MEMBRANE SYNTHESIS FOR DEMINERALIZATION PURPOSE

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CERTIFICATE

This is to certify that the thesis entitled "**Membrane Synthesis For Demineralisation Purpose**" has been carried out by Aihika Mandal in the fulfillment of the requirements for the degree of the Master of Chemical Engineering from Jadavpur University, Kolkata is recorded as bona fide work that has been conducted under the supervision of Prof. (Dr.) Chiranjib Bhattacharjee. The contents embodied in the thesis have not been submitted to any other university for the award of any degree or diploma.

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I hereby declare that this thesis contains literature survey and original research work by the undersigned candidate, as part of his Master of Chemical Engineering studies. All information in this document have been obtained and presented in accordance with academic rules and ethical conduct.

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Thesis Title: Membrane synthesis for demineralization purpose

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CERTIFICATE OF APPROVAL

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Abstract

In order to obtain highly efficient removal of Arsenic from contaminated water in lower operating cost, replacing Reverse Osmosis membrane with Ultrafiltration membrane incorporated with a highly efficient adsorbent can be a potential method. Layered Double Hydroxides (LDH) are a group of ionic lamellar compounds consists of positively charged Brucite-like layers with an interlayer region containing charge compensating anions and water molecules. Ion exchange is the most prominent and effective mechanism for removal of metal ions from water by LDH.

In this study, a number of Layer Double Hydroxides (doped with different metal ions) have been synthesized via co precipitation method. The structure and composition of pristine and doped LDH have been investigated by XRD, SEM, TG-DTA, FTIR. The comparative of pristine and doped LDH in terms of adsorption capacity has been shown via different adsorption model i.e., Langmuir model, Freundlich model.

Graphene Oxide is a carbonaceous material containing more oxygen rich polar. In order to design a highly efficient adsorbent for trapping arsenic ions from wastewater, a nanocomposite of layered double hydroxide with Graphene oxide have been synthesized via co-precipitation technique at inert atmosphere and its arsenic absorption will be further investigated under varying conditions such as pH, concentration, adsorbent loading and the time of contact.

Lastly a PSF polymeric membrane incorporating the nano-adsorbent has been prepared in the laboratory via phase inversion process for easy removal of contaminants from wastewater. Some characterizations of membrane have been carried out. The adsorption study by membrane is yet to be accomplished.

Chapter 1

Introduction

1.Introduction

Water is the most essential necessity of the mankind one cannot put a price on. But there is a very limited resource for drinkable and potable water. Though the hazardous materials that contaminate water can be occurred by some natural processes, anthropogenic activities are the main causes of the rapid increase of contamination. Due to fast industrialization and over population water resources are being polluted regularly by toxic chemicals or microorganisms which get mixed in water bodies and degrade the quality of water.

Wastewater released from chemical industries contains various hazardous organic and inorganic pollutants that are carcinogenic, toxic, mutagenic and non-biodegradable. In agricultural field, pesticides and fertilizer used by farmers may be useful to plant life but lead to serious hazards to human and animals. Sewer water carries chemicals and harmful bacteria and pathogens. Some naturally occurring minerals and gases can also contribute in water pollution.

Water contaminants can be categorized into the following types: Inorganic pollutants, organic pollutants, natural minerals, nutrients and agricultural pollutants, suspended solids and pathogens, thermal and radioactive pollutants etc.

Inorganic materials like Arsenic, Antimony, Chloride, Cadmium, Cobalt, lead, Iron, Fluoride, Magnesium, Manganese, Nickel, Nitrate, Mercury, Silica, Sulphate, Sodium, Silver, Potassium, Phosphorus, Nitrate, Phosphate, Zinc, Tin etc. which are present in the water can be considered as contaminants if their amounts cross the permissible limit. These heavy metals and other inorganic contaminants pose threat to human health and environment as a whole.

Humans suffer several health problems like respiratory diseases, cancer, cardiovascular diseases and neurological disorders due to water pollution. In rural areas mortality rate due to cancer is higher than urban areas because rural areas do not have modern water treatment facilities. People from lower economic classes are at higher risk due to improper supply of water, poor hygiene and sanitation. Pregnant women are also severely affected by this problem. Water contamination can also destroy crop production and has hazardous effect on aquatic life.

According to the information provided by CDC (Centre for Disease Control and Prevention), 780 million people in the whole world do not have access to clean water. WHO’s report suggests that by 2025, 50% of world’s population will live in water stressed area. In Asia several countries like China, Bangladesh, Nepal, Vietnam, Taiwan, Thailand and India are suffering from heavy metal contamination in drinking water. Reports show that in India Arsenic concentration (107 µg /L) in drinking water is approximately 11 times higher than the WHO’s guideline limit. Not only Arsenic, surveys have published that concentration of other inorganic pollutants like Iron, Lead, Uranium are also above the permissible limit.

Ecologists are raising concerns and various efforts have been made to reduce the intensity of this challenge by encouraging reuse, recycling and recovering water. The idea behind wastewater treatment is to develop methods to remove or reduce the amount of contaminants in water and release safe water for drinking.

There exist a number of methods to treat wastewater. The methods can be categorized into three major divisions: Physical Treatment Method, Chemical Treatment Method, Biological Treatment Method.

1.1. Physical treatment method:

This includes processes of removal of contaminants from waste water by physical forces without changing the chemical structure of the constituent material. These processes are very effective in separating hazardous material from a non-hazardous stream.

The physical processes that are commonly used are:

(i) Screening: For any wastewater treatment, screening would be the first step to retain solid contaminants found in wastewater. This method majorly separates floating solids and non-biodegradable matter that can be found in wastewater stream such as plastic, papers, tins, containers, Woods, rags etc. Screens can be categorized into three based on their opening size.

Course screen: This type of screens have opening from 6 to 150 mm. It is made off parallel wire, mesh or bars or perforated plates with openings of rectangular or circular shapes. Screens can be mechanically cleaned or hand cleaned as well. To reduce maintenance and operating problems and increase efficiency mechanically cleaned screens are designed.

Fine screens: These have openings which are less than 6 mm. They consist of wire cloth or perforated plates and used to remove fine solids. There are three types of fine screen such as static wage wire screen, static screen and drum screen.

Micro screens: These types of screens operate in gravity flow conditions and have variable low speed which is continuously back was washed. The fabrics that are used for filtration in this kind of screens have opening ranges from 10 to 35 micron and are seated on the periphery of the drums. The influent enters through the drum lined with fabric and are retained in the filtering fabric. Then they are collected by backwashing transported for disposal.

(ii)sedimentation: It is a unit operation for settling out the suspended solids and flocks in wastewater stream. This is done by lowering the velocity of wastewater below the suspension velocity to settle out the suspended particle by gravitational force. Wastewater are kept in stagnant in a large clarifier and the dissolves solids are settled at the bottom of the tank by gravity. The sediments which are found at the bottom is removed by slow moving horizon, Scrapper. But the drawback of this process is that this process is very slow and it takes a lot time to settle the suspended solid. And also TDS cannot be completely removed by this method.

(iii) Flocculation: Flocculation is one kind of sedimentation methods. But here some flocculent is added. Flocculent is generally a polymer that provides the base for settling the particles and it grows into a flock or flake which attract the contaminants out of the suspension. So, here agglomeration of particles is happening. Also using some certain physical techniques like mixing of suspension, agglomeration can be induced through flocculation. Here the particle size will increase, sub-microscopic micro flock to visible suspended particle and leads to production of large visible flocks. These are called pin flocks. Time off mixing, speed of mixing, etc are the influencing factor that determine the efficiency of flocculation process. In conventional plants flocculation process is followed by sedimentation and then filtration.

(iv) Flotation: By introducing of gas bubbles as transport medium, flotation is achieved. Suspended particulate matter is generally hydrophobic and it attach to the gas bubbles and then moves towards the surface of the solution contrary to the direction of the gravity and then it can be separated out from the water stream. To remove the surface inactive ions from any aqueous solution, some surfactant or collectors are added for ion flotation. Surfactants are generally defined as the ion which have the charge opposite to that of the metal ion to be removed from the waste water and collectors increase the natural hydrophobicity of the surface and it increases that chance of separation of hydrophobic and hydrophilic particles. Here the concentration is increased up to precipitation. So, rather than a solution it becomes a dispersion.

(v) Filtration: Membrane filtration process is a pressure driven separation process, which works by forcing the water through any porous media. When some pressure is applied to water, it is pumped through the membrane and it results in separation of undissolved or dissolved matter. In cross-flow filtration, the aqueous solution flow perpendicular to the membrane surface and only small amount of liquid passes through the membrane and collected as permeate. The concentrate is used to clean the membrane, it is circulated in loop to reduce concentration polarization. So, for this particular reason crossflow membrane is now preferred for filtration of solution that has high constant solid concentration. The relationship between the flux and the applied pressure is described by Darcy equation: $J=TMP/\mu R$, where TMP is the transmembrane pressure, J is the flux, μ is the viscosity, R is the total resistance. So, the porous media can be natural such as sand, gravel or clay or this porous media can be a membrane that are made of different materials majorly polymers. This process can produce demineralized water or partially softened water which is free from microorganisms and particulate matters. The size of the pores is generally the size of the materials which can be removed by filtration largely depends on the size of the pores in the membranes. So, there are mainly four types of filtration process based on the size of the substances it can filter from water microfiltration ultrafiltration, nanofiltration and reverse osmosis.

(vi) Centrifugation: By using centrifugal force, this process separates suspended particles or different matters from homogeneous solution. Physical properties like density, shape and size and chemical properties like viscosity and molecular weight are the deciding factors based on which this process separate particles. The working principle of this process is similar to gravity separation. But here the driving force is higher as it is resulted from the rotation of the fluids centrifugation uses centrifugal force to separate particles from the solution. It is a force which is filled by some object which is moving in a circular path. The force acts outwardly away from the centre of rotation. This process accelerates the rate of sedimentation by increasing the relative centrifugal force measures by rotation per minute.

(vii) Dialysis: In dialysis the solute migrates through a membrane that is impermeable to water. The processes can be differentiated by the driving force like pressure, concentration or electric potential difference and the type of membrane. In order to equalize the chemical potential on the both side of the membrane the impurities migrate through membrane. If the phase is removed continuously while the migration happens ,100% of the impurities will be removed. When an electric field is applied to an ion-rich liquid via electrodes between which a continuous potential difference exists, cations, move toward the cathode and anions move toward the anode. And then ions are discharged onto electrodes of the opposite sign and thus the ions are separate from the wastewater.

However, if we position a series of selective dialysis membrane between these electrodes;

- Cationic membrane will only be permeable to cations

Anionic membrane will only be permeable to anions

(viii) distillation: In this process we can separate liquids having different boiling point. Distillation is a process of converting a liquid into vapor and then condensing it back to liquid form in order to separates liquid from minerals or different liquid streams from a mixture. This separation process is based on the principle of boiling of different liquid stream at different temperature.

The mixture is fed in a distillation column and heated. Now the different component having different boiling points evaporates and recovered by condensation.

(ix) solvent extraction: Based on their relative solubilities components are separated by this process. It uses a solvent that has the ability to dissolve another compound. It is used to separate or remove some hazardous organic contaminants from wastewater smudges. Or sediments. It does not destroy contaminants. It concentrates them so that they can be removed or separated out using other technologies. Phenols crystals and other phenolic materials can be separated by using this method. Here a solvent is added in the waste stream and then the solute is removed from solvent and after that, three major operations occur. The first one is to extract solid solute from water into solvent, second one is where solute is separated from solvent and solvent is recycled in extractor.

(x) Adsorption: Adsorption for removing a wide range of compounds from wastewater or contaminated water absorption technique is used. It is mainly preferred for the removal of low concentration of non-degradable, organic or inorganic compounds that plays that are present in groundwater or wastewater or drinking and potable water. In this method, the molecules in a liquid bind themselves to the surface of any solid substance adsorbents has to have a very high internal surface area to increase the rate of absorption.

- Activated carbon is one of the most commonly used adsorbents and it is suited for removal of nonpolar compounds.
- Natural or synthetic zeolite has a very homogeneous distribution and polar binding sites they are more selective than activated carbon natural clay minerals which are used for adsorption of polar, organic and inorganic material.
- Silica gel and activated alumina are very polar adsorbent and they have large affinity for water and normally utilized to remove water from nonpolar medium
- Silicic acid

1.2. Chemical treatment methods:

In this method basically the chemical structure of the components of waste water is altered through chemical reaction to make the components less hazardous.

(i) Neutralization: Neutralization is done to adjust the pH value of wastewater stream to meet the requirements for various processing. Water which has pH of 6.5 to 8.5 is considered neutral, but when the pH is above 8.5 or below 6.5, then neutralization is needed wastewater. Water, which is acidic and contains some amount of heavy metal salt considered dangerous. So, neutralization involves two substances, of which one is acid one is base. Mixing those substance lose their properties. There are various methods of neutralization:

- By mixing acidic and basic wastewater
- By utilizing some chemical agents
- By filtrating acidic wastewater through materials which are neutralizing agent
- Absorption of acidic gases by basic water or absorption of ammonia by acidic water

The following factors effect the selection of this process
- Volume of wastewater
- Wastewater concentration
- Wastewater transportation method
- Availability and the cost of chemicals

So, neutralizing by mixing is conducted when two systems that generate acidic and basic wastewater are located nearby. No other contaminant be mixed in this wastewater in this case. Mixing is done in some large special tanks which can have mechanical agitator. Special neutralizing filters are used for achieving neutralization through filtration. Sulfuric, chlorine, nitric acid if the concentration in water below 1.5 g/L. CO_2, NO_2 and SO_2 are used for the treatment of basic wastewater but for the most cases of neutralization, a chemical agent is involved. Effluent flows into a holding tank or reserver where a pH sensor is installed. It provides the input to the pH controller device which operates the pump to inject caustic or acidic solution as required to neutralize the effluent. Then the mixer distributes the neutralizing chemical evenly throughout that tank to ensure complete and proper neutralization.

(ii) Reduction/oxidation (Redox): This method transforms toxic chemical compounds into less toxic compounds, which are less mobile or inert. Transfer of electrons from one compound to another is the basic principle of this process. Chemical redox method is used to treat residual contaminants in wastewater or groundwater as well. This process can be used to oxidize arsenic into less toxic compound, to reduce Cr(VI) to Cr(III) which is settled down as precipitation and improve separation by other methods, for oxidizing cyanide. Redox potential or ORP indicates that tendency to oxidize or reduce components in the wastewater. Some Commons oxidants and their application are:

- Oxygen: oxygen gas can be an excellent source of oxidizing power. It is used as general oxidant for aqueous waste treatment. Oxidation of Fe(II) and Mn(II) to Fe(IV) and Mn(IV), which precipitate, is a great example of redox by oxygen. It has been well established as a treatment process.
- Ozone: It is also a very good oxidizing agent and it has several advantages over chlorination. It does not live pre judicial decomposition products and it allows destruction of chelating and complexing agents.
- Chlorine: It is a powerful oxidant and it can support combustion. So it is a potential fire risk.
- Sodium hypochlorite: Sodium hypochlorite is used to store and dose chlorine.

Some common reductants and their applications are:

- SO_2: It is corrosive to metal in moist environment and it is psychologically harmful gas which has a pungent smell but, the aqueous solution of sulphites are strong reducing agent.
- Sulphur(IV): It is used to reduce Cr(VI) to Cr(III) which can precipitate .
- Hydrazine(N_2H_2): It is a strong reductant though it has some hazardous quality.
- Hydroxylamine(NH_2OH): The usage of this reductant is very limited because it is a comparatively less powerful reductant and does not form azine. .

(iii) Ion exchange: In water minerals and salts are dissociates into their constituent ions. These ions are attracted to their opposite charges. So, when the water is passed through an ion-exchanging resin hazardous cations and anions are held in the resins and non-hazardous $H^+ \ and \ OH^-$ ions are released.

Insoluble microporous resins are the main components of this process. The resins are supersaturated with loosely bound ions. Resins are mainly polymers that are capable of exchanging ions with ions present in passing solution. Some natural solids and living cells can act as resins but synthetically it is produced mainly from phenolic compounds and coal.

There are two types of ion exchanging resins; acid resin and basic resin. Acid resin contains acidic groups like –COOH, -SO_3H, and basic resin contains basic groups like –NH_3OH.

Acid resins exchange their H+ ion with other cations. This exchange happens because all the cations do not have same strength of positive charge. So, resin prefers more strongly charged ions then weakly charged H^+ ions and so hold other ions in water while releasing H+.

And same goes for anions. Strongly charged anions in the water are more likely to get attached to the resins than weaker H^- ions.

Water is passed through two large pressure vessel which contains man made ion exchanging resins. One of the vessels contains cation exchanging resins and other one contains anion exchanging resins. Acid resins exchange their H+ ions with other Cations i.e., Mg^{2+}, Ca^{2+} present in hard water.

Now in second vessel basic resins exchange their OH- ions with other anions i.e., HCO^-, Cl^-, SO_4^{2-}.

(iv) DE-chlorination: Before discharging the waste water into the environment dichlorination is done to remove the chlorine from disinfected wastewater. Most common dichlorination agent is sulfur dioxide. Other alternatives like carbon adsorption, sodium metabisulfite and hydrogen peroxide.

In water, chlorine dissolves and hydrolyze to form hypochlorite ions and hypochlorous ions which is known as free chlorine. They reacts with the organic compounds to form chlorinated organic matter. Free chlorine also combines with ammonia to form mono, di and tri-Chloramines in quantities, which are dependent on the ratio of chlorine to ammonia and nitrogen. When sulphites, salt or sulphur-dioxide are dissolved in water, aqueous sulfur compounds an oxidation state of +4 are produced. The sulphide iron reacts with free chlorine and combined form of floating precipitation.
(1) SO3-2 + HOCl → SO4-2 + Cl- + H+
(2) SO3-2 + NH2Cl + H20 → SO4-2 + Cl- +NH4+

(v) Precipitation: In this method dissolved components in the wastewater is precipitated by adding a reagent. The reagent and dissolved substance form an insoluble compound. Heavy metal ion(positive ion),as well as phosphate and sulfate ions(negative ion) can be removed from water via this method .Generally precipitation occurs in 1:1 mole means 1 mol of reagent and 1 mol of dissolved substance form the insoluble compound and precipitate. However in some case over dosage is required to removed certain matter from waste water stream. .
The formation if precipitate is a sign of chemical change where solid forms out of the solute phase and sink to the bottom of the solution. .
2 parameters are commonly used to describe the performance of the process:
(I) VRF (volume reduction factor):it the measure of the ratio of the volume of waste to be treated to the volume of the residues after the treatment. .

(II)DF (decontamination factor):It is defined as the radiation level prior to application of the process divided by the radiation level after the process is employed. It can be calculated in several ways, the value is dependent on the method used. In this case ,since the total activity discharged into the environment is the point of concern ,the DF can be calculated as :DF=total activity in feed/ total activity in effluent $=a_f v_f / a_e v_e$.
Where, a_f and a_e are the activities per unit volume of feed and effluent ,respectively And v_f and v_e are the volumes of feed and effluent, respectively.

1.3. Biological treatment method:

In this method micro-organisms are used to decompose organic waste into carbon dioxide, water or simple inorganic substance or into or simpler organic substances such as acid or aldehyde.

(i) Aerobic treatment: For the removal of BOD(biological oxygen demand) aerobic treatment is one of the most cost and energy efficient method. Here microorganisms are used. They are capable of converting complex material in the wastewater stream into a simpler one. This the water gets prepared for the further treatments. This process involves the presence of oxygen in the system. Oxygen is I produced by some aeration techniques and the oxygen helps micro-organisms to grow. These microorganisms then feed into the organic compounds in the wastewater and digest them. In this way, lower energy form of carbon compounds are produced from high energy form of carbon.

When the concentration of wastewater is high then, this treatment is preferred. So,it is generally used as a secondary treatment followed by anaerobic treatment.

(ii) Anaerobic treatment: This treatment occurs in the absence of oxygen or air. Anaerobic micro-organisms which can grow without oxygen are used here. They convert pollutants unto 'biogas' which is a combination of methane and carbon-di oxide. It is a relatively slower process.

1.4. Demineralization of water:

Minerals occurs naturally. They usually have a well-defined crystalline structure and specific chemical composition. Groundwater may pick up a variety of compound i.e. Ca, Mg, F, As, Cl, Fe while moving through rocks and soils.

There are mainly 5 processes by which demineralization of water is done:

1.4.1. Ion Exchange:

Introduction-

water minerals and salts are dissociated into their constituent ions. These ions are attracted to their opposite charges. So, when the water is passed through an ion-exchanging resin hazardous cations and anions are held in the resins and non-hazardous $H^+ \ and \ OH^-$ ions are released. Water softening is one type of ion exchange method which focus on reducing calcium and magnesium content from water. When there calcium/magnesium are present in water it is considered as ‘hard’ and this type of water decreases the efficiency of detergents in cleaning work.

So, Ion Exchange is done to recover metals from water, soften water, produce high purity of water for industrial application.

Ion exchanging resin-

Insoluble microporous resins are the main components of this process. The resins are supersaturated with loosely bound ions. Resins are mainly polymers that are capable of exchanging ions with ions present in passing solution. Some natural solids and living cells can act as resins but synthetically it is produced mainly from phenolic compounds and coal.

For softening water, the water is passed through a resin which contains Na+ ions, but when the water is passed through it the resin binds Mg2+ and Ca+ ions and release Na+ ions for making a softer water.

In case of removing all the minerals a resin which contains H+ ion is used. So H+ ion replace all the cations in the water. Then water is passed through a resin which contains OH- ions, which replace all the anions .Thus water becomes demineralized and all the H+ and OH- ions react together to produce more water.

There are two types of ion exchanging resins; acid resin and basic resin. Acid resin contains acidic groups like –COOH, -SO3H and basic resin contains basic groups like –NH3OH.

Acid resins exchange their H+ ion with other cations. This exchange happens because all the cations do not have same strength of positive charge. So resin prefers more strongly charged ions then weakly charged H+ ions and so hold other ions in water while releasing H+.

We can see in the order of affinity for cations which ones are more likely to get attracted by the resins:

Hg2+<Li+<H+<Cd2+<Cs+<Ag+<Mn2+<Mg2+<Zn2+<Cu2+<Ni2+<Co2+<Ca2+<Sr2+<Pb2+<Al3+<Fe3+

And same goes for anion. Strongly charged anions in the water are more likely to get attached to the resins than weaker OH- ions.

Order of affinity of anions:

OH-<HCO3-<Cl-<Br-<NO3-<HSO4-<PO43-<CrO43-<SO42-

<u>Procedure-</u>

Water is passed through two large pressure vessel which contains man made ion exchanging resins. One of the vessels contains cation exchanging resins and other one contains anion exchanging resins. Acis resins exchange their H+ ions with other Cations i.e. Mg2+, Ca2+ present in hard water.

2RCOOH+Ca2+ →(RCOO)2Ca+2H+

Now in second vessel basic resins exchange their OH- ions with other anions i.e. HCO3-, Cl, SO42-.

RNH3OH+Cl- →RNH3Cl+OH-

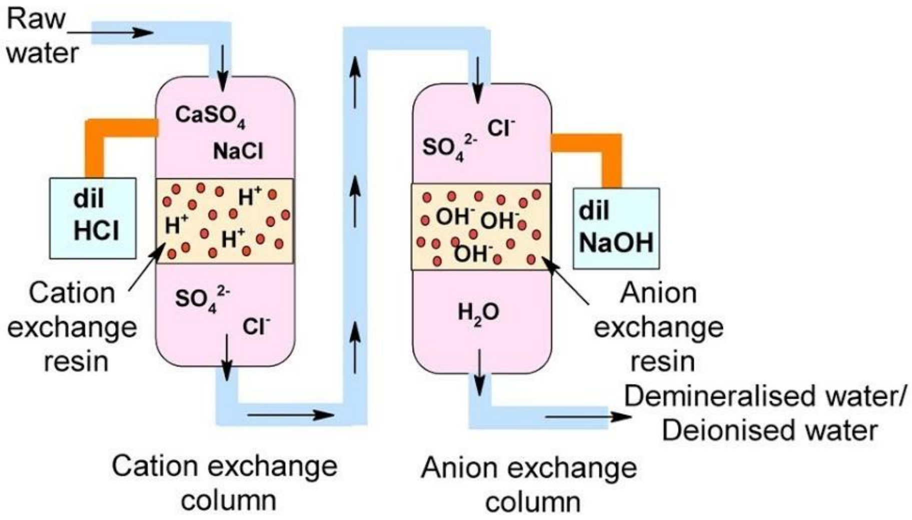


Fig1: Ion Exchange Column

<u>Recharge:</u>

Eventually the resin sites are occupied by the ions in the water and no further exchange can take place. So it is said to be exhausted and must be regenerated. Regeneration of resin means anionic or cationic functional groups are restored in the resin. This is accomplished by application of chemical reagents in the resins. There are different methods for regeneration also like co flow regeneration and reverse flow regeneration etc.

1.4.2. Electrodialysis:

Introduction-

This process involves a membrane. At a given potential by the effect of current, ions are migrated by the principle of electrochemical laws. There remain cathode and anode which attract actions and anions respectively to entrap them in semipermeable membrane. And therefore ions get separated from water and pure water is achieved.

The main component of this method is ion selective membrane. They are generally thin sheets of anion or cation exchange membranes which are installed with synthetic fibers as mechanical support. There are mainly 2 types of ion selective membranes:

CEM(cation exchange membranes): Allows positively charged ions to move across it but blocks the movement of anions. These membranes are characterized by the presence of fixed negative charge. Styrene divinyl benzene copolymer with sulfonic acid groups is an example of active sites in CEM.

AEM(anion exchange membranes): Allows the transportation of negatively charged ions but blocks actions. An example of AEM is Styrene divinyl benzene copolymer with tertiary amine compounds as active anion exchange sites.

Properties, these membranes should have:

1. high selectivity, lower electric resistance, lower water transfer
2. dimensional stability
3. resistance to chemical reactions
4. Mechanical strength to withstand pressure which is required for the operation

ED device: cell pair and stack-

An ED unit is constructed by placing some AEMs and CEMs together. It should have alternative compartments for concentrate and dilute solution and at both sides there remains electrode compartments.

When a required voltage is applied current flows through the ED stack and electrically charged solutes start to move to with respect to the electric field.

This results to the decrease of ionic solute content in the dilute compartment and enrichment in the concentrate compartment.

Repeating units of ED is called ED cell and few cell pairs to hundreds of cells together is known as ED stack.

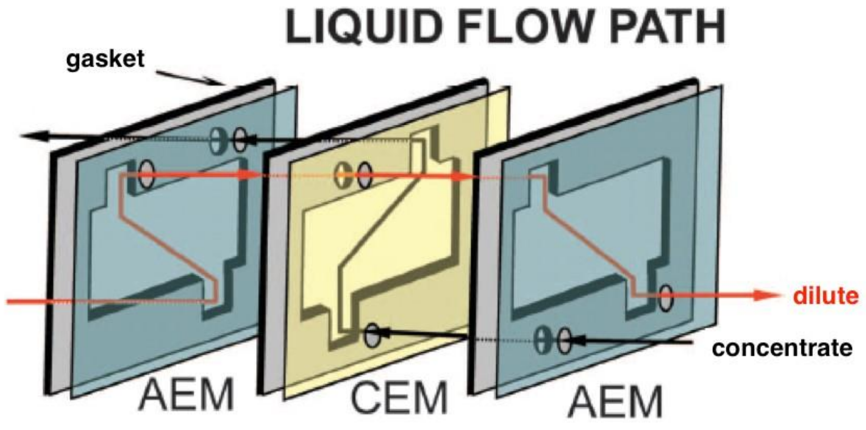


Fig2: AEM and CEM stack

Some development -

Membrane fouling is a very concerning problems on this process. There can be fouling by inorganic or organic substance.To avoid fouling there have been some developments like transport depletion, ion substitution, electro osmosis etc.Also the recent development like reverse ED has been able to increase the efficiency of the process.

1.4.3. Distillation:

Introduction-

In this process a liquid is converted into vapor and then is condensed back to former form to separate the minerals from liquid or different liquid streams. This separation process is based on the principle of boiling of different liquid stream at different temperature.

It may have many applications like:
1.desalination
2.in petroleum refining
3.to produce alcoholic beverages
4.cryogenic distillation leads to separation of air into its component
5.in chemical industry crude liquid product of chemical synthesis separation.

Distillation for the purpose of producing demineralized water is a very old purification process. In this process water is boiled and steam is cooled. When the steam is condensed, demineralized water is produced.
Though this process is effective in killing bacteria and viruses in water unlike other demineralization process but the produced DM water in this process is saturated with carbon

di oxide. And also a major drawback of this process is higher energy cost for converting water into steam is required.

Equipment needed-

Container vessel
Storage tanks
Pipes
Cooling chamber
Boiler
Condenser

There are different types of distillation plants i.e., batch distillation plant, continuous distillation plant etc.

Distillation process-

When a mixture of different compound is heated, the most volatile(have lowest boiling point) distils first, and others subsequently. The vapor in a suitable container is cooled and condensed into water. And thus, it is separated from minerals present in the surface or industrial water.

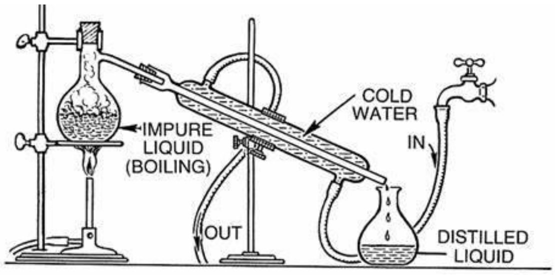


Fig3: Distillation process

1.4.4. Membrane filtration:

Introduction-

A pressure-driven separation technique called membrane filtration involves pressing water through a porous medium.

This porous medium may be composed of a membrane made of various materials, primarily polymers, or it may be natural, as in the case of sand, clay, or gravel.

High-quality demineralized or partially softened water that is free of impurities and microbes can be produced using membrane filtration.

Types of filtration –

The pore size of the membrane influences the size of the particle that can be separated by the process. There are mainly four types of filtration processes based on the size of the substances it can filter from water:

(a)Microfiltration (MF):

The pore size of a microfiltration membrane is around 0.1 micron. Utilizing the pressure as operation force a microfiltration membrane separates suspended particles and microorganisms from the process liquid when passed through membrane, eliminating all bacteria. Both the cross-flow and dead-end modes are typically used to operate it.

In cross flow the raw solution flows along the membrane surface with only a small portion of liquid passing through the MF membrane as a permeate. The concentrate is circulated in loop to reduce concentration polarization continuously and is used to clean the membrane. For this reason ,cross flow membrane is preferably applied for the filtration of liquids having a high solid concentration.

As a result of the liquid flowing perpendicular to the membrane surface during dead end filtration, the trapped particles get aggregated on the membrane surface and created a filter cake. Throughout the filtration process, the filter cake gets taller, which reduces permeate flux. Therefore, in this form of operation, the membrane needs to be cleaned frequently.

(b)Ultrafiltration (UF):

To produce potable water from raw water ultrafiltration can be used as it can remove macromolecules and particles. The pore size of this kind of membrane is 0.01 micron. This process is similar to micro filtration process as their pore sizes are different they operates in different pressure ranges and seperated different compounds. But both of the membranes separate pollutants by size exclusion method. It can be operated in cross flow or dead end mode. UF is generally used as a pre-treatment of Reverse Osmosis.

The relation between the applied pressure on the solution and flux through the membranes is most commonly described by Darcy equation:

$J=TMP/\mu R$

(c)NanoFiltration (NF):

The pore size of a nano filtration membrane lies in nano range. This membrane can remove nearly all viruses, most of the organic molecules and a variety of salts. Nano filtration is used to soften the water as it can remove divalent ions.

This membrane also works on the principle of size exclusion. Though it removes some of the compounds that only RO can remove. Though where , NF removes monovalent ions ranging from 50% to 90% , RO removes nearly all monovalent ions.

(d)Reverse osmosis (RO):

This process generally removes most of the dissolved salts(ions), particles, colloids, bacteria from the water. It is the best suited method for demineralization .The pore size of RO membrane is around 0.0001 micron.

Osmosis is a natural phenomenon in which solvent tend to migrate from low concentrated solution to the high concentrated solution through the semipermeable membrane.

In osmosis without any external force if a semi permeable membrane is placed between two compartments while in one compartment the concentration of salt is more than the other, the water will pass through the membrane from high saline water to lower saline water to reach the equilibrium on both sides.

In equilibrium the pressure difference generated between the two compartments due to the increased volume of water in one compartment known as osmotic pressure.

In RO process we need to apply a pressure to the more concentrated solution so that water flows in reverse direction into the less contracted solution through the semipermeable membrane. The external pressure applied has to overcome the osmotic pressure.

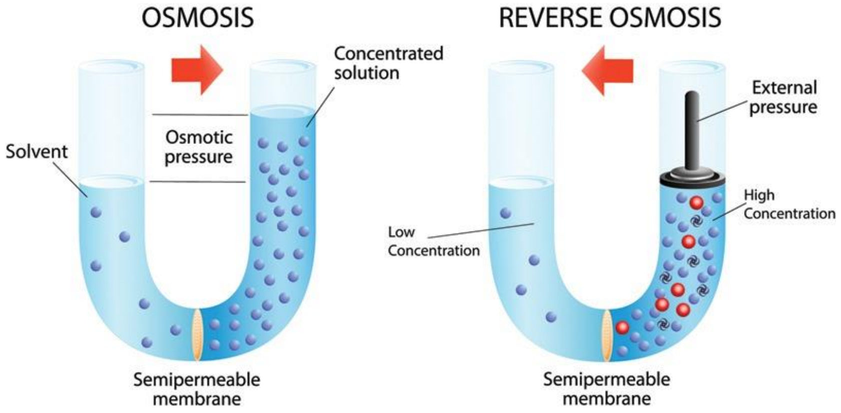


Fig4: RO mechanism

In practice, RO is applied as a cross flow filtration process. A high-pressure pump is on the salt side to force the water to flow across the membrane, leaving most part (95%-99%) of the dissolved salts behind the stream.

Chapter 2

Aim and Objective

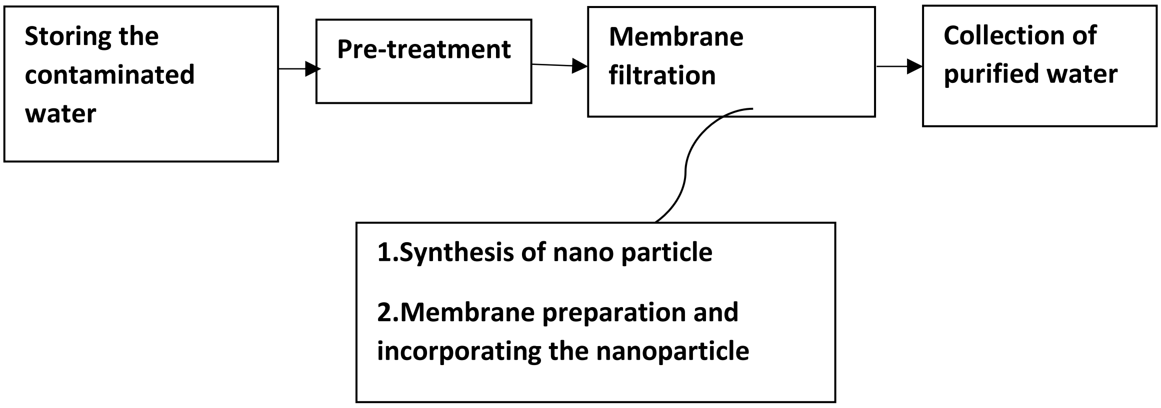
2.Aim and Objective

2.1. Aim:

Now, among the existing water treatment methods RO is the most efficient method for demineralization giving high removal. But the capital and operating cost of RO is also very high because high pressure is required. The objective of this research work is to replace RO membrane with UF membrane, giving high efficiency for Arsenic removal but operating in lower pressure range.

Here the aim is to synthesize a novel type absorbent, LDH (Layer double hydroxide) Nano particle and incorporate it in the UF membrane to increase the removal efficiency.

In water arsenic mainly occurs as arsenate As(V) ($H_2AsO_4^-$,$HAsO_4^{2-}$, AsO_4^{3-}) or Arsenite As(III)($H_2AsO_3^-$,$HAsO_3^{2-}$, AsO_3^{3-}) .LDH can absorb these ions by anion exchange method.



2.2. Objective:

1. Preparation of LDH nanoparticle
2. Characterization of Nano particle
3. Adsorption experiment for arsenic and other heavy metal from aqueous solution
4. LDH incorporated mixed matrix polymeric membrane fabrication
5. Membrane characterization
6. Adsorption experiments of mixed matrix membrane

Chapter 3

Literature Review

3.Literature Review

3.1. Layer Double Hydroxide:

Layer double hydroxides are two dimensional layered nanomaterials, belong to anionic clay family. The general formula of LDH is as follows: $[M_{1-X}^{2+}M_X^{3+}(OH)_2]^{X+}(A^{n-})_{X/n}$.m$H_2$O, where M^{2+} and M^{3+} represents metal cations having the valency of 2 and 3 respectively, such as $Mg^{2+}$and Al^{3+}in the layers of the LDHs. A^{n-} is interlayer anion, x is the molar ratio of (M^{2+} /M^{3+}) and m stands for the number of water molecules between the laminates. LDHs occur in nature as the by-products of some metabolism activities of certain bacteria, as minerals, and also in some man-made context i.e., results of corrosion of some metal objects.

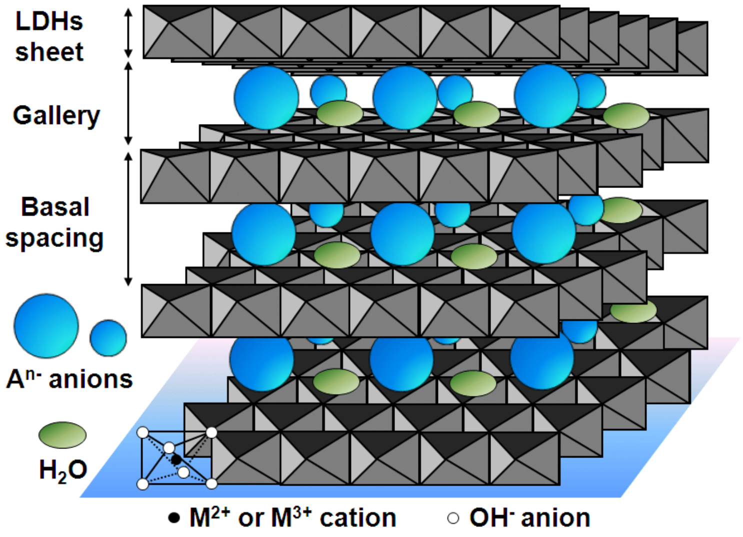


Fig5: LDH structure

3.1.1. Structure :

LDHs have Brucite(Mg$(OH)_2$) like structure. In Brucite hydroxide ions form hexagonal close packing in which Mg^{2+} ions occupy alternate octahedral sites. So hydroxide layers become neutral. These layers are stacked upon each other and bonded by van-der-waals force of attraction. If some trivalent ions substitute some divalent ions isomorphously in brucite structure, then it forms positively charged mixed metal hydroxide layers $[M_{1-X}^{2+}M_X^{3+}(OH)_2]^{X+}$. The intercalation of anions in interlayer region balances the residual positive charge in the hydroxide layers. Now the structure resembles layer double hydroxide structure. There remain water molecules in the interlayer region and they stabilize the crystalline structure of layer double hydroxide. (1)

The basal spacing in the LDH can vary from metal to metal.

(i)Metal cations:

Depending on their radii there can be different possible types of metal cations. If their ionic radii are similar to that of Mg^{2+}, it has been observed that $M^{2+} and\ M^{3+}$ react with hydroxyl group and form covalent bonds. Commonly found divalent metal ions in the layers are : Mg^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Cu^{2+}, Cd^{2+}, Ca^{2+} etc. and the trivalent metal ions which are commonly found in the layers are $Al^{3+}, Cr^{3+}, Fe^{3+}, Mn^{3+}, Ga^{3+}, In^{3+}, La^{3+}, Ru^{3+}$ etc. (1)

(ii)Interlayer Anions:

When M^{2+} ions are substituted by M^{3+} ions by Isomorphous Substitution and the layer becomes positively charged in LDH structure, anions get in the interlayer region to neutralize the positive charge. There remain weak forces among the interlayer anions. Under specific circumstances, by overcoming the applied force between layers, an anion can be inserted reversibly into the interlayer region without causing the original structure to be damaged.

The interlayer spacing can be altered through ion exchange between the interlayer anions of LDH and inorganic, organic anions, or coordinate compound. LDH's capacity for anion exchange depends on the nature of the interlayer anions. Low valent anions can be exchanged with ease while polyvalent anions are simple to insert into the interlayer zone.

Order of ability of anion exchange :

$$CO_3^{2-} > SO_4^{2-}, OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$$

Due to its weak association with the metal hydroxide layer, NO_3^- is the easiest to exchange with other anions, while CO_3^{2-} is the most difficult because of its significant affinity for the layer. (1)

3.1.2 LDH synthesis routes:

Depending on the type crystallinity, of cations in the laminates, the intercalating anions, the targeted physicochemical features (such as phase purity, crystallinity, porosity, shape, optical and electrical characteristics), there are various ways to synthesise LDH.

(i)Co-precipitation: One of the simplest and most popular way to make LDH is by co precipitation. By adding bases such as aqueous NAOH and KOH, LDH is created using this approach from an aqueous solution that contains bivalent and trivalent metal cations.

Initially, in the right proportions, aqueous solutions of both divalent and trivalent metal ions are taken into a reactor. The co-precipitation of both metal ions from the aqueous solution is accomplished by simultaneously adding base at controlled temperature while vigorously mixing.

Based on the nature of the metal ions, the pH of the reaction medium is maintained constant within the range of 7 to 10.

Finally, the precipitate is dried after being separated from the basic media. (2)

(ii)Urea Hydrolysis:

In this approach, an aqueous solution of the chosen metal ion that must be present in the LDH and urea in the stoichiometric molar ratio is subjected to hydrothermal treatment for two or three days at a temperature somewhere between 100 and reflux. The homogenous pH is elevated during the heating process of urea hydrolysis, which frequently results in the monodispersed particle of hydroxide and carbonate. This urea hydrolysis-based precipitation process yields LDH with a high crystalline content and a restricted particle size dispersion.

We shall use the synthesis of Mg-Al LDH as an example. In water, magnesium and aluminium nitrates and urea were dissolved. The molar ratio of Mg and Al was set at 2. Then the mixed aqueous solution of the metal salts and urea is placed in a stainless steel jacketed Teflon inner tank. The vessels were then inserted in an oven and heated to a target temperature of 90 to 120 degrees Celsius while being maintained there for 24 to 96 hours each treatment. Following this, the vessels were cooled down to room temperature. Then the products were air dried after being repeatedly centrifuged and rinsed with DI water. The end result of this urea technique has typically been reported as LDHs including carbonate anions. The temperature and reaction time were successful in controlling the particle size. It was shown that larger particles were produced by reactions that took place over longer time periods and at lower temperatures due to the slower urea hydrolysis at those temperatures.(2)

(iii)Hydrothermal crystallization: An aqueous suspension of two metal oxides one of trivalent metal ion M_2O_3 and another of divalent metal ion M_2O is subjected to hydrothermal treatment in a pressure vessel in an elevated temperature for few hours to few days depending on the requirement. During the process M_2O_3 crystallizes on the presence of M_2O which acts as a crystallizing agent.

Mg-Al LDH can be prepared in this method. MgO and Al_2O_3 is mixed is aqueous phase and subjected to hydrothermal treatment . MgO and Al_2O_3 are prepared by calcining Mg$(NO_3)_2$ .6H_2O and Al$(OH)_3$ at 600^oC for some hours.The aqueous suspension of the metal oxides is then put in to an autoclave and subjected to hydrothermal treatment at 110^oC for 5 to days .Then the product is centrifuged and washed and dried properly .to prepare Mg-Al-NO_3 LDH sodium carbonate or sodium bicarbonate is added in the mixture .(2)

(iv)Sol-gel method: This method is relatively new and fewer studies have been reported on this method. It leads to greater chemical homogeneity as a result of molecular level mixing of the reactants. In this approach, a metal hydroxide transition employing HCL or HNO_3 sol gel occurs as a result of the strong acid hydrolysis of the necessary metal precursors, such as metal-based alkoxides or acetyl acetonides, in an ethanol-water system.

Metal nitrates Mg$(NO_3)_2$.$6H_2O$ and Al$(NO_3)_3$.$9H_2O$ dissolved in 50 mL of deionized water are used as starting materials to create the Mg-Al LDH specimens using the sol-gel procedure. A 0.2 M solution of citric acid is added to the prepared combination. The resulting mixture is then agitated for an additional hour at 80^oC. In the end, 2 mL of ethylene glycol is added under vigorous mixing at 150^oC. The transition from sols to gels took place during the solvent's evaporation. The created gels are dried for 24 hours at 105^oC. Then gels were heated at 650^oC for 4 hours to produce the MMOs. By reconstructing MMOs in deionized water at 80^oC for 6 hours, LDHs were created.(2)

(v)Salt-oxide method: This approach involves electrically reducing nitrate ions to hydroxide ions, which raises the pH of the solution and causes the LDH film to precipitate.. This method is used to produce LDH film of desired film thickness, morphology and film density.
This approach is explained using the synthesis of Zn-Al LDH as an instance. Aqueous solutions containing Zn$(NO_3)_2$.$6H_2O$ salt as the Zn^{2+}source and Al$(NO_3)_3$.$9H_2O$ the Al^{3+} source were used to electrodeposit Zn-Al LDH films. DI water was utilised to prepare the solutions that were used in this work. When needed, NaOH and HNO_3 were added to the solutions to change the pH of the solution. An undivided cell with a traditional three-electrode arrangement was employed. Without stirring, cathodic depositions were performed using -0.8V ≤ E ≤ -1.8V at ambient temperature. The resulting film was then gently dried with a stream of nitrogen gas after each deposition and properly washed with deionized water. (2)

(vi)Mechanochemical synthesis: Preparation of LDH via solid state reaction is an good alternative to slurry and solution based methods. In this scenario, the chemical reaction is induced by mechanical energy. The initial material is ground using a mortar and pestle or just a ball mill employing mechanical forces like compression, shear, and friction.
A few examples of LDH synthesis in this method is discussed here;
To prepare a Li-Al LDH ,a mixture of Li OH-H_2O and Al$(OH)_3$ is grinded for 2-3 days and then the mixture is purged with water saturated under nitrogen media.Through mechanical mixing the LDH is formed.In this case water is important to promote interparticle diffusion.
Another example of LDH synthesis can be the preparation of Mg-Al LDH. Hydrated salts of $Mg(NO)_3$ and $Al(NO)_3$ is mixed and grinded and NaOH pellets are added as. LDH intercalated with $(NO)_3$ is the product of the synthesis.
So, it is clear that the mechanochemical synthesis method involves two steps –Dry grinding followed by wet grinding. (2)

3.1.3. Absorption phenomenon of heavy metals from waste water by LDH :

(i)LDH absorption properties:

- Absorption capacity: It is defined as the absorption of heavy metal ions done in one cycle. Total absorption in the entire life cycle is given very little attention.

- Recyclability: Considering the environmental issues and the cost impact recyclability of LDH is one of the critical properties.
- Stability: The temperature, pH, types and quantity of ions is variable ,so stability and selective absorbability are very important.

2 Effect of composition and structure of LDH on the absorptive properties:

(ii) Effect of valence, type, proportion of metal ions: The removal efficiency of LDH is directly influenced by the kind, quantity, and valence of metal ions in the LDH layers. Adsorption efficiency has been found to be higher when the adsorbing material's diffusion path is three to four times bigger than the adsorbing molecule. Larger diffusion paths and better heavy metal ion removal from wastewater are produced when the ratio of metal ions in the laminates is high.

It has been reported that Co/Fe LDH shows high adsorption capacities for Cr(VI) and methyl orange. The Co/Fe LDH was synthesized with various ratios of Co and Fe (2:1,3:1,4:1) using a coprecipitation method. The Co4Fe LDH shows a higher adsorption rate than other LDHs and had maximum adsorption. The pore size of Co4Fe LDH was much higher than Co2Fe and Co3Fe LDH.

Both Ni/Fe LDH and Mg/Al LDH had results that were close to this. The outcomes show that there were two mechanisms involved in the adsorption of Cr(VI): I anion exchange between the interlayer anion and the Cr(VI) oxoanions and (ii) surface complexation between the oxyanions of Cr(VI) and the hydroxyl groups of LDH. So it tis safe to say that, when LDH is produced using various metal ions, the adsorption effect varies. (1)

(iii)Effect of the anions: The types of interlayer anion can be categorized into the following groups:

- Inorganic anions i.e. $CO_3^{2-}, SO_4^{2-}, OH^-, Cl^-, Br^-, NO_3^-, I^-, SO_3^{2-}, S_2O_3^{2-}, ClO_3^-, IO_3^-, PO_4^{3-}$
- Organic anions i.e. dodecyl sulfonate, adipic acid, succinate, p-hydroxybenzoate, benzoate, dibenzoyl-D-tartaric
- Complex anions i.e. $Fe(CN)_3^{6-}, Ru(BPS)_3^{3-}, Fe(CN)^{4-}, Zn(BPS)_3^{4-}$
- Polyoxometalates i.e. $Mo_7O_{24}^{6-}, V_{10}O_{28}^{6-}, PW_{11}CuO_{39}^{6-}$
- A layered compound $[MgAl(OH)]^-$

Due to its flexible interlayer space and abundance of interlayer exchangeable anions, LDHs have the ability to adsorb polar molecular species as well as toxic anions that pollute water. Adsorption is directly impacted by the kind of interlayer anions. Low valent anions can be exchanged and polyvalent anions can be inserted easily.

Mg-Al LDH with different interlayer anions are prepared and the adsorption capacity for Cr(VI) of different LDHs are examined. It has been seen that removal efficiency is effected by the type of interlayer anion, following the order,$NO_3^- > Cl^- > SO_4^{2-}$.The reason behind this behavior is that NO_3^- is weakly bound to the metal hydroxide layer and the interlayer spacing is larger, as a result $NO_3^-$is easily exchanged with other anions.And in case of SO_4^{2-},it has two negative charge and is very strongly bound to the metal hydroxide layer.

(iv)Effect of surface groups and charge: Due to the isomorphous replacement of metal ions, LDH layers display surface charges. In LDH laminates, there are a lot of hydroxyl groups. The surface groups and charges have a significant impact on the ability of LDH to adsorb heavy metal ions.

To remove the ions Cu^{2+} and Zn^{2+} , Mg-Al oxide-calcinated LDH (CLDH) was developed. The highest adsorption capacities of the CLDH for the ions Cu^{2+} and Zn^{2+} were reported to be 422.08 mg/g and 508.21 mg/g, respectively. Through hydration and ionisation actions, CLDH enables the release of hydroxide ions from the LDH's surface. As a result of this event, the CLDH is now more effective at removing heavy metals from solution. The OH-ions and heavy metal ions now form octahedral sheets with shared edges and a positive charge. Since the water molecules and anions entered the LDH to restore the structure. Cu-O-Mg and Cu-O-Al peaks were discovered using XPS characterization, proving that $Cu^{2+}, Mg^{2+}, Al^{3+}$ and OH^-ions are mixed in the surface of the CLDH. (1)

(v)Effect on adsorption process condition:

a.Contaminant anions: Anions with smaller radii and higher charge are more easily inserted into the interlayer region of the LDH.

An experiment of As(III) uptake by Zn-Al-SO_4 LDH without competing anion was done in three different condition and the adsorption capacities were found to be 69%,61% and 54%.At the same time when the experiment was done for As(VI) ion the result was found to be 88%,86% and 82%.

As(VI) has smaller radii and higher valence state compared to As(III) ,and as a result diffusion of AS(VI) ion into LDH occur rapidly .And hence the adsorption capacities of As(VI) was higher than that of As(VI). The impact of the bivalent and the monovalent ion on the uptake on As(VI) : $CO_3^{2-} > SO_4^{2-} and\ Cl^- > NO_3^-.$

When removing As(VI), bivalent ions have a greater inhibitory effect than monovalent ions. In order to remove heavy metal ions with LDH, it is therefore important to pay closer attention to the inhibitory effect of contaminant anions and to choose an LDH with appropriate interlayer anions that match the radii and charge of both the contaminant anion and the target heavy metal ions.

b.pH: LDH is mostly alkaline and the pH value has a great effect on the adsorption capacities of the LDH.LDH at low pH is eutectic and the structure can change .The metal ions exists different ionic forms in different pH which effect the removal of heavy metal.

For the removal of $Cu^{2+}$with the $Fe_3O_4 - C - Mg - Al$ LDH it has been found that when the pH increases from 2 to 6 the adsorption increases but as the pH goes up from 6 to 12 the adsorption capacities decreases. When the pH range is 4 to 7 the removal is around 94% and then it decreases.

c.Temperature: Temperature has two main effects on the adsorption of the heavy metal ions. As the temperature increases the viscosity of the solution decreases, and the diffusion of heavy metal ions in the surface and the pores of LDH accelerates. In addition, changing the temperature will have effect adsorption capacity of the specific adsorbent .

A study has reported that the adsorption capacity of Cr(VI) by $Fe_3O_4 - C - Mg - Al$ LDH increases from 120.5 mg/g to 152mg/g if the temperature is increased from 15^0 to 40^0 .And again if the temperature is increased above 40^0 the adsorption capacity decreases rapidly.

d.Type of heavy metal ions: Heavy metal ions can be both anions and cations. Cation i.e.$Pb^{2+}, Cu^{2+}, Ni^{2+}$ are adsorbed via isomorphous replacement and the anions like $HCr_2O_7^+, HAsO_4^{2-}$ are removed by anion exchange procedure with the interlayer anion or via complexation reaction with hydroxyl groups in laminates or interlayer. The isomorphous replacement depends on the radii of the ions where as in the anion exchange depends on the charge and radii of the heavy metal ions.(1)

3.1.4. Removal mechanism:

(i)Ion Exchange: As there exists very weak bonding between the layers and the interlayer anions, anion Exchange occurs frequently in LDHs. Anion Exchange is the most effective and prominent mechanism for removal of metal ions from water. It has been observed that some metal ions exist in water as oxyanions. So when the contaminated water is passed through LDH the interlayer anion in LDH is replaced by the metal oxyanions present in water. It has been observed that basal spacing and exchangeability of anions are the two key factors that control anion exchange. As it has been discussed before Low valent anions can be exchanged with ease while polyvalent anions are simple to insert into the interlayer zone.

Order of ability of anion exchange :

$$CO_3^{2-} > SO_4^{2-}, OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$$

Due to its weak association with the metal hydroxide layer, NO_3^- is the easiest to exchange with other anions, while CO_3^{2-} is the most difficult because of its significant affinity for the layer. When heavy metal anions are close to interlayer galley, spatial hindrance will effect their intercalation. If the basal spacing is large then the ion exchange capacity has been seen to be larger. It has been observed that some ions having smaller radii face little spatial hindrance. So, when they are captured in the interlayer region of the LDH then they draw the adjacent layers closer preventing heavy metal ions from entering. So, it is crucial to control and immobilize basal spacing.

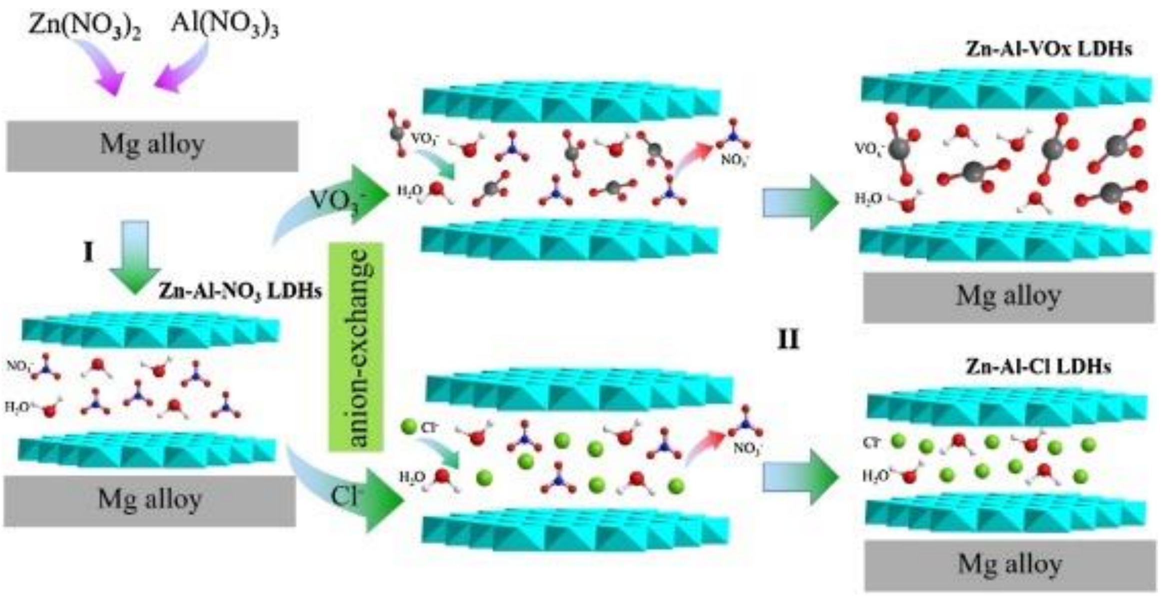


Fig6: Anion Exchange

(ii)Surface Reconstruction/ Memory Effect: Memory effect is a very unique and notable feature of LDH. LDH has ability to recover their original layered structure, after thermal decomposition, when immersed in the solution containing anions. Through surface reconstruction it recovers its original layered structure as well as absorb ions from contaminated water.

Many studies have shown that calcined LDH (LDO) has greater adsorption efficiency than pristine LDH for heavy metal anions. The possible reasons behind this can be: (i) the dihydroxylation of LDH results in enhancement of specific area and formation of mesoporous material. (ii) Rather than exchange inserting is more direct and efficient. The transformation of LDOs to LDHs with the hydration reaction of metal oxides is considered as the hydrodynamic spontaneous process. Calcination temperature has a great effect on memory effect. (5)

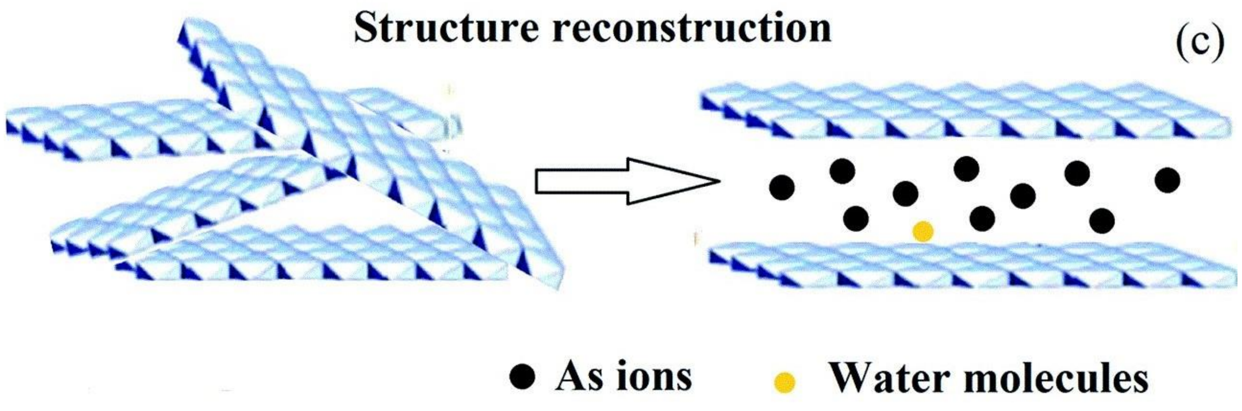
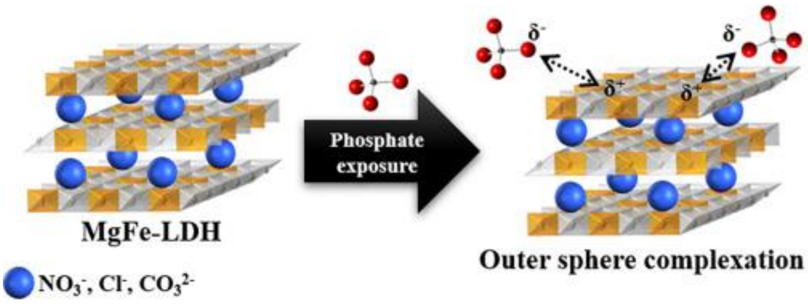


Fig6: Adsorption by surface reconstruction

(iii) Surface adsorption: Surface adsorption of metal anions by LDH can be achieved through physical or chemical adsorption. The interaction of heavy metal anions with surface hydroxyl groups (-OH), including the hydrogen bond and the complexation effect has been studied. As the -OH bonded with M^{3+} is more polarized than -OH bonded with M^{2+} , it co-ordinate with metal anions rapidly and more intensely. Other oxygen containing functional groups i.e., -COOH, -C-O, -C=O can interact with metal ions more closely in aqueous solution, LDH can be functionalised with materials containing those groups to enhance the adsorption capacity.

As for complexation, Both inner sphere complexation via chemical bonds and outer sphere complexation via ion pairs may occur. Based on the parameters i.e., active site density, surface protonation/deprotonation constant, specific area, point of zero potential are the factors that are responsible for adsorption characteristics of LDHs on heavy metal anion adsorption and their complexation mechanism under different experimental conditions. (6)



3.1.5. Examples of heavy metal removal from water by LDH:

At the beginning of the 20th century scientists identified LDH as minerals and then prepared as synthetic material later on. Successful structural determination was done in late sixties and early seventies. Because of its unique structure and tunable composition, interest has been growing leading to the application of this material in various field.

In 1999, M. Lehmann, A.I. Zouboulis and K.A. Matis studied removal of metal ions dilute aqueous solution by different types of inorganic sorbent material. For this study magnesium mineral, hydrotalcite(LDH), Goethite, Titanium-di-oxide, activated carbon and ferric hydroxide were examined for adsorption of Chromate anions and Zinc cations from dilute aqueous solution using batch adsorption experiment. As LDH is mainly anion exchanger, it gave high removal for Chromate anions compared to other sorbent materials. And for zinc cations high sorption was not expected. But in this paper, scientists have discussed that as $Mg_6Al_2(OH)_{16}.CO_3.4H_2O$ LDH has $(CO_3)^{2-}$ and $(OH)^-$ anionic groups which can act as proton acceptor, if the alkalinity of the aqueous solution can be increased using some base then precipitation of cationic metal species occurs and it increase the overall removal of cationic species. LDH gave nearly 100% removal for chromate anions at pH 4 or higher. But for zinc cations it gave about 40% removal.

Bhowmik et al., 2005 published a study on arsenic removal from groundwater using Layer Double Hydroxide as adsorbent. For this purpose a Mg-Al-Cl LDH was synthesized via coprecipitation method and then the adsorption experiments were carried out. The total arsenic content was reduced considerably after treating with LDH. Arsenic removal efficiency was increased considerably if pre oxidation treatment is done. It indicates that the removal for As(V) is much greater than As(III). As arsenic remain in aqueous solution as oxo-anions the interlayer anions got exchanged with $H_2AsO_4^-$,$HAsO_4^{2-}$ giving high adsorption for arsenic ions. Here in this experiment a little amount of H_2O_2 and HCl have been added in the aqueous solution to ionize As(III) to $H_2AsO_4^-$ or $HAsO_4^{2-}$.

In 2009 Sujata Mandal et al. studied the adsorption behavior of Selenite [Se(IV)] ions by LDH materials. Zn-Al, Mg-Al, Zn-Fe LDH were synthesized with varying composition and evaluated for Selenium adsorption in aqueous media. Highest Selenite removal was noticed for Zn-Al LDH with composition M^{2+}: M^{3+}=3. Uptake was nearly 60 mg/g. With this composition Mg-Al LDH showed removal of about 48 mg/g and Zn-Fe LDH showed removal of about 15mg/g. In this study, researchers have fitted the data in both Langmuir and Freundlich isotherm. Langmuir model gave a better fit for the isotherm data.

In 2007 A. Nakahira et al. published a paper on synthesis of LDH type clay substituted Ni and Fe ion for arsenic separation from aqueous solution. Ni-Fe LDH was synthesized via coprecipitation method with composition M^{2+}: M^{3+}=2. This study shows that Ni-Fe LDH gives high adsorption of As ions. A comparative adsorption study shows that the conventional Mg-

Al LDH has no affinity towards As ions. Though it was well known that LDH has great ability to anion exchange Kang et at., reported that due to the presence of $(CO_3)^{2-}$ ions in high quantity inside the LDH structure, As adsorption is inhibited. But in case of Mg-Fe or Ni-Fe ions ion-hydroxide remains in the brucite like structure of LDH in large amount. It contributed towards the better adsorption of arsenic. Further the change in interlayer spacing and layer spacing by incorporation of Ni or Fe ions can be the reason of greater affinity of LDH towards Arsenic.

In 2008, Teruhisa Hongo et al. studies and investigated synthesis of sulfate intercalated Zn-Fe LDH by coprecipitation method and adsorption of several harmful anions like chromate, borate, fluoride, selenate, arsenate, phosphate. Where Zn-Fe LDH shows phosphate, chromate and selenate adsorption of about 100%, 91% and 97% respectively, whereas Mg-Al LDH adsorbs only about 20% of the phosphate. Both LDH shows negligible amount of fluoride ions adsorption. In LDH adsorption occurs by two mechanisms: anion exchange and surface adsorption. Surface adsorption is faster because it involves strong interaction (Coulomb force) between negative ion and positive external surface. Surface adsorption process depends on variable charge density, whereas anion exchange depends greatly on intercalated anion type. The strong interaction between Positive layer and $(CO_3)^{2-}$ inhibits anion exchange. So typical Mg-Al LDH intercalated with $(CO_3)^{2-}$ ion exhibits lower adsorption.

In 2010, Yunfeng Xu et al. studied removal efficiencies of Arsenate and Phosphate ions by Mg-based and Ca-based layer double hydroxide materials. Two types of Mg-based LDHs, Mg-Fe and Mg-Al and two types of Ca-based LDHs, Ca-Al and Ca-Fe were prepared. Cl intercalated Mg-Al LDH showed excellent capture of arsenate ions from aqueous solution. The initial concentration of arsenate was taken 0.15 mg/L and after treating with LDH it becomes as low as 0.007mg/L. As per the isothermal data the maximum adsorption amount of arsenate by Mg-Fe was 16.4 mg/g after 18 hours. Isotherm data was fitted in Langmuir Model. The adsorption behaviour of arsenate by La based LDH was totally different. It suggested a Freundlich model. Ca-Fe LDH showed about 98% removal of arsenate ion. Ca-Al LDH exhibited adsorption efficiency of nearly 160 mg/g for phosphate ion.

In 2009 Liang et al. published a report on pb(II) uptake by Mg-Fe LDH. Sorptive kinetics at various initial concentration of Pb(II) and LDH loading was studied. This report shows that the initial rate of sorption was very rapid and it was followed by a slow approach to equilibrium. Pseudo second order model and double exponential model can describe the sorption kinetics. As per the isotherm study, it was seen that with the increasing initial concentration of Pb(II) the uptake also improved. For 395 mg/L of Pb(II) concentration, Mg-Fe showed an uptake of 869 mg/g. LDH surface has protonated hydroxyl group which may form outer surface complexes with heavy metal cation via electrostatic interaction. But it was not the case in this study. Scientists concluded that surface-induced precipitation was the reason behind Pb(II) uptake.

In the paper entitled “Nickel–iron layered double hydroxide (LDH): Textural properties upon hydrothermal treatments and application on dye sorption” Fatiha Saiah et al. pointed out that LDH can be used for dye removal also. A sorption kinetics study of Evan’s Blue on Ni-Fe LDH was carried out and it was seen that EB removal percent was increased with increasing contact time. Due removal of nearly 100% was observed.

In 2009 Wang et al. investigated the effect of surface charge density and interlayer anion orientation for arsenate removal. Mg-Al-NO_3 LDH with varying Mg/Al ratio of 2:1, 3:1 and 4:1 were prepared using a constant pH coprecipitation method. The maximum adsorption for these LDHs noticed were 1.56, 1.08 and 0.36 mmol/g respectively. The low adsorption by 4:1 can be described by the fact that arsenate ion had low access to the interlayer spacing, so arsenate adsorption occurred only on the external surface of the material. In 4:1 LDH the interlayer anions are parallel to the hydroxide sheets and in 2:1 or 3:1 the anions remain in perpendicular positions to the hydroxide sheets, so that they can be replaced easily by other anions, relative to their counterpart with a horizontal orientation. Thus if we compare the arsenate adsorption, 2:1 and 3:1 show greater removal than 4:1.

Competitive adsorption between Fluoride and Arsenate on Mg-Fe Calcined LDH was studied by Dongjuan Kang et al. in 2013. Batch experiments were conducted under various condition i.e., M^{2+}/M^{3+} ratio, initial concentration, calcination temperature, solution pH, contact time and competitive adsorption. This study found that Mg-Fe CLDH with a M^{2+}/M^{3+} ratio of 5, calcined at 400^{o}C and at pH 7 had the maximum adsorption capacity of 50.91 mg/g and 50.24mg/g for fluoride and arsenate. For LDH Mg/Fe ratio had a very negligible effect on the adsorption of ions but for CLDH this ratio had a great impact on the adsorption capacity. This study established the fact that CLDH gives greater adsorption than LDH. Because in LDH there remains a strong interaction between carbonate ion and positive layer but after calcination the layered crystalline structure get destroyed and amorphous phase of magnesium iron mixed metal oxide was formed, and also BET surface area was increased. The calcination temperature also effected the adsorption. LDH calcined at 400^{o}C had the highest removal. At lower calcination temperature magnesium iron mixed oxides can not be formed, so that there exists a temperature range where stable phase of $MgFe_2O_4$ spinel and MgO can be formed and the hydrotalcite-like structure can not be reconstructed.

In 2013, Wen et al. reported a Mg-Al LDH and Graphene Oxide nanocomposite for efficient removal or arsenic from groundwater. The nanocomposites with varying GO amounts were prepared via hydrothermal process. A maximum adsorption capacity of 181 mg/g was observed for LDH/GO nanocomposite containing 6% of GO. The kinetics suggest a second-order model for adsorption behavior.

3.1.6. LDH based membrane fabrication:

LDH-based membranes can be classified into the following categories based on the available literature:

(i) LDH supported membrane: LDH is supported on a membrane in this type of membrane for simple separation and improved stability.

(ii) Nanocomposite or mixed matrix membrane: LDH nanoparticles are inserted into the polymer matrix to improve permeability, selectivity, and mechanical strength (Ly et al., 2020).

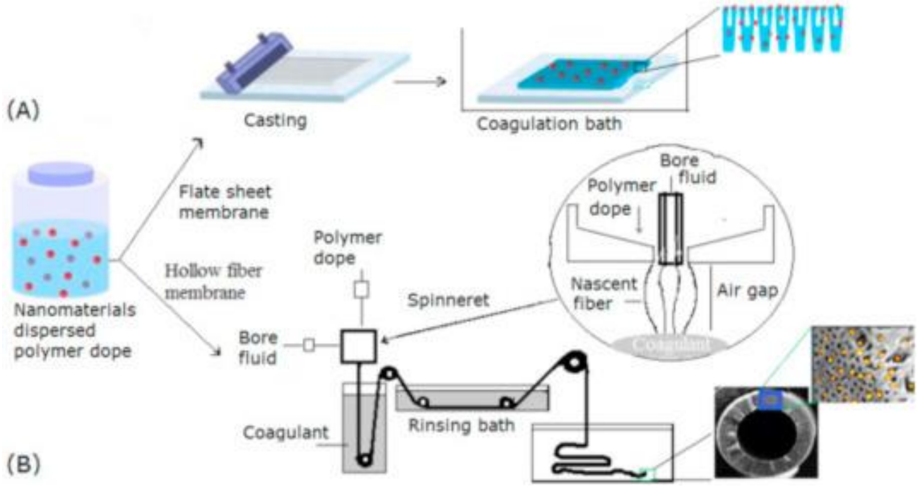
Fabrication of LDH-based membranes can be done using a variety of methods. Phase inversion, interfacial polymerization, vacuum filtering, covalent dip coating, in situ growth, and the utilization of oil-water-based two-phase systems are all typical techniques. Each method is given a brief summary. (31)

(i)Phase Inversion: For the manufacture of membranes, phase inversion is a popular process. This is a method of converting liquid-phase membranes to solid-phase membranes in a controlled manner. Precipitation from the vapour phase, controlled evaporation, thermal phase separation, or immersion precipitation are all methods for achieving phase inversion membranes. Immersion precipitation is a common technique that involves dissolving a polymer or polymer mixture in a suitable solvent and then casting it on a support layer. After that, the sample is immersed in a coagulation bath containing a separate solvent. Solvent exchange causes precipitation to occur. Before the casting step in MMMs, the nanomaterial is dispersed in the polymer solution and becomes part of the membrane structure. Nanomaterials (NMs) can also be generated in situ during the casting process in the presence of the solvent. Pore size and distribution are affected by the presence of NMs. The size, loading, and kind of NMs, as well as how they interact with the polymer, determine the membrane's performance. NMs, depending on their type, can increase membrane qualities such as hydrophilicity, anti-fouling, and anti-microbial activity.(32)

Another approach for making LDH-based MMMs used vapour induced phase separation and phase-inversion precipitation. A certain amount of LDH NPs was fully distributed in a binary solution comprising PEG/DMAc in this process. For a few hours, the solution was swirled and sonicated. To obtain a polymeric solution with the desired polymer concentration, weighed quantities of polymers were added to each mixture. It was then stirred for several hours at a specific temperature. The dope solution was then degasified for several hours at a specific temperature. The flat-sheet MMMs were then cast on a glass frame using a casting knife with a 300 m air gap. After that, the polymer solution was evaporated for 30 seconds at room temperature before being soaked in a deionized water coagulation bath under the same conditions. The membranes were stored in a deionized water tank after phase immersion precipitation.(33)

Another typical approach for membrane fabrication is interfacial polymerization. In NF and RO, it is commonly used to synthesize active layers of membranes. The interfacial polymerization process of 1,3-Phenylene diamine (MPD) in the aqueous phase and 1,3,5-Benzenetricarbonyl trichloride (TMC) in the organic phase, utilizing PSf UF membrane as support, produced Zn–Al LDH modified polyamide NF membranes. Thin film nanocomposite (TFN) RO membranes with cationic and anionic nanosheets were prepared using Montmorillonite (MMT) and LDH as additives.(34)

Fig8



(**ii)Vacuum filtration:** The membrane is coated with the polymer utilizing various ways in this method. A membrane, for example, can be submerged in a polymeric solution. After that, a vacuum filtration assembly filters the desired coating/modification substance through this membrane. To make GO/LDH/PDA/CA nanocomposite membrane, self-assembled GO-LDH suspensions were filtered via PDA/CA membrane. Similarly, Fe-cage intercalated Co–Al LDH dispersions were filtered via a vacuum-assisted assembly through a hydrolyzed PAN UF membrane. The resulting LDH/Fe-cage composite membranes were dried for 24 hours at 40 degrees Celsius.(35)

In situ growth of LDH on ceramic tubular substance: The urea hydrolysis approach was used to develop Co-Al LDH in situ on the tubular Al2O3 substrate. $Co(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$, urea, and NH_3F were dissolved in 500 ml deionized water (molar ratios for Co:Al:urea = 3:1:10) and then transported to a Teflon-lined stainless-steel autoclave. The Al_2O_3tube was immersed in the precursor solution for a period of time at a temperature of 80 - 120^{o}C. (10 - 18 h). The resulting Co-Al LDH composite membrane was carefully washed with deionized water after cooling to room temperature to eliminate the dispersed particles on the surface. The Co-Al LDH composite membrane was then allowed to dry at ambient temperature.(36)

(iii)Electrospinning: A polymer is normally dissolved in a suitable solvent in this process. A suitable method is used to add the needed amount of nanomaterial, such as LDH, to this solution. A spinneret is used to feed the electrospinning solution at a high voltage, and membrane fibres are collected over aluminium foil support on a rotating metal drum. After that, the membrane is vacuum dried to remove any remaining solvent or moisture. Figure 5 depicts the electrospinning arrangement. This method was used to make an EDTA-intercalated LDH/PAN membrane.(37)

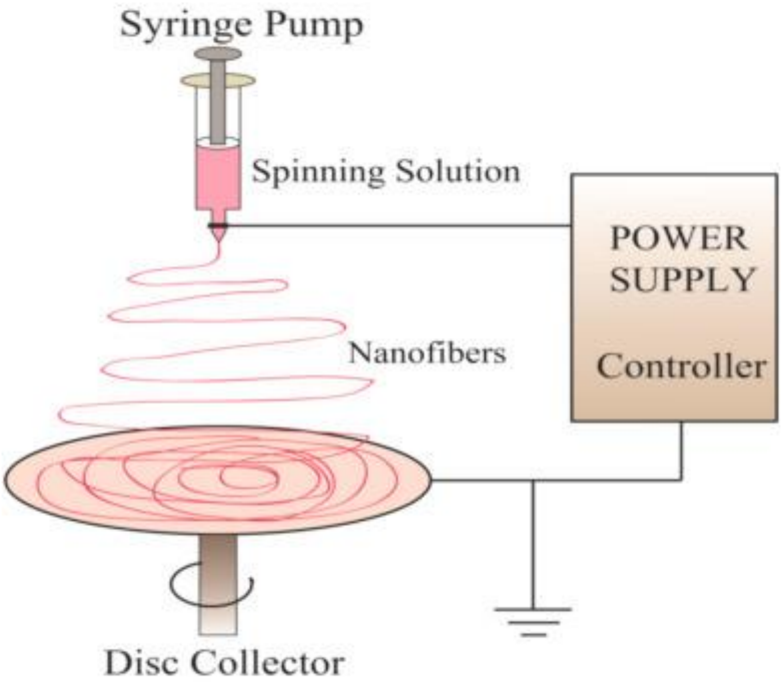


Fig9: Membrane fabrication by electrospinning

<u>(iv)Covalent dip coating:</u> Another frequent method for modifying membranes is to dip coat them. A PVDF membrane was functionalized utilizing a covalent dip-coating approach after it was produced using non-solvent phase induced phase separation. On methacrylic acid grafted membranes, amine-terminated silica NPs and amine-terminated LDH NSs were functionalized at the same time (Ma et al., 2020). Figure 6 shows the step-by-step approach. The goal of this synthesis was to create a membrane that was both superhydrophilic and somewhat oleophobic.(38)

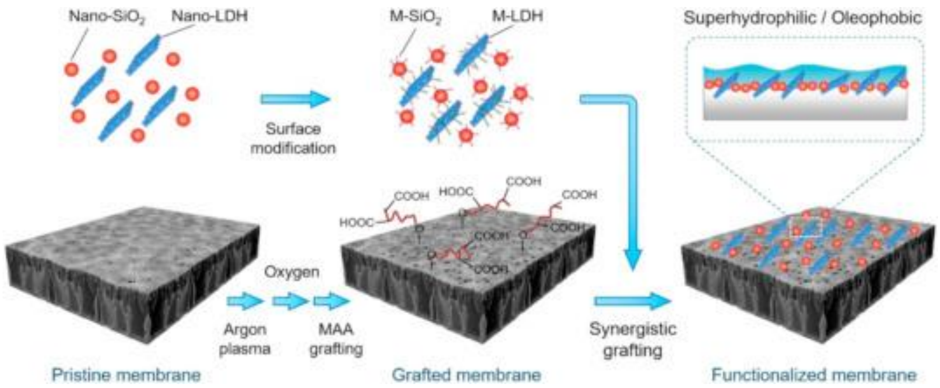


Fig10: Membrane fabrication by covalent dip coating

3.1.7. Application of LDH based membrane in inorganic matter separation:

Application of LDH based membrane for removal of inorganic anions like Phosphate, fluoride, arsenate, arsenite and metal cations like magnesium, copper, chromium is a potential method for wastewater treatment.

A phase inversion technique was used to manufacture a mixed matrix membrane based on integrating exfoliated Mg–Al–Fe LDH layers into polyethersulfone for the adsorptive removal of phosphate and fluoride ions from water. Exfoliated LDH-based membranes have a higher phosphate ion adsorption capacity than non-exfoliated LDH-based membranes. The phosphate adsorption was unaffected by chloride and sulphate ion interference. The membrane also demonstrated adequate fluoride ion adsorption capability. The presence of Fe in LDH facilitates the replacement of intercalated anions due to its large radius and low charge density, which can weakly hold the anions. The membrane performed excellently under dynamic settings and had a high reusability potential. By incorporating additional species into the interlayer gaps of LDH, it is possible to improve the replacement of intercalated anions, and this property can be employed in the treatment of anions. Anions can be treated with this feature.(39)

By intercalating chelating chemicals in the LDH, the selectivity for metal ions can be enhanced. Cu (II) was adsorpted from wastewater using an EDTA intercalated Mg–Al LDH/PAN membrane, for example. The Mg–Al LDH/PAN membrane was used in this study, and the characteristics of its two primary components were exploited. Mg–Al LDH/PAN has a large surface area, which makes separation easier and reduces the likelihood of aggregation, while EDTA adds selectivity against Cu (II) ions. With a concentration range of 0.6 to 40 mg/L, Mg–Al LDH/PAN membranes had a maximum adsorption capacity of 120 mg/g.(40)

The phase-inversion method was used to make a PES/LDH blend flat sheet membrane, which was used to remove fluoride ions from aqueous samples. The membrane has a 2.63 mg g1 adsorption capacity and could be regenerated with 0.1 M NaOH. However, when regeneration times increased, a modest decrease in adsorption capacity was noted.(41)

For the removal of Cr (VI) from wastewater, an LDH/Eggshell membrane bio-composite was prepared. LDH was grown in situ using ESM as a template. The intercalated carbonate ions were replaced with chloride ions when the composite membrane was treated with a combination of NaCl/HCl. The adsorption capacity of the Mg–Al–Cl– -LDH/ESM composite was higher than that of ESM and Mg–Al–CO32– -LDH/ESM composite. The removal efficiency was over 90%, and equilibrium was reached in less than 30 minutes. For some metal ions, replacing intercalated anions with appropriate equivalents may improve removal efficiency.(42)

An electrospinning method was used to create a Mg–Al LDH/PS fibrous membrane. It was used to remove Cd (II) from aqueous samples via adsorptive removal. The exchange of Mg (II) ions with Cd ions was primarily responsible for the membrane's removal effectiveness (II).

The interchange of divalent LDH ions with divalent pollutant ions is a key feature of our research. This aspect could be examined further for other types of divalent ions.(43)

Cu2+ and MB were removed from wastewater using an LDH/GO/PVDF composite membrane. Electrostatic interactions between positively charged LDH layers and negatively charged GO layers created the LDH/GO composite. Vacuum suction filtration was used to load this compound onto the PVDF membrane. Because the manufacture of this composite membrane does not require the use of organic solvents, it can be deemed environmentally friendly. The addition of LDH to the GO sheet was said to improve the interlayer gap and the composite's hydrophilicity. The pure water flux was greatly increased with the addition of LDH content, while the contact angle was reduced. For a longer period of time, the composite membrane showed an improved and consistent clearance rate of Cu2+ and MB.When exposed to an ultrasonic bath, the LDH/GO/PVDF composite membrane outperformed the GO/PVDF membrane. The rationale for increased stability Electrostatic interactions, complexation, and hydrogen bonding between LDH and GO were found to be responsible for the LDH/GO/PVDF composite membrane. Electrostatic interactions, complexation, and hydrogen bonding between LDH and GO were found to be responsible for the LDH/GO/PVDF composite membrane.(44)

Chapter 4

Methodology

4. Methodology

4.1. Materials: Magnesium Nitrate, Aluminium Nitrate, Manganese Nitrate, Cupper Nitrate, Ferric Nitrate, Nickel Nitrate, Graphene oxide, NaOH pellets, De-Ionized water, Nitrogen Gas

4.2. Synthesis of LDH

- The following types of LDH were synthesized in laboratory via coprecipitation method
    1. Mg-Al LDH
    2. Mn doped Mg-Al LDH
    3. Cu-Al LDH
    4. Mg-Fe LDH
    5. Ni doped Mg-Fe LDH
- LDH-GO nanocomposite
    1. Cu-Al LDH/GO
    2. Mg-Fe LDH/GO

Procedure:

. Mg-Al LDH: Magnesium Nitrate and Aluminium Nitrate salt were taken in the ratio of 2:1. 100 ml aqueous solutions (0.2 mol Mg salt solution and 0.1 mol Al salt solution) were prepared for both salts. Then the solutions were mixed by magnetic stirring. Another solution containing Sodium Hydroxide was prepared. The base was added in the salt solution dropwise under vigorous mixing. When the basic solution dripped in the salt solution local precipitation can be seen. To remediate that it is suggested to add base dropwise under vigorous mixing. When the pH of the solution reaches to 10 the addition of basic solution was stopped. Then the mixture was kept on magnetic stirrer for 24 hours for maturation. After 24 hours the precipitation is centrifuged and washed with DI water thoroughly. Then the precipitate was taken in a petri dish and dried in vacuum oven at 60^{o}C for 24 hours. And lastly it is crushed using a mortar and pastel.

Mn doped Mg-Al LDH: The synthesis procedure of Mn doped Mg-Al LDH is quite similar to the pristine one. Only difference is that an aqueous solution of Manganese Nitrate is also prepared. In the salt solution mixture the salts are taken in following quantity Mg: Mn: Al =2:2:1 (0.64 mol, 0.64 mol, 0.32 mol).

For Cu-Al LDH synthesis, initially two solutions were prepared. 1st solution comprised of $Cu(NO_3)_2.3H_2O$, $Al(NO_3)_3.9H_2O$ in the molar ratio of 2:1 and 2nd one comprised of 2 M NaOH aqueous solution. NaOH solution was added dropwise into the 1st solution under vigorous mixing until the pH level reached 10.7. This NaOH solution was acted as precipitating agent.

Liquid was stirred for 24 hours and then the precipitate was centrifuged. Lastly it was dried and crushed.

For the synthesis of Mg-Fe LDH salt solution comprising of $Mg(NO_3)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$ in the molar ratio of 2:1 was prepared by mixing the precursor salt into DI water by magnetic stirring. This solution was added dropwise by using burette in a 2.4 molar NaOH solution under vigorous mixing. The pH was maintained at 10. The solution was kept under mixing for about 24 hours and then the precipitate was centrifuged and dried. The reaction was conducted in N_2 atmosphere to avoid intercalation of any carbonate ion. Nitrogen gas was bubbled the whole time reaction took place.

The Ni doped Mg-Fe LDH synthesis was done the same way as the previous one. Additionally the $Ni(NO_3)_2.6H_2O$ was added in the salt solution in the molar ratio of Mg: Ni: Fe=2:2:1.

Fig11: LDH synthesis by coprecipitation

For preparing LDH/GO nanocomposite LDH and graphene oxide were taken in 2:1 ration to make an aqueous solution. Then the mixture was subjected to probe sonication. After that the product was collected via centrifugal process and oven dried at 60°C.

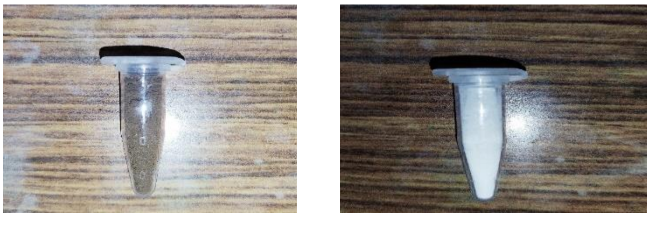


Fig13: Mn doped and pristine Mg-Al LDH

4.3. Characterization of LDH:

X-ray diffraction analysis was conducted to determine the crystallographic information of the material. XRD analysis works on the principle of Bragg's law:$2d\sin\Theta=n\lambda$ [Where; d is spacing between diffracting planes, Θ is incident angle, n is an integer, λ is the beam wavelength]. It was done by using Cu K-α radiation (λ=1.5Å) in the 2Θ ranges of 5^0 to 80^0 for the powdered sample.

Thermogravimetric analysis (TGA) of Cu-Al LDH powdered sample is done in the temperature range of 35^0C to 950^0C.

Micro-morphology of Ni doped Mg-Fe LDH was obtained by using Scanning Electron Microscopy(SEM).

Fourier transform infrared spectroscopy(FTIR) of sample is carried out to identify the chemical bonds present in the sample. It creates a sample profile by producing infrared absorption spectrum.

4.4. Adsorption Experiments for As(V):

To perform adsorption experiments, a series of Arsenate ion solution, having varying concentrations of Arsenate (from 0.1 ppm to 100 ppm) were prepared from an arsenate salt. As a typical batch experiment, adsorbent is added (0.5 g/L loading) into the solutions and stirred magnetically for some particular duration. Next the adsorbents are filtered from the solutions. The initial and final concentrations of Arsenate are measured by ICP-OES instrument.

Experiments have been carried out to study the effect of initial concentration of adsorbate, pH, temperature, time, adsorbent loading on the adsorption capacity of the nanomaterial.

- Ci: initial conc. of Arsenate solution
- Ce: Equilibrium conc. of arsenic in solution
- Qe: Equilibrium adsorption amount/adsorption capacity

$$Qe=\frac{Ce-Ci}{Dosage\ of\ adsorbent}$$

4.5. Membrane preparation: Mixed matrix membranes can be fabricated through various different strategies. Here I have used Phase Inversion procedure for the synthesis of the membrane. The phase inversion membranes, here, have been achieved by immersion precipitation method. In this method, we have to dissolute polymer or some polymeric mixture into a suitable solvent. We have used Polysulfone (PSF) as polymer and N-Methyl-2-Pyrrolidone(NMP) as solvent. First , we have dispersed LDH nano particles into the solvent through sonication for 30 mins ,then Polymer is added into the solution. Then the mixture is casted on a support layer. Then, it is submerged into a coagulation bath containing the nonsolvent. In my case the nonsolvent is water. Due to solvent and nonsolvent exchange, precipitation takes place The combination of mass transfer and phase separation effect the membrane structure. The presence of LDH nano particle in the membrane effects the pore size and distribution.

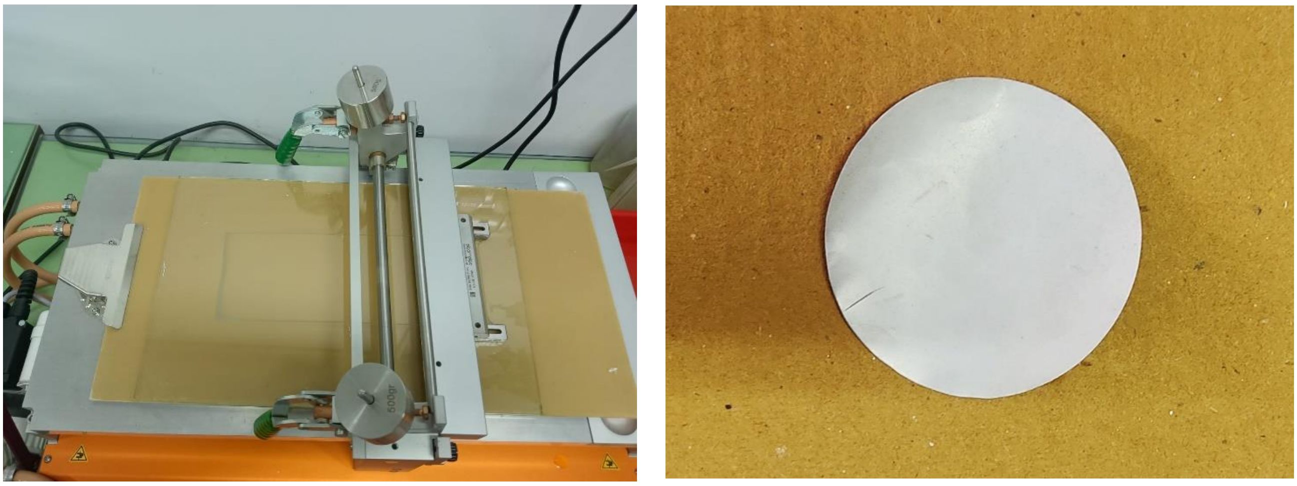


Fig 13: Membrane Casting and prepared membrane

4.6. Membrane characterization: Compaction study was conducted with DI water to get steady flux. Initial permeation was observed at pressure 4.5 bar. Compaction was done at 6 bar.

Contact angle was measured to check if the membrane is hydrophilic or hydrophobic.

SEM images were taken of membranes.

FTIR spectroscopy for dry membrane was done.

Chapter 5

Result and Discussion

5. Result and discussion

5.1. XRD:

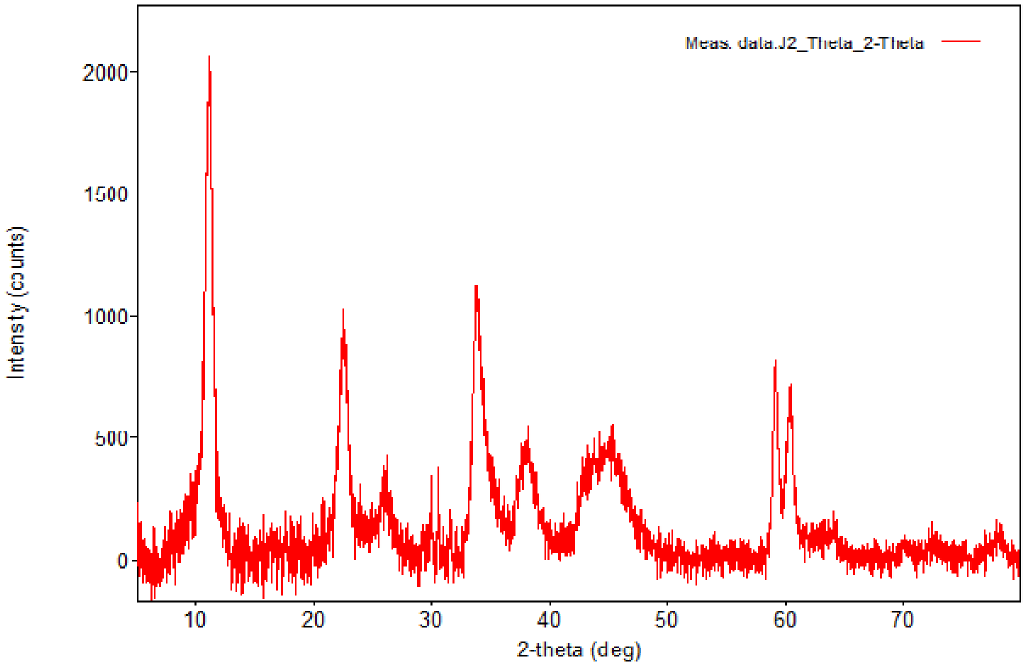


Fig 14: XRD pattern for Mg-Fe/GO nanocomposite

The crystallinity of the material is descried by the sharp peaks of the XRD plot. The peak in the XRD plot at 2Θ=11.1^{0} strongly suggests the characteristic reflection of GO when in conjugation with Mg-Fe LDH. Peaks at 2Θ=60^{0} is characteristic of layer double hydroxide structure. Also the lattice distance at 11.1^{0} is 7.96nm, at 22.4^{0} is 3.98nm, at 33.75^{0} is 2.65, at 37.87^{0} is 2.37nm, at 45.1^{0} is 2nm and at 60^{0} is 1.53nm. This XRD plot confirms the formation of Mg-Fe/GO nanocomposite having a highly crystalline hexagonal structure. The split peak at 33.75^{0} suggests the plot is comparable to existing XRD patterns of Nitrate-intercalated LDH.

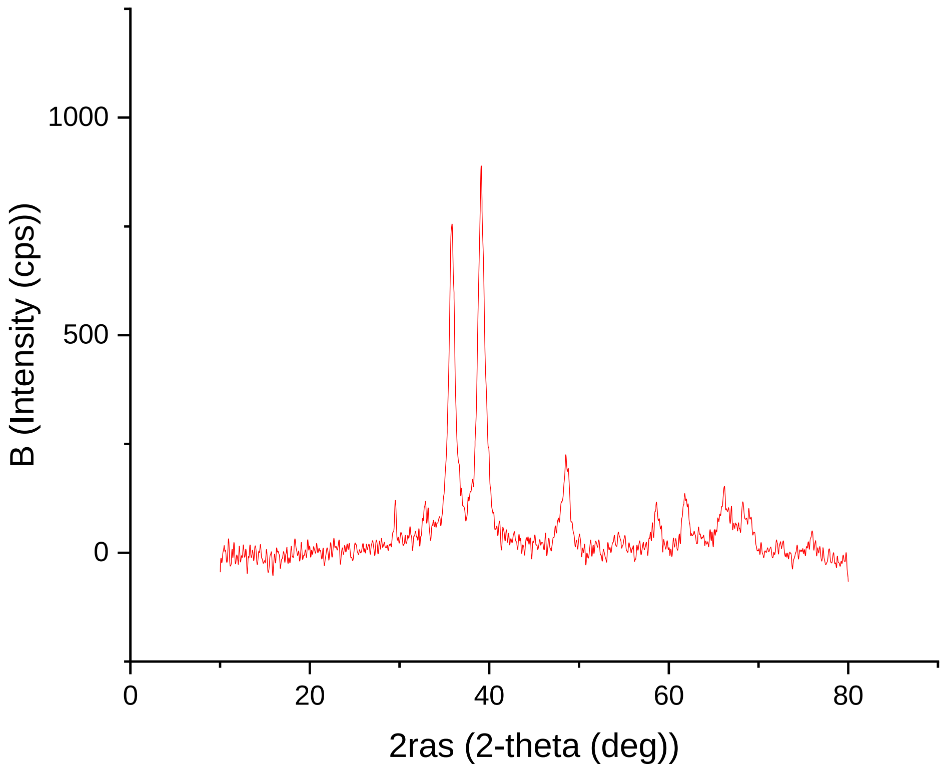


Fig15: XRD pattern for Cu-Al LDH

Diffraction patterns exhibited at 2ϴ=10.2, 20.5, 31.3, 33.6, 35, 40, 51 suggests the formation of layered double hydroxide structure of Cu and Al. The sharp peaks confirm the crystalline structure in LDH. At 2ϴ=60^{0} there exists a peak which denotes the layered hexagonal plate like structure of LDH.

5.2. TGA Analysis:

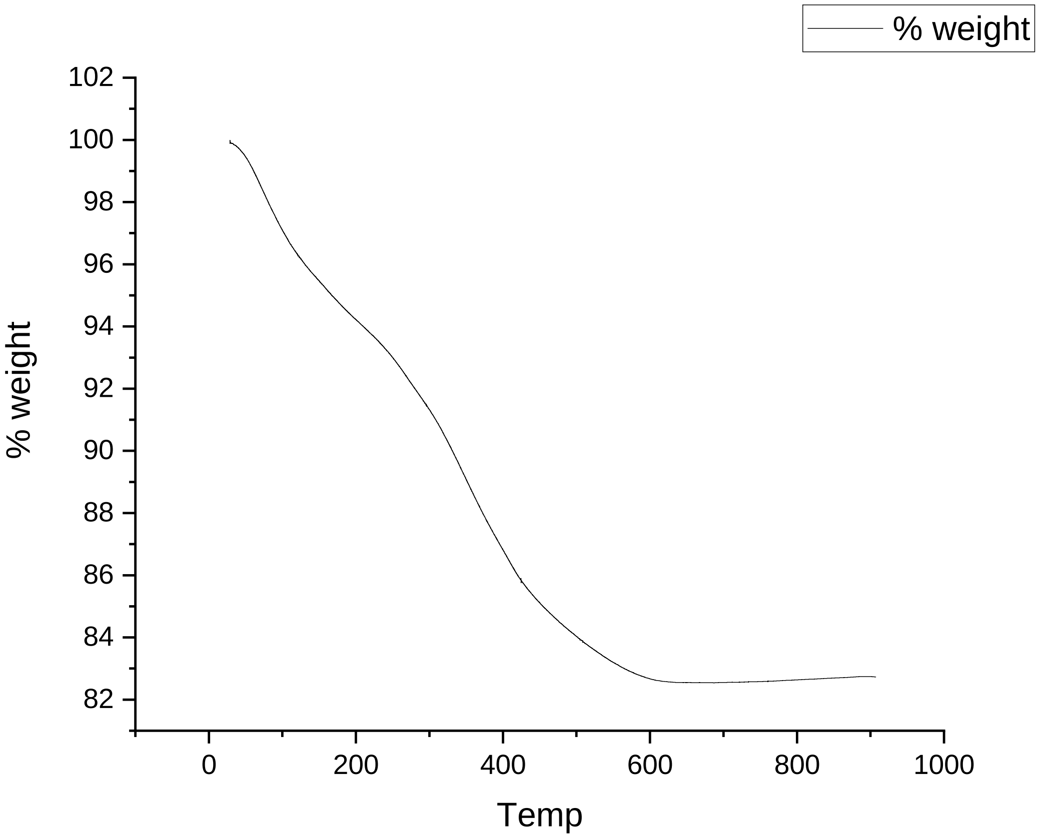


Fig16: TGA data for Cu-Al LDH

The thermogravimetric analysis of Cu-Al LDH is comparable with the previous TGA data of LDH like material. The curve suggests an initial weight reduction between initial temperature and 200°C which is caused by evaporation of water molecule which exists in the interlayer region by physisorption. Between 200°C and 450°C, another weight loss is observed. It is caused by the dihydroxylation of cationic layers and reduction of nitrates to nitrites. Further decomposition of hydroxyl groups and nitrate decomposition contributes the wight loss beyond 450°C. Further increase in temperature from 450°C to 950°C causes complete dihydroxylation of Cu-Al hydroxide layers and decomposition of nitrates. At a temperature beyond 600°C the layered structure of LDH collapses and forms of new crystalline phase.

5.3. SEM:

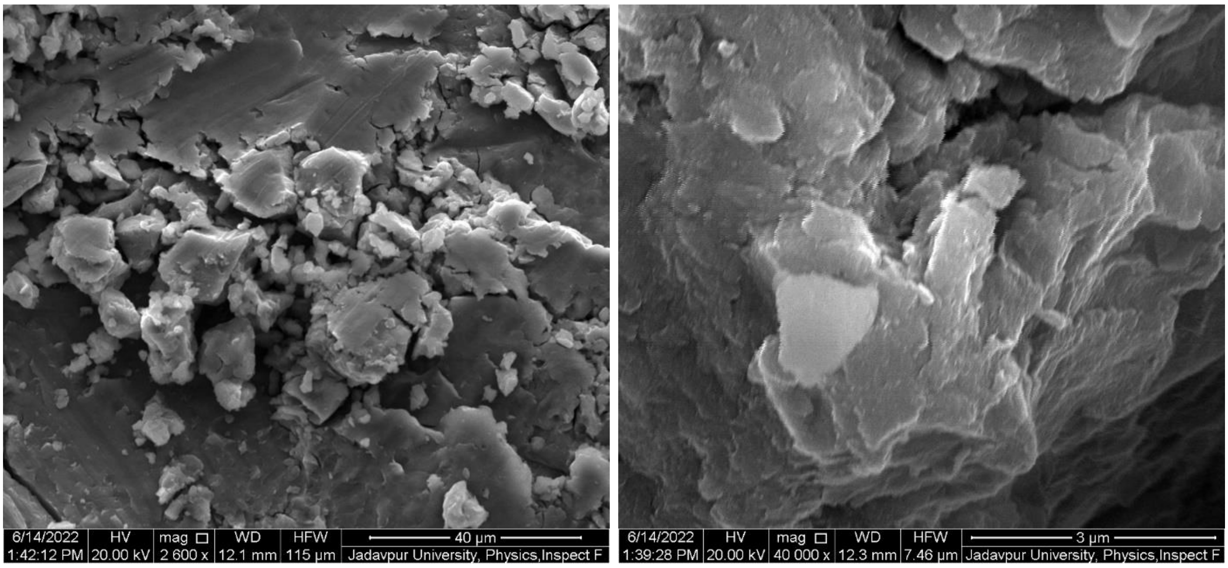


Fig17: SEM images of Ni doped Mg-Fe LDH

Scanning electron micrographic images are shown here. LDH has hexagonal plate like structure and is crystalline. But in the image plates are not visible separately, they are stacked upon each other. This is because LDH has the strong affinity for agglomeration. To reduce the chance of agglomeration different methods and techniques can be applied i.e., exfoliation, ultrasonication etc.

5.4. FTIR:

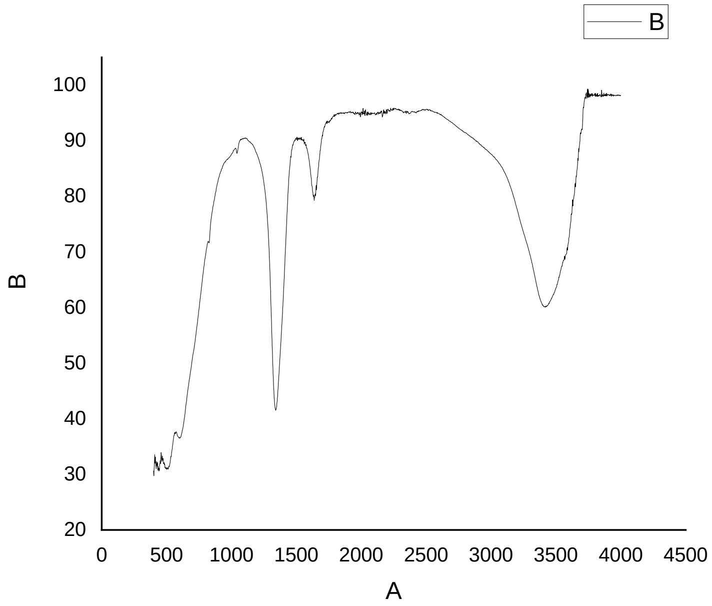


Fig18: FTIR of Ni doped Mg-Fe LDH

The characteristic absorption band around 1400 cm^{-1} noticed in the IR spectrum due to the presence of NO_3^- group. The strong absorption band at 3441 cm^{-1} observed in the plot was attributed to O-H stretching of interlayer water and metal-hydroxides. This is due to the formation of hydrogen bond with the interlayer anion and in the cation surface. The absorption band observed in lower frequency region (<800°C) suggests the vibration of lattice i.e., O-M-O vibration at 571cm^{-1} and M-O-H vibration at around 450cm^{-1}.

5.5. Adsorption Isotherm:

A comparative adsorption study between Mg-Al LDH and Mn doped Mg-Al LDH was carried out for As(V).

Experiment No.	Ci(mg/L)	Ce'(mg/L)	Ce(mg/L)
1	144	127	110
2	25	16.54	10
3	12	7.8	4.8
4	4.5	0.998	3.9
5	2	1.889	1.67
6	0.5	0.432	0.401

[Where Ci= Initial arsenate conc., Ce’: final conc. after treating with pristine Mg-Al LDH, Ce: final conc. after treating with Mn doped Mg-Al LDH]

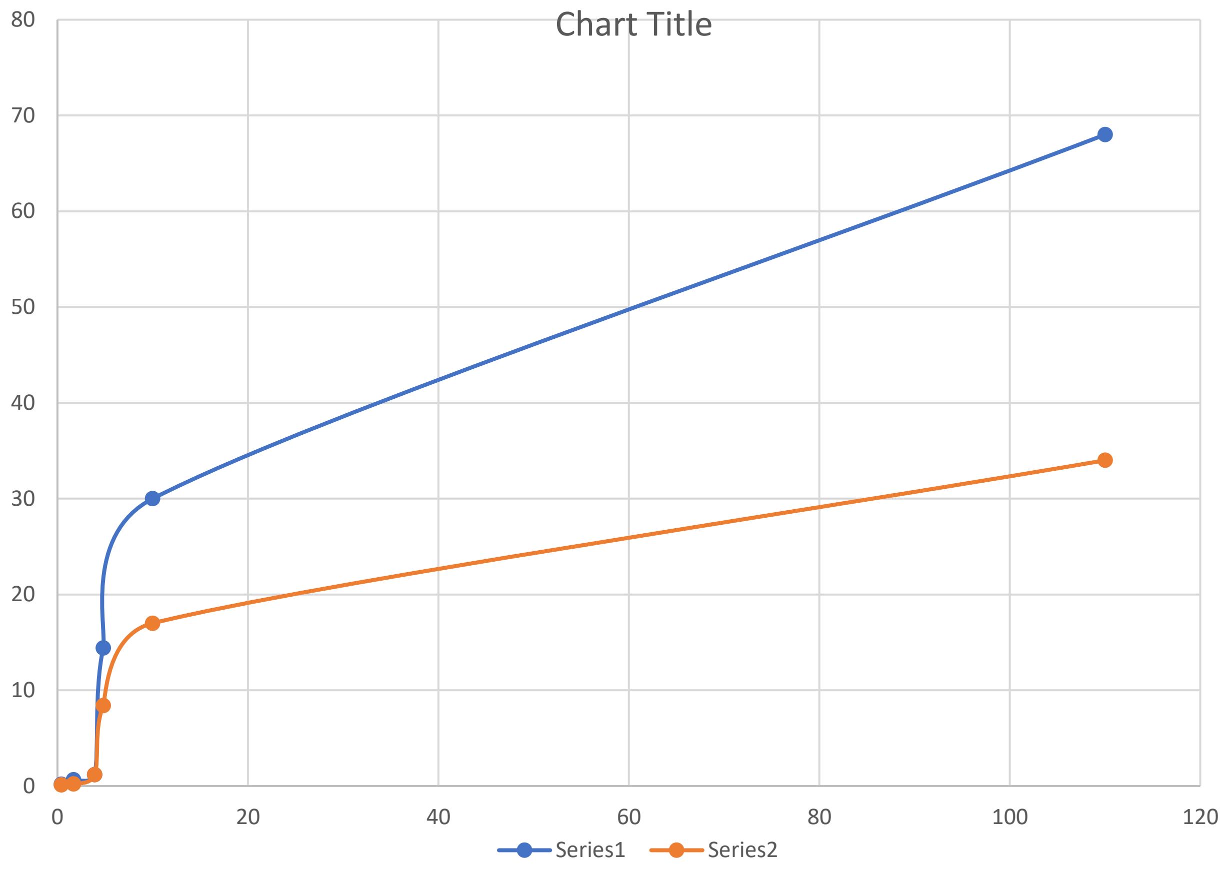


Fig19: Ce vs qe plot

It can be observed from the isotherm that with increasing initial concentration of As(V) the adsorption capacity increases. And also the adsorption capacity of the doped LDH seems higher than the pristine one. The Mn doped Mg-Al LDH has shown the adsorption capacity of 68 mg/g for As(V).

As LDH has greater affinity for carbonate ions, it can be assumed that there remained some carbonate ions in the interlayer region that hindered the entrapment of As(V). Otherwise if the inert atmosphere is ensured during the synthesis and adsorption experiments, the capacity would have been higher.

Now the isotherm plot is fitted in both Langmuir and Freundlich model.

Langmuir Model: $\frac{1}{q_e} = \frac{1}{K_L q_{max}} \frac{1}{C_e} + \frac{1}{q_{max}} \quad [K_L = \frac{1}{slope * q_{max}}]$

Freundlich Model: $\mathrm{Log}q_e = Logk_f + \frac{1}{n}LogC_e$ $[k_f = inverse \log{(intercept)}, \frac{1}{n}$ =Slope]

The equilibrium between the adsorbate and adsorbent system is described by the Langmuir adsorption isotherm, where the adsorbate adsorption is restricted to one molecule layer at or prior to the relative pressure achieving unity. Although Langmuir's initial isotherm hypothesis from 1918 is largely acceptable for characterising ionic or covalent chemisorption processes the adsorbent and the adsorbate create chemical bonds, and the equation is followed in many systems with somewhat low coverage and are easily expandable to describe the actions of the system of binary adsorption. Langmuir goes on to say that the rate directly proportional to the fractional surface coverage of adsorption and desorption, as well as desorption from the surface at equilibrium, rates are equal.

When a single molecule occupies a single surface site, the Langmuir adsorption isotherm assumes that there is no lateral interaction between adjacent adsorbed molecules, describing the surface as homogeneous.

The Freundlich adsorption isotherm was proposed by Freundlich in 1906 as an empirical equation, but it is consistent with the thermodynamics of heterogeneous adsorption.

1/n is the intensity of the adsorption. The higher fractional values of 1/n suggest that the system has strong adsorption forces. The favourability and capacity of the adsorbent/adsorbate system are related to the magnitude of 1/n. The n value between 1 and 10, indicating favourable adsorption.

Experiment No.	Ci(mg/L)	Ce(mg/L)	1/Ce	Log Ce	Ln Ce	qe(mg/g)	1/qe	Log qe
1	144	110	0.009091	2.041393	4.70048	68	0.014706	1.832509
2	25	10	0.1	1	2.302585	30	0.033333	1.477121
3	12	4.8	0.208333	0.681241	1.568616	14.4	0.069444	1.158362
4	4.5	3.9	0.25641	0.591065	1.360977	1.2	0.833333	0.079181
5	2	1.67	0.598802	0.222716	0.512824	0.66	1.515152	-0.18046
6	0.5	0.401	2.493766	-0.39686	-0.91379	0.198	5.046154	-0.70333

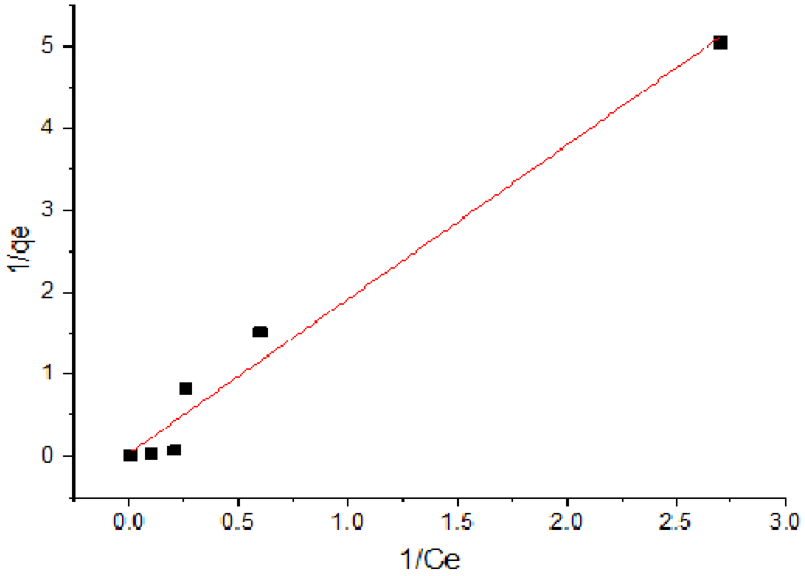


Fig20: Langmuir isotherm

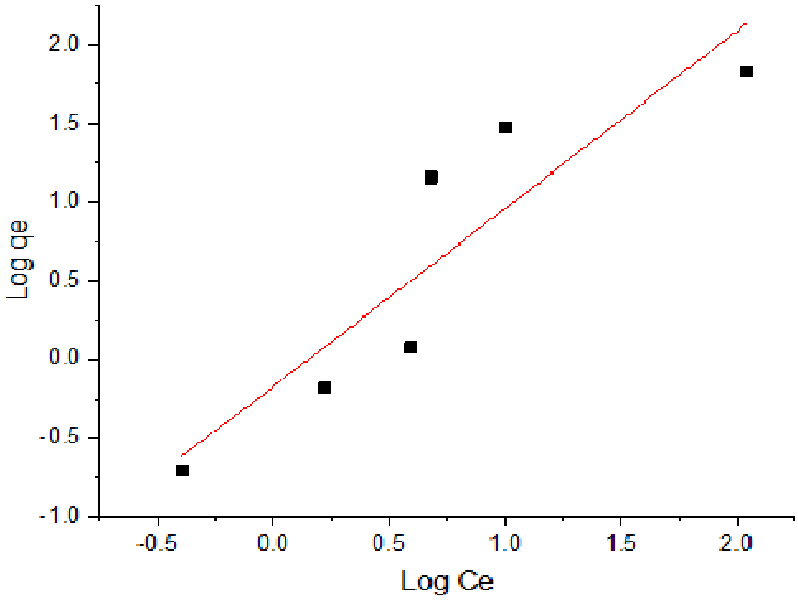


Fig21: Freundlich isotherm

		Intercept	Slope	q_max(mg/g)	K_L	R square
Langmuir:		0.0337	1.87997	29.6735905	0.017926	0.97925

	Intercept	Slope	1/n	Kf	R square
Freundlich:	-0.16914	1.13012	1.13012	0.677423	0.82172

Looking at the R square value it can be said that Langmuir isotherm model is better fitted here. So, it can be confirmed that monolayer adsorption is happening here. And also, ionic or covalent bonds are formed between the adsorbate and adsorbate.

It can be assumed that as the As(v) concentrations taken were high Langmuir model gave better fitting. But for a better fitting in Freundlich model we have to conduct the experimental runs in lower concentration also.

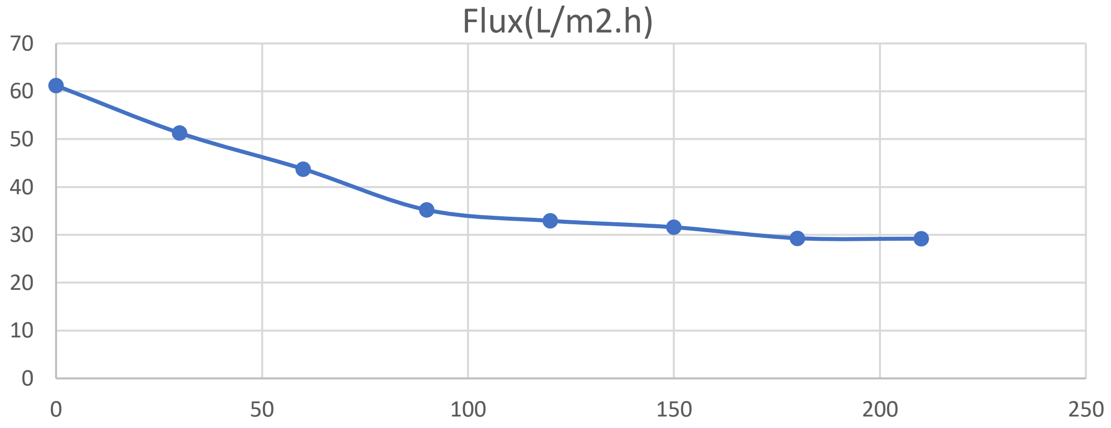
5.6. Membrane Compaction:

Membranecompactionphysical compression of membrane under certain pressure, resulting the decrease in transport characteristics of membrane. Because polymeric membranes are flexible in nature TMP(transmembrane pressure) effect the hydraulic performance of membrane. When pressure is applied on membrane the flux reduces with time. This phenomenon is caused due to pore construction, deformation of matrix and other factors. Compaction is generally conducted at a pressure higher than that at the time of initial permeation to ensure achievement of steady flux. Compaction is generally irreversible. So, when the pressure is reduced the polymeric membrane can not go to its older form. (48)

The following is the table of compaction time vs flux:

Time (min)	Flux(L/m2.h)
0	61.21
30	51.29
60	43.76
90	35.21
120	32.93
150	31.59
180	29.3

Compaction factor=$\frac{Initial flux}{Final\ flux} = \frac{61.21}{29.30}$=2.1



5.7. SEM of Membrane:

Fig23: SEM images of membrane

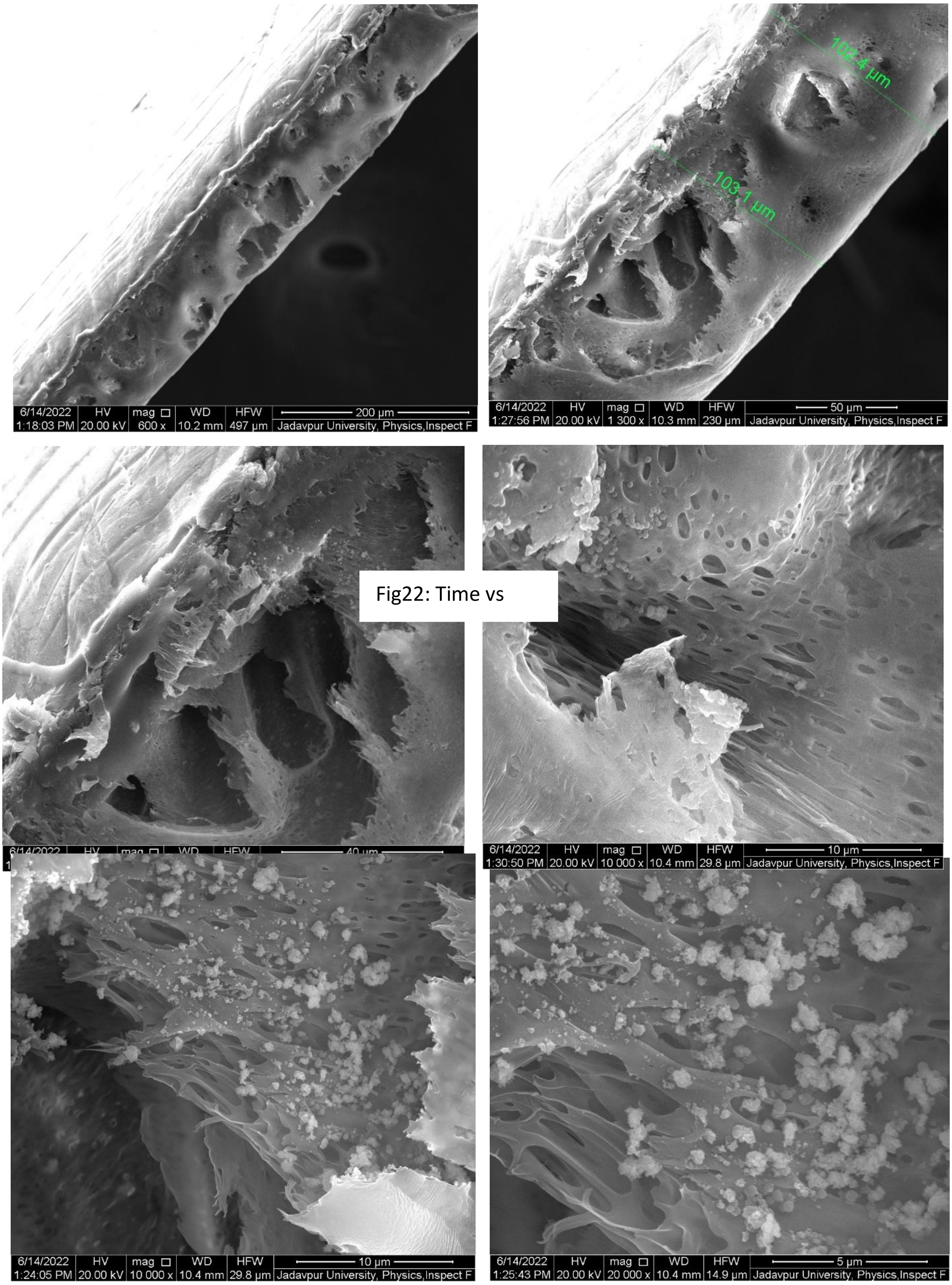


Fig22: Time vs

Sem images of cross-section of mixed matrix membrane are shown here. The porous structure od membrane is clearly visible. And the existence of nanoparticle inside membrane matrix can be noticed. Though the nanoparticles observed in the matrix are in agglomerated form. They need to be exfoliated in order to get single crystals separately.

5.8. FTIR of Membrane:

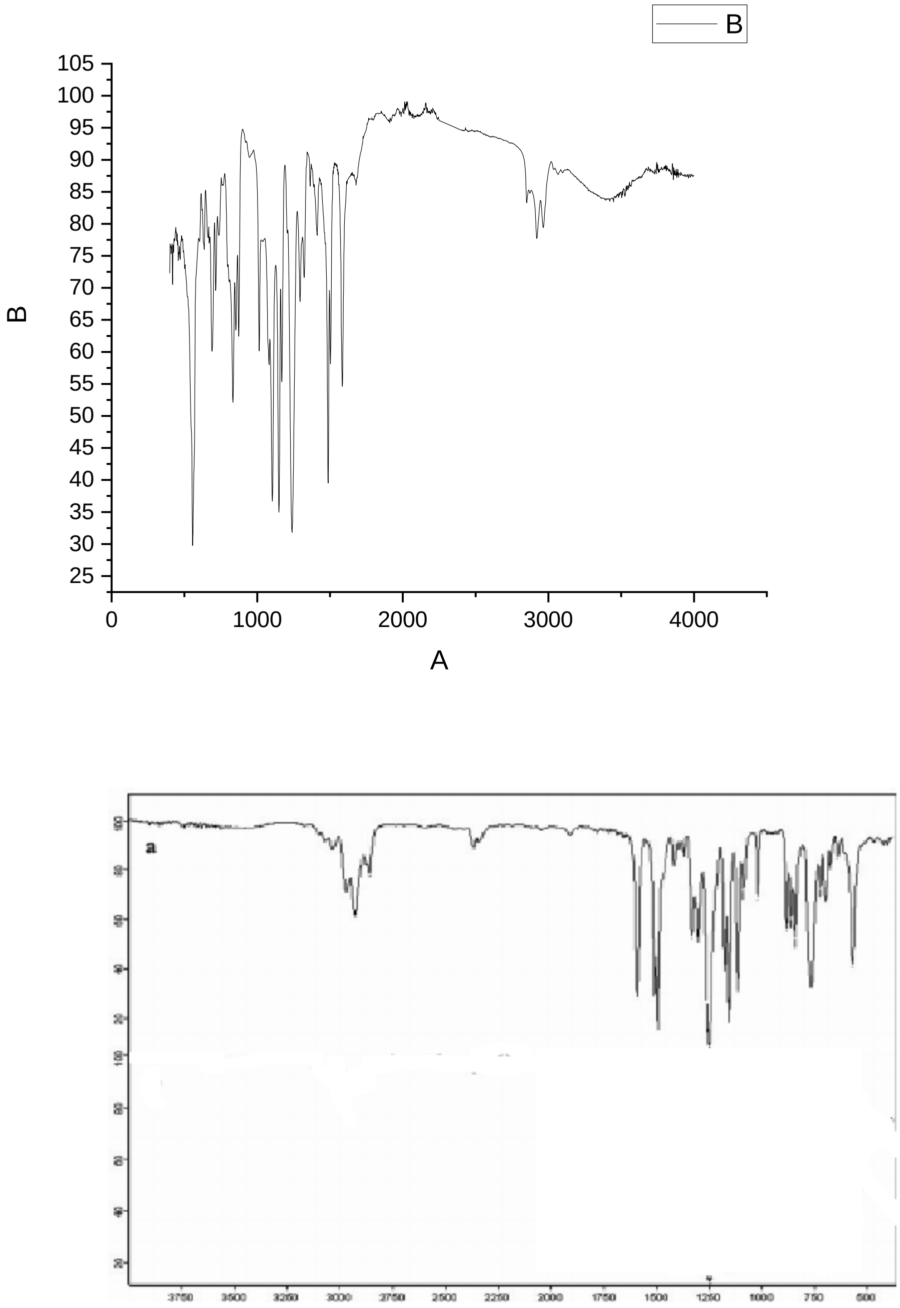


Fig24: FTIR of NP based psf membrane and pure psf membrane

For comparison a typical polysulfon membrane FTIR spectroscopy is added. We can observe all the characteristic peaks i.e., 2879 cm^{-1}(aromatic CH), 2966 cm^{-1}(aliphatic CH), 1241cm^{-1} (C-O), 1488 cm^{-1}(aromatic bond), 1044(SO_3H) of polysulfone are present in the mixed matrix membrane. (19)

5.9. Contact Angle of membrane:

Fig25: Contact angle measurement

Contact angle of the membrane was found to be 71.29^{0}. This information suggests that the membrane is semi-hydrophilic.

Conclusion:

Layer Double Hydroxide Nanoparticle is currently gaining a lot of attention because of its very unique properties i.e., large specific surface area, adjustable layer spacing, good anion exchangeability, tunable composition, high adsorption, simple and cheap preparation. And undoubtedly, it has a lot of potential to be an example of an affordable yet very efficient nano adsorbent. But several aspects like surface modification, doping with metal cations, antimicrobial study, simultaneous removal of different ions, "Memory Effect" are yet to be explored. The use of Membrane technology and adsorption technology together can be very useful for wastewater treatment. Instead of polymeric membrane, nowadays scientists are exploring the possibilities of nanoparticle based ceramic membrane as it is more resistant to fouling and chemical attack then polymeric membrane.

Further Plans:

1. Completing all the remaining characterization of the LDH nanoparticle.
2. Conduct the As(III) and As(V) adsorption experiments which are due.
3. Conduct the adsorption experiments for the mixed matrix membrane.

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