PREPARATION, CHRACTERIZATION AND APPLICATION OF MIXED MATRIX MEMBRANE FOR HEAVY METAL REMOVAL FROM WASTE WATER

Thesis submitted towards the partial fulfillment of Masters of Engineering in Chemical Engineering, Jadavpur University, India.

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Certificate

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I hereby declare that this thesis "Preparation, characterization and application of mixed matrix membrane for removal of heavy metals from wastewater" contains literature survey and original research work by the undersigned candidate, as a part of my M.E Degree in Chemical Engineering during academic session 2021- 2023. All the information that has been provided in this document is in accordance with academic rules and ethical conduct. I also declare that, as required by this rules and conduct, I have fully cited and referred all materials and results that are not original to this work.

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ABSTRACT

Removal of heavy metal ions from wastewater is of prime importance for a clean environment and human health. Different reported methods were devoted to heavy metal ions removal from various wastewater sources. These methods could be classified into adsorption, membrane separation, chemical, electric, photocatalytic-based treatments. Wastewater treatment using mixed matrix membrane could provide tremendous results as it could play two roles in pollutant removal by covering adsorption and size exclusion of water contaminants simultaneously. Ceramic membranes with excellent thermal and chemical stability, mechanical strength, fouling resistance are most suitable for wastewater treatment.

Keywords: heavy metals, mixed matrix membrane, adsorption

1. INTRODUCTION

"When the wells dry, we know the worth of water", Franklin (1746) quoted those prophetic words nearly two and a half centuries ago. Now, those wells are in danger of running dry, and we are facing a critical shortage of clean and fresh water. The problem is not the supply of water. Earth has virtually the same amount of water today as it had at dinosaur's period. We are the cause for acute shortage of fresh water (drinking) due to our flagrant abuse of one of our precious and limited resources. Water pollution due to organic contaminants is a serious issue because of acute toxicities and carcinogenic nature of the pollutants.

1.1. IMPORTANCE OF THE WORK

Removal of heavy metal ions from wastewater is of prime importance for a clean environment and human health. The presence of heavy metals in wastewater has been increasing with the growth of industry and human activities, e.g. plating and electroplating industry, batteries, pesticides, mining industry, rayon industry, metal rinse processes, tanning industry, fluidized bed bioreactors, textile industry, metal smelting, petrochemicals, paper manufacturing, and electrolysis applications. The heavy metal contaminated wastewater finds its way into the environment, threatening human health and the ecosystem. The heavy metals are non-biodegradable and could be carcinogenic. Presence of these metals in water in improper amounts could result in critical health issues for living organisms. The most popular heavy metals are lead (Pb), zinc (Zn), mercury (Hg), nickel (Ni), cadmium (Cd), copper (Cu), chromium (Cr), and arsenic (As). Although these heavy metals can be detected in minor amount; however, they are still hazardous to human health. The aforementioned metals and others such as silver (Ag), iron (Fe), manganese (Mn), molybdenum (Mo), boron (B), calcium (Ca), antimony (Sb), cobalt (Co) etc. are commonly available in wastewater and need to be removed.

Due to the discharge of large amount of metal-contaminated wastewater from industries, bears heavy metals, such as Cd,Cr,Cu,Ni,As,Pb and Zn, which are the most hazardous among the chemical-intensive industries. Because of their high solubility in the aquatic environments, heavy metals can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders .Therefore, it is necessary to treat metal contaminated wastewater prior to its discharge to the environment. Heavy metal removal from inorganic effluent can be achieved by conventional treatment processes such as chemical precipitation, ion exchange, and electrochemical removal. These processes have significant disadvantages, which are, for instance, incomplete removal, high-energy requirements, and production of toxic sludge. Numerous approaches have been studied for the development of cheaper and more effective technologies, both to decrease the amount of wastewater production and to improve the quality of the treated effluent. Adsorption has become one of the alternative treatments, in recent years; the search for low-cost adsorbents that have metal-binding capacities has intensified. The adsorbents may be of mineral, organic or biological origin. Membrane separation has been increasingly used recently for the treatment of inorganic effluent due to its convenient operation. There are different types of membrane filtration such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). And electrotreatments such as electrodialysis has also contributed to environmental protection. Photocatalytic process is an innovative and promising technique for efficient destruction of pollutants in water. Although many techniques can be employed for the treatment of inorganic effluent, the ideal treatment should not only be suitable, appropriate and applicable to the local conditions, but also be able to meet the maximum contaminant level.

1.2. BRIEF ABOUT MIXED MATRIX MEMBRANE

Mixed Matrix Membrane is the incorporation of solid phase in a continuous polymer matrix.

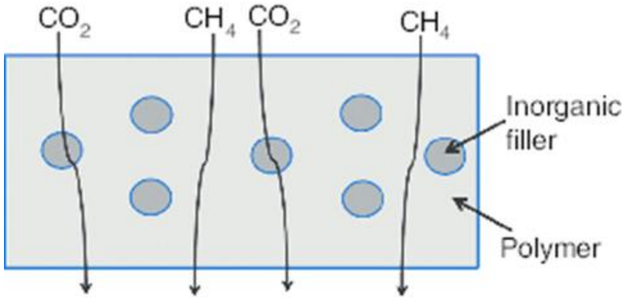


Fig-1 (Mixed Matrix Membrane)

From early 90's it has been observed that pure polymeric membranes had reached upper limit regarding mass transport properties. It has been found that incorporation of some inorganic materials in pure polymeric membrane increases the mass transport efficiency among them and from this scenario the concept of mixed matrix membrane has arrived. There are basically 3 types of mixed matrix membranes : solid, liquid and solid-liquid. These membranes are considered as a new generation membranes. These are used for the removal of O_2 and CO , treatment of wastewater, as catalysts and for many other purposes.

Specific characteristics and features:

- Various inorganic particles are sewn in the polymer matrix.
- These particles may act as molecular sieves which increases the permeability of the membrane.
- Sometimes inorganic particles can cause disruption in polymer matrix which increases the interfacial void and decreases the efficiency of gas separation in the membrane.
- In asymmetric mixed membrane the skin layer acts as filter where the porous structure gives mechanical strength.
- It is necessary that the polymer chains be attached directly to the filler particles embedded in polymer matrix

- Pores of the filler material must not be blocked by polymer chains neither should be chain rigidification around filler particles.
- It should be defect-free.
- It must pose as high chemical resistance.
- It must have high thermal stability.
- It must be mechanically strong.
- High selectivity and permeability.
- For gas separation purposes, nonporous membranes are preferred and in case of porous membranes it must be made sure that pore dia. is less than the mean free path of the gas molecules.

1.3. Heavy Metals in industrial waste water

Toxicity : Heavy metals are generally considered to be those carcinogenic metals whose density exceeds 5g per cubic centimeter. A large number of elements fall into this category, but the ones listed in Table.1 are those of relevance in the environmental context. Arsenic is usually regarded as a hazardous heavy metal even though it is actually a semi-metal. Heavy metals cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person’s immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, nervous system, and damaging of the fetal brain. At higher doses, heavy metals can cause irreversible brain damage. Children may receive higher doses of metals from food than adults, since they consume more food for their body weight than adults. Wastewater regulations were established to minimize human and environmental exposure to hazardous chemicals. This includes limits on the types and concentration of heavy metals that may be present in the discharged wastewater. The MCL standards, for those heavy metals, established by USEPA are summarized in Table 1.

Heavy metal	Toxicity	MCL (mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.05
Chromium	Kidney damage, renal disorder, human carcinogen	0.01
Copper	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	0.8
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system	0.00003

Table. 1 (Toxic metals and their maximum concentration limit)

1.4. VARIOUS SOURCES OF HEAVY METALS :

Industrial wastewater streams containing heavy metals are produced from different industries. Electroplating and metal surface treatment process generate significant quantities of wastewater containing heavy metals (such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium) from a variety of applications. These include electroplating, electroless depositions, conversion-coating, anodizing-cleaning, milling, and etching. Another significant source of heavy metals waste results from printed circuit board (PCB) manufacturing. Tin, lead, and nickel solder plates are the most widely used resistant over plates. Other sources for the metal wastes include wood processing industry where a chromated copper-arsenate wood treatment produces arsenic containing wastes; inorganic pigment manufacturing producing pigments that contain chromium compounds and cadmium sulfide; petroleum refining which generates conversion catalysts contaminated with nickel, vanadium, and chromium; and photographic operations producing film with high concentrations of silver and ferrocyanide. All of these generators produce a large quantity of wastewaters, residues, and sludges that can be categorized as hazardous wastes requiring extensive waste treatment.

1.5. WATER SCARCITY AND RECYCLE OF WATER :

Every continent suffers from increasing water scarcity, largely due to climate change, as well as over-use, misuse and abuse of water. Some of the causes of water scarcity include excess ground-water tapping, polluting fresh-water bodies, and excess industrialization and agriculture. Water scarcity is more prominent in arid regions but sustainable water delivery has already reached its limit in most regions. At present over 2 billion people are living in water-stressed areas. There is a highly complex relationship between global development and water demand. Some of the various measures employed to mitigate this crisis include: limiting the supply of water, recycling water, adopting desalination techniques, using water treatment plants and creating water awareness programs.

Recycling water is an essential measure to address this crisis, and brings with it numerous potential benefits. It can be carried out in different ways, depending on the water source, the contaminants present, the scale of water availability, the economy of recycling, and the use of the utility post-recycle. Advanced water recycling methods are employed to address existing water challenges in water-scarce regions. However, recycling water in water-scarce regions is a major challenge, as there is little availability of water at the source. The water to be recycled will have high levels of contaminants, increasing the energy used by and the cost of the recycling process. On the other hand, recycling this water may still provide economic and financial benefits in these regions. A few examples of local water recycling are: using process water for cooling or heating purposes; collecting rainwater for gardening, washing and cleaning purposes; treating rainwater to make it potable; and utilizing waste water from washing machines for flushing toilets and washing cars.

1.6. DIFFERENT WAYS OF REMOVAL OF HEAVY METALS FROM INDUSTRIAL WASTE WATER :

ADSORPTION BASED SEPARATION : Adsorption mechanism is defined by the physiochemical properties of adsorbent, heavy metal and other operating conditions such as temp, pressure, p^H value, adsorption time, initial concentration of metal ions and many more.

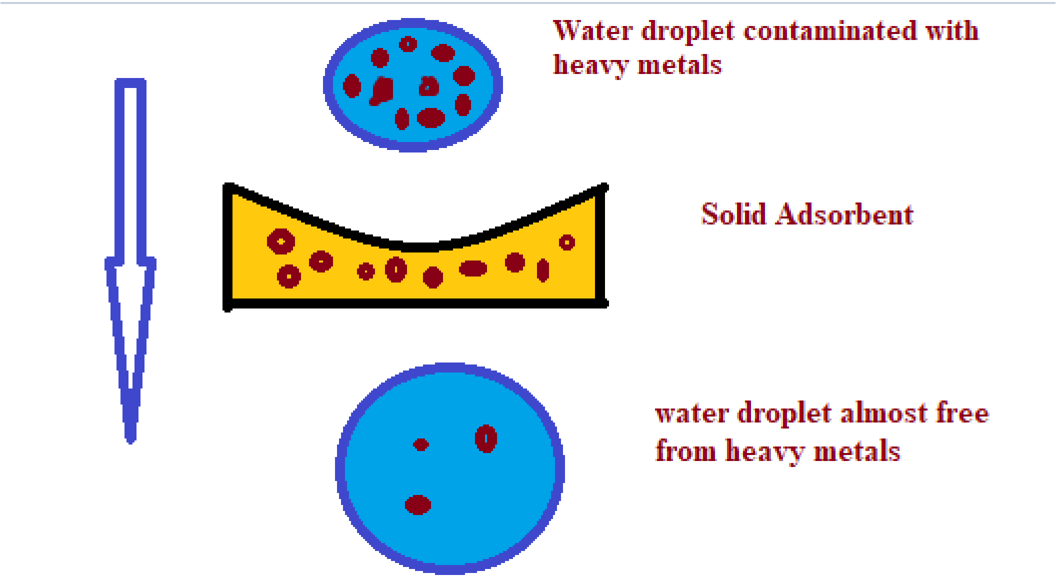


Fig 2 (Adsorption of particles)

Different types of adsorptions have been documented in various articles. Here few of them are mentioned.

1.6.1. CARBON BASED ADSORBENTS : Carbon-based nanoporous adsorbents, especially carbon-based nanoporous adsorbents, especially activated carbons (ACs), carbon nanotubes (CNTs), and graphene (GN), are extensively used in the applications of heavy metal removal owing to their tremendous surface area (500–1500 m^2/g)⁽¹⁾

The carbon surface charges can be enhanced by surface functional groups (such as carboxyl, phenyl, and lactone groups, to improve the heavy metal uptake(2). Among various modification methods, nitrogenation, oxidation, and sulfuration are the most commonly employed techniques to enhance the specific surface area, pore structure, adsorption capacity, thermal stability, and mechanical strength (3). However, they depend mainly on the adsorbent materials, which sometimes are very expensive(4) . Subsequently, adsorbent's cost should be considered in choosing the most suitable adsorbents. Surface modification often reduces its surface area and, in turn, increases the content of surface functional groups. Consequently, more metal ions can be adsorbed(5) . The adsorption uptake increases by increasing the adsorbent surface area, adsorbent dose, initial concentration of metal ions, and contact time. Although the multi-wall carbon nanotubes (MWCNTs) have received particular interest for heavy metal removal(6) , they are highly hydrophobic and suffer from rapid aggregation in aqueous solution due to large Vander Waals forces, decreasing the adsorption potential.

1.6.2. CHITOSAN BASED ADSORPTION : Chitosan (CS) is a natural adsorptive polymer that has an affinity toward pollutants in wastewaters because it has amino (–NH_2) and hydroxyl (–OH) groups (7). Despite its unique features, it suffers from low mechanical strength and poor stability (8), making the regeneration inefficient. Also, it is challenging to use CS in its powder or flake form because of its low porosity, low surface area, resistance to mass transfer, and high crystallinity. Consequently, structural and chemical modifications have been proposed to overcome these drawbacks. Cross-linking chemical modification imparts strength to CS by bridging between polymer chains and the functional groups. However, this approach reduces the uptake.(9)

1.6.3. MINERAL ADSORBENTS : Mineral adsorbents such as faujasite, silica, and clay are considered good candidates for water purification with low operating costs (10). Clay has extraordinary cation exchange capacity (CEC), cation exchange selectivity, surface hydrophilicity, high swelling/expanding capacity, and surface electronegativity (11). In addition, acid washing, thermal treatment, and pillar bearing could enlarge the pore size, pore volume, and specific surface area, leading to a remarkable increase in the adsorption efficiency (11). Using natural minerals could be cost-effective. However, the removal efficiency might decrease after a few cycles (12). Therefore, different modification methods, such as calcination and impregnation, have been proposed to enhance the removal efficiency of such adsorbents (13) . The preparation of twodimensional nanosheets and one-dimensional nanotubes-based clay adsorbents might lead to innovative low-cost and high performance adsorbents.

1.6.4. MAGNETIC ADSORBENTS : Magnetic adsorbents are a specific material matrix that hosts iron particles . The base materials could be carbon, CS, starch or biomass. The adsorption process is affected by magnetic field, adsorption process is affected by magnetic field, surface charge and redox activity characteristics. Different magnetic adsorbents were proposed in the literature, such as zero-valent iron nanoparticles (ZVI NPs), iron oxides (hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), magnetite (Fe_3O_4), and spinel ferrites. The mechanism and kinetics of the sorption process rely on several parameters, such as surface morphology and adsorbent magnetic behavior. They are also affected by experimental conditions such as pH, irradiation time, adsorbent concentration, wastewater temperature, and the initial dosage of pollutants(14). Some studies have focused on coating Fe_3O_4 particles for removing heavy metal ions. Co-precipitation, high-gravity technology, and grafting are the most commonly used methods (15)

1.6.5. BIOSORBENTS : The most recent studies show that biosorption is a great way to remove heavy metals from industrial waste water. The presence of various functional groups i.e carboxyl, amino, hydroxyl, phosphate, thiol on the surface expedite the biosorption process (16). The solution pH affects the biosorbent surface charge density and ionization of functional groups located on the biosorbent surface . The biosorbent amount is a vital factor affecting the removal efficiency due to offering more vacant biosorption sites. The biosorbent capacity could increase at higher temperatures due to decreased solution viscosity, reduction in Gibb’s free energy, and bond rupturing. These reasons increase the collision frequency (mobility and kinetic energy) between biosorbent and metal ions and enhance the biosorbent active sites, leading to a higher affinity (16). In turn, the bonding force between biosorbent and pollutants could decline at higher temperatures, and thus the biosorbent sorption uptake reduces. It was elucidated that the removal efficiency increases as the mixing agitation rate increases. (17)

1.6.6. METAL-ORGANIC FRAMEWORK ADSORBENTS : Metal-organic frameworks (MOFs) are generally synthesized via reticular synthesis in which metal ions are strongly bonded to organic linkers. Researchers proposed thousands of MOFs. It was noticed that most of the organic ligands used to form many MOFs are very expensive and toxic(18). Zirconium-MOFs is a promising nanostructure materials for sorption applications due to the easy incorporation of functional groups and hydrolytic-thermal stability such as amine, carboxylic, hydroxyl, and oxygen or by using the cross-linking method. (19) Composite based MOF adsorbents could obtain further enhancement in the adsorption capacity of MOFs. Despite the exciting features of MOFs and their good capability to remove heavy metal ions, they have micropores (i.e tinypores). inaccessible for some target metals. Also, most of them have low stability in water. Mn, Fe, and Cu have been used to form MOFs, but most of them resulted in poor chemical stability. Therefore, further research is still needed to tune the MOFs' structure and scale up these materials to implement them into industrial wastewater applications. Moreover, different functionalization methods should be proposed and applied to enhance MOFs' stability and sorption kinetics.

1.6.7. MEMBRANE BASED FILTRATION AND SEPARATION : Over the years, technological advancement in membrane development has led to an increase in the use of membranes for filtration and extraction of heavy metal ions from wastewater. A simplified schematics for different membrane-based filtration processes is illustrated in Fig. 3a–c, while Fig. 3d demonstrates various pollutants that can be separated by different membrane techniques (20) **.**

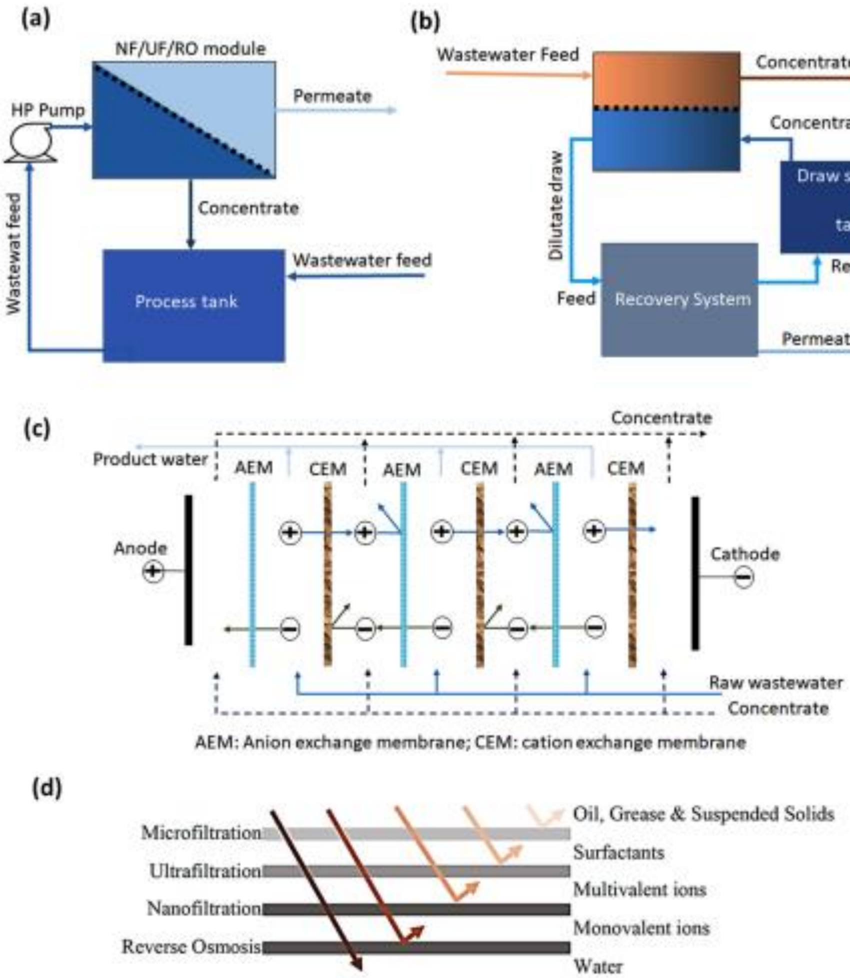


Fig. 3 (different membrane based treatment for pollutants removal from waste water and salty water, a. nanofiltration, ultrafiltration, Reverse Osmosis, b. forward osmosis process, c. Electrodialysis method

ULTRAFILTRATION : Ultrafiltration (UF) is used at low transmembrane operating pressure (TMP) because UF membrane pores may be larger than the heavy metal ions, additives may be bonded to metal ions to enlarge the size of the metal ions. Therefore, micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) are proposed. MEUF is formed by bonding UF and surfactant. MEUF has high flux and high selectivity, leading to low-energy consumption, high removal efficiency, and less space demand (21). MEUF is most suitable for wastewater whose heavy metals are in low concentrations (22). In MEUF, a surfactant is mixed with wastewater in a concentration above the critical micellar concentration (CMC).

Beyond CMC, surfactant monomers assemble and increase the creation of some micelles in the solution. The surfactant contains a hydrophobic tail and a hydrophilic head. The inner hydrophobic core of the micelles could solubilize organic matters (having low molecular weight) as a solubilizate, while the surface adsorbs counter metal ions on their surface due to electrostatic interactions (23). Surfactants, whose electric charge is the opposite of the metal ions, usually attain the highest retentions. In this regard, polyelectrolytes (PE), cationic surfactants, and anionic surfactants (e.g., sodium dodecyl sulfate (SDS)) are used for effective heavy metals extraction (24). A summary of different studies on the MEUF process is given in Supplementary. The performance of MEUF depends on several factors, including the added solutes, type of surfactant, operating conditions, and kind of membrane used. PEUF is formed through the integration of UF and binding polymers. The functional groups of the bonding polymers could be sulfonate, phosphonic, carboxylated, or amine and they are bonded via chelating or ionic bonds(25). PEUF are also known as polymer-supported, complexation, polymer-assisted, size enhanced, and complexation enhanced ultra-filtrations. While permitting water and un-complexed components to permeate the membrane pores, the PEUF process blocks and extracts polymerbonded metal ions (26).

NANOFILTRATION : Nanofiltration is used to concentrate constituents whose molecular weight is >1000 Da and remove solutes whose size of 0.0005–0.007 μm with molecular weights >200 Da (27). Thus, the operating range of NF is between UF and reverse osmosis (RO) processes (28). The NF membranes are composed of polymer composites of multiple-layer thin-film of negatively charged chemical groups. Anti-fouling NF membranes containing CeO_2/Ce_7O_{12} and PES were synthesized through phase inversion and used to extract Fe^{3+}, Al^{3+}, Co^{2+}, Cd^{2+}, Cu^{2+} and humic acid from wastewater and reached extraction efficiency between 94 and 98% (29).

MICROFILTRATION : Microfiltration (MF) employs a microporous membrane to remove micron-sized particles, bacteria, viruses, protozoa, contaminants, pollutants, etc., from a solvent/fluid/solution60. MF process is also a low pressure-driven membrane process, whose membrane pores are in the range of 0.1–10 μm60. Some of the MF membranes are made of silica, ceramics, zirconia, alumina, PVC, polysulfone, PTFE, polypropylene, PVDF, polyamides, polycarbonate, cellulose acetate, cellulose esters, or composite materials. The commercial application of MF is widely found in pharmaceutical and biological industries. However, the application of the MF system may be found in particle removal of the rinse water in the semiconductor industry, sterilization of beer and wine, other juices and cider clarification, and wastewater treatment . The application of MF in heavy metal removal has not drawn enough attention because of its low removal ability. However, it has been used by modifying membrane or chemical pre-treatment of the feed solution. Depending on the mode of application, the MF process is available in two main configurations: crossflow and dead-end.

REVERSE OSMOSIS : RO is a pressure-driven separation process that employs a semipermeable membrane (pore size 0.5–1.5 nm) to allow only smaller molecules to pass. RO process reverses the normal osmosis process by applying pressure (20–70 bar) that is greater than the osmotic pressure of the feed solution. The molecular size of the solutes blocked is usually in the range of 0.00025–0.003 μm. RO process could extract 95–99% of inorganic salts and charged organics. RO process is compact and attained high rejection efficiency. However, membrane fouling and degrading are the major drawback of RO systems (27). The RO separation process was used to extract heavy metal ions, including Ni^{2+}, Cr^{6+}, and Cu^{2+} from electroplating wastewater, with a removal efficiency of >98.7562.

FORWARD OSMOSIS: Forward osmosis (FO) is an osmosis process that requires a membrane to balance selectivity and permeated water flux (20). In FO a semi-permeable membrane separates a feed solution from the draw solution, as shown in Fig. 3b. The drawn solution is usually at a higher osmotic pressure compared to the feed solution. Due to the osmotic pressure difference between the feed and draw solutions, water transports from the feed solution to the draw solution, thereby keeping the rejected solutes on the feed side and treated water on the draw solution (30). FO does not require hydraulic pressure; thus, it is energy-saving. FO process is also environmentally friendly, easy cleaning, and low fouling; therefore, it is widely used in wastewater treatment. Nevertheless, FO has limitations, such as drawn solution re-concentration, membrane selection challenges, internal and external concentration polarization. (31)

ELECTRODIALYSIS : Electrodialysis (ED) is used to separates ions at the expense of electric potential difference. ED uses a series of cation exchange membranes (CEM) and anion exchange membranes (AEM), alternatively arranged in parallel, to separate ionic solutes(20) . In the ED process, the anions pass through AEM, while cations pass through CEM. In such a case, the treated stream (diluate) is produced from half of the ED stack channels, while the concentrated stream is expelled from the other half, as shown in Fig. 3c. ED offers high water recovery, no phase change, no reaction, or chemical involvement66, and can operate over a wide range of pH values. However, ED also exhibits membrane fouling, high cost of membranes, and demand for electric potential. ED has been used to separate $Ni^{2+,}$ Pb^{2+} , K^+ from synthetic solution through a novel ED heterogeneous CEM (consisting of 2-acrylamido-2-methyl propane sulfonic acid-based hydrogel and PVC) to attain extraction efficiency of 96.9%, 99.9%, and 99.9% for Ni^{2+}, Pb^{2+} ,and K^+, respectively (32). A batch ED process was employed to recover Pb^{2+} and reached a maximum separation efficiency of ~100% 68(1). A pilot-scale ED system has also been used to extract Cu^{2+}, Ni^{2+}, and traces of Cd^{2+}, Fe^{3+}, Cr^{6+}, and Zn^{2+} and exceeded 90% removal. Rate (33). As^{3+} and As^{5+} were removed from metallurgical effluent by ED and attained a removal efficiency of 91.38% (34).

OTHER MEMBRANE BASED METHODS : Membrane distillation (MD) and liquid membrane (LM) are also used for wastewater treatment. MD is a hybrid thermally driven membrane separation process that consists of cold and hot compartments separated by a microporous hydrophobic membrane. MD allows only vapor to permeate its pores while blocking other molecules. MD exists in four configurations: direct contact MD, air gap MD, sweeping gas MD, and vacuum MD. MD process has been reported to achieve over 96% removal of Ca^{2+}, Mg^{2+}, Fe^{3+}, and Fe^{2+}.On the other side, LM is made of a liquid phase or thin-layer organic phase, which acts as a barrier between two aqueous phases. LM is immiscible to the feed solution and retentate solution (20), and combined stripping and extraction processes in a single stage (35). LM is highly selective, relatively efficient, and can achieve specific molecular recognition. However, the membrane’s long-term stability is poor (36). LM process exists as a supported liquid membrane (SLM), emulsion liquid membrane (ELM), bulk liquid membrane (BLM), and polymer inclusion membrane (PIM) (20). Among these types, the SLM process is an attractive alternative to traditional solvent extraction for heavy metal removal(35). SLM achieved a removal efficiency of 89% for Zn^{2+}, Cd^{2+}, Cu^{2+}, and Fe^{3+} (37).

CHEMICAL BASED SEPARATION : Chemical methods for removing heavy metals from wastewater are mature and used early. In this section, the chemical-based methods will be discussed including precipitation, coagulation, flocculation, and flotation.

PRECIPITTION : Chemical precipitation (the so-called coagulation precipitation) is broadly used in industries and is considered one of the most effective and mature methods. It changes the form of dissolved metal ions into solid particles to facilitate their sedimentation. The reagent coagulation (coagulant) precipitates metal ions by changing pH, electro-oxidizing potential, or co-precipitation(38). It is usually followed by the removal of sediments. Hydroxide precipitation is broadly used due to its relatively inexpensive, simple, and tunable pH 7 . It is implemented by adding a hydroxide to the stirred wastewater to form insoluble metal hydroxide precipitates. For example, a metal ion could react with calcium hydroxide (lime) to produce metal hydroxide precipitates and calcium ions as:

$\text{Metal}^{n+} + Ca(OH)_2 = \text{Metal}(OH)_n + Ca^{2+}$

It was found that pH values of 9–11 improved this process efficiency(39) . However, a high p^H value is considered a disadvantage of this method since it requires a large dosage of precipitates. One of the most effective hydroxide precipitates for treating inorganic effluents of heavy metal concentration of 1000 mg/L is lime (CaO or $Ca(OH)_2$) (40). It can be seen that the majority of metals removed by this method are Zn^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Cr^{2+}. The sulfide participation method distinguishes itself by higher removal efficiency and lesser dissolved solids increment than the hydroxide method. This method was reported to treat toxic heavy metal ions (41). Lower sulfide results in a higher zinc concentration in the effluent, while higher sulfide leads to a malodor problem due to high residual sulfide. Also, it could produce hydrogen sulfide gas which is malodorous and toxic. For these reasons, the sulfide precipitation is recommended to be executed at a neutral p^H (42). Metal Sulfide precipitation follows

$\text{Metal}^{n+} + S^{2-} = \text{Metal}_n S \downarrow$

As an alternative method to hydroxide precipitation, carbonate precipitation shows good effectiveness and optimum precipitation at lower p^H values (43). It could be achieved using sodium carbonate or calcium carbonate

$\text{Metal}^n + nNaCO_3 \rightarrow n\ \text{Metal}(CO_3) + nNa^+$

$n\text{Metal}(CO_3) + H_2O \rightarrow CO_2 \uparrow + (MeOH)_n\ CO_3 \downarrow$

It could have less sludge volume, but it could release CO_2 bubbles and needs higher reagents for efficient precipitation (43). Fenton reaction is usually used to improve the removal efficiency of the chemical precipitation methods. The Fenton or Fenton-like oxidation is used for the de-complexation of heavy metal complexes. However, the pH is adjusted by the chemical precipitation mechanism (e.g., NaOH). Fenton chemistry is not straightforward, and it is performed through numerous reactions, depending upon various active intermediates, such as $[Fe^{IV}O]^{2+}$ and hydroxyl radicals (44). The classical Fenton reaction is(45)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + HO-$$

$$HO. + \text{dye} \rightarrow \text{oxidized dye} + H_2O$$

COAGULATION AND FLOCCULATION : Coagulation is the destabilization of colloids by neutralizing the forces that keep them parted, while flocculation is the agglomeration of destabilized particles (46). Traditional coagulants are aluminum, ferrous sulfate, and ferric chloride, using to neutralization of ion charges. Flocculation bonds the particles forming large agglomerates with the help of a flocculant, such as polyaluminum chloride (PAC), polyferric sulfate (PFS), polyacrylamide and other macromolecule flocculants (47). The PE were reported as one of the most practical flocculations, but the produced sludge might be toxic(46). The flocculants are generally not natural and nonbiodegradable (48). The process is illustrated in Fig. 5, including the sedimentation. Some weaknesses are toxicity and health hazardousness of inorganic coagulants, a large volume of sludge, selective for some metals and inefficient in emerging contaminants, increasingly effluent color, inefficient when using natural coagulants, and complex of scaling up (49). The typical heavy metals removed by this method include Cu^{2+}, Pb^{2+}, and Ni^{2+}. Other metals such as As^{2+}, Se^{2+}, Cr^{2+}, Sb^{3+}, Sb^{5+}, Ag^{2+} could also be efficiently removed.

FLOTATION : Flotation is used to remove various metal ions. Dissolved air flotation, ion flotation, and precipitation flotation were extensively studied. In the dissolved air flotation, air (or gas) is fed to wastewater to generate micro-bubbles that could attach the metal ions, developing lower density agglomerates, leading to raising. the flocs through the wastewater. The accumulated slug at the top surface can easily be removed (50). The ion flotation process relies on the increase of hydrophobicity of metal species by using surfactants; therefore, the hydrophobic species are removed by air bubbles. The added surfactant facilities as collectors, while frothers control the indexes of ion flotation (51). When the concentration of metal ions is low within a large quantity of wastewater, the ion flotation appears inefficient (52). The ion flotation process showed low-energy consumption, limited volume demands, reduced sludge volumes, and selective treatment (53). The precipitation flotation process is basically a chemical precipitate process that implements microbubbles. That precipitation flotation takes a short time to complete efficiently(54). Generally, the flotation processes have advantages such as rapid operation, compact process, and a moderate cost. Significant attention has recently been paid to ion flotation among all flotation processes. Since ion flotation depends on surfactants as collectors, efficient and non-toxic surfactants are required. Chemical synthetic surfactants have been introduced to have strong collection ability, good selectivity, and easy construction. However, the cost and toxicity issues limit them. On the other side, biosurfactants sound more environmentally friendly, but they exhibited low removal rates, large dosage quantity, and longtime process. In this regard, nanoparticles have been proposed as new collectors that showed both benefits of synthetic- and biosurfactants.

ELECTRIC BASED SEPARATION : In this section different Electrochemical methods i.e Electrochemical Reduction (ER), EC, Electroflotation, Electrooxidation and Ion Exchange methods are discussed. In an electrochemical system, oxidation is performed at the anode (positive side), where electrons transfer to the cathode (negative side) at which the reduction process occurs.

ELECTROCHEMICAL TREATMENT : In an electrochemical system, oxidation is performed at the anode(positive side), where electrons transfer to the cathode (negative side), at which the reduction process occurs. These two chemical reactions are called redox (reduction-oxidation), leading to water purification through metal removal. For example:

$\text{Metal}^{n+} + n\,H_2O \rightarrow \text{Metal}^{m+}(H_2O)_n\ \text{solution}\downarrow + me^-\ \text{metal}$

Selection of the anode and cathode mainly decides the type of the electrochemical method and influences the removal efficiency towards specific metal ions. The electrochemical processes are primarily classified into ER, EC, EF, and EO processes. In the ER method, also known as electrodeposition and electroplating, targeted atoms or molecules are deposited on the surface of the cathode. Sludge, which requires further treatment, is not formed in this treatment . It is worth noting that cathodes with high overpotential toward hydrogen evolution are more efficient in pollutant removal/reduction (55) . The cathodes made of carbon-based or sulfur mixture with different ratios in acidic conditions are suitable for removing Hg^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+} from wastewater (56). Iridium oxide-coated titanium anode was found as a perfect material for Cd^{2+} removal with an efficiency of 100% regardless of its initial concentration. More attention should be paid to the reactor design and the operating conditions to enhance the performance of the wastewater treatment. Energy consumption is a barrier that should be solved to commercialize this type of treatment in industrial applications. In the EC method, steel (iron) or aluminum electrodes, which are non-toxic and reliable, are mostly used(57).

$\text{Metal} \rightarrow \text{Metal}^{n+} + ne^-$

$2H_2O(l) + 2e^- \rightarrow H_2 + 2OH^-$

Cations from anode destabilize colloidal particles and also from polymeric hydroxide complex metal ions(i.e coagulants), which react with pollutants (negatively charged) present in wastewater as :

$\text{Metal}^{n+}\text{ (aq)+ nOH}^{-} \rightarrow \text{Metal(OH)}_{n}\text{ (S)}\downarrow$

Therefore, metal hydroxide (larger particles) whose density is higher than water forms and precipitates (settle down), while floc (fine particles) floats. The coagulants are generated in situ due to anode oxidation, which is considered a further advantage of EC methods over other technologies. Generally, it was found that lower energy consumption and higher removal efficiency are achieved when the alternating current is used rather than the direct current. Also, the rise in temperature, voltage, and pH reduces the test duration. EC drawbacks are the electrodes passivation and relatively high energy consumption and the challenge of large-scale applications at lower energy consumption (58). Many successful approaches were proposed to alleviate the passivation of the electrode, such as aggressive ion addition, alternating current operation, polarity reversal operation, ultrasonication, mechanical cleaning of electrodes, chemical cleaning of electrodes, hydrodynamic scouring. However, each route has drawbacks, such as generating hazardous byproducts, costly, additional treatment and infrastructure and increasing sludge production. Accordingly, the EC process is still not fully mature application.

ION EXCHANGE TREATMENT :

The ion exchange method is a reversible chemical reaction used to replace the undesirable metal ion with harmless and environmentally friendly ones. A heavy metal ion is removed from a wastewater solution by attaching it to an immobile solid particle as a replacement with the solid particle cation, as shown in Fig.6. The material of solid ion-exchange particles could be either natural, e.g. inorganic faujasites, or synthetically produced, e.g., organic resins. The ion-exchange method can remove target (some or all) heavy metal ions, such as Pb^{2+}, Hg^{2+}, Cd^{2+}, Ni^{2+}, V^{4+}, V^{5+}, Cr^{3+}, Cr^{4+}, Cu^{2+}, and Zn^{2+} from wastewater(59). The ion exchange mechanism for metal removals can be explained in the following reaction as the ion exchange particle having ion exchanger of $M^{-}EC^{+}$ (M^{-} is the fixed anion and EC^{+} is the exchange cation;

Na^+ and H^+ are frequently used as exchange cations) to exchange its cation (EC^+) with the wastewater cation (WC^+) (60)

$M^- EC^+ + WC^+ \leftrightarrow M^-WC^+ + EC^+$

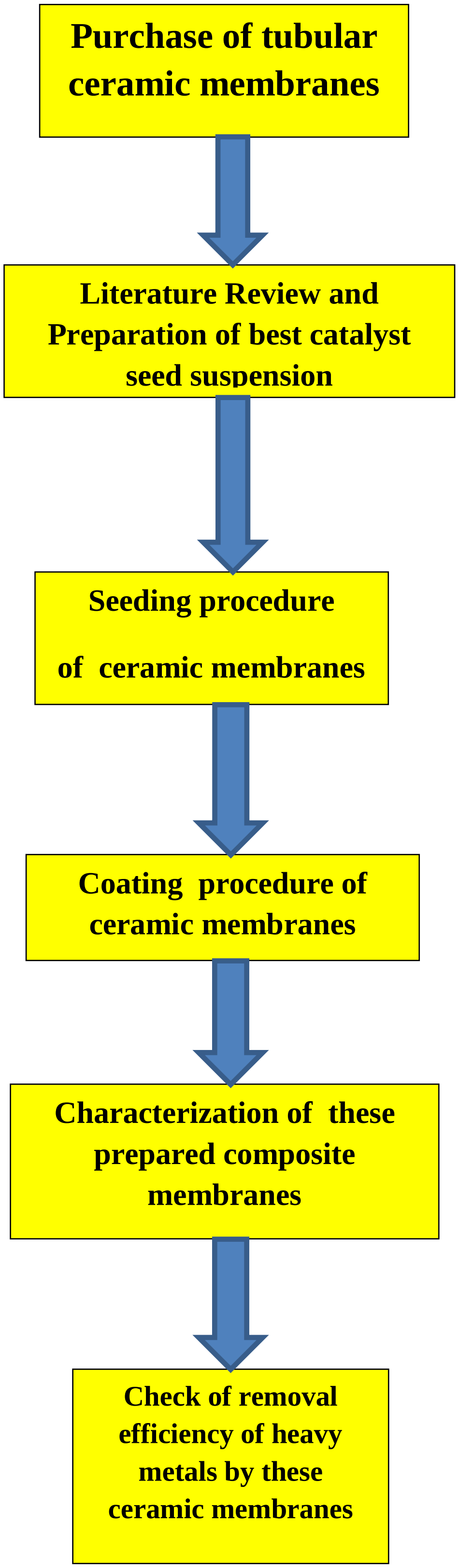
Different types, such as Amberlite(61) and Diaion CR11(62), were investigated for cations removal. Faujasite has an excellent ion exchange capability owing to its negative charge resulting from Si^{4+} which resides in the middle of the tetrahedron and undergoes isomorphous replacement with Al^{3+} cations. MOFs have recently been suggested as good candidates for the ion-exchange removal process . Some reported MOFs used for ion-exchange reactions include AMOF-1 (for Cd^{2+}, Pb^{2+}, and Hg^{2+} removal)(63)

PHOTOCATALYTIC BASED SEPARATION : The photocatalytic process was reported as a simple process for wastewater treatment that uses light and semiconductors, such as titanium dioxide (TiO_2) (64). Three key steps are taken in this process: charged carrier photogeneration, charged carrier separation and diffusion to the photocatalyst surface, and redox reaction on the photocatalyst surface. The effluents of real soil washing wastewater were treated using an outdoor dual solar photocatalytic process of flat plate collector for the removal of 93.5% Cu^{2+}, 99.6% Fe^{3+}, and 99.4% Zn^{2+} (65). A simulated ultraviolet (UV)–solar TiO_2 photocatalysis has been used for the removal of ethylenediamine-N, N′-disuccinic acid (EDDS), and Cu^{2+} from wastewater (0.2 mM EDDS and 0.2–1.4 mM CuSO4) to obtain 100% conversion efficiency at 24% mineralization degree. In another study, maximum removal efficiencies of 41% Cu^{2+}, 100% Fe^{3+} , 100% Zn^{2+} and 100% EDDS were obtained from synthetic soil washing solution (3.6×10^{-1} mM EDDS, 8.0×10^{-2} mM Cu^{2+}, 1.0×10^{-1} mM Fe^{+3} and 8.0×10^{-2} mM Zn^{+2}) (66). Using visible light irradiation, a synthesized rhodium/antimony co-doped TiO_2 nano-rod and titanate nanotube (RS-TONR/TNT) was used to extracts Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, and organic pollutant from wastewater with 70 and 80% degradation efficiency for dye and Bisphenol A, respectively. The photocatalytic process using $CeO_2/BiOIO_3$ composites with Ce^{4+}/Ce^{3+} redox centers was used to attain 86.53% Hg^{2+} removal efficiency under visible light absorption and photocatalytic activity (67). In an aqueous solution containing As^{5+} and Cr^{6+} (concentration of 0.10 mg/L), a synthesized 3D-Fe_2O_3 was used to achieve nearly 100% removal rates using solar light irradiation and photocatalytic activity. A fabricated CH-GEL/ZSPNC hybrid nanocomposite ion exchanger achieved 90% Ni^{2+}, 94.9% Zn^{2+}, 95% Mg^{2+}, 100% Pb^{2+}, 90.3% Cd^{2+}, 88.9% Cu^{2+} and 84% Rhodamine-B (dye) extraction efficiencies using solar light(68). A fabricated CS/silver bio-nano-composites (CS/PVDC/Ag) was utilized in photocatalytic oxidation process for 97% Cu^{2+}, 88% Pb^{2+}, 89% Cd^{2+} and 77% dye removal (69). Although this technology shows the in site generation of reactive radicals, no chemicals used, no sludge production, it has some drawbacks. It is still on a laboratory scale, low throughput, dependent on pH, and inefficient when different metals are present (70).

2. OBJECTIVE

In this work faujasite coated composite ceramic membranes will be fabricated by in-situ hydrothermal crystallization technique. Efficiency of these membranes will be checked in removing various heavy metals like Arsenic. Various Characteristic features such FESEM Analysis, flux of these membranes will be checked in this project. Faujasite will be synthesized in this project work and characteristics will also be analyzed. Efficiency of zeolite coating will be checked in this work.

3. PLAN OF WORK



4. LITERATIURE REVIEW

4.1. Studies on removal of arsenic using cellulose acetate-zinc oxide nanoparticle mixed matrix membrane

Mixed matrix membranes were prepared by varying compositions of cellulose acetate, acetone and formamide for synthesis of ultrafltration and nanofltration membranes coated with nanoparticles for removal of arsenic from synthetic solution. Zinc oxide nanoparticles were synthesized by in situ ultrasonic technique and their characterization was done using XRD and SEM. In this study batch experiments were done to characterize the maximum removal effiency of arsenic by cellulose acetate–ZnO composite membrane. Experiments showed that 58.77% of arsenic removal was obtained for the feed concentration of 1000 mg/L at a pH range of 6.8±0.6. Nanoparticles-embedded membranes show higher removal efficiency, high flux and permeation rate than cellulose acetate membranes without embedded nanoparticles.

4.2. Fabrication of Zinc doped Aluminium Oxide / polysulfone mixed matrix membranes for heavy metal removal

In this work removal of heavy metals were done from wastewater to make it drinkable. In this work Zinc doped Aluminium Oxide (Zn:Al_2O_3) nanoparticles were incorporated into Polysulfone (PSf) to fabricate composite membranes for the efficient removal of heavy metals from water. These Zn:Al_2O_3 nanoparticles were prepared by the solution combustion method and these particles have a very high surface area (261.44 m^2 /g) with an approximate size of 50 nm. X-ray Photoelectron Spectroscopy was conducted to check oxidation state of nanoparticles and this analysis showed that the Al and Zn nanoparticles were in þ3 and þ2 oxidation states, respectively. Cross-sectional Scanning Electron Microscopy images revealed the finger-like morphology and porous nature of the membranes. Synthesized membranes showed enhanced hydrophilicity, surface charge, and porosity which enabled the removal of arsenic and lead with efficiencies of 87% and 98% respectively. A study of the antifouling properties carried out at various pressures with a feed solution containing Bovine Serum Albumin (BSA) showed 98.4% of flux recovery ratio and reusability up to three continuous cycles. This work demonstrates a rational design of novel mixed matrix membranes exhibiting characteristics of hydrophilicity, surface charge and adequate porosity to realize the efficient removal of heavy metals.

4.3. Fabrication of polycarbonate mixed matrix membrane containing hydrous manganese oxide and alumina nanoparticles for heavy metal decontamination

Here novel ultrafiltration polycarbonate (PC) mixed matrix membranes (MMMs) containing hydrous manganese oxide (HMO) and alumina nanoparticles were fabricated for the removal of Cd^{2+} and Cu^{2+}. Weight percent of HMO and alumina nanoparticles in the polycarbonate mixed matrix membrane was changed in a certain range. Synthesized composite ceramic membranes were characterized in terms of structural morphology and hydrophilicity using FESEM, water contact angle and FTIR analysis. The effects of hydrous manganese oxide and alumina loadings on the pure water flux, mean pore size, porosity and water contact angle of membranes and removal of Cd^{2+} and Cu^{2+} were further studied. By increasing the loading of manganese oxide and alumina nanoparticles in the casting solution, the mean pore size of membrane increases while the membrane porosity decreases. Increase in hydrous manganese oxide and alumina loadings resulted in an increase in water flux of the membrane. It can be attributed to enhancement in mean pore size and decrease in contact angle. Furthermore UF experiments showed that the composite membranes had very fast kinetics and demonstrated the highest Cd^{2+} and Cu^{2+} removal efficiency. Furthermore, these data were higher than the removal efficiency of mixed matrix membranes prepared by alumina nanoparticles (about 91% and 81% for Cd^{2+} and Cu^{2+} , respectively) . Due to the higher adsorption capacity of manganese oxide nanoparticles compared to alumina these generic results revealed that hydrous manganese oxide nanoparticles can be a good candidate for membrane preparation and can be conveniently used in the Cd^{2+} and Cu^{2+} removal from polluted water resources.

4.4. Fabrication of PES/MnO mixed matrix membrane for Cd removal

This work represents potential of novel nanocomposite mixed matrix membrane impregnated with manganese oxide (MnO_2) nanoparticle for cadmium removal. Membranes were fabricated using polyethersulfone (PES) by phase inversion technique with different Manganese Oxide nanoparticle loading. These membranes were characterized by their structural morphology, surface chemistry and cadmium adsorption capability. The results suggested that PES membrane incorporated with 2.0 ratio of MnO_2/PES exhibited the best result in both cadmium adsorption (51.7 mg/g) and water permeability (1462 $L/m^2.h.bar$)

4.5. Impact of Graphene Oxide Mixed Matrix Membrane on removal of heavy metals from waste water

The graphene oxide (GO) impregnated mixed matrix membrane (MMM) was prepared by non-solvent induced phase inversion method. MMM was characterized in terms of molecular weight cut-off, porosity, permeability, average pore size, pore size distribution, contact angle, zeta potential and mechanical strength. The membrane became highly permeable, hydrophilic and charged on addition of GO. The surface morphology and roughness were studied through scanning electron and atomic force microscopy. Efficacy of MMM for removal of heavy metals was explored using the developed MMM. It showed high adsorption capacity for Pb^{2+} (79 mg/g), Cu2+ (75 mg/g), Cd^{2+} (68 mg/g) and Cr^{6+} (154 mg/g) at natural pH, 6.7, 6.5, 6.4 and 3.5, respectively. The steady state permeate flux was around 30 l/m^2 h for 50 mg/l feed concentration at 414 kPa transmembrane pressure drop and 40 l/h cross flow rate. Rejection of Pb, Cu, Cd and Cr were in between 90% and 96% for various operating conditions and the breakthrough time was around 10 h for different metal ions. The membrane was regenerated in-situ, by acidic solution at pH 5.5.

4.6. Study on novel ultrafiltration grade nickel iron oxide doped hollow fiber mixed matrix membrane: Spinning, characterization and application in heavy metal removal

Nickel iron oxide nanoparticles incorporated hollow fiber mixed matrix membranes were prepared to achieve high throughput and high selectivity for heavy metals. Fibers were characterized in terms of their morphology, permeability, molecular weight cut off, zeta potential, surface roughness and adsorption capacity of various toxic heavy metal species. Scanning Electron Microscope images showed that tear drop like pores in cross section of the fibers were changed into finger like macro-pores on addition of nanoparticles. Increase in pore-size and porosity was observed with nanoparticle concentration. Membrane permeability increased almost twice by addition of 3 wt% nanoparticles compared to pure polysulfone membrane. Similar concentration of nanoparticles made the membrane more hydrophilic reducing its contact angle from 77° to 64° and at the same time, molecular weight cut off of the hollow fibers increased from 17 kDa to 34 kDa. Surface zeta potential of the fibers decreased with pH and the membrane with 3 wt% nanoparticles showed a surface potential about −16 mV at pH 9. The maximum adsorption capacity of membrane with 3 wt% nanoparticles was the highest for lead (52 mg/g) followed by copper (42 mg/g), zinc (35 mg/g) and cadmium (24 mg/g). Nickel (17.5 mg/g) and chromium (18 mg/g) had comparable adsorption capacity. Thus, the mixed matrix membrane developed in this study has significant potential in removal of heavy metals from aqueous solution.

4.7. Study on Fabrication of rGO-CuO and/or Ag_2O nanoparticles incorporated polyvinyl acetate based mixed matrix membranes for the removal of Cr^{6+} from anti-corrosive paint industrial wastewater.

In this work fabrication of ternary system mixed matrix membrane were done based upon polyvinyl acetate incorporated reduced graphene oxide (r GO) and CuO or Ag_2O nanoparticles as filler in different weight ratios via non-solvent induced phase inversion separation method. Fabricated membranes were characterized for chemical composition porosity , pore distribution, surface roughness, thickness, water contact angle and mechanical strength. Scanning electron microscopy and atomic force microscopy analyses revealed that pure PVAc exhibited smooth and uniform surface while PVAc/rGO/Ag_2O and PVAc/rGO/ACuO membranes possessed rough and uneven topography and higher surface porosity. PVAc/rGO/CuO and PVAc/rGo/Ag2O membranes exhibited total permeate flux of 1.60×10^{-2} g/m^2.s and 1.28×10^{-2} g/m^2.s corresponding to net removal of 99.9% and 98.0% respectively from model wastewater of Cr^{6+} under the optimized experimental conditions. Under these optimized conditions, PVAc/rGO/CuO membrane achieved Cr^{6+} removal of 99.9% from anti-corrosive paint industrial wastewater (as real sample) with a flux of 1.90 × 10-2 g/m^2 .s, which was much higher than other membranes. The uptake of Cr^{6+} from real solution was confirmed by EDX and AFM analysis of the post-separation membrane. Newly designed PVAc/rGO/CuO membranes can be used for potential applications for the remediation of Cr^{6+} and other similar pollutants from industrial wastewater.

4.8. Preparation and Characterization of hydrous ferric oxide ultrafiltration mixed matrix membrane for removal of Lead (II) from aqueous solution

Polysulfone (PSf)/ hydrous ferric oxide nanoparticles (HFO NPs) ultrafiltration mixed matrix membranes (MMMs) were prepared for adsorptive removal of lead Pb (II) from aqueous solution. Morphological and physiochemical properties of prepared HFO NPs and mixed matrix membranes were characterized using TEM, BET, XRD, FTIR, SEM, AFM, pure water flux analysis. Results revealed that the self-synthesized HFO NPs possessed a specific surface area (SSA) of 233.49 m^2/g. Increasing weight ratio of HFO NPs in PSf membranes significantly enhanced membrane pure water flux from 229.5 L/m^2.h to 942.1 L/m2.h attributed by the improved membrane hydrophilicity (contact angle 8.0^o) coupled with greater surface roughness (74.8 nm) and overall porosity (88.8%). Adsorption study showed that removal of Pb(II) was strongly dependent on p^H in which the optimum pH was 6.5 to 7.0. Membrane M-1.5 (mass ratio of 1.5 HFO NPs: PSf) possessed the highest adsorption capacity of Pb(II) which was 13.2 mg/g. The adsorption mechanism of Pb(II) onto PSf/HFO MMMs was best fitted to Langmuir isotherm whereas the kinetic mechanism was best described by pseudo-second order model. The UF filtration study showed that this adsorptive MMMs produced permeate of high quality with Pb(II) content (< 15µg/L). The recovery of 96% demonstrated by the MMMs confirmed the superior potential of dual-function membrane for heavy metals removal.

4.9. Efficient removal of lead ions from aqueous solution by graphene oxide modified polyethersulfone adsorptive mixed matrix membrane

Graphene oxide (GO) and polyvinylpyrrolidone (PVP) were used for heavy metal removal .PVP with four different amounts of GO were impregnated in the membrane matrix by the physical blending method. Porosity, contact angle, water flux and Fourier transform infrared spectroscopy tests were conducted for all prepared membranes. Viscid behavior of polymer dope solution was examined. PVP enhanced the GO distribution within the membrane surface to some extent via hydrogen bond. The addition of nanoparticles enhanced the membrane physicochemical properties with water permeation, Pb^{2+} rejection and adsorption capacity. Permeate flux of modified membrane was found to be 150.21 L/m^2h and it is 8.03 times higher than unmodified membrane .

5. EXPERIMENTAL PROCEDURE :

5.1. Materials: Alumina, China clay, binder, Aerosil 200, Sodium Hydroxide pellets, Raw Aluminium sources, Millipore water, Arsenic (V) salt, Triethanolamine(TEA).

5.2. Fabrication of faujasite coated tubular ceramic membrane

5.2.1. Fabrication of tubular ceramic support : Weighed amount of Alumina(620 g) and China Clay were mixed in 5:1 with distilled water to form a uniform dough like mass. Specified amount of binder(70 g) was added to the mixture. The prepared mass was left to dry naturally for at least a fortnight. Once fully dried the hardened mass was passed through a screw type extruder with water jacketing to obtain the tubular membrane structure. The dimensions of the membrane were 8 mm outer diameter and 100 mm long. The length of membrane in extrusion process was kept 10-15% higher than the desired length to account for the shrinkage associated with the ceramics. Again, these tubes were sun-dried for a fortnight before firing the same in a Silicon carbide furnace at the desired temperature of 1425^0 C. Once fired the membranes were stored in a dry place before further use. While performing the permeation study of the prepared membranes it was observed that there were pockets of air entrapped within them which interfered with the experimental procedure. So to get rid of this problem, membranes were placed in a distilled water bath overnight so that the capillary pores got conditioned properly.

Fig.4 (Prepared tubular ceramic membrane)

Details of tubular ceramic membrane :

Length = 10.5 cm

Inner dia=0.313 cm

Outer dia= 0.618 cm

Effective area= $(2\times \pi\times r_{out}\times l)= 20.386\ cm^2$

Effective Volume= $\pi\times(r_{out}^2 - r_{in}^2)\times l= 2.338\ cm^3$

5.2.2. Synthesis of faujasite solution : 15 g of sodium hydroxide (NaOH) pellets were dissolved in Millipore water and Aluminium foil of cigarette cover was added into the solution. In another mixture Aerosil 200 was mixed in Millipore water and triethanolamine (TEA). Both of these mixtures were mixed stirred for 24 hours long at 400 rpm and then mixed. The mixture was kept on stirring for 18 hours long. After that the solution was kept stagnant for 24 hours long. Two visible separate layers were formed from this solution. The upper layer was like a gel which was faujasite seeds solution and the lower layer looked hazy white which mainly consists of paper particles that remains in the metal foil of cigarette cover. Upper layer was separated by simple gravity filtration technique and used for further process.

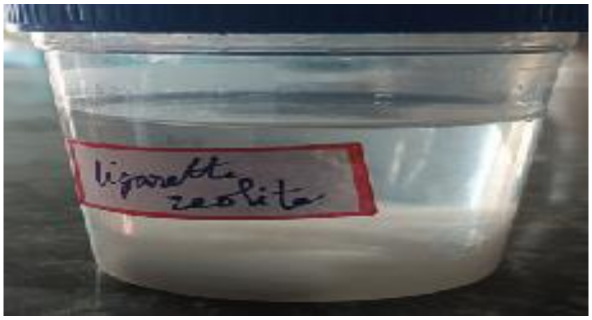


Fig.5 (Faujasite gel along with unwanted solution of paper particles)

5.2.3. Synthesis of faujasite coated ceramic membrane: Finally outer layers of the ceramic membranes were polished with abrasive paper and placed in a ultrasonic bath to remove detached powder that generated during burnishing. Burnished membrane was dipped in faujasite gel solution and was placed in a Teflon coated stainless steel autoclave reactor and heated for 200^0 C for 10 hours long until faujasite particles got impregnated inside the pores of membrane by in-situ hydrothermal crystallization procedure. After synthesis membranes were washed by Millipore water quite a few times and dried at 100^0 C for 5 hours and then calcined at 450^0 C for 10 hours long.

Fig.6 (In-Situ Hydrothermal Crystalization Set-up)

5.3. Characterization : Excess faujasite gel was poured inside Teflon-coated stainless steel autoclave reactor and then heated in 200^0 C for 10hours long until faujasite powder was formed by hydrothermal crystallization technique. Then faujasite powder was washed several times by Millipore water and then calcined under the same condition as used for faujasite coated ceramic composite membrane.

5.3.1. Porosity : Determination of porosity needs dry weight(W_{dry}) and wet weight (W_{wet})of the membrane. To find dry weight membrane was dried at 150^0 C for 8 hours long and then measured . To find wet weight membrane was submerged in water for 24 hours long, taken out and then every droplets of water were cleared from membrane surface by tissue paper, then dry weight of membrane was measured. Then from dry weight (W_{dry}) , wet weight (W_{wet}) and volume of membrane ($V_{membrane}$) using the following formulae (19) porosity of membrane was calculated.

$$\text{Porosity} = \frac{W_{\text{wet}} - W_{\text{dry}}}{\rho_{\text{water}} V_{\text{membrane}}} \times 100 \qquad (1)$$

5.3.2. Pure Water flux test : Membrane's performance in varying pressure was measured by measuring water flux. For this a dead end UF setup was used which is illustrated in figures Fig. 1 and Fig. 2. The water flux was measured at different pressures. At each time of flux calculation first 50 ml of filtrate was discarded and results were calculated based upon second 50 ml filtrate collected. Following formulae was used for calculating flux,

$$\boxed{J_w = Q/A\Delta T} \tag{2}$$

Where J_w is flux and Q is water flux(m.s^{-1}) and A is area (m^2)and ΔT is sampling time(s)

Fig 7(Schematic of UF setup used for heavy metal removal test)

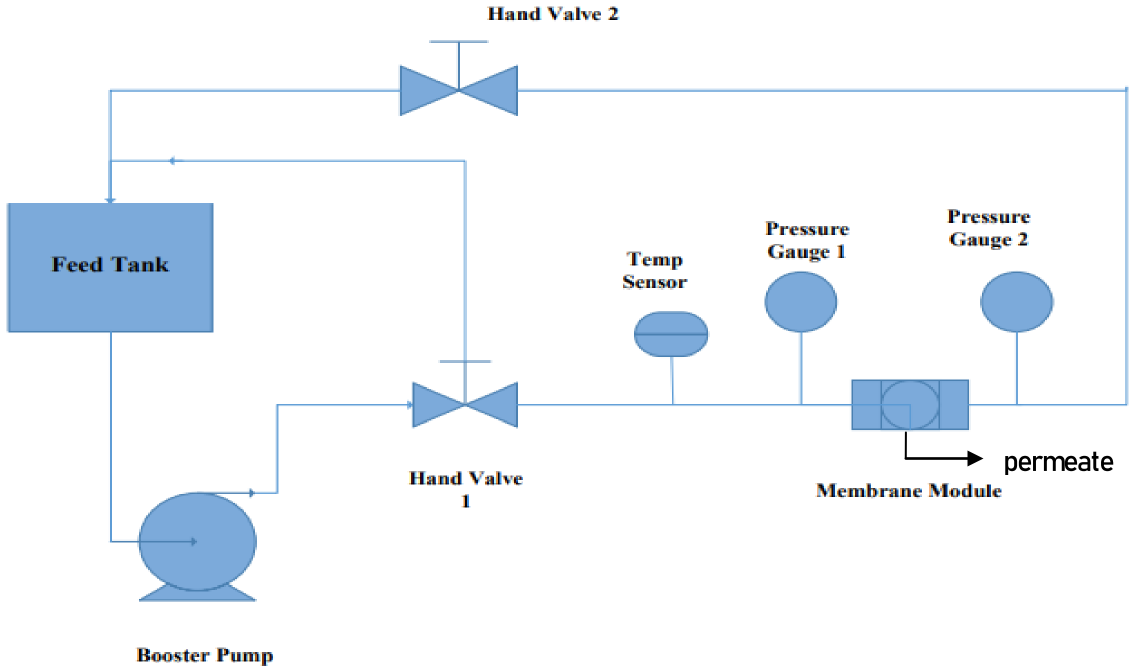


Fig.8 (process flow diagram of the UF setup)

5.3.3. Arsenic Removal test : Performance of the faujasite coated membrane in removal of Arsenic ions (As(V)) was tested. UF feed tank was filled with 500 ml of 1000 ppm solution of AsV. Before filling up the tank it was cleared with Millipore water. At each time of varying pressure first 10 ml of filtrate was rejected and the next 10 ml was collected for determining concentration of Arsenic salt. To determine Arsenic concentration ICP-OES instrument was used. To determine rejection following formulae is used.

$$\boxed{R = (1 - C_p / C_F) \times 100} \qquad (3)$$

Where C_F is concentration of Arsenic in feed and C_p is concentration of Arsenic in permeate. After every experimental run membrane setup was cleared by Millipore water at a high pressurized condition .

5.3.4. XRD Analysis : X-ray diffraction of calcined faujasite powder was performed in a machine (Bruker AXS instrument) with Cu K@ radiation source. The graph was taken for a 2θ range of 5^0 to 50^0.

5.3.5. FT-IR Analysis : FT-IR Analysis was performed using a Shimadzu IRAffinity-1 model spectrometer in the wavenumber range of 4000–800 cm^{-1} . Spectra was taken at room temperature and pressure.

5.3.6. TGA Analysis : Thermogravimetric analysis (TGA) of the faujasite powder (before calcination) was carried out using a Perkin Elmer Simultaneous Thermal Analyzer (STA 6000) under a flowing nitrogen atmosphere with a heating rate of 25^0C min^{-1} from 50^0C to 600 ^0C in a ceramic crucible. The crucible was first covered with alumina powder and then the sample was poured into it.

5.3.7. FESEM Analysis : A Field Emission Scanning Electron Microscope (FESEM, FEI INSPECT F50) was used to examine the surface properties of the faujasite coated mixed matrix membrane. A very small amount of the sample was placed onto the stub and coated with gold.

5.3.8. EDS Analysis : Energy Dispersive Spectroscopy was done for both faujasite powder and membrane surface in an EDS BRUKER instrument. For knowing surface morphology of cigarette foil used EDS Analysis was also done.

5.3.9. Point of Zero Charge Measurement : Solid addition method was used to determine point of zero charge of the composite membrane (20). 50 mg of solid sample was collected from coated membrane, powdered in mortar and pestle. This powder was mixed in 50 ml of 0.001 M NaCl solution at various P^H(2-14) and then placed in a shaking bath for 24 hours long. Initial P^H ($P^H{}_i$) was adjusted using 0.1 M HCL or NaOH. After shaking for 24 hours long final P^H ($P^H{}_F$) value was also measured. Difference in initial and final p^H was calculated and that was denoted by ΔP^H . A plot of ΔP^H and $P^H{}_i$ was drawn taking them in Y and X axes respectively. The value of $P^H{}_i$ at which ΔP^H was zero was denoted by point of zero charge or $P_{PZC.}$

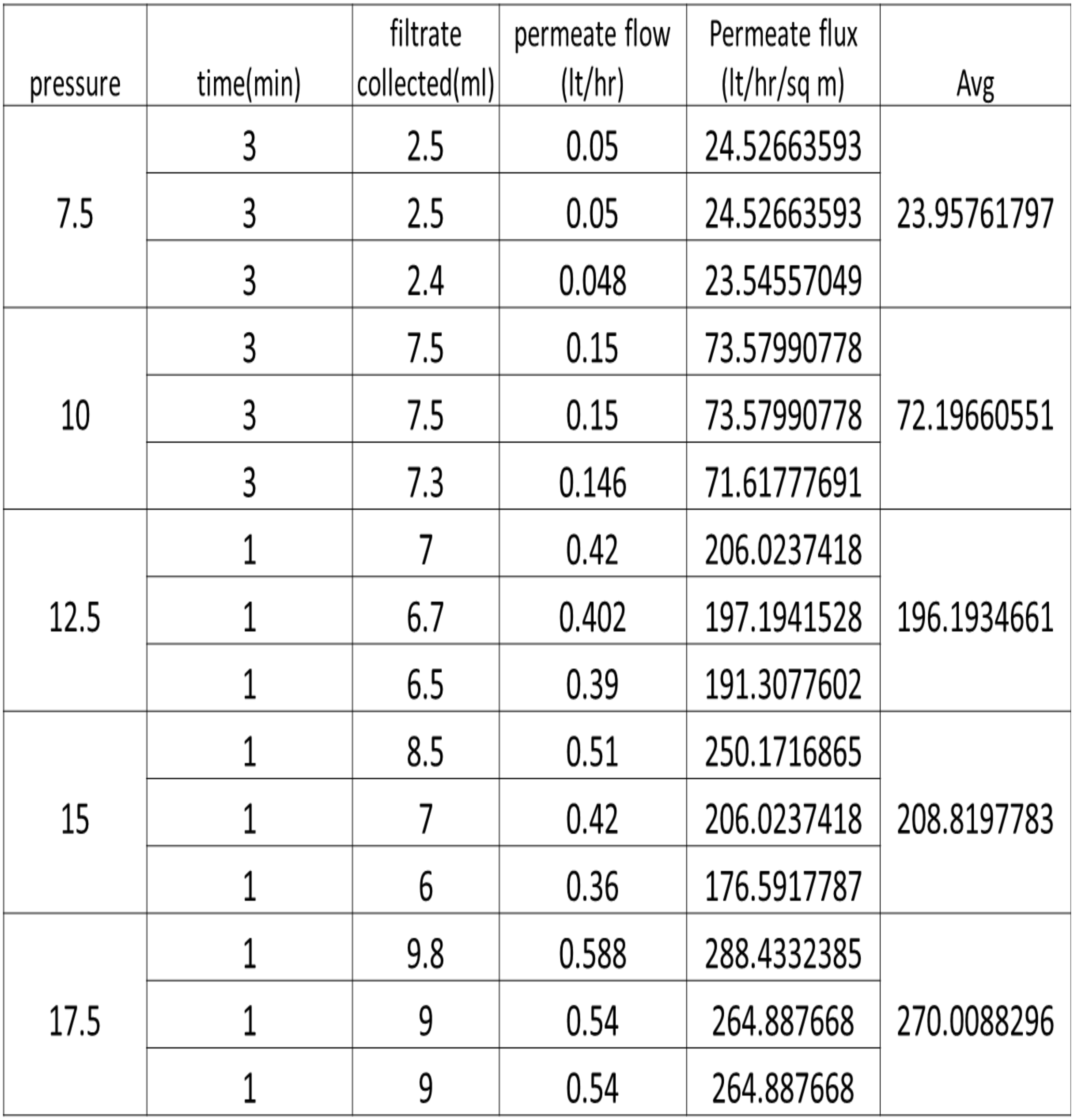
6. RESULTS AND DISCUSSIONS:

6.1. POROSITY : Porosity of raw ceramic membrane was found to be 39%; whereas faujasite coated composite ceramic membrane showed porosity around 35%. Impregnation of faujasite nanocrystals and microcrystals inside the pores of ceramic membrane justified this reduction in porosity .

Characteristics	Dry Membrane	Faujasite coated Membrane
Dry Weight	3.7531 g	3.931%
Wet Weight	3.7166 g	4.75 g
Outer Dia	0.618 cm	0.618 cm
Inner Dia	0.313 cm	0.313cm
Length	10.5 cm	10.5 cm
Volume	2.338 cm^3	2.338 cm^3
Porosity	**38.99%**	**35.03%**

Table. 2 (porosity calculations)

6.2. WATER FLUX TEST : Effect of pressure on water flux was measured for both raw and coated membrane for varying pressures of 7psi to 18 psi. First droplets of permeate were found at a transmembrane pressure of around 6 psi, before this pressure no permeate flow was observed. How flux changes with pressure is showed in this graph. Due to hydrothermal crystallization of faujasite seeds inside the pores of ceramic membrane there was a reduction in flux value of composite ceramic membrane.



pressure	time(min)	filtrate collected(ml)	permeate flow (lt/hr)	Permeate flux (lt/hr/sq m)	Avg
7.5	3	2.5	0.05	24.52663593	23.95761797
	3	2.5	0.05	24.52663593	
	3	2.4	0.048	23.54557049	
10	3	7.5	0.15	73.57990778	72.19660551
	3	7.5	0.15	73.57990778	
	3	7.3	0.146	71.61777691	
12.5	1	7	0.42	206.0237418	196.1934661
	1	6.7	0.402	197.1941528	
	1	6.5	0.39	191.3077602	
15	1	8.5	0.51	250.1716865	208.8197783
	1	7	0.42	206.0237418	
	1	6	0.36	176.5917787	
17.5	1	9.8	0.588	288.4332385	270.0088296
	1	9	0.54	264.887668	
	1	9	0.54	264.887668	

Table.3 (Flux calculations of raw membrane)

Pressure(psi)	Permeate flow (L/hr)	Permeate Flux (L/hr/m2)	Avg Permeate Flux (L/hr/m^2)
7.5	0.135	2.75211	2.7929
	0.132	2.690952	
	0.144	2.935584	
10	0.6	12.2316	12.43546
	0.624	12.720864	
	0.606	12.353916	
12.5	1.14	23.24004	24.05548
	1.2	24.4632	
	1.2	24.4632	
15	1.68	34.24848	31.80216
	1.56	31.80216	
	1.44	29.35584	
17.5	1.5	30.579	32.20988
	1.56	31.80216	
	1.68	34.24848	

Table.4 (Flux calculations of coated membrane)

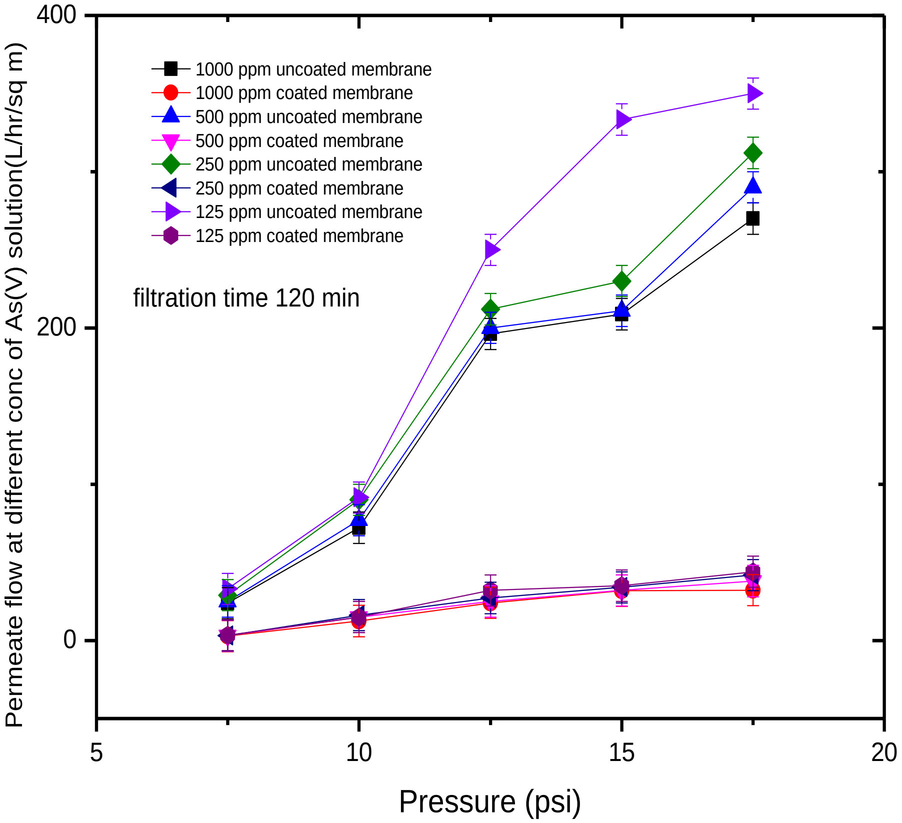
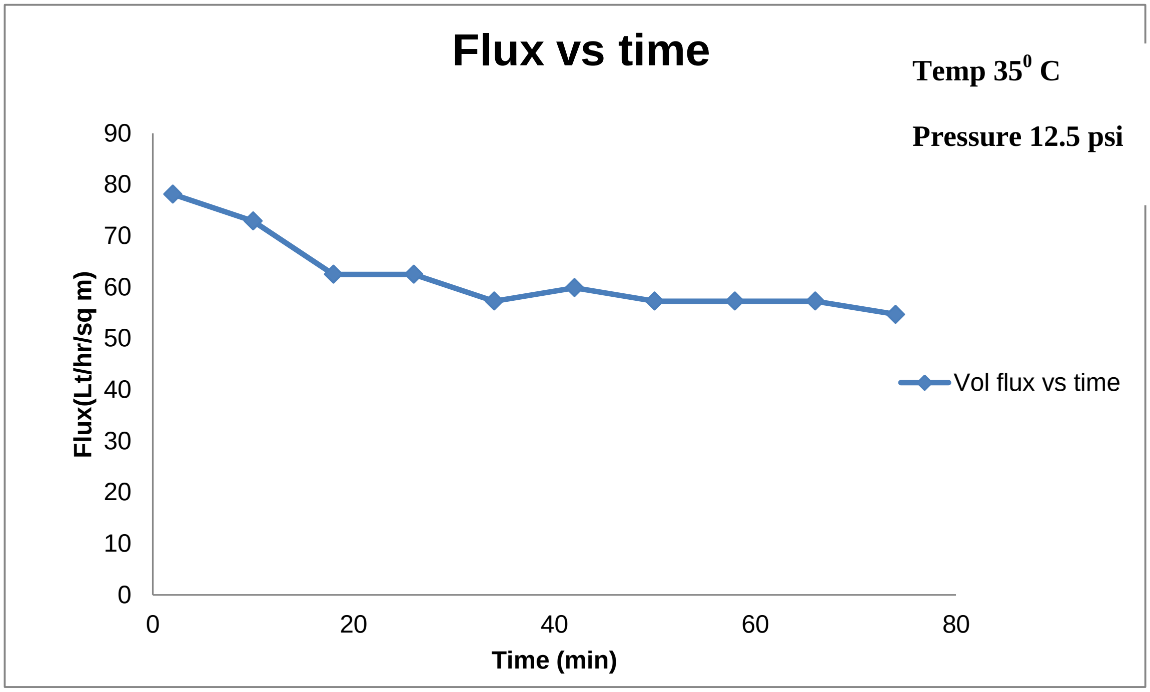


Fig. 9 (Graphical representation of flux for coated membrane and raw membrane)

Steadystate flux: Steady-state flux value was calculated for both raw and coated membrane. Flux was calculated for 5 minutes each and this calculation was continued until 70% reduction value in flux was achieved. For raw membrane approximately after 140 minutes steady state flux was achieved, whereas for coated membrane steady state was achieved after 54 minutes.

Time	ml	Volumetric flux(L/hr/sq m)
2	3	78.2
10	2.8	72.9
18	2.4	62.5
26	2.4	62.5
34	2.2	57.3
42	2.3	59.9
50	2.2	57.3
58	2.2	57.3
66	2.2	57.3
74	2.1	54.7

Table.5 (Variation of flux with time for raw membrane)



` **Fig.10** (Variation of flux with time (raw membrane))

Time (min)	Vol of filtrate(ml)	Volumetric flux(L/hr/sq m)
5	10.5	273.4375
13	10.5	273.4375
21	10.5	273.4375
29	10.6	276.0416667
37	10.5	273.4375
45	10.5	273.4375
53	10	260.4166667
61	10	260.4166667
69	9.2	239.5833333
77	8.5	221.3541667
85	8.5	221.3541667
93	8.3	216.1458333
101	8.2	213.5416667
109	8	208.3333333
117	7.7	200.5208333
125	7.5	195.3125
133	7.2	187.5
141	7	182.2916667
149	7	182.2916667
157	7	182.2916667

Table. 6 (Variation of flux with time for coated membrane)

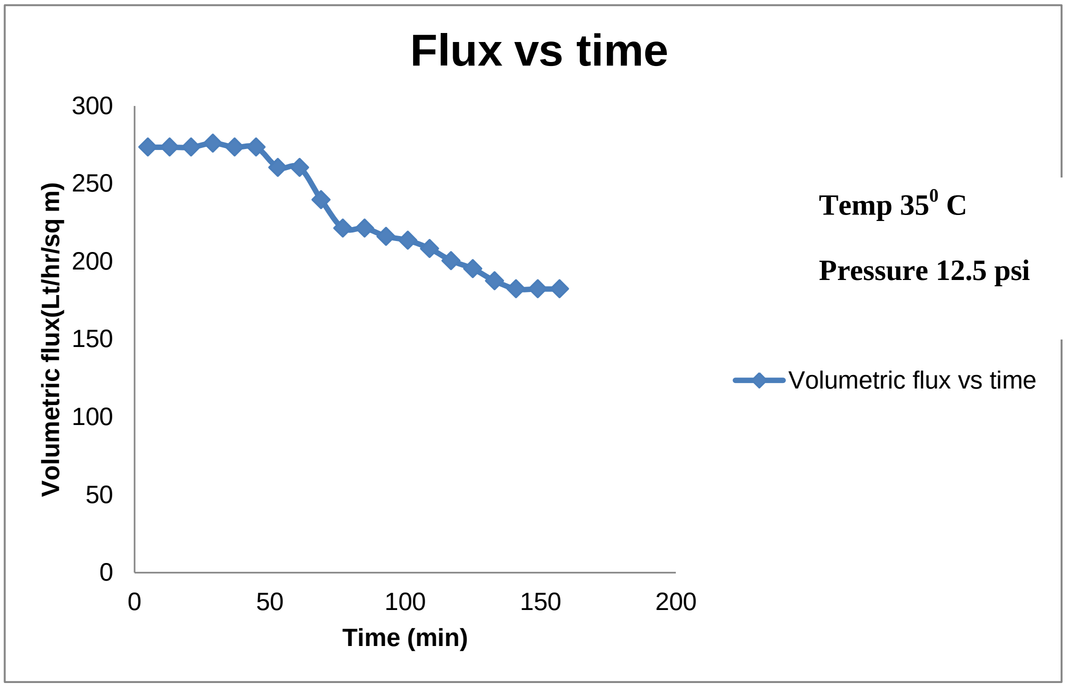


Fig.11 (Graphical Representation of flux vs time for coated membrane)

6.3. Arsenic removal test : Arsenic removal results for both raw membrane and coated membranes were satisfactory. Coating operation made the mixed matrix membranes more efficient in removing Arsenic salt. Accumulation of arsenic salts in feed size creates a layer of ions and this layer effects permeate concentration. This phenomenon is called concentration polarization (71) . Besides concentration polarization, concentration of solute in feed, interaction of solute with membrane surface effect plays very important roles in determining both permeate flux and rejection.

pressure	initial conc(ppm)	conc(ppm)	removal	Rejection(%)
7.5	1000	878	122	12.2
10	1000	966.9	33.1	3.31
12.5	1000	984.1	15.9	1.59
15	1000	858	142	14.2
17.5	1000	846	154	15.4

Table . 7 (Removal of Arsenic salt by raw membrane)

Pressure	Initial conc(ppm)	Conc(ppm)	Removal	Rejection(%)
7.5	1000	606.2	393.8	39.38
10	1000	677.6	322.4	32.24
12.5	1000	898	102	10.2
15	1000	776	224	22.4
17.5	1000	871	129	12.9

Table.8 (Removal of Arsenic by coated membrane)

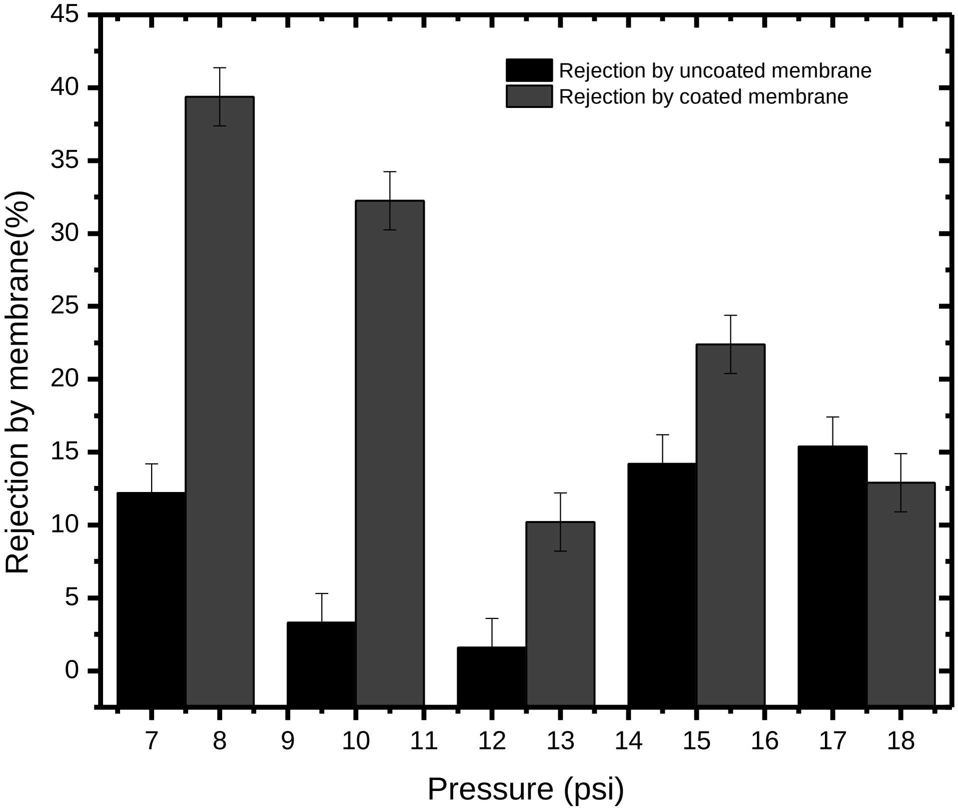


Fig. 12 (Graphical Representation of Removal of Arsenic by raw and coated membrane)

Available data points were fitted in adsorption isotherm i.e a graph was plotted taking (removal/weight of membrane) in Y axis and pressure in X axis.

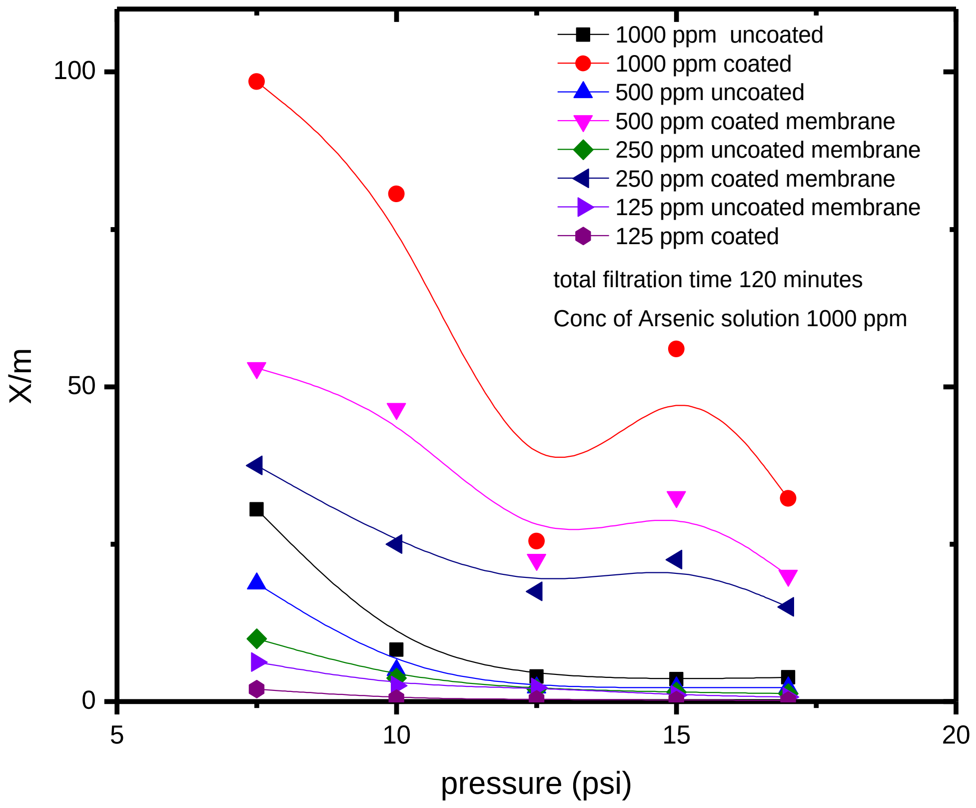


Fig.13 (Adsorption isotherms for raw and coated membrane)

Effect of Feed Concentration on Permeate Rejection : Concentration of feed plays a vital role in permeate concentration. In this figure X represents adsorbed amount of solute and m denotes mass of the adsorbent. This has been observed with increasing feed concentration amount of rejection is decreasing. This phenomenon is justified by Donan Exclusion Effect (72) . With increasing As(V) concentration, Donnan effect declines and surface concentration increases which leads to high amount of concentration polarization. Consequently, the solute permeation by diffusion increases and hence the permeate concentration also raises.

Initial conc(ppm)	Final conc(ppm)	Removal(ppm)	Rejection(%)
1000	968	32	3.2
500	480	20	4
250	239.25	10.75	4.3
125	112.25	12.25	10.2

Table.9 (Effect of concentration of As(v) on solute rejection)

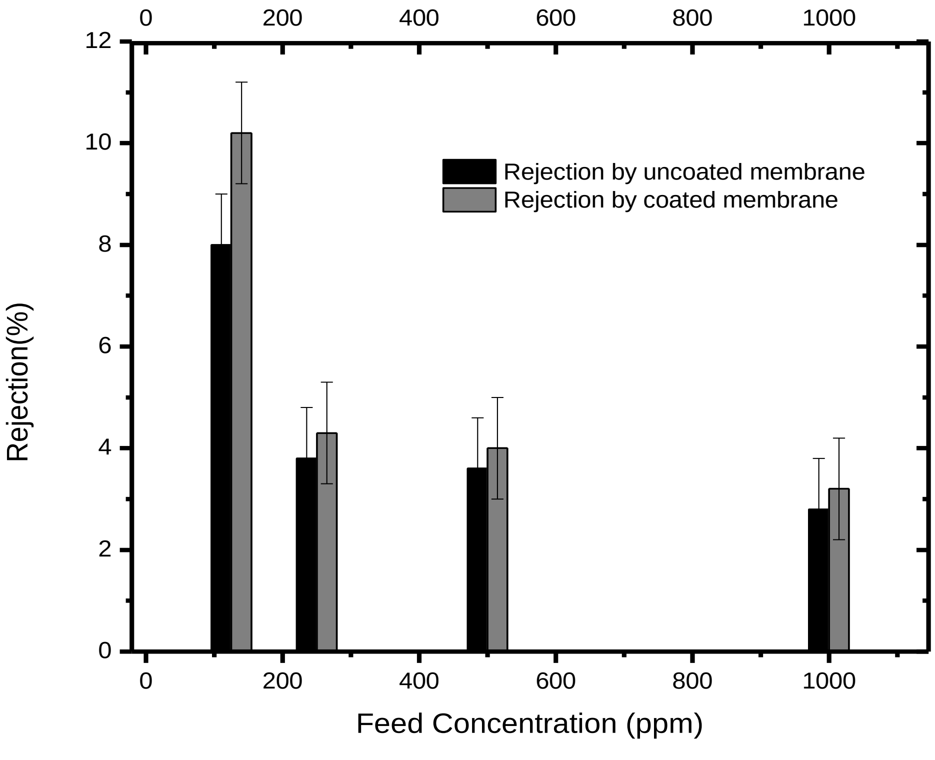


Fig. 14 (Effect of concentration on rejection)

6.4. Characterization of faujasite powder by XRD test : Faujasite data was subjected to analysis for its structure and purity verification by means of XRD patterns as shown in figure 16. The obtained XRD pattern closely matches with Analcime C Faujasite(peaks at 26^0 ,30^0) [Fig.15] with some extra bonds that denote CaO (at 32^0 ,37^0 C). The peaks obtained before and after calcination were almost same.

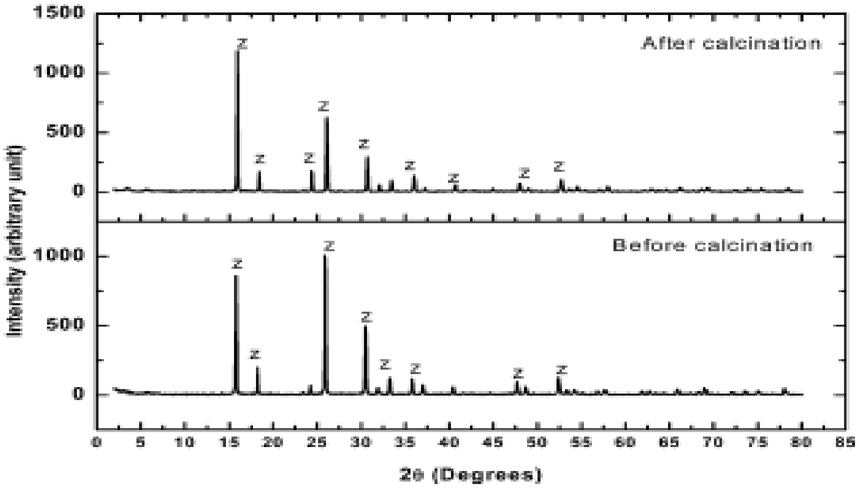


Fig.15 (XRD image of faujasite in literature)

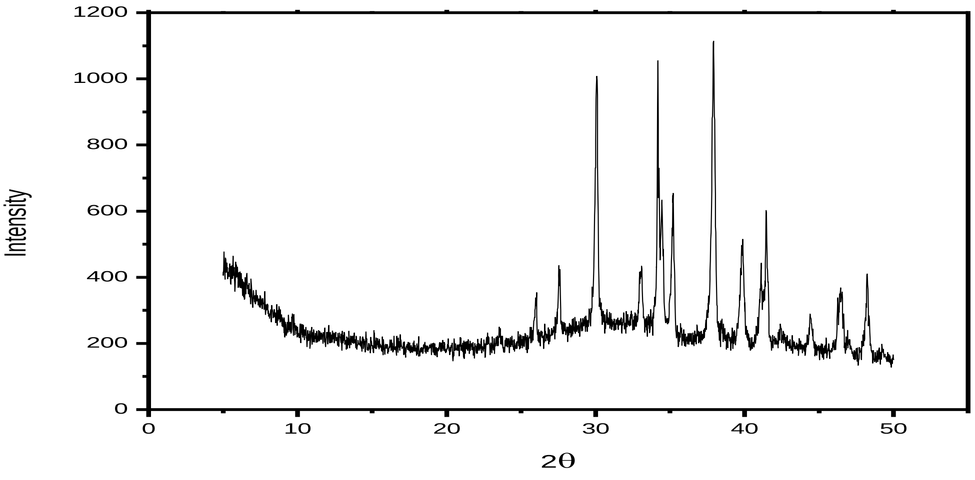


Fig.16 (XRD Analysis of synthesized Faujasite nanoparticles)

6.5. FTIR analysis: The bands (assymetric and symetric) for streching vibration of hydroxyl group appear in the waverange of 3000-3500 cm^{-1} and exhibit high density. H-O-H bending vibration appears at 1600 cm^{-1} . Bending vibration of tetrahydral bonds appear in the region of 615-450 cm$^{-1.}$

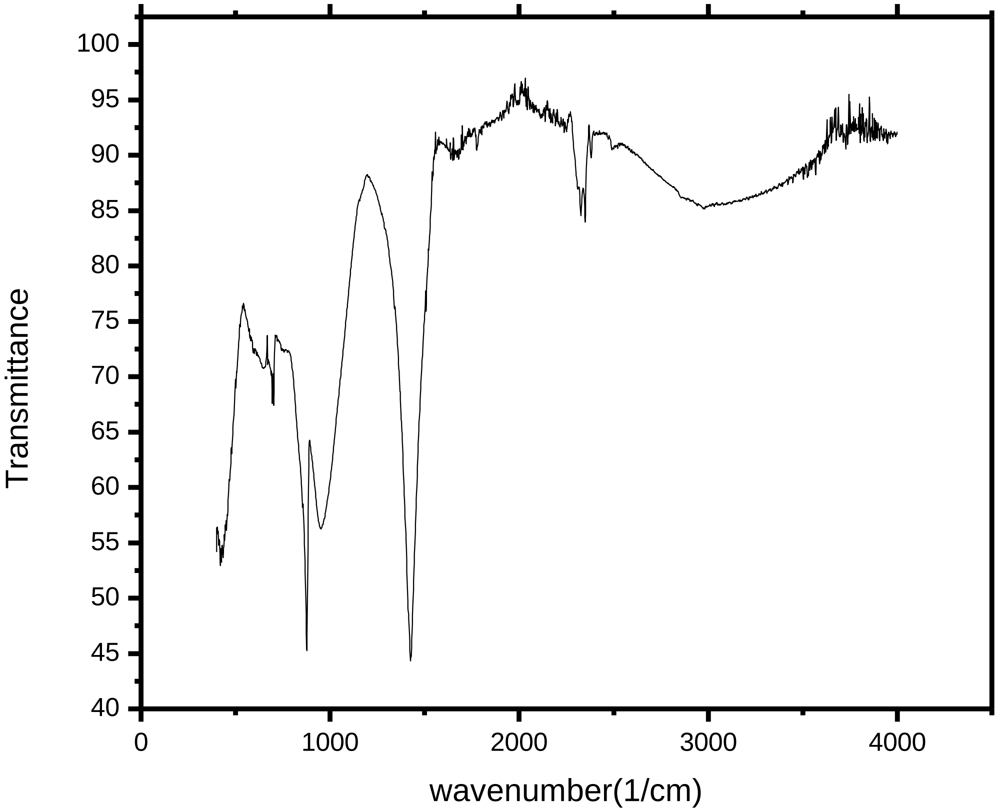


Fig. 17 (FT-IR spectra of synthesized faujasite powder)

6.6. TGA analysis : Thermogravimetric Analysis of the synthesized faujasite type zeolite particles showed that total weight loss is approximated to be 30%. Weight loss around 100^0 C-150 ^{0}C was due to removal of unbound moisture absorbed by the micro faujasite particles. At higher temperature reduction of weight percentage is due to removal of structural hydroxyl groups. After 400^0 C no major change in weight percentage was observed. Therefore sintering temperature was fixed at 450^0 C.

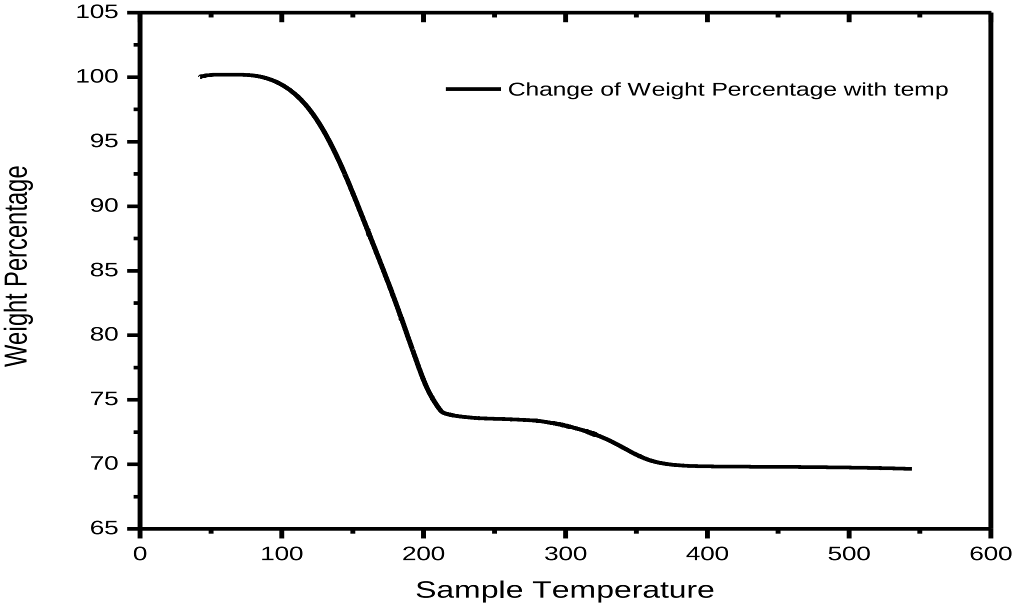


Fig.18 (TGA Analysis of Faujasite microcrystals)

6.7. FESEM analysis : FESEM images shows faujasite microcrystals on membrane surface. In figure 19.b and 19.d faujasite micro crystals were shown in red color. Identification of these white cystals as faujasite type of faujasite was done by surface morphology analysis i.e EDS analysis of faujasite coated membrane surface. Faujasite crystals were mostly round shaped. Most of the faujasite crystals were impregnated on the membrane surface but few were also covered the pores which means that more number of coatings will be reducing the pore size of the membranes. Average size of membrane pores was found to be 1.3 μm. Average size of faujasite microcrystals were found to be 1-20 μm. Hydraulic permeability also can be calculated from this observation. For this the formulae of average pore radius calculation can be used.

$$\boxed{r=(8\mu l L_h/\,\varepsilon)^{0.5}} \tag{4}$$

Here μ is water viscosity, l is pore length, L_h is permeability, ε is porosity. Considering pores as cylinder and pore diameter equals to 4V/S (V is pore volume and S is cross-sectional area of pore) (23) pore length equals to D/4 (D is pore diameter). Putting all values for faujasite coated membrane water permeability is coming out to be $0.7*10^{-8}$ $m^3\ m^{-2}s^{-1}Kpa^{-1}$.

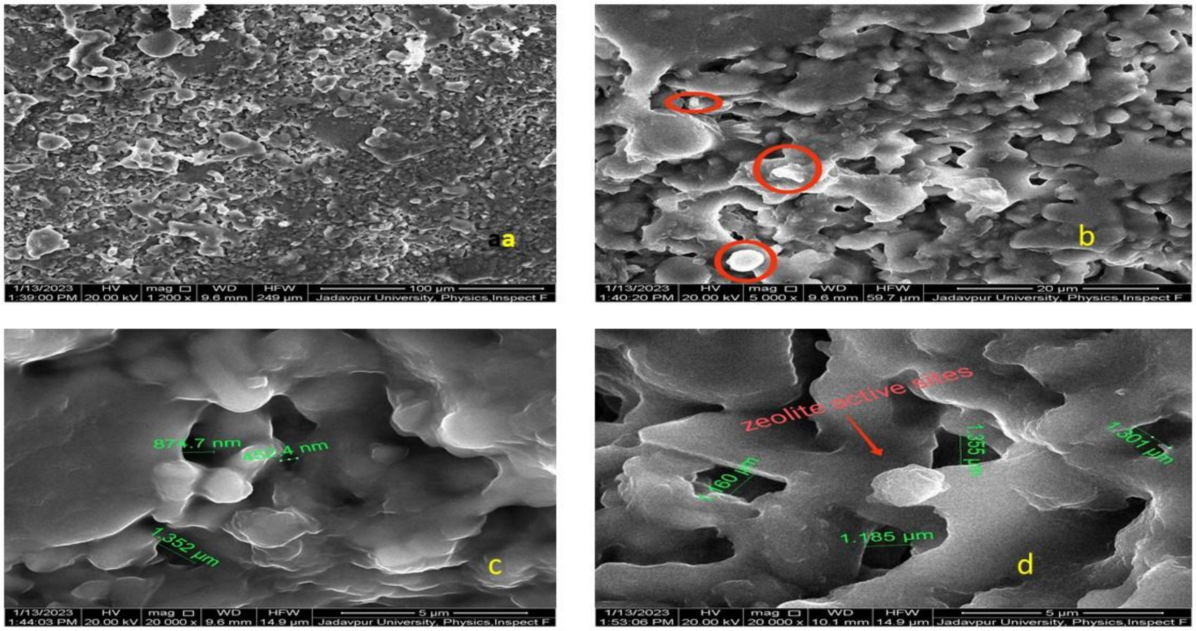


Fig.19 (FESEM images of (a), (b) membrane surface ; (c)membrane pore size; (d) membrane pores modified by faujasite microcrystals.)

6.8. EDS analysis : EDS Analysis of Aluminium foil was done to determine Al content in that foil. Table.10 shows that Al content foil used in cigarette used is around 32%. EDS Analysis of coated membrane was also done. Existence of Ca was traced in surface morphology of coated membrane(Table.11) which proves that coating by faujasite solution was successful as Calcium was not used in manufacturing process of raw membrane, Ca is present only in the foil of cigarette among all reactants to prepare faujasite solution.

Element	Weight Percentage (%)
Aluminium (Al_2O_3)	32.36
Calcium (CaO)	27.78
Oxygen	39.87

Table.10 (EDS Analysis of foil inside cigarette packet)

Element	Weight Percentage
Sodium (Na_2O)	43.93
Aluminium (Al_2O_3)	9.43
Calcium (CaO)	0.45
Silicon(SiO_2)	10.44
Oxygen	35.75

Table. 11 (EDS Analysis of coated membrane)

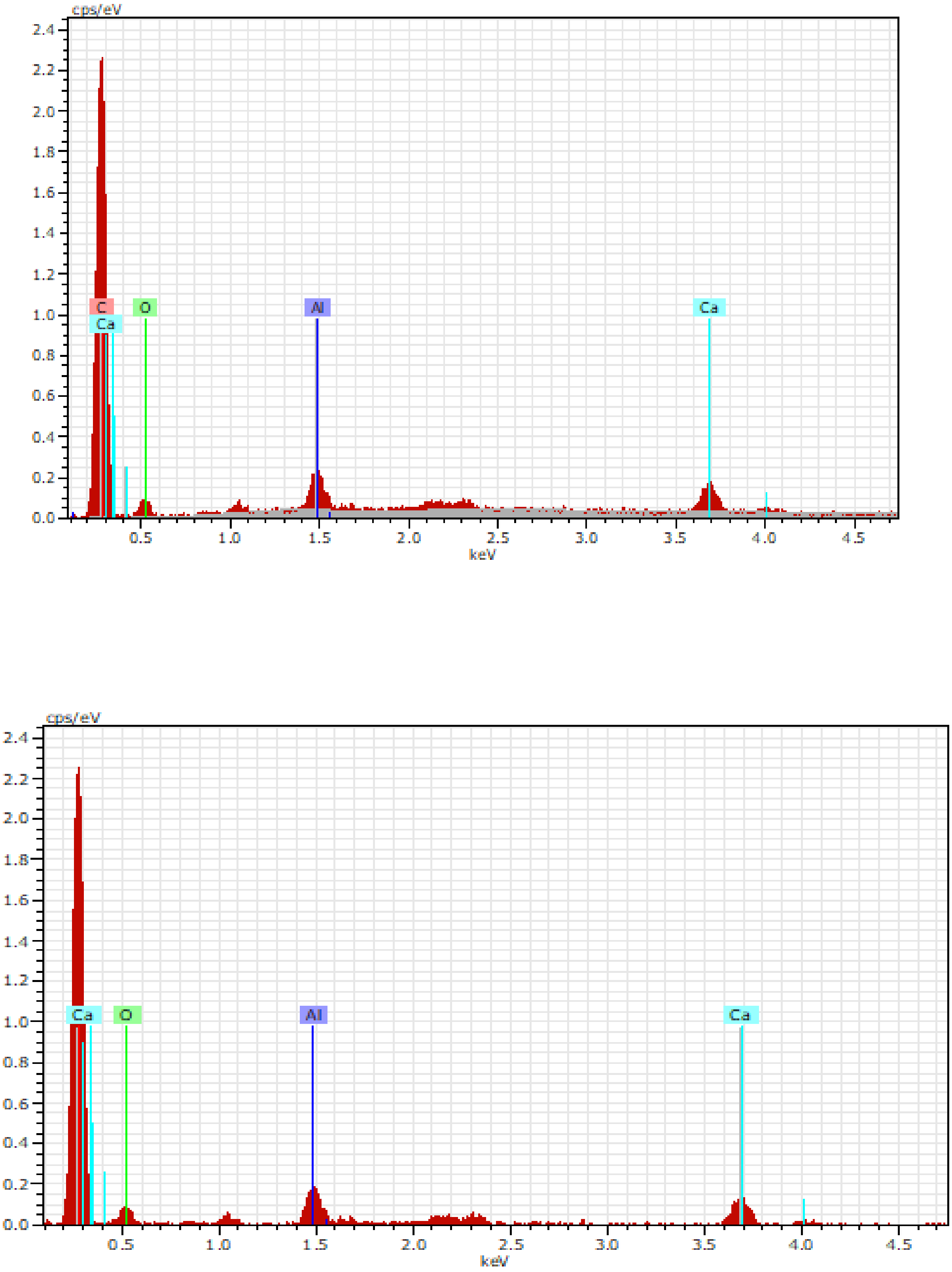


Fig.20 (EDS spectra of Cigarette foil)

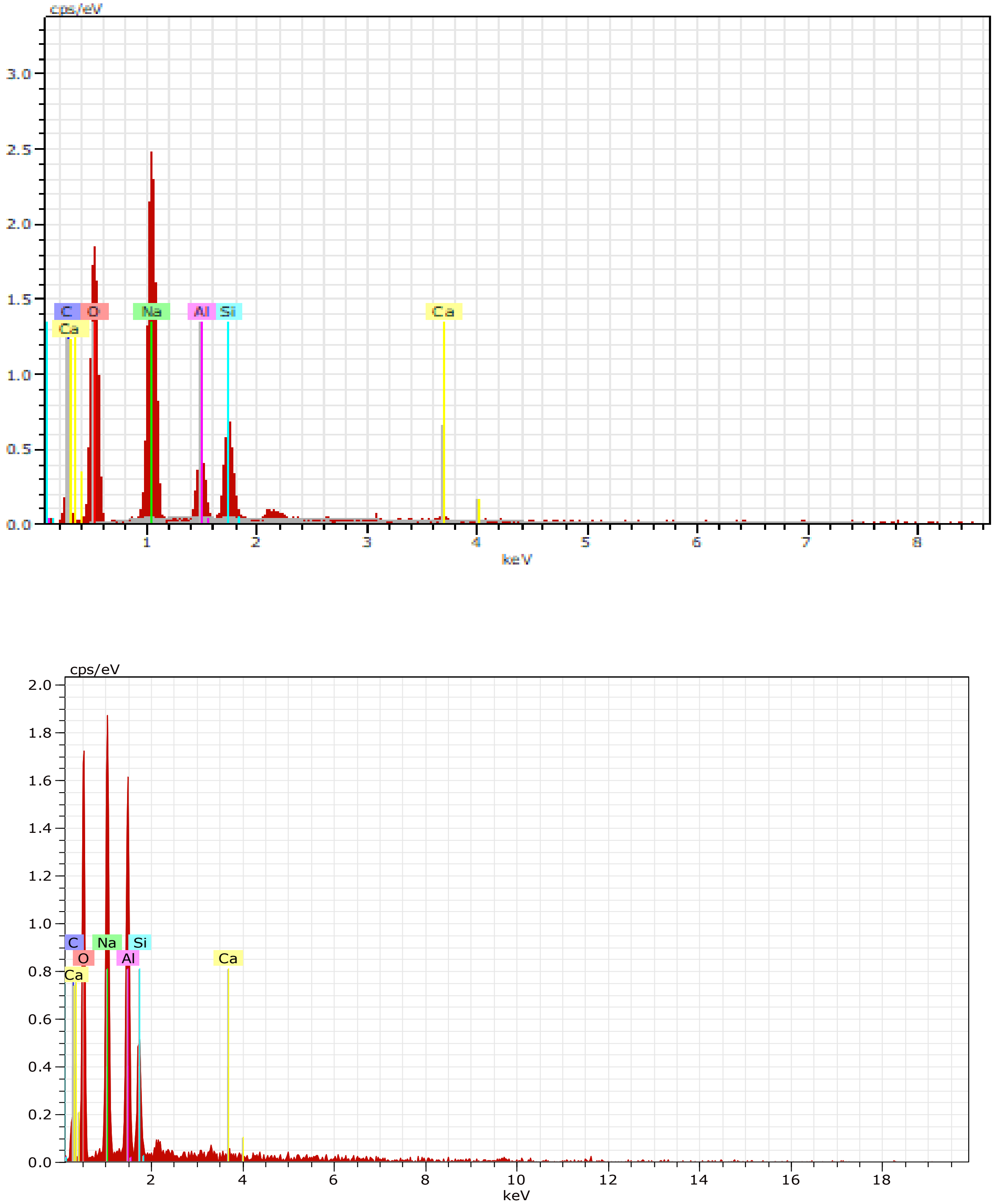


Fig.21 (EDS spectra of coated membrane surface)

6.9. Analysis of point of zero charge : To find point of zero charge of the coated membrane a wide variation of pH was considered. Point of zero charge helps us to know how membrane surface changes its polarization with varying pH. Point of zero charge for this membrane was found to be 9.85. This implies that at lower pH of 9.85 membrane surface will act as positively charged and above 9.85 membrane surface will be negatively charged.

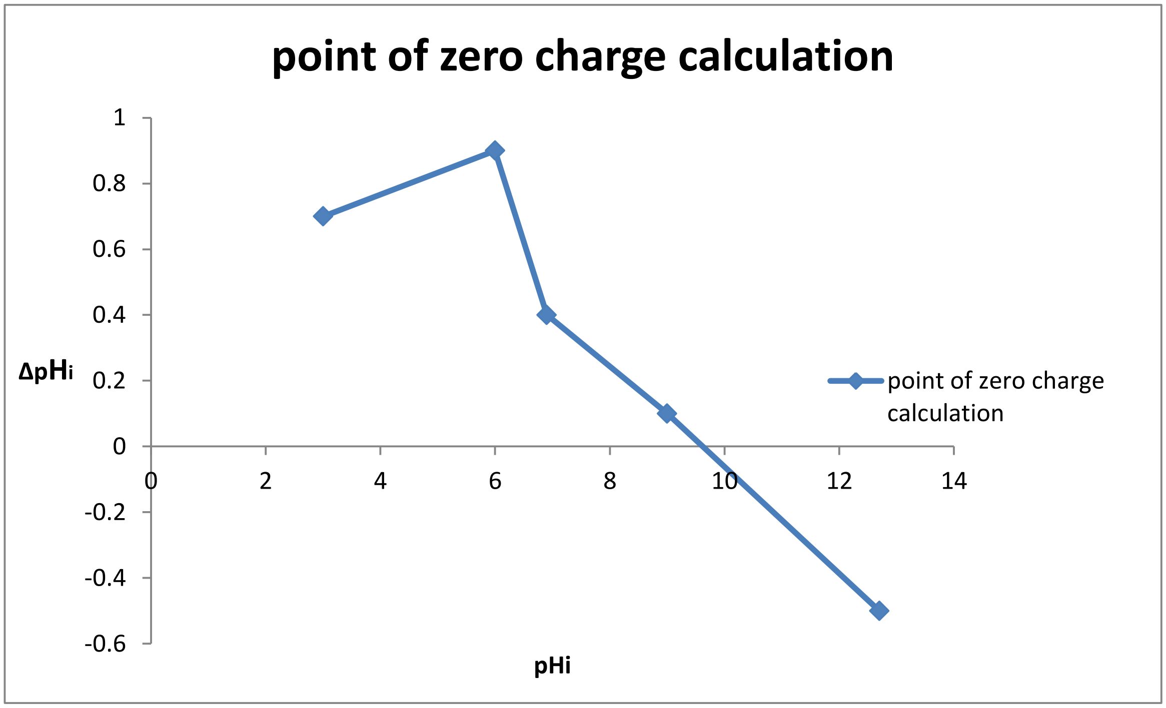


Fig. 22 (point of zero charge calculation for coated membrane)

7. CONCLUSIONS

In this work faujasite type of zeolite is synthesized from a waste source of Aluminium and then faujasite coated ceramic membrane is fabricated through in-situ hydrothermal crystallization technique which proved to be very efficient in removing heavy metals. Average porosity of fabricated of membrane is 35%, average pore dia is 1.3 µm, permeability $2.8*10^{-8}$ m^3 $m^{-2}s^{-1}Kpa^{-1}$. Average size of faujasite microcrystals were varying from 1-20 µm. How varying pressure was effecting permeate flux and Arsenic removal was shown in this work. This work shows quite a high removal efficiency of heavy metals such as Arsenic compared to other works mentioned in literature review.

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