromium, sulfides, suspended solids and dissolved solids. Membrane filtration has got tremendous potential in tannery wastewater treatment. The filtration process can be evaluated in terms of sludge filterability, fouling rate and fouling reversibility. During membrane filtration of tannery wastewater treatment, membrane fouling poses a significant problem as rapid declination of permeation flux occurs. It is very useful to systematically investigate the mechanisms and components in tannery wastewater that contribute to fouling and determine fouling profile with the help of flux operation data. From the experiment the fouling profile (the saturation time for fouling, membrane resistance, cake resistance and total resistance) has been developed.

Flux profile for raw composite waste water as feed was **34 LMH** after **7200 min** of operation at **1.0 kg/cm^2** pressure. During RO study, flux rate was **9.5 LMH** after **2400 min** of operation at **100 psi** pressure. About **93%** reduction of TOC was obtained with complete removal of organic matter represented in terms of BOD & COD. Heavy metals like Fe, Mn, Co were completely removed and values of toxic heavy metals like Pb, Cr, Cu were within permissible limit. The water quality obtained after combined process seems to be very good and can be reusable in some process.

CHAPTER 4

Ceramic Membrane based Contactor for enhanced Arsenic and Iron oxidation

4.1 Introduction

Oxidation of arsenite into arsenate has also proven effective in the presence of manganese oxide and iron oxide[49] and have been proven as effective oxidation agents for arsenite. Potassium permanganate is commonly used as an oxidation agent for small municipal systems. Once converted to arsenate, the arsenic is removed by one or more treatment options. The technologies for arsenate removal are ion exchange, activated alumina, reverse osmosis, modified coagulation/filtration, modified lime softening (for waters with pH 9 to greater than 10.5), electrodialysis reversal, and oxidation/filtration (for waters with a 20:1 iron: arsenic concentration ratio). More recently, iron-based adsorbents have been developed to treat remove arsenic from drinking water with much success and are commercially available under various chemical compositions and brands.

Membrane contactor can be a viable option for rapid oxidative conversion of Arsenic (III) to Arsenic (V) and Iron (II) to Iron(III). There are several processes for gas-liquid contacting. These are mainly bubble column, tray tower, packed tower, venturi scrubber, falling liquid film, sieve trays, static in line mixing, tubular flow, stirred tank reactor etc. Usually, the main challenge in designing and operating these devices is to maximize the mass transfer rate by producing as much interfacial area as possible. Membrane contactors, which is a relatively a new development, can cater the need for maximizing the mass transfer rate because of the high interfacial area for gas liquid contacting for the application for rapid oxygen transfer to the liquid phase containing Arsenic(III) and Iron(II) rich water. With a high oxygen transfer rate, it is anticipated that rapid and maximum conversion of Arsenic (III) and Iron (II) will take place.

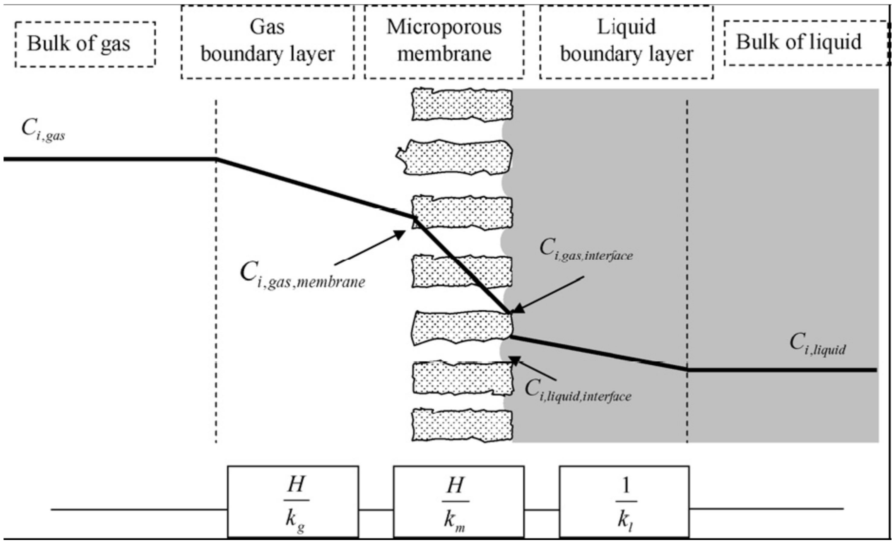


Fig 4.1: Mass transfer regions and resistance-in-series in membrane contactor.

The advantages of membrane contactors are as followings:

i. Avoidance of operational problems occurring in conventional absorption/column systems where gas and liquid flows are in direct contact.

ii. Use of compact membranes result in smaller equipment sizes with capital cost reductions.

iii. Operational problems avoided include foaming, flooding entrainment and channeling, and result in the free choice of the gas and liquid flow rates and a fixed interface for mass transfer in the membrane/solvent system.

In this study, advantage of the availability of higher interfacial area for gas liquid contacting for the application for rapid oxygen transfer to the liquid phase containing Arsenic(III) and Iron(II) rich water was investigated.

4.2 Materials & methods

In this section information regarding the materials and oxidation systems based on membrane contractor used for carrying out the experiment under varying the process parameters, as well as on the analytical methods employed for monitoring the Fe (II) to Fe (III) and As (III) to As (V) conversion has been elaborated.

4.2.1. Characterization of Ceramic membrane, Deionizer Water (DIW) & Tap Water (TW)

The 19-channel ceramic membrane is used, with identification number of KM/B29/F19C/200mm circular shape channel configurations. The dimension and physical properties of above said element is given below in table 4.1. The XRD analysis of this membrane is shown in fig. 4.1a and the FESEM & EXD analysis are represented in fig. 4.1b. Deionized water (DIW) used for preparation of feed solution has been prepared from Millipore unit and the characteristic of the DIW is shown in table 2. The Tap Water (TW) used for preparation of feed solution is the service water of the Kolkata city supplied by the municipal corporation and the characteristics of the TW is shown in table 4.2.

Table 4.1: Dimension and physical properties of the element

Identification of the ceramic membrane	KM/B29/F19C
Outer Diameter (OD) in mm	34.07
Inner channel Diameter (ID) in mm	4.22

Length of the membrane in mm	200
Apparent Porosity (%)	46.9
Bulk Density (gm/cc)	2.99
Water Absorption (%)	16.30
Effective filtration area in m^2	0.0503

Table 4.2: Physical & chemical characteristics of Deionized water & Tap water

Parameters	Deionized water(DIW)	Tap water (TW)
Turbidity (NTU)	0.021	1.05
pH	6.24	7.57
TDS(mg/l)	0.25	93
Cod. ((µs/cm)	2.52	194
Cl (ppm)	0.540	18.02
Na (ppm)	-	18.2
K (ppm)	-	7.84
Ca (ppm)	-	37.3
Mg (ppm)	-	15.2

4.2. 2. Preparation of Feed solutions

(A) The varying concentration of Fe (II) solutions (2 -10 ppm) of feed were prepared by diluting 100 ppm Fe (II) stock solution using Deionized water (DIW) & Tap water (TW) and pH was varied with addition of dilute acid /alkali.

(B) As (III) solutions of varying concentration typically mentioned as feed solution (0.1 - 1 ppm) consisted of Deionized water(DIW), Tap water (TW) and As (III) and have been prepared from 1L of “mother solution” containing 10 ppm of As (III). The pH was adjusted with addition of dilute acid /alkali.

4.2.3 Oxidation systems based on batch mode through direct injection method and direct injection with MnO_2 dose

Oxidation study of Fe(II) to Fe(III) under various condition for optimization of the process parameters have been carried out in batch mode through direct injection as mention below and the effect of air and pure oxygen(98%) purging were studied.

Table 4.3: Experimental parameters Batch mode through Direct Injection method for Fe (II) to Fe(III) conversion study

Experimental parameters for Fe (II) to Fe(III) conversion study					
Feed	Feed temp (^{O}c)	Feed vol.	Oxidizing agent	Fe (II) conc. of feed (ppm)	Feed pH variation
Tap water/ DIW	Room temp	5 L	Pure oxygen/Air	2/5/8/10	4/5/6

In this mode of experiment, oxidizing agent pure oxygen (98%) / Air is added directly in the feed solution containing Fe(II) through a pipe line connected to an oxygen cylinder for pure oxygen and compressor gas storage vessel for air system. Aquarium diffusers were used for better bubbling. The flow of gas is controlled by gas flow meter. The system is shown in Fig. 4.2. Under this system studies was carried out by varying the feed concentration, pH and oxidizing agent for optimizing the process parameter.

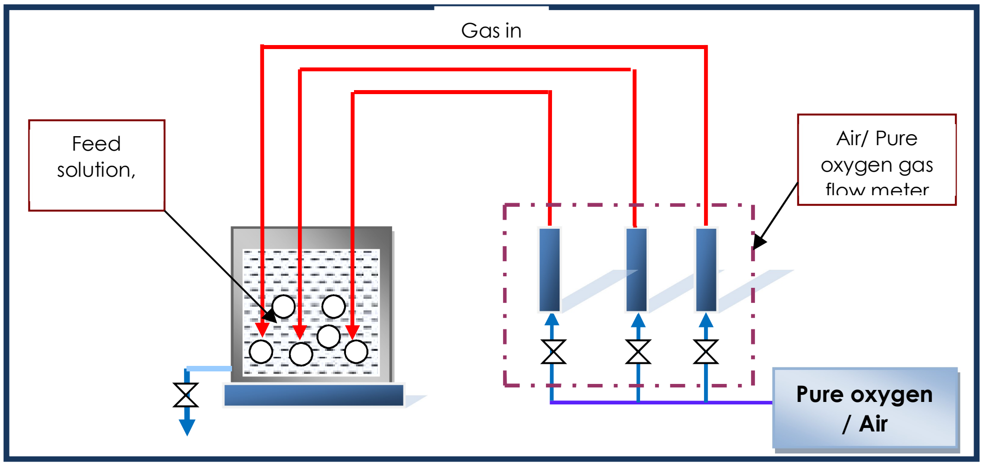


Fig. 4.2 Schematic of Batch mode through Direct Injection method

The conversation of As(III) to As(V) studied was carried out in batch mode through direct injection and MnO_2 dose as mentioned below and pure oxygen (98%) and Air were used as an oxidizing agent for aerating the feed solution.

Table 4.4: Experimental parameters Batch mode through Direct Injection method for As (III) to As(V) conversion study

Experimental parameters for As (III) to As(V) conversion study					
Feed	Feed temp (^{O}c)	Feed vol.	Oxidizing agent	As (III) conc. of feed (ppm)	Feed pH variation
Tap water/ DI water	Room temp	2 L	Pure oxygen/Air	1.0	5/6/7

In this system oxidizing agent pure oxygen (98%) / Air is added directly in the feed solution containing As(III) through a pipe line connected to an oxygen cylinder for pure oxygen and compressor gas storage vessel for air system. The flow of gas is controlled by gas flow meter. The system is shown in Fig. 4.3. Under this system studies was carried out varying the feed concentration, pH and oxidizing agent for optimizing the process parameter.

Table 4.5: Experimental parameters Batch mode through Direct Injection method with MnO_2 dose for As (III) to As(V) conversion study

Experimental parameters for As (III) to As(V) conversion study						
Feed	Feed temp (^{O}c)	Feed vol.	Oxidizing agent	As (III) conc. of feed (ppm)	MnO2 dose	Feed pH variation
Tap water/ DI water	Room temp	2 L	Pure oxygen/Air	1.0	0.1/0.25/ 0.5	5/6/7

In this system oxidizing agent pure oxygen (98%) / Air is added in the liquid through a pipe line connected to an oxygen cylinder for pure oxygen and compressor gas storage vessel for air system. The system is shown in Fig. 4.4. The flow rate of gas is controlled by gas flow meter and MnO_2 power was dose in the feed solution initially in varying concentration to enhance the conversion rate and MnO_2 act as a catalyst.

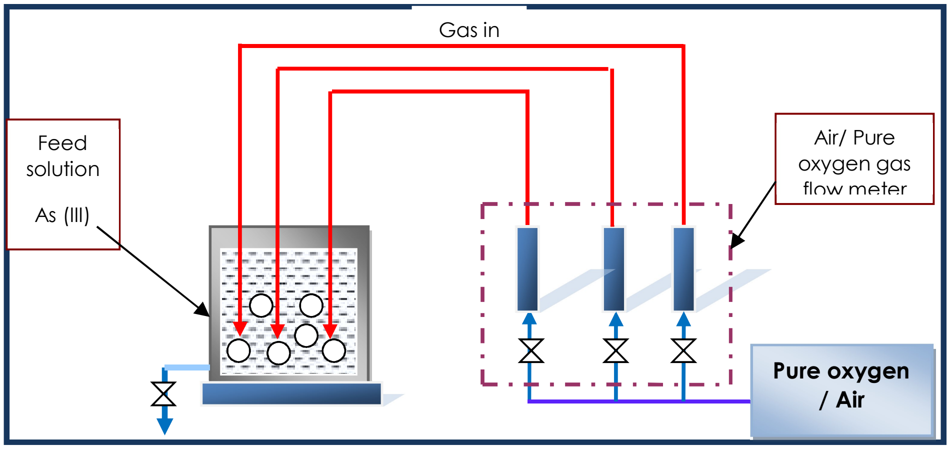


Fig. 4.3 Batch mode through Direct Injection method

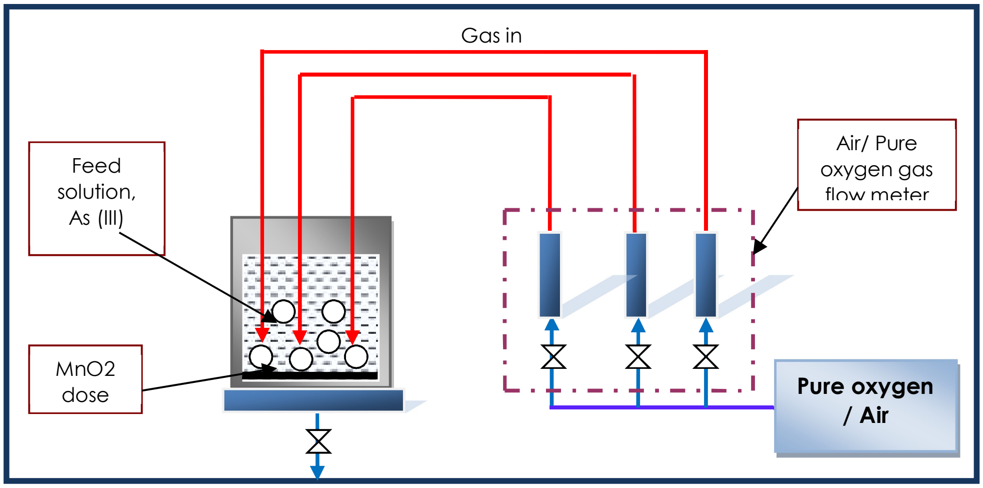


Fig. 4.4 Direct inject method with MnO_2 dose

4.2.4 Method for Coating and characterization

Manganese dioxide coating was conducted for catalytic oxidation application for conversion of As (III) to As (V). Commercial MnO_2 powder (Merck, India, assay≥70%, molecular weight 86.93) was crushed using agate mortar and used for slurry preparation having average particle diameter of 248.2 nm (78.8-825 nm) measured using Zetasizer Nano-S, Malvern, UK. The MnO_2 powder slurry was prepared by adding 2.0 wt % of MnO_2 to 250 g of total slurry along with 32 wt% dolapix and 3.5 wt% PEG (300 Da). 32 wt% hydroxyethylcellulose in Milli Q water was finally added. For coating, 200 mm long, 19-channel, defect free ceramic tubes were cleaned and used. Tubes were coated using dip coating method. The tubes were immersed in the slurry for 5 min and allowed for air drying overnight. Then the tubes were fired at 500ºC for 3 h (1ºC/min heating rate) in a horizontal furnace. A dark colored coating was obtained on the inner surface of tube. Tubes were washed thoroughly with Milli Q water. Then some tubes was immersed in 100 ml water for 65 h, filtered using Whattman-44 filter paper and the filtrate was analyzed for leaching of Mn. There was no leaching of Mn, indicated that a stable coating was obtained.

4.2.5 Characterization of MnO_2 powder and coated membrane

To obtain the morphology and stability of MnO_2 coating and its dispersion on the surface of the ceramic tube was evaluated by SEM at 20KV (Cambridge Instruments Stereoscan 360), X-ray diffraction (Philips PANalytical X'Pert Pro XRD). Fig 4.5b depicted the XRD analysis of 19 channel clay alumina support. FESEM of support showed the porous structure and peaks of alumina from EDAX analysis (Fig 4.5a).

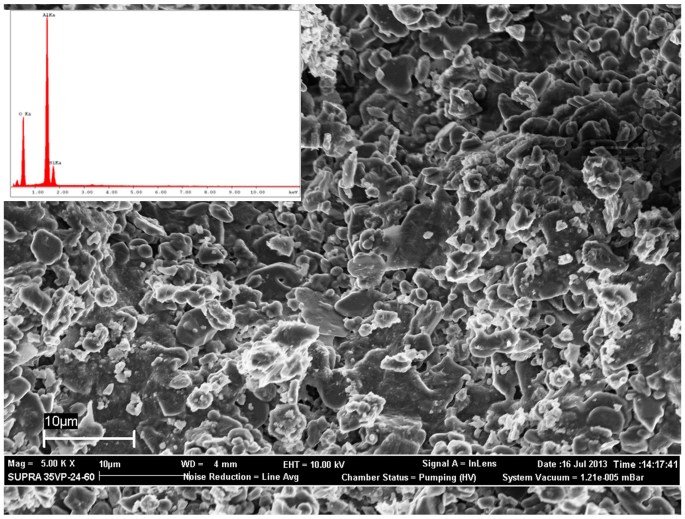


Fig. 4.5a FESEM and EDX analysis of 19-channel clay-alumina support tube

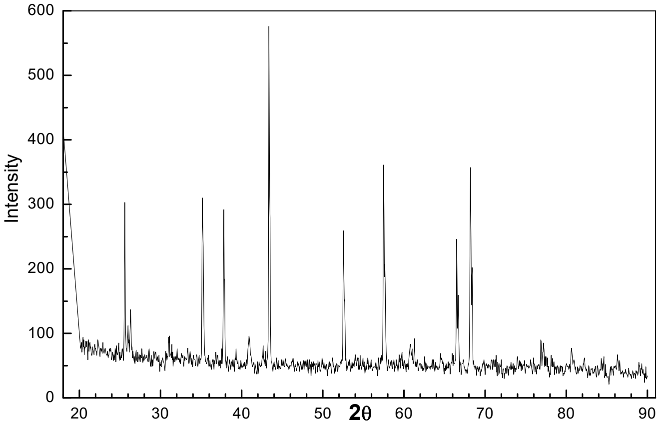


Fig. 4.5b XRD analysis of 19-channel clay-alumina support tube

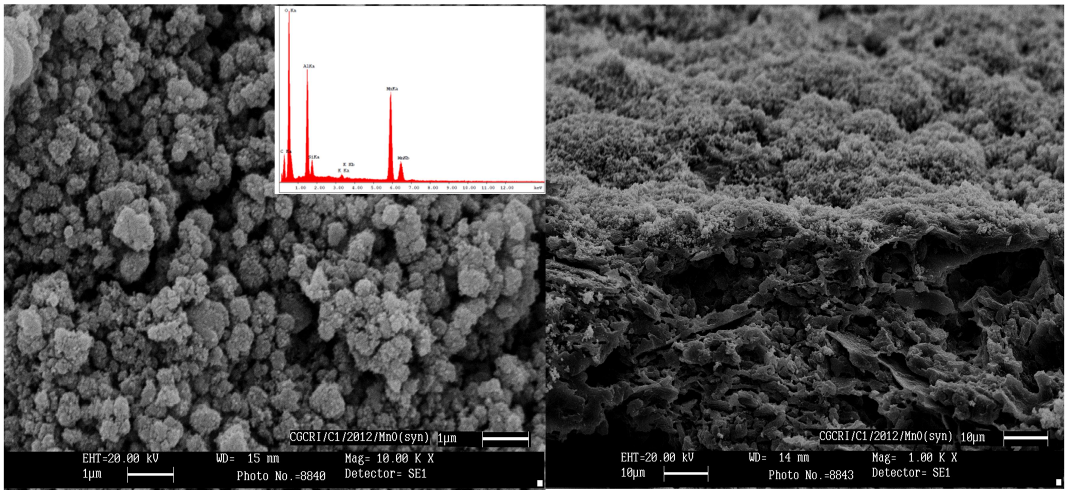


Fig. 4.5c FESEM and EDX of MnO_2 coated membrane supported the presence of manganese layer coated on ceramic support

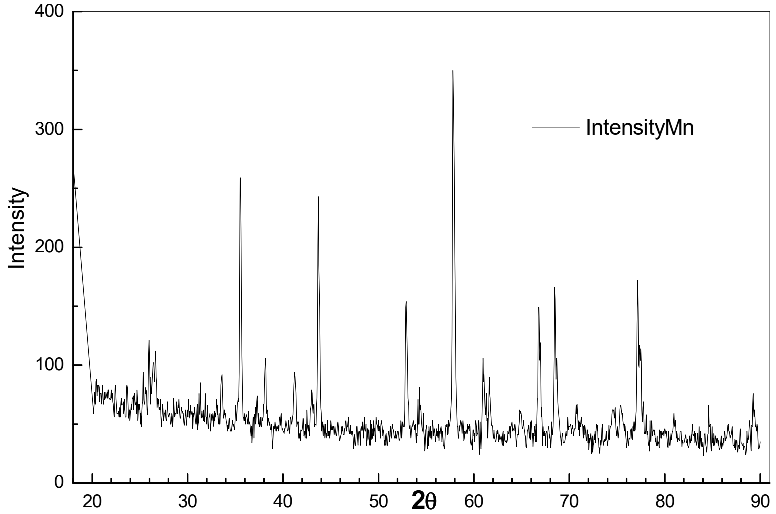


Fig 4.5d XRD analysis of MnO_2 coated membrane (KM/B29/F19C/200mm/MnO_2 coated)

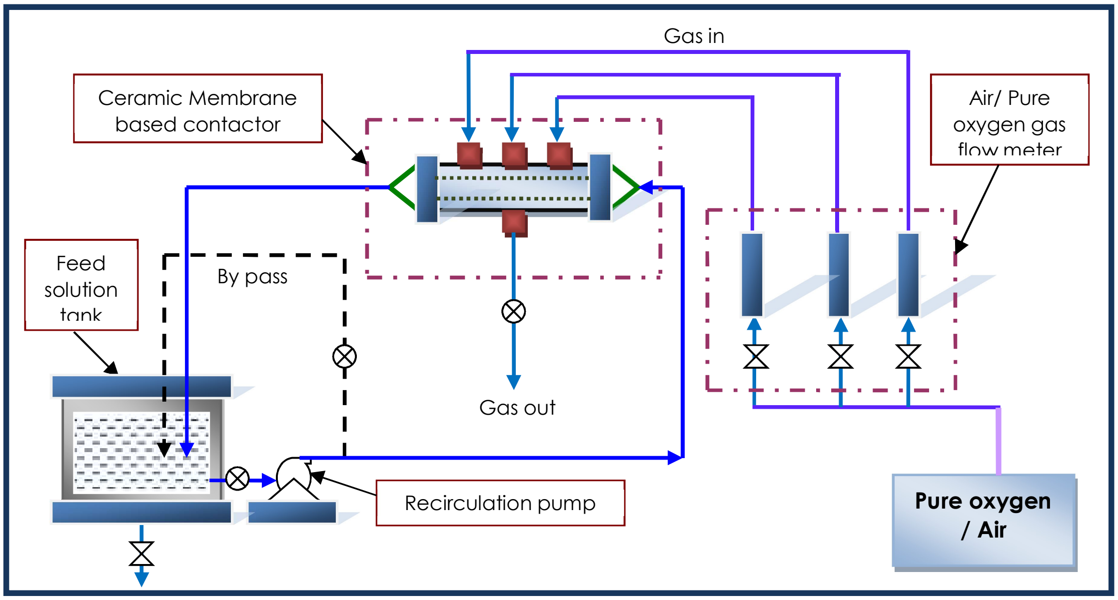
Fig. 4.5e Stereoscopic image of MnO_2 coated membrane (KM/B29/F19C/200mm/MnO_2 coated)

Table 4.6 Experimental parameters for As(III) to As(V) conversion in Ceramic Membrane Contactor

Experimental parameters for As(III) to As(V) conversion					
Feed	Ceramic membrane	Feed vol.	Oxidizing agent	Variation of As (III) conc. (ppm)	Feed pH variation
Tap water	KM/B29/19C/200mm/support	5 L	Pure oxygen/Air	0.1/0.2/0.3/0.4/ 0.5	5/6/7
Tap water	KM/B29/19C/200mm/ MnO2 coated membrane	5 L	Air	0.1/0.2/0.3/0.4/ 0.5	5/6/7

The lab unit for carrying out the oxidation study of As (III) to As (V) conversion with membrane contactor is shown in figure 4.6a and 4.6b. It consists mainly of a membrane module, a pump for recalculating the feed stream, a tank containing feed, gas flow meter for controlling & measuring the pure oxygen (98%)/air gas flow rate.

In the membrane contactor module a tubular microporous uncoated ceramic support of KM/B29/19C/200mm and a tubular microporous coated ceramic membrane of KM/B29/19C/200mm/MnO2 was used to conducting the study under varying process parameters to evaluate the performance of contactor and optimize the process parameter.



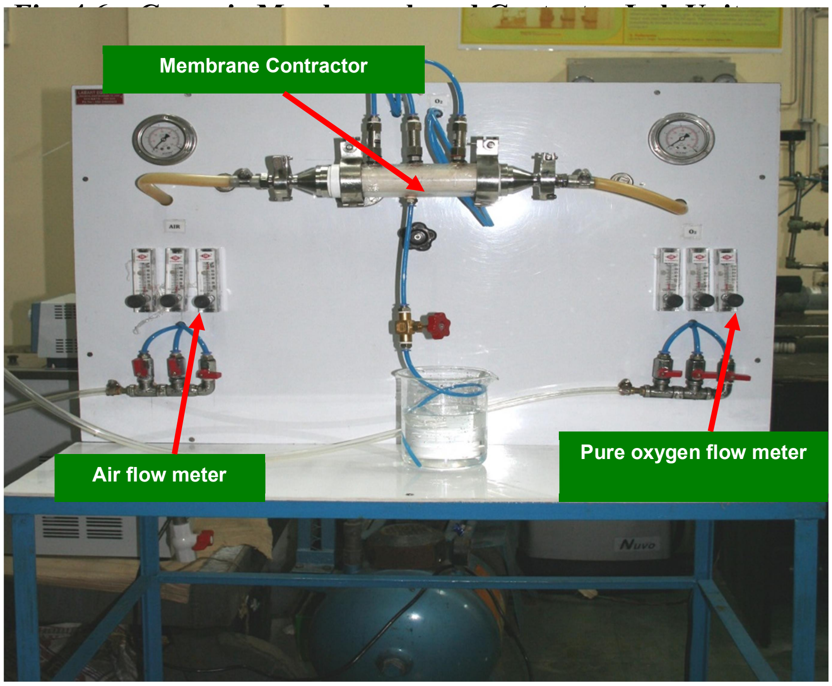


Fig. 4.6b Photograph of Ceramic Membrane based Contactor lab unit

The feed solution is recirculated to the inner channel of the membrane at the desired flow rate and pure oxygen / air stream is sent in cross-flow mode to the shell-side., Gas phase (Pure oxygen/Air) penetrate through the micro pores and the interface between gas and water is established at each pore mouth due to certain pressure of gas. Therefore, the gas, after diffusing through the micro pores, reaches the liquid Stream at the pore mouth and the contact between the two phases is established (fig. 4.7)

From the interface, the pure oxygen / oxygen contained into the air has to dissolve into the aqueous feed and to diffuse towards the bulk, so that it can be able to meet the As (III) present and to react with it to convert into As (V).

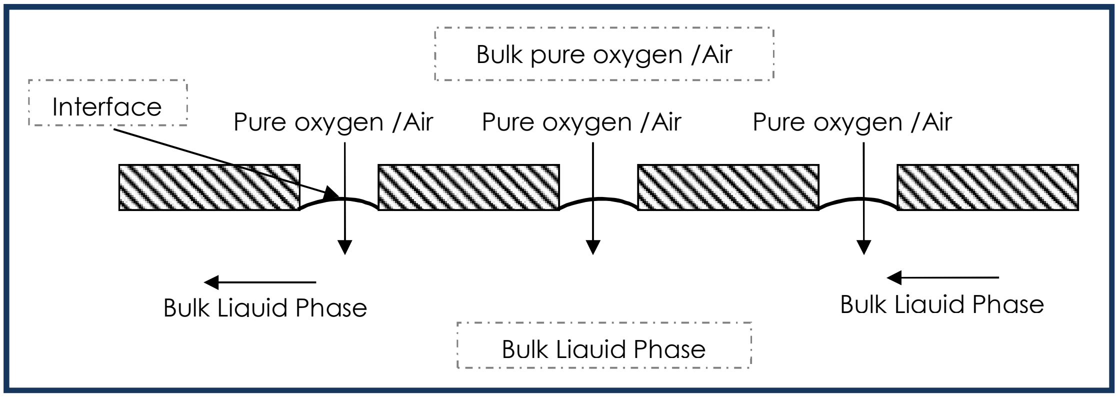


Fig. 4.7 Gas liquid mass transfer interface

4.2.6 Analytical methods

During the experiment the pH, DO and temp of feed solution has been recorded by portable type multiparameter meter (make, Hach). The concentration of Fe(II) and As (V) content into the feed solution has been determined by a UV visible spectrophotometer (carry 50 Bio, make: Varian). In particular, a colorimetric method has been applied for preparing both samples & standards and the absorbance has been measured at 510 nm and 863 nm for Fe(II) & As(V) respectively. The Rate constants of Fe(II) oxidation under various condition is shown in table 4.7.

4.2.7 Results and discussion

The results of the oxidation of Fe (II) to convert Fe(III) carried out in batch mode through direct injection method & As (III) to convert As (V) carried out on Direct Injection method, Direct Injection method with MnO2 dose and Ceramic Membrane based Contactor system under varying process parameters and discussed in the following part.

During the study the performance evaluation of the system at different parameters to convert Fe(II) to Fe(III)and As(III) to As(V) has been analyzed and presented below.

4.2.7.1 Rate of Deaeration of feed by nitrogen and pH variation

Initially the feed water was deaerated using nitrogen before preparing the synthetic feed solution to remove the dissolved oxygen and stop the effect of DO on oxidation. In both cases of DI water and Tap water around 90% of DO removed with in 30 mins of purging is shown in fig. 9. The variation of pH for both of liquid is very little during deaeration.

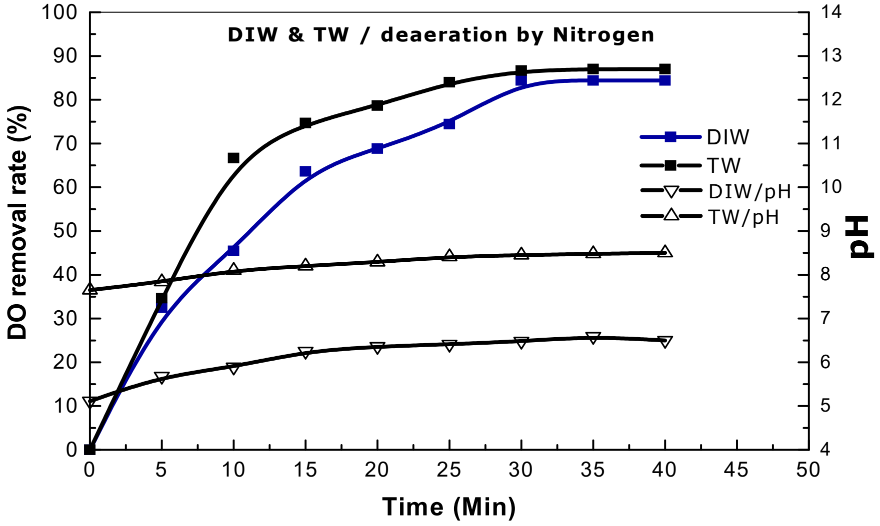


Fig. 4.8 Rate of deaeration of feed solution

Figure 4.9 shows the oxidation degree Fe(II) achieved in time as a function of feed type. Deionized water (DIW) and Tap water (TW) are used for preparation of feed solution. 95% of oxidation is obtained in both cases of DIW and TW in around 20 mins. As it was observed that the better degree of oxidation was achieved for Tap water in less duration compare to DIW. So, TW have been used preparing the feed sol. to conduct the study.

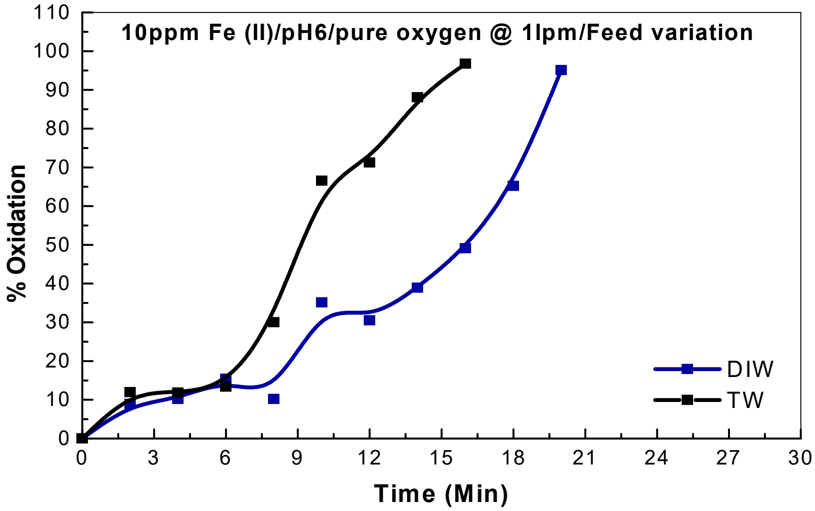


Fig 4.9 Fe(II) oxidation with time as function of feed , direct injection pure oxygen (98%)@ 1 lpm, feed Vol. ,5L; Conc. of Fe (II) 10ppm; pH6

4.2.7.2 Oxidation of Fe (II) with time as function of pH

Fig. 4.10 represented that the degree of oxidation was higher with pH closer to the neutral, compare to acidic pH in presence of pure oxygen to feed solution containing 10 ppm of Fe(II). Maximum oxidation of about 98% obtained at pH 6 in 16 10 minutes and at neutral pH its oxidation was fast just in a few mins.

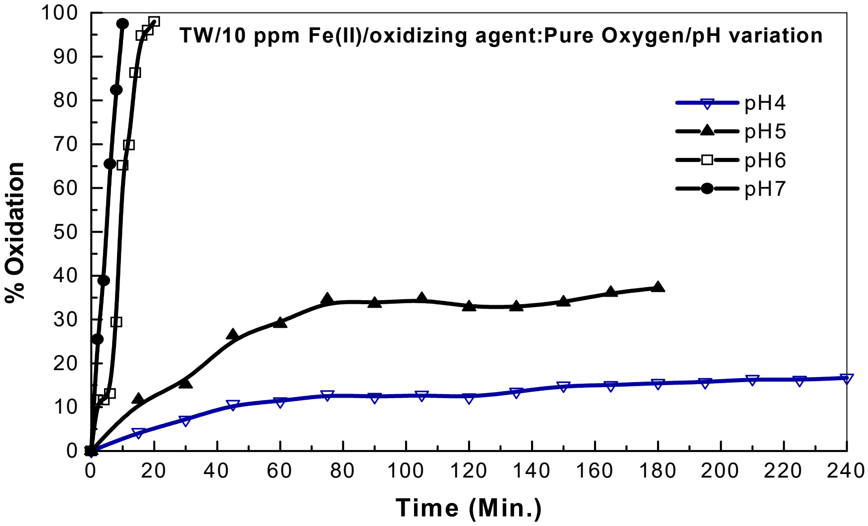


Figure 4.10 Fe(II) oxidation with time as function of feed pH , direct injection of pure oxygen (98%)@ 1 lpm, feed Vol. ,5L; Conc. of Fe (II) 10ppm

4.2.7.3 Oxidation of Fe (II) with time as function of feed Conc.

From the above results, pH 6 was considered as optimum pH for maximum oxidation. Effect of varying Fe(II) concentration at pH 6 was observed (Fig 4.11). Maximum oxidation of about 100% was achieved for 2ppm Fe(II) solution after 10 minutes of experiment. The oxidation of higher conc. might achieve 100% if operated for longer time or increase the rate of oxidant.

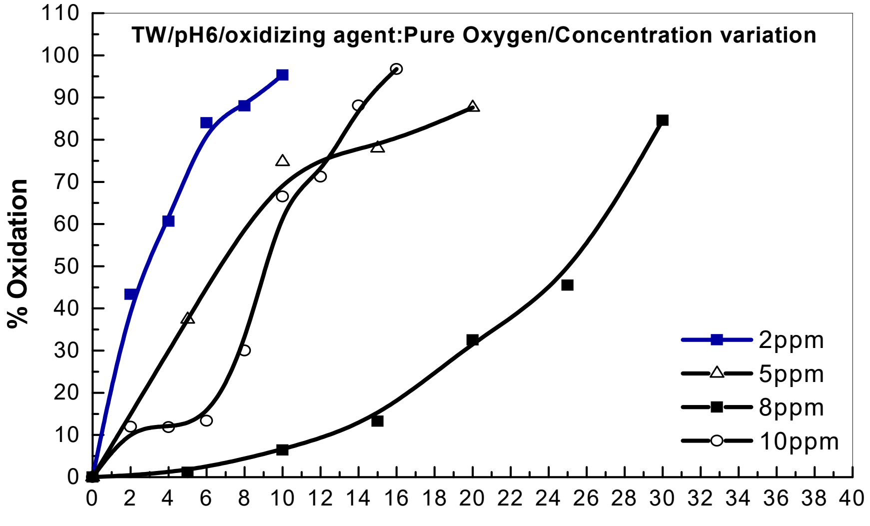


Figure 4.11 Fe(II) oxidation with time as function of feed conc. , direct injection of pure oxygen (98%)@ 1 lpm, feed Vol. ,5L; pH6

4.2.7.4 Oxidation of Fe (II) with time as function of oxidizing agent

Fig. 4.12 and 4.13 represents the oxidation degree was the function of oxidizing agent under varying pH condition. The oxidation rate increases when pure oxygen is used compared to air at pH 5 and pH 6.

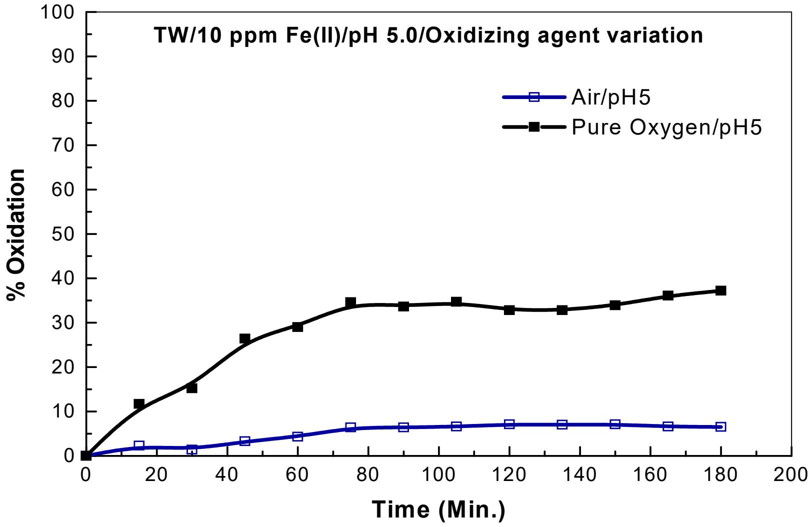


Figure 4.12 : Fe(II) oxidation with time as function of oxidizing agent , direct injection rate 1 lpm, feed Vol. , 5L; pH5

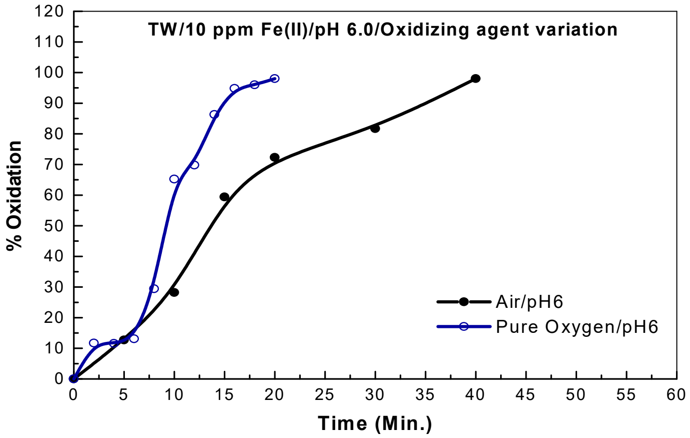


Figure 4.13 Fe(II) oxidation with time as function of oxidizing agent. , direct injection rate 1 lpm, feed Vol. , 5L; pH6

Table 4.7 : Rate constants of Fe(II) oxidation under various process parameters

Fe(II) oxidation to Fe(III) in batch study with purging of air/oxygen through aquarium aerator			
Feed Fe(II)	**pH**	**1st order rate constant (s^{-})**	**Purging**
2.0 ppm in TW	6.0	5.46×10^{-3}	Pure oxygen (98%), flow rate:1.0 lpm
5.0 ppm in TW	6.0	2.03×10^{-3}	Pure oxygen (98%), flow rate:1.0 lpm
8.0 ppm in TW	6.0	0.703×10^{-3}	Pure oxygen (98%), flow rate:1.0 lpm
10.0 ppm in TW	6.0	2.37×10^{-3}	Pure oxygen (98%), flow rate:1.0 lpm
10.0 ppm in TW	6.0	1.433×10^{-3}	Pure oxygen (98%), flow rate:1.0 lpm
10.0 ppm in TW	6.0	8.959×10^{-4}	Air, flow rate:1.0 lpm
10.11 ppm TW	4.0	4.5100062×10^{-6}	Pure oxygen (98%), flow rate:1.0 lpm
10.07 ppm TW	5.0	5.622027×10^{-5}	Pure oxygen (98%), flow rate:1.0 lpm
De-aeration by purging of nitrogen gas			
TW	7.6	1.4382134×10^{-3}	Change of DO level in water due to purging of nitrogen gas followed the first order rate law.
DIW	7.7	1.0686531×10^{-3}	

4.2.7.5 Oxidation of As (III) with time as function of feed and pH

Figure 4.14 & 4.15 shows the oxidation degree achieved in time with direct injection of air to feed solution containing 1.0ppm of As (III) at three different pHs of 4, 5 & 6. Deionized water (DIW) and Tap water (TW) are used for preparation of feed solution. 7%, 15% & 10% of oxidation is obtained in case of DIW and 6%, 20% & 10% of oxidation is obtained in case of TW for pH 5, 6 & 7 respectively. To maintain the experimental system closer to real, Tap water was used for further study.

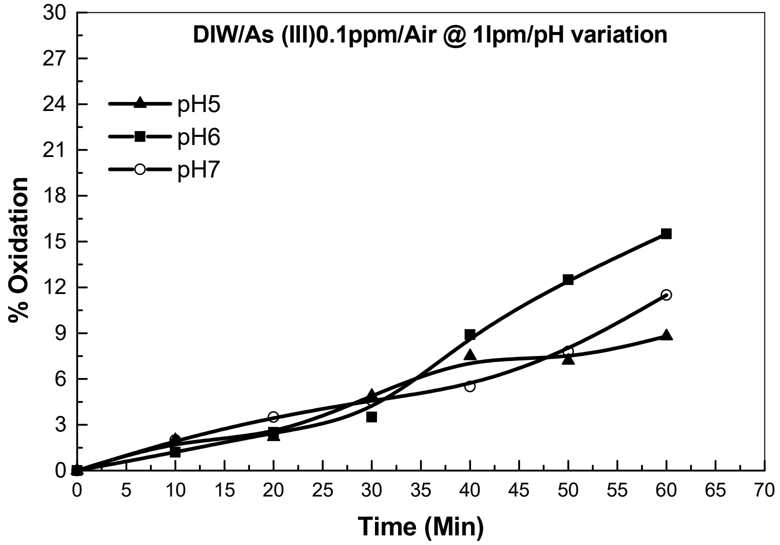


Figure 4.14 As (III) oxidation with time as function of feed pH, Direct injection of air; feed, Deionized water (DIW); feed sol. Vol., 2L; Conc. of As (III), 1.0ppm; Air @ 1 lpm

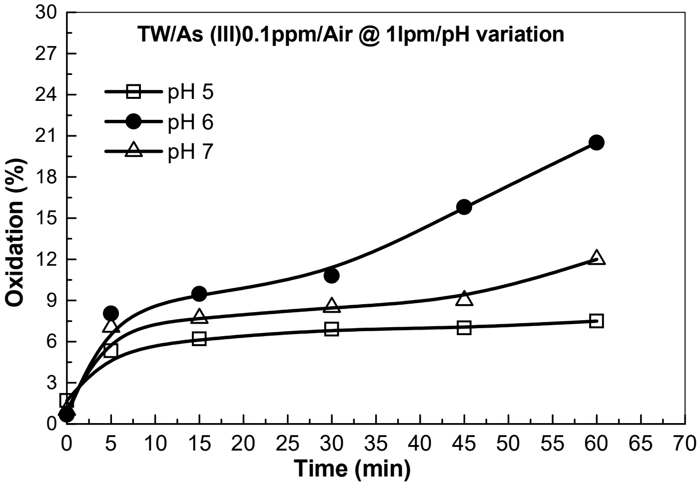


Figure 4.15 As (III) oxidation with time as function of feed pH, Direct injection of air; feed, Deionized water (DIW); feed sol. Vol. 2L; Conc. of As (III), 1.0ppm; Air @ 1 lpm

4.2.7.6 Oxidation of As (III) with time as function of oxidizing agent

The oxidation degree achieved in time with direct injection of pure oxygen (98%) to feed solution containing 1.0ppm of As (III) at three different pHs of 5, 6 & 7 is shown in figure 4.16 Tap water (TW) is used for preparation of feed solution. 9%, 22% & 13% of oxidation is obtained for pH 4, 5 & 6 respectively.

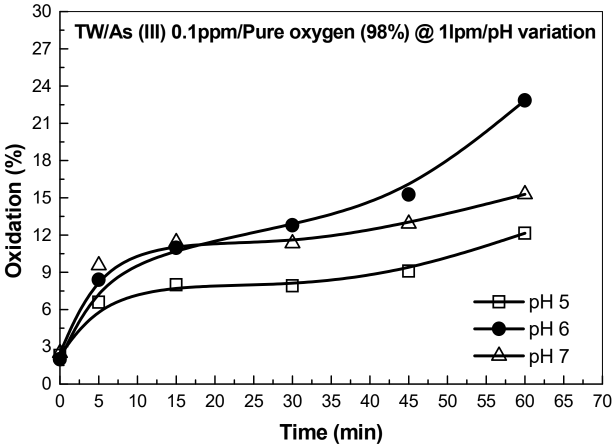


Fig 4.16 As (III) oxidation with time as function of feed pH, direct injection of pure oxygen (98%); Tap Water feed (TW); feed Vol. 2L; Conc. of As (III), 1.0ppm; pure oxygen @ 1 lpm

It was observed that the rate of oxidation for both air and pure oxygen were comparable under similar condition.

4.2.7.7 Oxidation of As (III) with time: effect of MnO2 catalyst

Figure 4.17 & 4.18 shows the oxidation degree achieved with time in presence of MnO_2 (constant dose of 0.1 mg/L) and varying dose (0.1-0.5 mg/L) as a catalyst in direct injection of pure oxygen to feed solution containing 1.0ppm of As (III) at three different pH of 5, 6 & 7. In case of 0.1mg/L MnO_2 dose about 18% oxidation was obtained and in case 0.5 mg/L dose 24% oxidation was obtained. FESEM and EDX of MnO_2 power after treatment with As(III) was shown in figure 4.19.

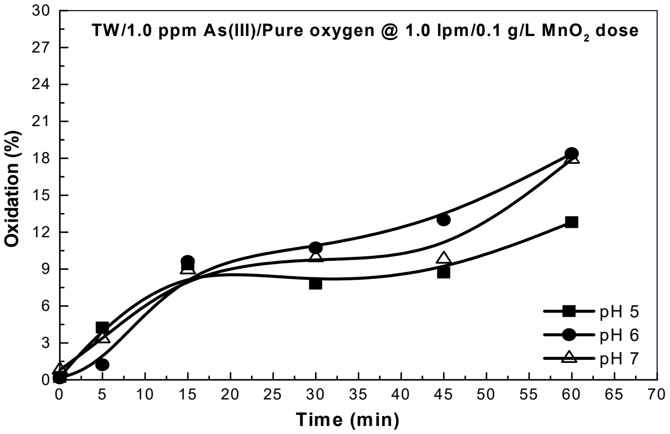


Fig. 4.17 As(III) oxidation with time in presence of MnO2 as a catalyst using direct injection of pure oxygen (98%), feed Vol. 2L; Conc. of As (III) 1.0ppm; pH 5/6/7; Pure oxygen @ 1 lpm

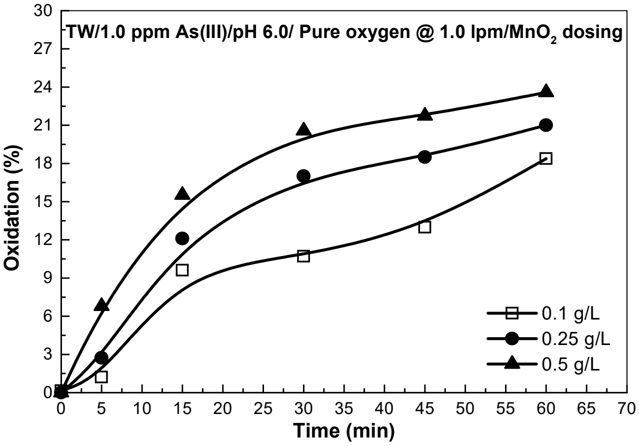


Fig. 4.18 As(III) oxidation with time in presence of MnO2 dose variation using direct injection of pure oxygen (98%) @ 1 lpm, feed Vol. 2L; Conc. of As (III) 1.0ppm; pH 6

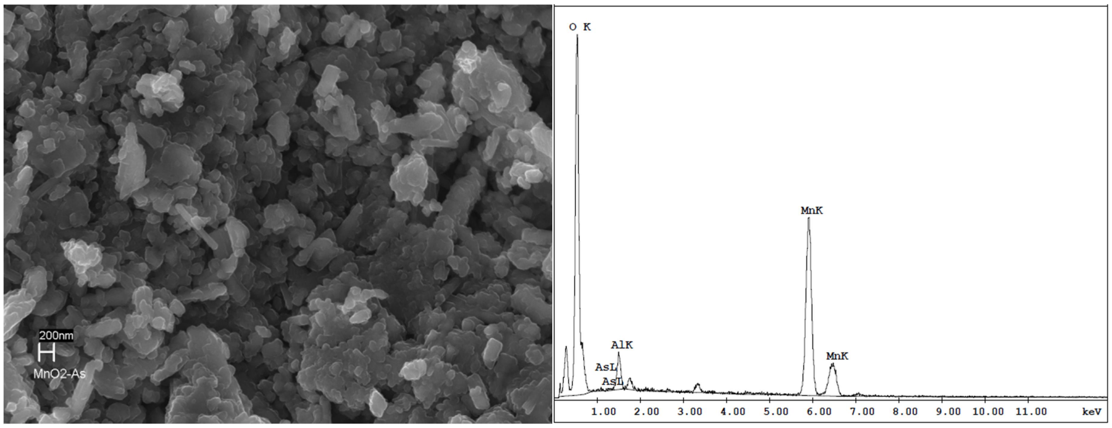


Fig. 4.19 FESEM and EDX of MnO$_2$ powder after treatment with As(III)

4.2.7.8 Oxidation of As (III) with time as function of pH and Pure oxygen using membrane contactor (uncoated support membrane)

The oxidation achieved with ceramic membrane based contactor (uncoated support membrane) in presence of pure oxygen (98%) to feed solution containing 0.1 ppm of As (III) at three different pH of 5,6 & 7 is shown in figure 19. Maximum oxidation of about 55% was obtained at pH 6 after 60 minutes (Fig 20).

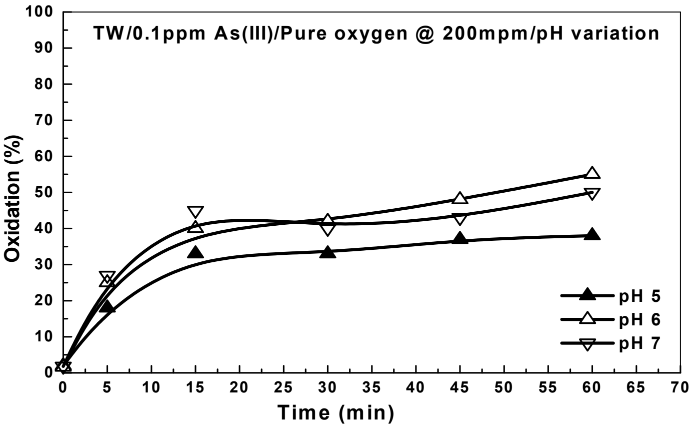


Fig. 4. 20 As(III) oxidation with time as function of pH and pure oxygen using ceramic membrane based contactor (uncoated support), feed Vol. 5L; Conc. of As(III), 0.1ppm; Pure oxygen @ 200 ml/m

4.2.7.9 Oxidation of As (III) with time as function of concentration and Pure oxygen using membrane contactor (uncoated support membrane)

From the above results, pH 6 was considered as optimum pH for maximum oxidation. Effect of varying As concentration at pH 6 was observed (Fig 21). Maximum oxidation of about 55% was achieved for 0.1 ppm As (III) solution after 60 minutes of experiment. Degree of oxidation decreased with increasing concentration of As (III) with constant pure oxygen supply. The oxidation might increase if operated for longer time or increase the rate of oxidant.

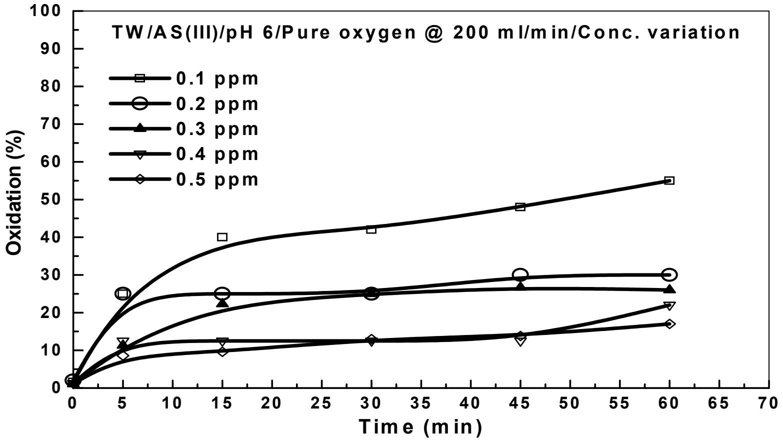


Fig. 4. 21 As(III) oxidation with time as function of conc. using ceramic membrane based contactor (uncoated support membrane), feed Vol. 5L; pH 6; Pure oxygen @ 200 ml/m

4.2.7.10 Oxidation of As (III) with time as function of pH and Air using membrane contactor (uncoated support membrane)

The oxidation degree achieved in time with ceramic membrane based contactor (uncoated support membrane) in presence of air to feed solution containing 0.1 ppm of As (III) at three different pH of 5,6 & 7 is shown in figure 4. 22. Maximum oxidation of about 52% was obtained at pH 6 after 60 minutes.

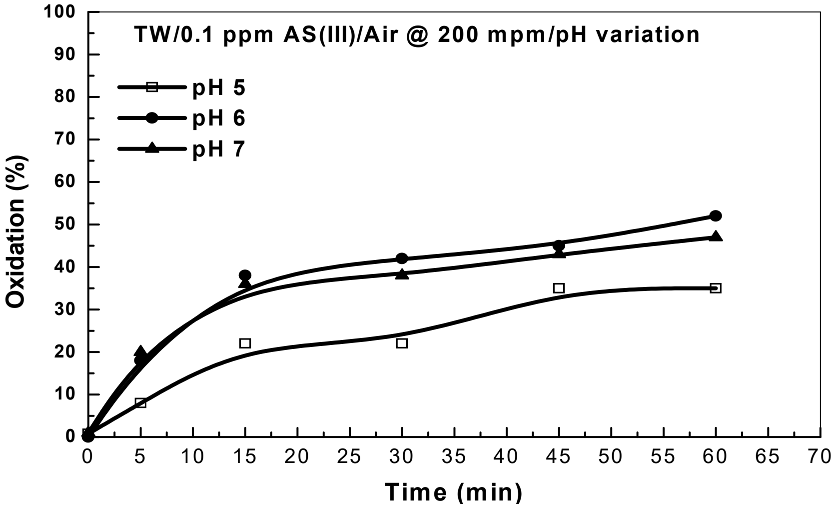


Fig. 4. 22 As(III) oxidation with time as function of pH and air using ceramic membrane e based contactor (uncoated support membrane), feed Vol. 5L; Conc. of As(III),0.1ppm; Air @ 200 ml/m

4.2.7.10 Oxidation of As (III) with time as function of concentration and air using membrane contactor (uncoated support membrane)

From the above results pH 6 was considered as optimum pH for maximum oxidation. Effect of varying As concentration at pH 6 was observed (Fig 4.23). Maximum oxidation of about 52% was achieved for 0.1 ppm As (III) solution after 60 minutes of experiment. Degree of oxidation decreased with increasing concentration of As (III) with constant air supply. The oxidation might increase if operated for longer time or increase the rate of oxidant.

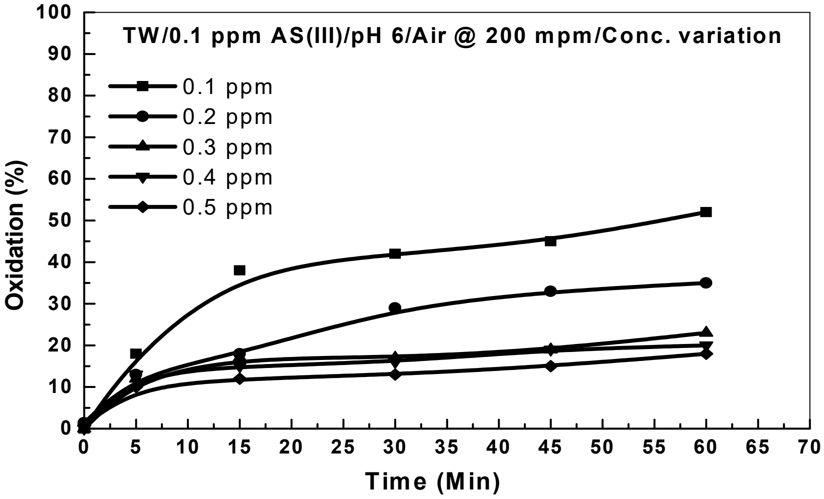


Fig. 4.23 As(III) oxidation with time as function of conc. and air using ceramic membrane based contactor (uncoated support membrane), feed Vol. 5L; pH 6; Air @ 200 ml/m

It was observed that the rate of oxidation for both air and pure oxygen were comparable using uncoated support membrane under similar condition. So, air was selected as an oxidizing agent for conducting the experiment based on MnO_2 coated membrane contractor and results were shown in below.

4.2.7.10 Oxidation of As (III) with time as function of pH and Air using membrane contactor (coated membrane)

The oxidation degree achieved in time with ceramic membrane based contactor (coated support membrane) in presence of air to feed solution containing 0.1 ppm of As (III) at three different pHs of 5, 6 & 7 is shown in figure 4.24. Maximum oxidation of about 90% was obtained at pH 6 after 60 minutes and also 75% and 65% was obtained at pH 5 and 7 respectively. In case of coated membrane, MnO_2 act as catalyst to enhance the oxidation rate in same duration of experiment.

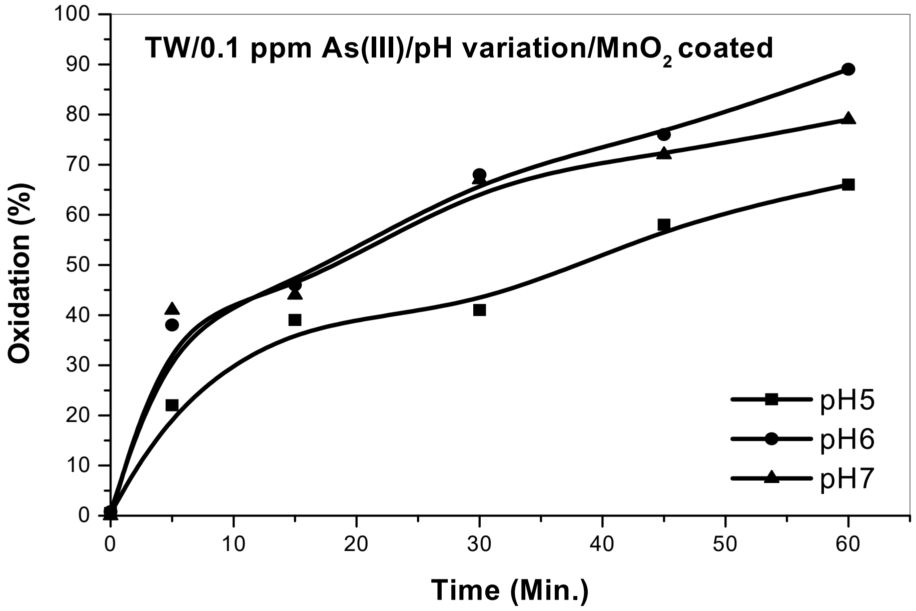


Fig. 4.24 **As(III) oxidation with time as function of pH and air using ceramic membrane based contactor (MnO_2 coated), feed Vol. 5L; Conc. of As(III), 0.1ppm; Air @ 200 ml/m**

4.2.7.11 Oxidation of As (III) with time as function of concentration and air using membrane contactor (coated support membrane)

From the above results pH 6 was considered as optimum pH for maximum oxidation. Effect of varying As concentration at pH 6 was observed (Fig. 4.25). Maximum oxidation of about 90% was achieved for 0.1 ppm As (III) solution after 60 minutes of experiment and 70%, 62%, 52% and 50% oxidation was achieved for 0.2ppm, 0.3ppm, 0.4ppm and 0.5ppm As(III) concentration respectively. The oxidation might increase and achieved 100% oxidation if operated for longer time or increases the rate of oxidant.

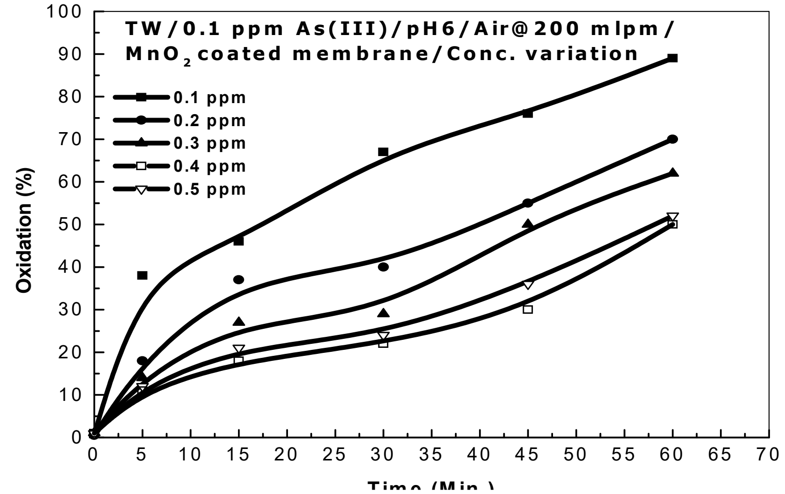


Fig. 4.25 **As(III) oxidation with time as function of conc. and air using ceramic membrane based contactor (MnO_2 coated), feed sol. Vol., 5L; pH 6; Air @ 200 ml/m**

4.2.8 Conclusion

The oxidation of Fe(II) to Fe(III) has been carried out in batch mode of direct injection method. Fe(II) oxidation is significantly higher with purging of air/oxygen and the oxidation is faster near to neutral pH. Catalytic coating has significant role on Fe(II) oxidation.

The oxidation of As(III) to As(V) has been carried out in direct injection method, direct injection method with MnO_2 as catalyzing agent and ceramic membrane based contactor system. The effect of various operating condition has been studied.

Effect of deionised water and tap water on degree of As (III) oxidation was observed. The obtained results suggested that minute variations of about ± 1-2% were noted. Moreover the characteristics of tap water were closer to that of groundwater; it would be feasible for real system applications. Therefore tap water was selected for further conduction of experiments.

Presence of MnO_2 as catalyst in direct injection method using pure oxygen/air as compared to only direct injection method did not show any significant results. Results also suggested that pure oxygen had more potential in oxidizing As (III) to As (V) as compared to air.

Application of membrane contactor (uncoated support membrane) resulted in enhanced degree of oxidation of As (III). Effect of pH on As (III) conversion showed that maximum conversion of about 60% occurred at pH range of 6 after 60 minutes of experiment.

Effect of oxidizing agent such as pure oxygen and air on degree of As(III) oxidation in membrane contactor (uncoated support membrane) system was observed. The obtained results suggested that minute variations of about ± 2-3%. Therefore air was selected for conducting the experiments based on coated membrane contactor.

Application of membrane contactor (coated membrane) resulted in enhanced degree of oxidation of As (III). Effect of pH on As (III) conversion showed that maximum conversion of about 90% occurred at pH range of 6 after 60 minutes of experiment in presence of air. The oxidation might increase and achieved 100% oxidation if operated for longer time or increases the rate of oxidant.

CHAPTER 5

Arsenic removal from groundwater using Ceramic Membrane Technology

5.1 Introduction

5.1.1 Background

Arsenic is a natural component of the earth's crust and is widely distributed throughout the environment in the air, water and land. It is highly toxic in its inorganic form. Arsenic contamination of groundwater is widespread and there are a number of regions where arsenic contamination of drinking-water is significant. It is now recognized that at least 140 million people in 50 countries have been drinking water containing arsenic at levels above the WHO provisional guideline value of 10µg/L. The greatest threat to public health from arsenic originates from contaminated groundwater. Inorganic arsenic is naturally present at high levels in the groundwater of a number of countries, including Argentina, Bangladesh, Chile, China, India, Mexico, and the United States of America.

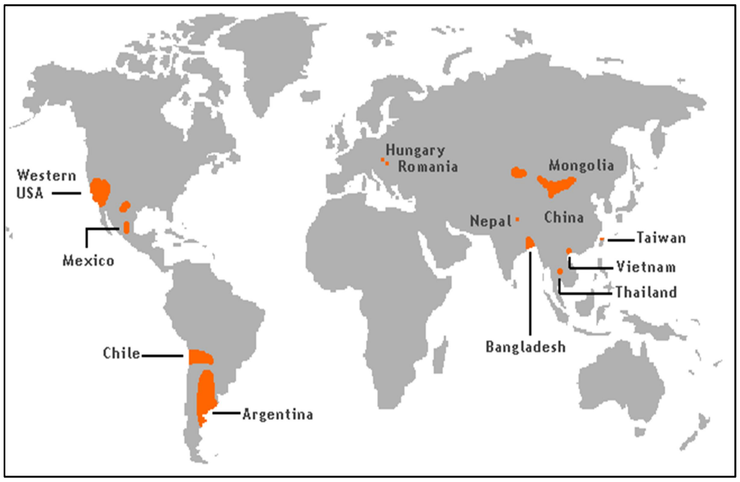


Fig: 5.1 Arsenic contamination of ground water

Drinking-water, crops irrigated with contaminated water and food prepared with contaminated water are the sources of exposure. Fish, shellfish, meat, poultry, dairy products and cereals can also be dietary sources of arsenic, although exposure from these foods is generally much lower compared to exposure through contaminated groundwater. In seafood, arsenic is mainly found in its less toxic organic form.

Inorganic arsenic is a confirmed carcinogen and is the most significant chemical contaminant in drinking-water globally. Arsenic can also occur in an organic form. Inorganic arsenic compounds (such as those found in water) are highly toxic while organic arsenic compounds (such as those found in seafood) are less harmful to health. The immediate symptoms of acute arsenic poisoning include vomiting, abdominal pain and diarrhoea. These are followed by numbness and tingling of the extremities, muscle cramping and death, in extreme cases. The first symptoms of long-term exposure to high levels of inorganic arsenic (for example, through drinking-water and food) are usually observed in the skin, and include pigmentation changes, skin lesions and hard patches on the palms and soles of the feet (hyperkeratosis).

Fig: 5.2 Skin damages by Arsenic contamination

These occur after a minimum exposure of approximately five years and may be a precursor to skin cancer. In addition to skin cancer, long-term exposure to arsenic may also cause cancers of the bladder and lungs. Other adverse health effects that may be associated with long-term ingestion of inorganic arsenic include developmental effects, diabetes, pulmonary disease, and cardiovascular disease. Arsenic-induced myocardial infarction, in particular, can be a significant cause of excess mortality. In China (Province of Taiwan), arsenic exposure has been linked to "Blackfoot disease", which is a severe disease of blood vessels leading to gangrene. This disease has not been observed in other parts of the world however, and it is possible that malnutrition contributes to its development. Arsenic is also associated with adverse pregnancy outcomes and infant mortality, with impacts on child health, and exposure in utero and in early childhood has been linked to increases in mortality in young adults due to multiple cancers, lung disease, heart attacks, and kidney failure. Numerous studies have demonstrated negative impacts of arsenic exposure on cognitive development, intelligence, and memory.

The most important action in affected communities is the prevention of further exposure to arsenic by the provision of a safe water supply for drinking, food preparation and irrigation of food crops.

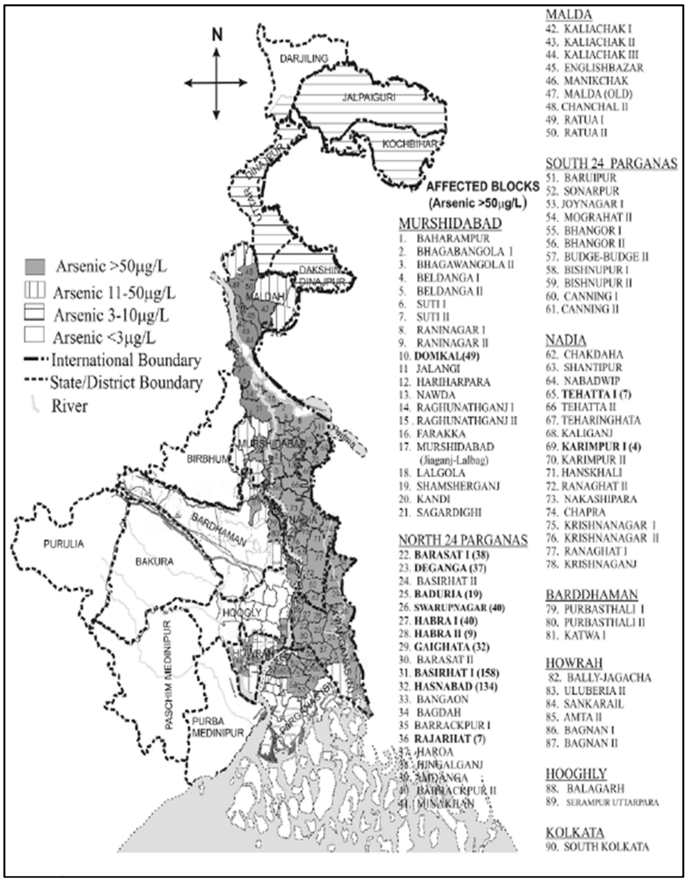


Fig: 5.3 Area of arsenic contaminated groundwater in West Bengal

In USA, under EPA's technology demonstration programme, 39 locations were chosen for technology demonstration. Out of 39 plants, 22 were based on Adsorptive media, 7 were for removal of Arsenic by Iron removal, 2 were for adsorptive media with Iron removal, 4, were based on coagulation-filtration and 2 were based on Ion exchange. The demonstration plants used mostly packed bed tanks/columns filled with media and the inlet arsenic concentration was relatively low(average 50 microgram/litre). Higher capacity plants installed with huge capital cost using adsorption techniques have been tried under field condition under this programme but their use is restricted to lower As level with reduced iron content and the limit of 10 microgram per litre could be achieved after a prolonged operation.

The highest arsenic concentration in natural water was reported in Western USA (48 000 μg/L). High amount of arsenic in groundwater was also reported in southeastern Asia (Bangladesh, India, China, Taiwan, Philippines), North and South America, and some parts of Europe (Hungary, Romania, Serbia and Monte Negro). In countries like India and Bangaldesh, several Arsenic removal plants, mostly attached hand pump had been tried. In a recent study, it has been found that 25% of the installed units are defunct and 53% of the working plants does not meet the WHO recommended limit for Arsenic. The present focus on arsenic remediation in third-world countries is on using iron containing compounds because they are both cheap and effective. Absorbents are not as effective in the field because of the presence of Mg2+ and Ca2+ and other naturally occurring ions, which compete with arsenic for adsorbent sites. Arsenic removal technologies indicates that iron filings, ferric salts, granular ferric hydroxide, alumina manganese oxide, lanthanum hydroxide, Aqua-bind, and Kimberlite tailings are potentially low-cost sorbents that can remove arsenic after simple mixing in a relatively short time. Fixed column of sorbents can remove arsenic simply by passing groundwater through the column, but are ineffective when Iron is present in groundwater. Many synthetic adsorbents are available in the market which is very effective but the high cost of adsorbent is a limiting factor for use of such adsorbents. Naturally occurring solids also remove arsenic well, but the removal rate is often very slow and the product water contains bacteria.

Activated alumina, Al_2O_3, having good sorptive surface is an effective medium for arsenic removal. When water passes through a packed column of activated alumina, the impurities including arsenic present in water are adsorbed on the surfaces of activated alumina grains. Eventually the column becomes saturated, first at its upstream zone and later the saturated zone moves downstream towards the bottom end and finally the column get totally saturated.

Regeneration of saturated alumina is carried out by exposing the medium to 4% caustic soda, NaOH, either in batch or by flow through the column resulting in a high arsenic contaminated caustic waste water. The residual caustic soda is then washed out and the medium is neutralized with a 2% solution of sulfuric acid rinse. During the process about 5-10% alumina is lost and the capacity of the regenerated medium is reduced by 30-40%. The activated alumina needs replacement after 3-4 regeneration.

In USA, under EPA's technology demonstration programme, 39 locations were choosen for technology demonstration. Out of 39 plants, 22 were based on Adsorptive media, 7 were for removal of Arsenic by Iron removal, 2 were for adsorptive media with Iron removal, 4, were based on coagulation-filtration and 2 were based on Ion exchange. The demonstration plants used mostly packed bed tanks/columns filled with media and the inlet arsenic concentration was relatively low(average 50 microgram/litre). Higher capacity plants installed with huge capital cost using adsorption techniques have been tried under field condition under this programme but their use is restricted to lower As level with reduced iron content and the limit of 10 microgram per litre could be achieved after a prolonged operation. A survey conducted by CGCRI in 8 different places in Nadia district and three different places in Murshidabad districts of west Bengal shows groundwater Arsenic level upto 80 microgram per litre. CSIR-CGCRI has proven technology proven under field condition (plant in operation for five years) for treatment of groundwater containing upto 130 microgram per litre.

Few other technologies have been developed by Indian researchers and some of those are in use in field. ARI Groundwater Arsenic Treatment Technology by Agarkar Research Institute uses 'integrated microbial oxidation alumina oxidation-adsorption process' suitable for domestic use as it gives around 40 LPH output. There has been 5 installations reported.

Hand Pump Attached Arsenic Removal unit by Jadavpur University is based on the double principle of oxidation & Co-precipitation and adsorption. The oxidation of As (III) to As (V) is achieved by adding chlorine. Co-precipitation for removal of arsenate is achieved by adding alum (aluminum sulphate) in right proportion. During up-flow movement of water, arsenate or arsenite, if present are removed through adsorption process in activated alumina layer. The iron in water is also removed in the purification process. It is a community filter capable of achieving 800 to 1000 LPH capacity. This has been demonstrated in 4 locations of West Bengal.

Tezpur University has developed Arsiron Nilogon technology. This filter removes arsenic and iron by Oxidation-Coagulation at Optimized pH (OCOP). Here the arsenic and the iron present in groundwater are oxidised from As(III) (arsenite) and Fe(II) (ferrous) states to As(V) (arsenate) and Fe(III) (ferric), respectively by using an oxidizing agent, viz., potassium permanganate ($KMnO_4$) and then coagulated using a coagulant, viz. ferric chloride ($FeCl_3$) at an optimized pH range controlled by adding sodium bicarbonate (baking soda or cooking soda, $NaHCO_3$) before oxidation and coagulation. Aeration of the water reduces the required quantity of KMnO4. The water is then filtered using any filter, preferably a sand-gravel filter fitted with a filtration assisting device. Capacity can be upto 500 LPH. There has been 25 installations reported.

IIT Madras has developed AMRIT is an affordable solution for providing clean drinking water in arsenic affected areas. It is a gravity-fed water purification unit in which arsenic and iron containing water is passed through a composite filter unit to obtain water, conforming to international standards. The solution has been implemented at various levels - homes, small communities and large scale water supply programs. The community based plants are 100-1000 LPH capacity whereas the capacity with motor driven pumps can be higher. 200 household units demonstrated in Yadgiri District of Karnataka, Murshidabad district of West Bengal and in Bihar 160 units of community filter demonstrated in villages spread across the districts of Murshidabad and Nadia, (West Bengal).

Indian Institute of Technology, Kharagpur has developed he Laterite based Arsenic filter which uses naturally abundant raw laterite modified by suitable chemical treatment. The capacity of domestic filter is in the range of 40-120 litres/day and for community scale it is in the range of 500-2000 litres/day. 25 household filter units installed in West Bengal.

All the above technologies are based on packed bed configuration which has got certain disadvantages in the form of bed material replacement and more maintenance effort are needed to keep the units running.

5.1.2 Methodology

Arsenic & iron contaminated ground water is pumped into a storage tank containing the nano colloidal adsorbent media (quantity/dose of media depends on the concentration of arsenic), aerated and mixed for a predetermined time. The oxygen supplied enables oxidation of Arsenite (Trivalent form of Arsenic) to Arsenate (Pentavalent form of Arsenic) and Ferrous (Bivalent for of Iron) to Ferric (Trivalent form of Iron) in the storage tank. Adsorbent particles thereupon attach these Arsenates and Ferrics on their surfaces to form a conglomerate, with an increase in particle size in the contaminated water. The contaminated water along with the colloidal media is then re-circulated through tubular ceramic membrane(having invisible micropores on the surface) module under pressure for separation of the media particles attached with Arsenic and Iron in the retentate stream and production of safe drinking water as the permeate. The technique is essentially a hybrid process comprising of adsorption of arsenic by the colloidal media particles suspended in water followed by crossflow microfiltration for solid-liquid separation using multichannel ceramic membranes. In case of presence of iron only (absence of arsenic), colloidal adsorbent media is not required. Similarly, water containing high particulates causing turbidity is also removed by cross flow microfiltration.

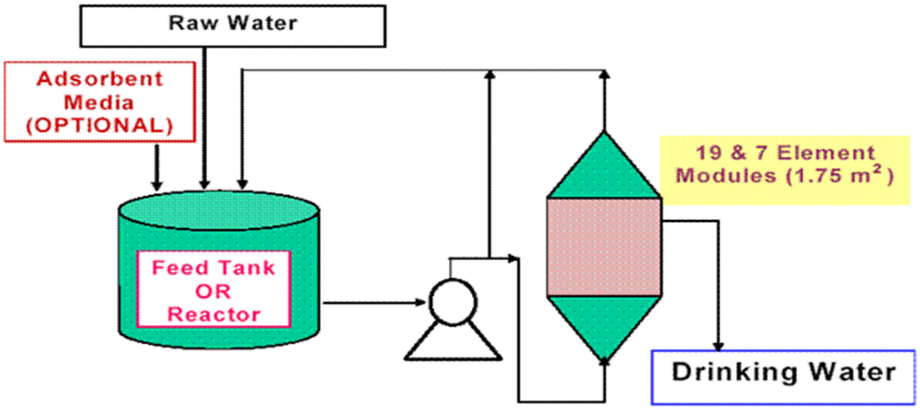


Fig. 5.4 Schematic of Ceramic Membrane based Plant

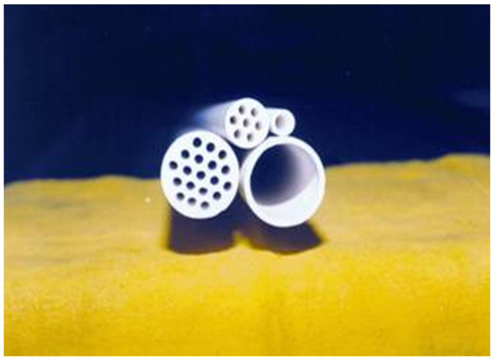


Fig. 5.5 Typical Ceramic Membranes

The novelty of the process is deployment of a hybrid process comprised of two steps : adsorption of arsenic by the colloidal media particles suspended in water and application of membrane based separation technique for solid-liquid separation using ceramic micro-filtration membrane modules. The efficiency of removal is higher due to intimate contact of arsenic species with colloidal adsorbent media followed by complete separation of fine particulates of iron and media by membrane through cross-flow microfiltration process. CSIR-CGCRI technology use colloidal adsorbent media where as other technologies use granular media loaded in packed bed. Use of colloidal media is a very novel idea which results into a much better adsorption of arsenic particles; hence the level of purification achieved is also higher compared to other processes. In case of presence of iron only (absence of arsenic), colloidal media is not required.

Besides that, ease of operation and maintenance particularly electrically operated semi automatic plant with minimum human intervention, ease of periodical cleaning (once in 3-6 months) of the modules, back washing with minimum amount of filtered water, no loss of water, smaller space requirement for plant installation, lower sludge volume, etc. make this process ideal for rural area.

Typical community level or small plants are generally made of Food grade Stainless Steel with SS piping, valves, SS impeller for pump and Food grade PVC storage tanks. The use of Stainless steel makes these plants costly and capacity enhancement of the same system was not wise as due to higher price of the Stainless steel. Higher capacity plants are developed using the innovative idea of using PVC modules and piping and also MS modules which has brought down the cost of the plant.

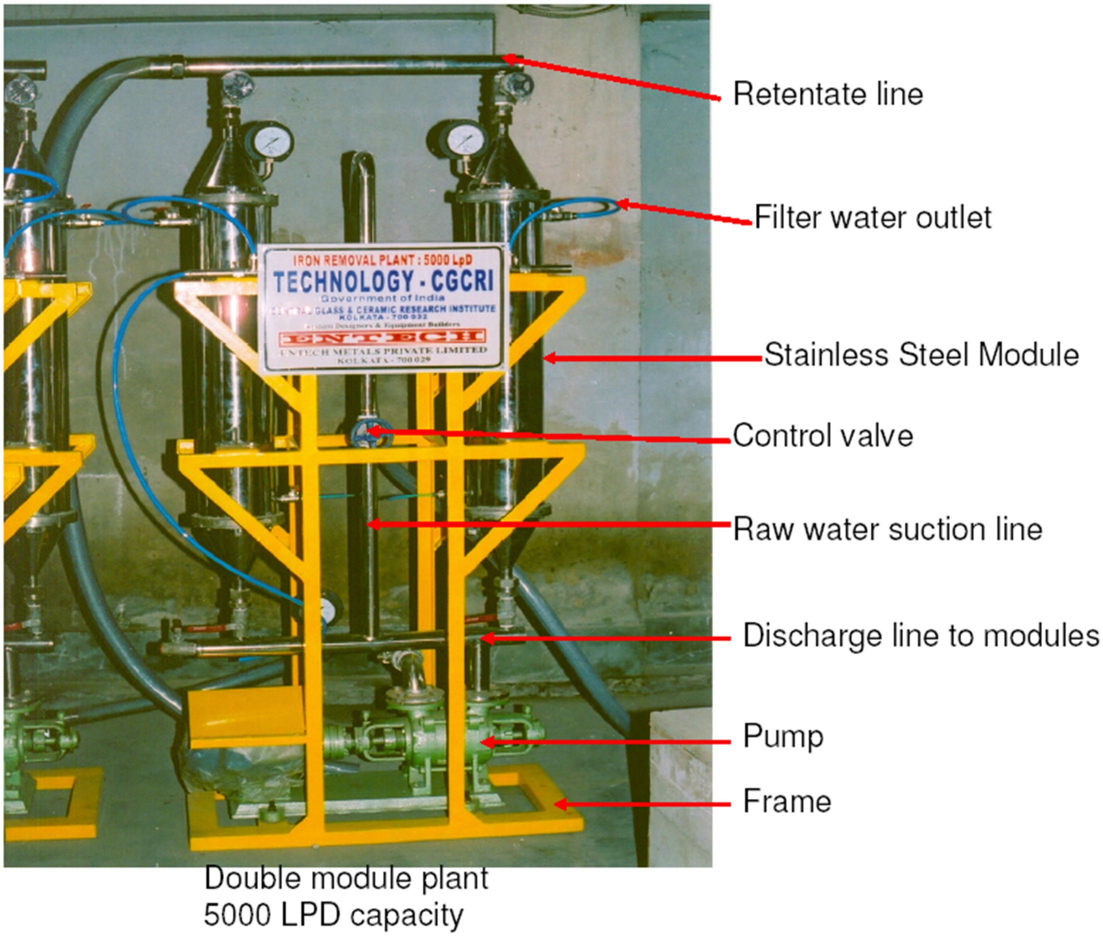
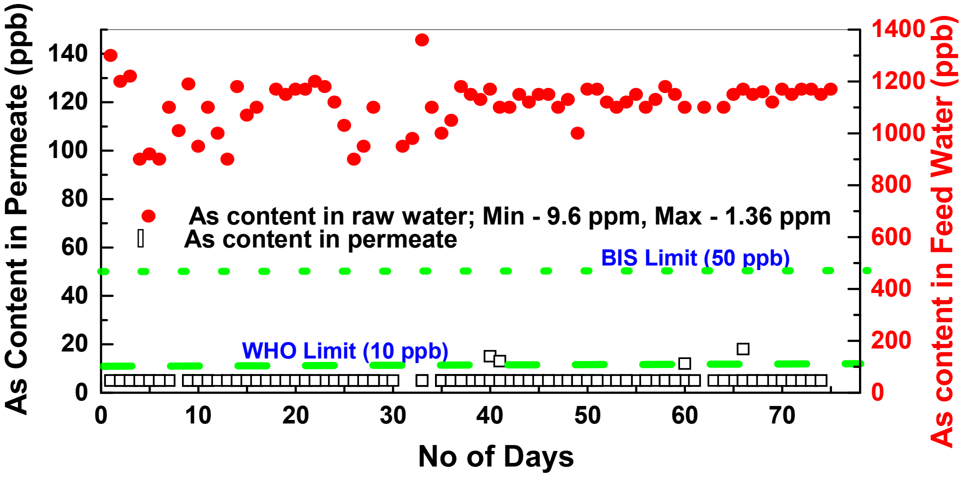


Fig 5.6 Typical SS body 5000 LPD capacity plant

Fig 5.7 Typical SS body 60 LPH capacity test plant

5.2 Results and Discussion

The results of the test plant are shown in the following graph. Form the graph it is evident that the ceramic membrane based plant can effectively reduce the Iron and Arsenic value in the treated water very consistently.



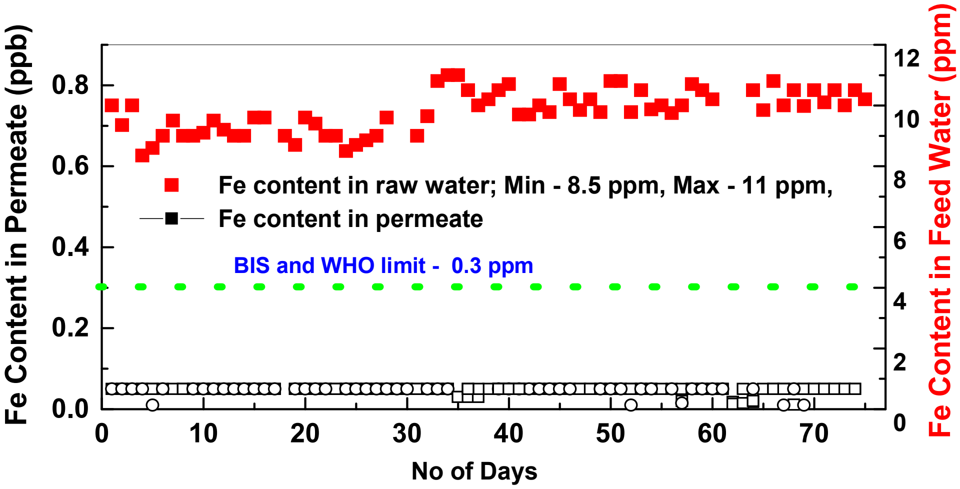


Fig 5.8 Arsenic and Iron removal performance in test plant

Fig 5.8 A 500 LPH capacity Ceramic Membrane plant of CSIR-CGCRI, Kolkata

Table 5.1 Water quality parameter of Raw and filter water of 500 LPH Ceramic Membrane based plant

Concentration (ppm)	Raw source water	filter water
Al	0.18	0.18
Ti	Not detected	Not detected
Ca	102.38	101.12
Mg	22.13	22.05
Fe	1.47	0.01
Na	15.96	14.88
K	2.45	2.44
P	0.48	0.47
Mn	0.03	0.03
Cr	Not detected	Not detected
Cu	Not detected	Not detected
Pb	0.07	0.07
Zn	0.16	0.15
As	30.16	Bellow detection limit

Table 5.1: Typical cost estimate for a Ceramic membrane based plant

Expenditure (per day)	Amount (Paisa per Litre)
Electricity Cost (For 1800 L in 14 hours with 2 hour mixing)	6.0
Media Cost (@ 20 g media per 1000 L of 1 ppm GW)	0.2
Repairing, Sludge Disposal, etc. (@ Rs. 100/- pm)	0.2
Production Cost	6.4
Man Power for O&M (@ Rs. 3000/- pm for 2 persons)	12.0
Bottling & Distribution (in 5 Litre PET Jar)	30 - 40

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