SYNTHESIS AND CHARACTERIZATION OF NOVEL ADSORBENT FOR GROUND WATER REMEDIATION PURPOSE

Thesis submitted towards the fulfillment of M.E. in Chemical Engineering, Jadavpur University, Kolkata

Submitted by

Raja Mandal

M.E. in Chemical Engineering

University Roll No: 002210302004

Examination Roll No: M4CHE24004

Registration No: 131124 of 2015-16

Jadavpur University

Kolkata-32

Under the Guidance of

Prof. Chiranjib Bhattacharjee

Chemical Engineering Dept

Jadavpur University

Kolkata-32

CERTIFICATE

This is to certify that the thesis entitled "**Synthesis and Characterization of Novel Adsorbent for Ground Water Remediation Purposes**" has been carried out by Raja 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.

28/08/2024

Dr. Chiranjib Bhattacharjee

Prof. (Dr.) Chiranjib Bhattacharjee

Supervisor
Professor (On Lien)
Department of Chemical Engineering
Jadavpur University, Kolkata-700032

Ranjana Das 28/08/2024

Dr. Ranjana Das
Co-supervisor
Associate Professor
Department of Chemical Engineering
Jadavpur University, Kolkata-700032

Dr. Ranjana Das
Associate Professor
Chemical Engineering Department
Jadavpur University
Kolkata - 700032

Rajna Dutta 29/08/24

for Prof. (Dr.) Papita Das (Head of Department)
Department of Chemical Engineering
Jadavpur University, Kolkata-700032

HEAD (Officiating)
CHEMICAL ENGINEERING DEPARTMENT
JADAVPUR UNIVERSITY
Kolkata-700 032

Dipak Laha 29.8.24

Dean FET
Jadavpur University, Kolkata-700032

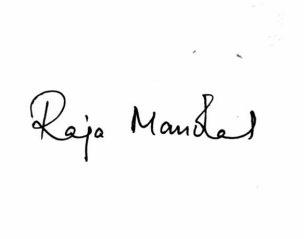
DEAN
Faculty of Engineering & Technology
JADAVPUR UNIVERSITY
KOLKATA-700 032

Declaration of Originality and Compliance of Academics Ethics

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.

I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Thesis Title: **Synthesis and characterization of novel adsorbent for ground water remediation purposes**



……

Raja Mandal

M.E. Student

Roll No: 002210302004

CERTIFICATE OF APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject and presented in a manner satisfactory to warrant acceptance as pre requisite to the degree for which it has been submitted. It is understood that by this approval the undersigned do not necessarily endorse or approve any statement made, opinion expressed or conclusion drawn there in but approve the thesis only for which it is submitted.

Committee of the final exam

…….

Signature of the Examiner

……..

Signature of Supervisor

To Maa, Baba

To Meethi

To my beloved Molian, River shilaboti

To the songs of Yuksom

To the light of Sharchi

To the old Willow tree of Mussoorie

To the air of Rishikesh……

ACKNOWLEDGEMENT

On the very backdrop of the completion and representation of my thesis work, I take this very opportunity to convey my sincere thanks and deepest sense of gratitude to Prof. (Dr.) Chiranjib Bhattacharjee, Dept. of Chemical Engineering, Jadavpur University for his continuous and indispensable support, esteemed guidance and kind encouragement throughout the length of my M.E. Course and in completion of my thesis work. For this committed help and support on his part, I express my sincere obligations and owe him profound respect.

I would like to express my gratitude to Associate Prof. (Dr.) Ranjana Das, Dept. of Chemical Engineering, Jadavpur University, for her extensive guidance throughout the period of the thesis work. Her painstaking efforts and tremendous support have been very encouraging which has always inspired me in applying myself sincerely to my work.

I also like to express my heartfelt thanks to Aishwarya Das, Anubhab Das, Somakraj Banerjee, the research scholars of Membrane Research Laboratory for their earnest support and guidance throughout the course of the project work.

And, finally I wish to thank Prof. Papita Das, Head of the Department, all departmental staffs, my classmates who have extended their kind co-operation and have contributed directly or indirectly towards the completion of my thesis work and throughout my M.E. Course.

ABSTRACT

Arsenic pollution has become a worldwide environmental concern. Dangerous arsenic concentrations in natural waters threaten the health of millions of people, and this has received significant attention. Among the various technologies that have been developed for arsenic removal from water, the use of adsorption technology is considered to be a prevailing method, because the adsorption approach usually has high removal efficiency and the advantage of convenience of handling. In recent years, layered double hydroxides (LDHs) have become prime candidates for arsenic removal, due to their hydrophilic nature and cationic layered structures. Ion exchange is the most prominent and effective mechanism for removal of metal ions from water by LDH.

In this study, Ni doped Mg- Fe LDH with four different Mg/Ni/Fe (2:2:1, 2:1:1, 1:2:1, 1:1:1) have been synthesized via co-precipitation method. A series of batch experiments were performed under various conditions, such as M2+/M3+ ratio, initial anions concentrations, contact time, solution pH and competitive adsorption, for the adsorption of arsenic (V) and lead (II) on Ni doped Mg/Fe LDH. It is found Ni doped Mg/Fe with Mg/Ni/Fe ratio 2:2:1 at pH 6 shows maximum removal of 91% for arsenic(V) and 81.5 % for Lead (II). The equilibrium and kinetic adsorption data were best fitted into the Freundlich isotherm for higher concentration of arsenate and adsorption data were best fitted into Langmuir isotherm for higher concentration of lead (II). The adsorbents were characterized by TGA, SEM, XRD, FT-IR and XPS, and the analysis results demonstrated that the adsorption mechanism involved surface adsorption, ion exchange interaction and concomitant intercalation of lead and arsenate ions into the interlayer region.

LIST OF TABLES

Table No	*Contents*	*Page*
1	Total groundwater resources and its withdrawal rates in 2017	13
2	Concentration of heavy metals and other elements in groundwater reported worldwide in comparison with the WHO and USEPA standards	15
3	Comparative Arsenic adsorption data in higher conc. of LDH with different synthesis ratio	56
4	Comparative Arsenic removal data in higher conc. of LDH with different synthesis ratio	56
5	Comparative Arsenic adsorption data in lower conc. of LDH with different synthesis ratio	57
6	Comparative Arsenic removal data in lower conc. of LDH with different synthesis ratio	58
7	Comparative Lead adsorption data in higher conc. of LDH with different synthesis ratio	59
8	Comparative Lead removal data in higher conc. of LDH with different synthesis ratio	59
9	Comparative Lead adsorption data in lower conc. of LDH with different synthesis ratio	60
10	Comparative Lead removal data in lower conc. of LDH with different synthesis ratio	61
11	Arsenic adsorption data in higher concentration	63
12	Lead adsorption data in higher concentration	65
13	Arsenic adsorption data in lower concentration	67
14	Lead adsorption data in lower concentration	69
15	Effect of contact time for arsenic removal	71
16	Effect of pH for arsenic removal	72

LIST OF FIGURES

Fig No	*Contents*	*Page*
1	Schematic diagram of Adsorption Process	16
2	Ground water existing treatment method	17
3	Adsorption behaviour and mechanism of LDH	27
4	Structural Representation of LDH (Layered Double Hydroxide	27
5	Representative structure of LDH materials.	27
6	3D representation of hexagonal LDH metal structure	28
7	Schematic representation of a co-precipitation setup for LDH synthesis.	29
8	The synthesis methods, structure and applications of Layered Double Hydroxides	32
9	Anion Exchange	35
10	Adsorption by surface reconstruction	36
11	Synthesis set up for LDH	47
12	Ni doped Mg Fe after centrifugation	48
13	Powdered form of Ni doped Mg Fe LDH	48
14	TGA data analysis for Ni doped Mg Fe	51
15	FTIR data analysis for Ni doped Mg Fe	52
16	SEM data analysis for Ni doped Mg Fe	53
17	XRD data analysis for Ni doped Mg Fe	54
18	Effect of molar ratio of metals (Mn, Mg, and Fe) on the adsorption capacity of resultant Mn/Mg/Fe-LDH samples towards As(V)and Lead (II	55
19	As removal % comparison between two Ni doped LDH with different synthesis ratio.	57
20	As removal % comparison between two Ni doped LDH	58

LIST OF FIGURES

Fig No	*Contents*	*Page*
21	Lead removal % comparison between two Ni doped LDH with different synthesis ratio.	60
22	Lead removal % comparison between two Ni doped LDH with different synthesis ratio.	60
23	Langmuir Isotherm for Arsenic adsorption	61
24	Freundlich isotherm for Arsenic adsorption	63
25	Langmuir Isotherm for Lead adsorption	64
26	Freundlich isotherm for Lead adsorption	65
27	Langmuir Isotherm for Arsenic adsorption	66
28	Freundlich isotherm for Arsenic adsorption	67
29	Langmuir Isotherm for Lead adsorption	68
30	Freundlich isotherm for Lead adsorption	69
31	Effect of contact time for arsenic removal	71
32	Effect of pH for arsenic removal	72

CONTENTS

Chapter 1

1.1 Introduction…….14-18

1.2 Ground water remediation techniques……...18-27

1.2.1 Physical treatment
1.2.2 Chemical treatment
1.2.3 Biological treatment

1.3 What is LDH……27-30

1.3.1 Structure of LDH

1.4 LDH synthesis routes……...30-33

1.4.1 Co precipitation method
1.4.2 Hydrothermal crystallization
1.4.3 Urea hydrolysis
1.4.4 Sol gel method
1.4.5 Salt-oxide method
1.4.6 Mechanochemical synthesis

1.5 Absorption phenomenon of heavy metals from waste water by LDH……33-35

1.5.1 LDH adsorption properties
1.5.2 Effect of composition and structure of LDH on the absorptive properties
1.5.3 Effect on adsorption process condition

1.6 LDH removal mechanism……35-37

Chapter 2

2 Literature Review……...39-44

Chapter 3

3 Aim and objectives ……...46

Chapter 4

4 Methodology……..48-50

4.1 Materials
4.2 Synthesis of LDH
4.3 Characterization of LDH
4.4 Adsorption experiment for heavy metal

Chapter 5

5.1 Result and discussion……..52-55

5.1.1 TGA analysis

5.1.2 FTIR analysis

5.1.3 Sem analysis

5.1.4 XRD analysis

5.2 Adsorption studies……56-62

5.2.1 Comparative adsorption studies for Arsenic removal

5.2.2 Comparative adsorption studies for Lead removal

5.3 Adsorption isotherm……63-71

5.3.1 Adsorption isotherm plot

5.3.2 adsorption data for lower concentration

5.4 Effect of contact time……72

5.5 Effect of pH……73

Chapter 6

6.1 Conclusion……..75

6.2 References……....77-83

Chapter 1

1.1 Introduction:

Water is a fundamental resource for life. Sustainable development and efficient management of this scarce resource has become a challenge in India. There are competing needs for water due to population growth, urbanization, and fast industrialization as well as the need to increase agricultural output.

Groundwater makes up about thirty percent of the world's fresh water supply, which is about 0.76% of the entire world's water, including oceans and permanent ice.[1] Groundwater accounts for 99% of the liquid freshwater stock on Earth and is the world's most accessed freshwater reservoir.[2] It has been an extremely important source of water for many years, especially in arid climates. Groundwater has emerged as the main source for agriculture, domestic and the industry. It is important to realize that groundwater is not a resource that could be utilized indiscriminately.

	North Africa	Sub Saharan Africa	Central America	North America	South America	Asia	Middle East	Eastern Europe	Oceania
Total groundwater (10^9 m^3/year)	15	1404	222	1903	2475	3202	5	837	93
Groundwater withdrawal (10^9 m^3/year)	25	6.5	4.5	147	24	594	28	13	7.5

Table No 1: Total groundwater resources and its withdrawal rates in 2017

It is impossible to overestimate the significance of groundwater as a dispersed supply of drinking water for millions of families in both rural and urban areas.
According to some estimates, it accounts for nearly 80 per cent of the rural domestic water needs, and 50 per cent of the urban water needs in India.[3]

In India, where groundwater is widely utilized for farming and industrial purposes, many kinds of land and water-based human activities contaminate this valuable resource. Ground water contamination is nearly always caused by human activity. Groundwater is especially at risk in places with high population density and intense human land use.

Groundwater pollution varies from surface water contamination in that it is invisible, and recovery of the resource is challenging with existing technologies. To begin to address prevention or remediation, we must understand how surface waters and ground waters

interrelate with each other. If a water supply well is located near a source of contamination, it may get contaminated. If there is a river or stream close by, the ground water may contaminate it as well. Many factors can lead to the contamination of ground water.

These include activities that occur on the land surface, like spilling or releasing industrial waste, sources below the water table but above it, such as leaking underground petroleum storage systems or septic tanks, structures below the water table, including wells, and contaminated recharge water.

The numbers of classes of contaminants detected in groundwater are increasing rapidly, but they can be broadly classified into three major types: chemical contaminants, biological contaminants, and radioactive contaminant.

Nitrogen contaminants, such as nitrate, nitrite, and ammonia nitrogen, are prevalent inorganic contaminants. Nitrate is primarily derived from anthropogenic sources, such as agriculture (fertilizers, manure) and household wastewater. Other common inorganic contaminants found in groundwater include anions and oxyanions, such as F^-, SO_4^{2-}, and Cl^-, and major cations, such as Ca^{2+} and Mg^{2+}. Metals such as zinc (Zn), lead (Pb), mercury (Hg), chromium (Cr), and cadmium (Cd), as well as metalloids like selenium (Se) and arsenic (As), are commonly found in groundwater.[4] Exposures at high concentrations can lead to severe poisoning, although some of these elements are essential micronutrients at lower doses. In groundwater, more than 200 organic contaminants have been detected, and this number is still increasing.[5] Common organic contaminants include hydrocarbons, halogenated compounds, plasticizers, pesticides, pharmaceuticals, and personal care products and natural oestrogens, among others.

Biological contaminants include algae and microbiological organisms including bacteria, viruses, and protozoa. More than 400 types of bacteria have been found in human and animal faeces, as well as over 100 types of viruses.[6]

In addition to coming from natural radioactive deposits, human sources such as nuclear power plant waste, nuclear weapons testing, and improper disposal of medical radioisotopes can also produce radioactive pollutants in groundwater.

Arsenic is ranked as a Group 1 human carcinogen by the International Agency for Research on Cancer (IARC), and As^{3+} can react with sulfhydryl (–SH) groups of proteins and enzymes to upset cellular functions and eventually cause cell death. A few large aquifers, in various parts of the world, have been identified with problems of high arsenic concentration in

ground water.[7] The most noteworthy occurrences of arsenic in ground water, are in parts of Argentina, Bangladesh, Chile, China, Hungary, India, Mexico, Romania, Taiwan, Vietnam, and many parts of U.S.A. The main source of arsenic poisoning is through drinking water. According to the BIS (Bureau of Indian Standards), the limit for arsenic in drinking water is 0.01mg/L (IS 10500 -1993 Amended 2003). However, affected West Bengal State is following the earlier standard as per BIS (1993) of maximum permissible value 0.05 mg/L (for detection) and 0.01mg/L (for removal).[8]

Elements $\mu g/L$	Bangladesh (Dhaka)	China (Dong ting Lake Plain)	India (Tamil Nadu)	Pakistan (Northern)	WHO 2017	USEPA 2018
Arsenic	2	7.4	-	-	10	10
Chromium	1.5	21	30	89	50	100
Copper	9.6	1.7	40		2000	1300
Lead	49.6	9.1	-	55	10	1.5
Nickel	-	0.32	-	92	20	100

Table No 2: Concentration of heavy metals and other elements in groundwater reported worldwide in comparison with the WHO and USEPA standards.[9]

Groundwater has been treated using a variety of technologies, including chemical, biological, and physical processes, all with varying degrees of success.
Among of them adsorption is considered as an efficient treatment technique for the removal of both toxic elements and pathogens by utilizing different novel adsorbents.

Adsorption is a part of surface chemistry. In adsorption solid surface has the tendency to attract and retain the molecule of the phase with which it comes into contact. These molecules so attracted remain only at the surface and do not go deeper in to the bulk.

The accumulation of the molecular species at the surface rather than in the bulk of a solid is termed as adsorption. The molecular species which accumulates at the surface is termed as Adsorbate. The material on the surface of which adsorption take place is coined as Adsorbent. Solids, particularly in finely divided state, have larger surface area and therefore LDH (Layered Double Hydroxide), Graphene Oxide, Charcoal, Silica gel, Alumina gel, clay, Colloids, or material in finely divided state are good adsorbent.

During Adsorption there is always a decrease in the residual forces of the surface such that there is always a decrease in the surface energy appears in the form of heat. Adsorption is

therefore an exothermic process. It means ΔH of the adsorption is negative. When a gas is adsorbed, due to the restriction of freedom of movement of its molecules there is a decrease in the entropy of the gas after adsorption. Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system.[10]

$\Delta G = \Delta H - T\Delta S$, For $\Delta G < 0$ and $\Delta H > T\Delta S$

As adsorption proceeds ΔH becomes less and less negative. Rate of adsorption is proportional to the number of active sites of the solid surface of adsorbent. As the number of active sites decreases rate of adsorption also decreases which means less amount of heat is released. Eventually ΔH becomes equal to TΔS and $\Delta G = 0$. At this state, equilibrium is attained.

Two type of adsorption phenomenon is seen.

1. Physical Adsorption:
2. Chemical Adsorption:

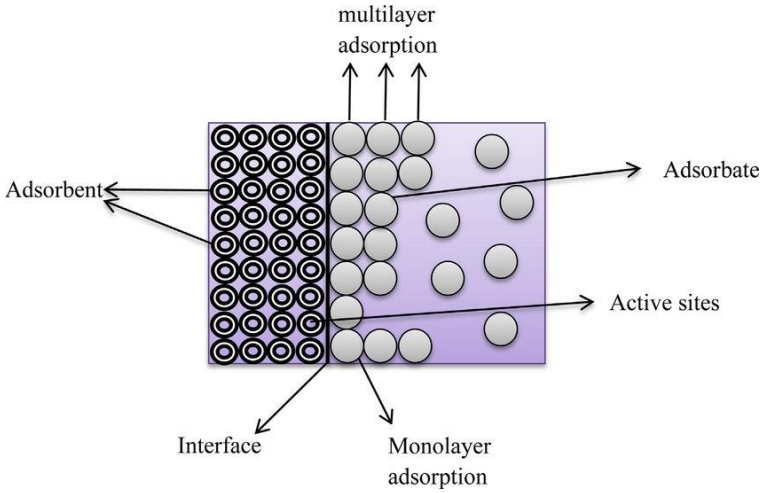


Fig 1: Schematic diagram of Adsorption Process

In most of the cases, this process is described at the equilibrium by means of some equations that quantify the amount of substance attached on the surface given the concentration in the fluid. These equations are called isotherms (the most famous are the Langmuir and the Freundlich equations) because of the dependence of their parameters on the temperature, which is one of the most important environmental factors affecting adsorption. Adsorption has a fundamental role in ecology: it regulates the exchanges between geosphere

and hydrosphere and atmosphere, accounts for the transport of substances in the ecosystems, and triggers other important processes like ionic exchange and enzymatic processes.[11]

In my research work, LDH is used as a nano adsorbent for the removal of heavy metal like Arsenic (As), Lead (Pb).

1.2 Ground Water Remediation Techniques:

Contamination of groundwater is a major global problem and has prompted development of proper ways of remediating the water sources. In recent years several methods of physical, chemical and biological treatments of wastewater have been discovered and enhanced. It is a critical area of research aimed at addressing the contamination of groundwater resources. Adsorption-based methods using novel adsorbents have emerged as promising approaches. This literature review provides an overview of the advancements in the synthesis and characterization of adsorbents, highlighting their potential applications and performance for groundwater remediation.

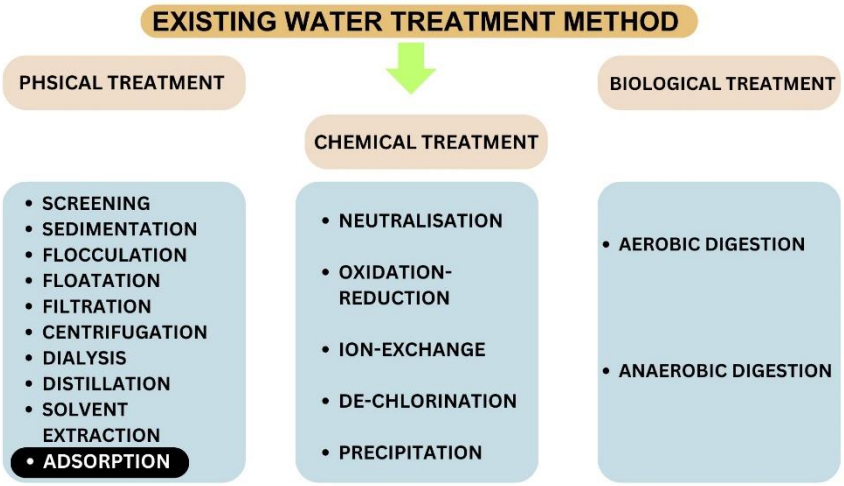


Fig 2: Ground water existing treatment method

1.2.1 Physical Treatment:

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 number 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 like 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.

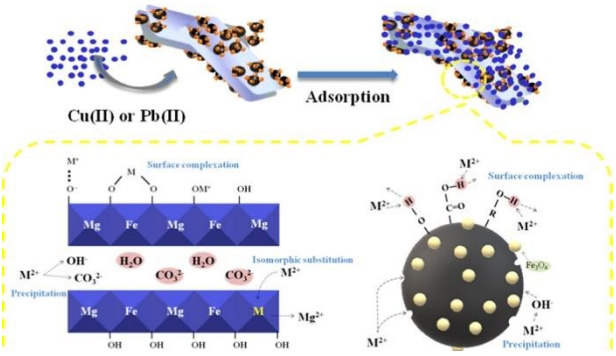


Fig 3: Adsorption behavior and mechanism of LDH [12]

Activated carbon is one of the most 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.

LDH (layered double hydroxide) has been using as novel adsorbent because of their high surface area, iron exchange mechanism.

1.2.2 Chemical Treatment:

In this method basically the chemical structure of the components of waste water is altered through chemical reaction to make the components less hazardous. The physical processes that are commonly used are:

(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 affect 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:

(i) 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.

(ii) 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.

(iii)Chlorine: It is a powerful oxidant and it can support combustion. So, it is a potential fire risk.

(iv)Sodium hypochlorite: Sodium hypochlorite is used to store and dose chlorine.

Some common reductants and their applications are:

- Sulphur di oxide (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 sulphite is 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^{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 sulphur dioxide. Other alternatives like carbon adsorption, sodium metabisulfite and hydrogen peroxide.

In water, chlorine dissolves and hydrolyse to form hypochlorite ions and hypochlorous ions which is known as free chlorine. They react 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 sulphur compounds an oxidation state of +4 are produced. The sulphide iron reacts with free chlorine and combined form of floating precipitation.

$SO_3^{2-} + HOCl \rightarrow SO_4^{2-} + Cl^- + H^+$

$SO_3^{2-} + NH_2Cl + H_20 \rightarrow SO_4^{2-} + Cl^- + NH_4^+$

(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 sulphate 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.

Two 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 $=afvf/aeve$. Where, af and ae are the activities per unit volume of feed and effluent, respectively and vf and ve are the volumes of feed and effluent, respectively.

1.2.3 Biological Treatment:

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 can convert 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.

1.3 What is LDH?

Layer double hydroxides are two dimensional layered nanomaterials, belong to anionic clay family. The general formula of LDH is as follows: $[M_{1-x}^{2+} M_x^{3+} (OH)_2]^{x+} (A^{n-})_{x/n}. mH_2O$, 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 in some man-made context i.e., results of corrosion of some metal objects.

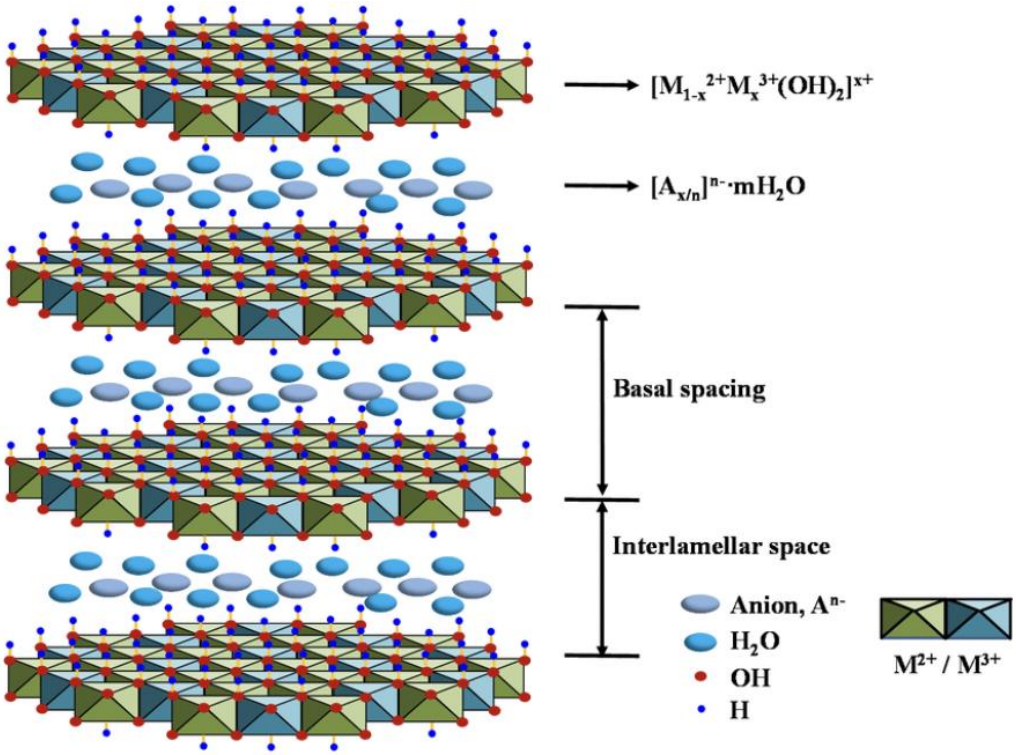


Figure 4: Structural Representation of LDH (Layered Double Hydroxide [13]

1.3.1 Structure of LDH:

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 $[M_{1-x}^{2+}\ M_x^{3+}\ (OH)_2]^{x+}$.

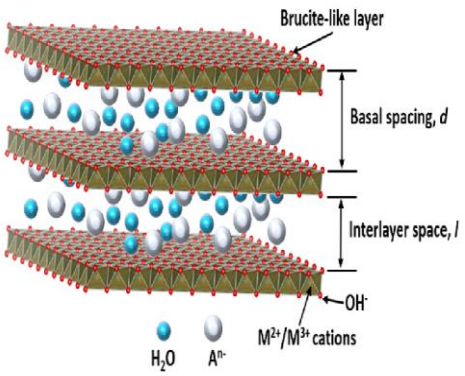


Fig 5: Representative structure of LDH materials.[14]

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.

The basal spacing in the LDH can vary from metal to metal.[15]

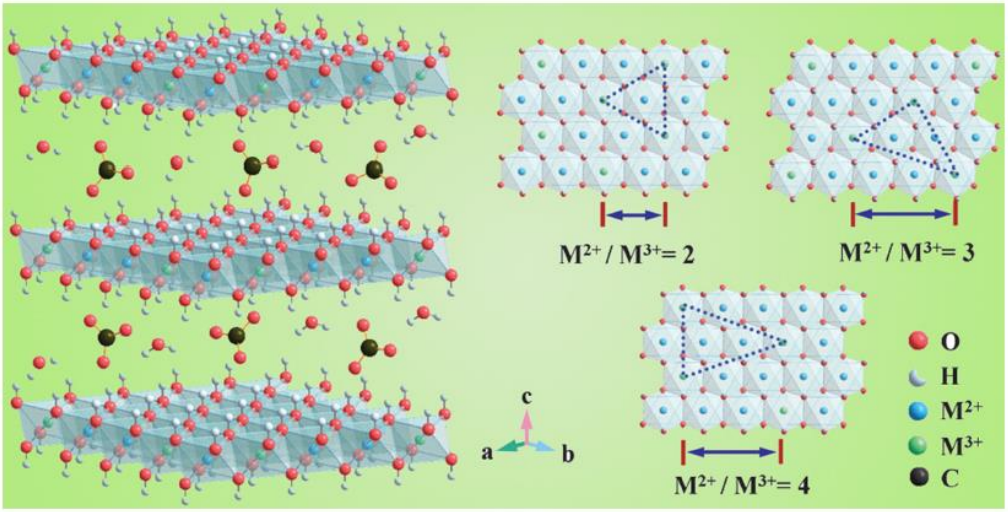


Fig 6: 3D representation of hexagonal LDH metal structure [16]

(i) Metal cations:

Depending on their radii there can be different possible types of metal cations. If their ionic radii are like 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. [17]

(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. [18]

1.4 LDH Synthesis Routes:

Layered Double Hydroxides (LDHs) are a class of materials with applications in catalysis, environmental remediation, drug delivery, and more. There are several synthesis routes for LDHs, each offering different control over composition, morphology, and properties. Here's an overview of the main synthesis methods:

1.4.1 Co-precipitation Method: The most commonly used method involves the simultaneous precipitation of metal cations and hydroxide anions from aqueous solutions under controlled pH. The pH is typically maintained by adding a base (e.g., NaOH or NH4OH). 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.[19]

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. Ni doped Mg Fe LDH was synthesized using co-precipitation method.

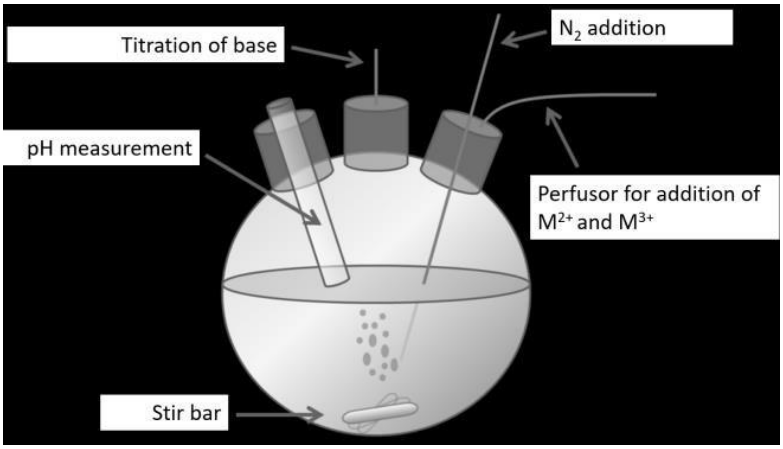


Fig 7: Schematic representation of a co-precipitation setup for LDH synthesis.[20]

Advantages: Simple and scalable, with good control over composition and crystallinity.

1.4.2 Hydrothermal Crystallization: In this method, the precursor solution is treated at high temperatures and pressures in a sealed autoclave. This promotes the formation of highly crystalline LDHs. 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°C for some hours. The aqueous suspension of the metal oxides is then put in to an autoclave and subjected to hydrothermal treatment at 110°C 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. [21]

Advantages: Produces LDHs with high crystallinity and well-defined morphology.

1.4.3 Urea Hydrolysis: This method involves the slow release of hydroxide ions via the hydrolysis of urea, leading to the precipitation of LDHs. It is often used to synthesize LDHs with uniform particle sizes and shapes. 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. [22]
Advantages: Provides better control over particle morphology.

1.4.4 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^{o}C. In the end, 2 mL of ethylene glycol is added under vigorous mixing at 150^{o}C. The transition from sols to gels took place during the solvent's evaporation. The created gels are dried for 24 hours at 105^{o}C. Then gels were heated at 650^{o}C for 4 hours to produce the MMOs. By reconstructing MMOs in deionized water at 80^{o}C for 6 hours, LDHs were created. [23]
Advantages: Allows for the fine control of particle size and porosity.

1.4.5 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 was 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 $-0.8V \leq E \leq -1.8V$ 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. [24]

1.4.6. Mechanochemical synthesis: Preparation of LDH via solid state reaction is a 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. [25]

Advantages: Environmentally friendly (solvent-free) and suitable for large-scale production.

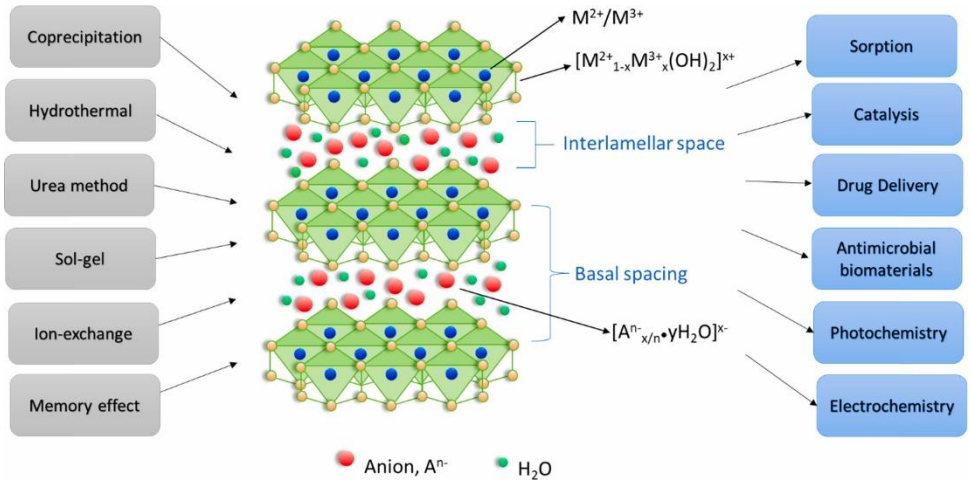


Fig 8: The synthesis methods, structure and applications of Layered Double Hydroxides [26]

1.5 Absorption phenomenon of heavy metals from waste water by LDH:

1.5.1 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. [27]

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

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 Co/Fe 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) oxyanions and (ii) surface complexation between the oxyanions of Cr(VI) and the hydroxyl groups of LDH. So it is safe to say that, when LDH is produced using various metal ions, the adsorption effect varies. [28]

1.5.3 Effect on adsorption process condition:

(i) 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-$SO4$ 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. [29]

(ii)pH effect: 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 exist different ionic forms in different pH which effect the removal of heavy metal. For the removal of Cu^{2+} with the $Fe3O4 - C - Mg - Al$ 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 decrease. When the pH range is 4 to 7 the removal is around 94% and then it decreases.

(iii)Temp effect: 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 15º to 40º .And again if the temperature is increased above 40º the adsorption capacity decreases rapidly.

(iv) Type of heavy metal ions: Heavy metal ions can be both anions and cations. Cation i.e.Pb, Cu^{2+}, Ni^{2+} are adsorbed via isomorphous replacement and the anions like $HCr_2O_7^{+}$, $HAsO4\ 2-$ 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.[30]

1.6 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 affect 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. [31]

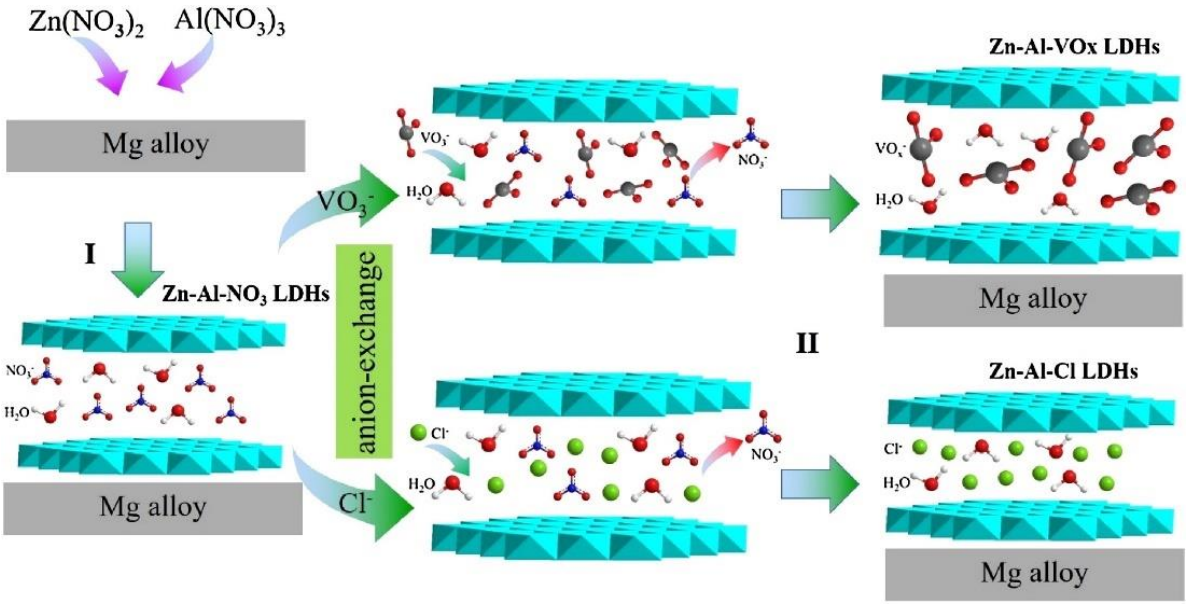


Fig 9: Anion Exchange [32]

(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. [32]

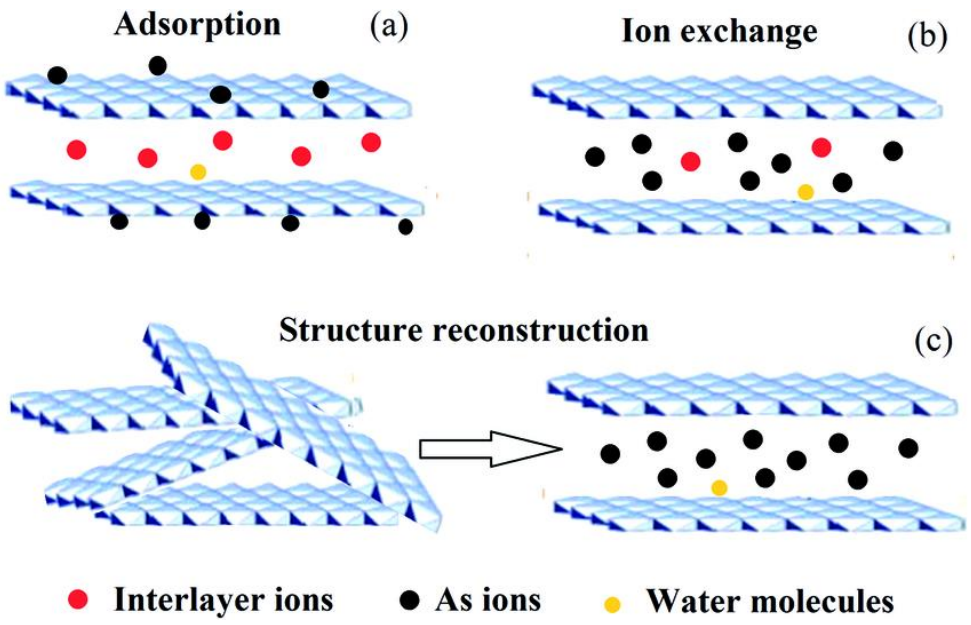


Fig 10: Adsorption by surface reconstruction [33]

Chapter 2

2 Literature Review:

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

Existing Research work on LDH :

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 $(CO3)^{2-}$ 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 $H_2AsO_4^-$, $HAsO_4^{2-}$.

In 2009 Sujata Mandal et al. studied the adsorption behaviour 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+}) =3 . 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 sulphate 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 was 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. So, 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 400ºC 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 400ºC had the highest removal. At lower calcination temperature magnesium iron mixed oxides cannot 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 cannot 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 behaviour.

In 2016, Ling et al synthesized Co/Fe LDHs with different ratios of Co/Fe (2:1, 3:1, and 4:1), using a coprecipitation method and reported the Co/Fe LDHs to have high adsorption capacities for methyl orange and Cr (VI). The Co/Fe (4:1) LDH had the maximum adsorption of 27.62mg /g among these LDHs and showed a higher initial adsorption rate than the other two LDHs. The average pore size of Co4Fe1-LDH (4:1) was 8.40, which was much larger than those of Co3Fe1-LDH (3:1) and Co2Fe1-LDH (2:1). The results showed that the adsorptive behaviour involved two processes: external surface adsorption and interlayer anion exchange.

In 2016 Lu et al. synthesized Ni/Fe LDHs with different ratios of Ni/Fe (4:1, 3:1, 7:3, and 1:1), using a simple coprecipitation method and reported that the Ni/Fe (4:1) LDH had maximum adsorptions of 205.76 and 26.78mg /g for methyl orange and Cr (VI), respectively.

In 2016 Eshaq et al. successfully synthesized a Mg-Zn-Al LDH and its corresponding oxide, which were applied in the adsorption of Cr (VI) in water. The maximum adsorption capacities were 29.25 and 33.82mg /g for Mg-Zn-Al LDH and calcined Mg-Zn-Al LDH, respectively. The results indicated that the adsorption of Cr (VI) through rehydration was

more significant than the adsorption through anion exchange by the calcined LDH. Cr (VI) was removed from water via two methods: (1) anion exchange between the Cr (VI) oxyanions and the interlayer anions of the LDH and (2) surface complexation between the Cr (VI) oxyanions and the surface and interlayer hydroxyl groups of the LDH. Thus, the adsorption effects vary greatly with LDHs synthesized with different metal ions. Hence, LDHs with a larger ratio of metal ions (M^{2+} /M^{3+}) should be chosen when enhancing the metal ion ratio or when changing the metal ion species for modification. Furthermore, the metal ions and interlayer anions should be adjusted in this situation.

In 2016 Khitous et al. synthesized Mg/Al LDH materials with different anions ($NO3^{-}$, $SO4^{2-}$, and Cl^{-}) to study the effect of the different interlayer anions on the removal of Cr (VI). The maximum adsorption capacity of the LDH was 71.91mg /g. The removal efficiency of the LDH for Cr (VI) depended on the nature of the interlayer anion, following the order of $NO3^{-}$> Cl^{-}> SO_4^{2-}. This could be due to the weak interaction between NO3- and the metals in the laminates, which caused the LDH with NO3- to have the largest interlayer spacing, allowing for the easiest ion exchange with NO_3^{-}. $SO4^{2-}$ was most difficult to exchange because $SO4^{2-}$ has two negative charges that bind strongly with the metal hydroxide layer. Generally, the removal efficiency follows the order of NO_3^{-}/LDH > Cl^{-}/LDH > SO_4^{2-}/LDH. NO3-/LDH should be synthesized to achieve the best removal efficiency when designing LDHs to adsorb heavy metal ions.

Anions with high charges and small ionic radii more easily insert into LDH interlayers. In 2014 Bagherifam et al. studied the removal capacity of a Zn-Al-SO4 LDH for As (III) and As (VI) in soil with SO_4^{2-} and CO_3^{2-} coexistence and reported maximum adsorption capacities of 34.24 and 47.39mg /g, respectively. In three different conditions, without adding competing anions, adding SO_4^{2-} and CO_3^{2-} led to As (III) removal rates of 69%, 61% and 54, while the rates were 88%, 86% and 82% for As (VI), respectively. The effects of competitive anions on the uptake of As (III) and As (VI) by Zn-Al-SO_4 layered double hydroxide.

In 2015 Zhang et al. employed Fe_3O_4/C/Mg/Al LDH nanoparticles to remove Cr (VI) in solution and found that Cr (VI) could be adsorbed by this material with high efficiency, which was greatly affected by the pH value. When the pH value ranged between 2 and 6, the adsorption capacity increased sharply and reached a maximum of 143.3mg /g at a pH value of

6. When the pH value ranged between 6 and 12, the equilibrium adsorption capacity decreased with increasing pH value.

A similar tendency was also observed in a study by Li et al. in 2009. When the pH value was 6, the Fe_3O_4@C@MgAl-LDH nanoparticles showed their best adsorption capacity for Cr (VI) of 152mg /g, which was attributed to the high positive charge on the surface of the

Fe_3O_4@C@MgAl-LDH nanoparticles when the pH value was below 6, accelerating the diffusion of $Cr_2O_7^-$ and the subsequent adsorption of Cr (VI) by the Fe_3O_4@C@MgAl-LDH nanoparticles.

In 2002 Daneshvar et al. found that temperature might have two main effects on the adsorption process. An increasing temperature would lead to a drop of solution viscosity, which is conducive to accelerate the diffusion of heavy metal ions in external boundaries and holes. In addition, changing the temperature will change the equilibrium adsorption capacity of the specific adsorbent.

Arabinda Baruah et al. synthesized N-doped graphene oxide NiFe-CO_3-LDH (LDH-NGO) nanocomposites by chemical precipitation and probe-ultrasonic methods and studied its toxic heavy metal ions in aqueous solutions at different pH values. The adsorption capacity is given, and the corresponding kinetic rate equation and adsorption isotherm are given. The research found that it can also be used in a wide pH range (5–11), and the adsorbent can be easily regenerated. Therefore, the material has strong application potential in the treatment of industrial wastewater poisoned by heavy metals. In summary, the combination of LDHs materials and common inorganic nanomaterials can further increase the adsorption active sites on the adsorption capacity of the original LDHs materials, thereby improving the adsorption activity.

Hajar Azad et al. prepared a new self-supporting polyvinyl alcohol butyl-polyacrylonitrile/zinc sulphide layered double hydroxide nanocomposite membrane (PVB-PAN/Zn Al-LDH NCM) by phase inversion method. It is used to remove the salt and heavy metals in the aqueous solution. The introduction of Zn-Al-LDH nanosheets significantly improved the mechanical strength, surface porosity, roughness, hydrophilicity, average pore size, and membrane morphology. In addition, the prepared PVB-PAN/Zn-Al-LDH nanomembrane has a significant effect on the removal of Pb^{2+} and Cd^{2+} in the aqueous solution.

Chapter 3

3. Aim and Objectives:

1. Synthesis of novel adsorbent for groundwater remediation purposes
2. Detailed & confirmatory characterization of nano adsorbents.
3. Performance study and removal efficiency study of the nano adsorbent.
4. Focusing on process development for removing contaminants to obtain contaminant-free water.

Chapter 4

4. Methodology:

4.1 Materials: Magnesium Nitrate, Ferric Nitrate, Nickel Nitrate, NaOH pellets, H_2SO_4, De-Ionized water, Nitrogen Gas.

4.2 Synthesis of LDH:

This synthesis of LDH was prepared in laboratory via co precipitation method.

- Ni doped Mg - Fe LDH

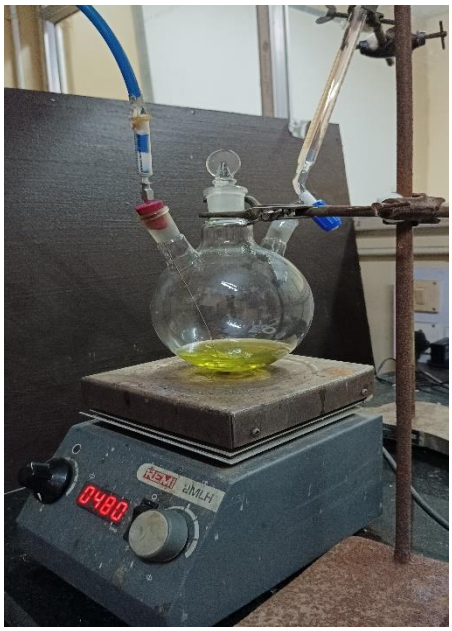


Fig 11: Synthesis set up for LDH

4.2.1 Procedure: For the preparation of Ni doped Mg - Fe LDH Magnesium Nitrate ($Mg(NO_3)_26H_2O$), Nickel Nitrate($Ni(NO_3)_2.6H_2O$) and Ferric Nitrate($Fe(NO_3)_3.9H_2O$) were taken in the molar ratio of 2:2:1,1:2:1, 2:1:1, 1:1:1 by mixing the precursor salt into DI water by magnetic stirring with constant Nitrogen flow into the mixture for 30 mins. 2.4 Molar of NaOH solution was prepared by mixing NaOH pellets with de-ionized water.

The NaOH 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. The whole process is done under constant

Nitrogen flow. Then the whole 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 60ºC for 24 hours. And lastly it is crushed using a mortar and pastel.



Fig 12: After Centrifugation



Fig 13: Final Ni doped Mg-Fe 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 5º to 80º for the powdered sample.

Thermogravimetric analysis (TGA) of Ni doped Mg- Fe LDH powdered sample is done in the temperature range of 35ºC to 900ºC.

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 experiment for heavy metal:

To perform adsorption experiments, a series of Arsenate(V), Arsenite (III), Lead (II) ion solution, having varying concentrations from 10 ppb to 1000 ppb were prepared from salt. As a typical batch experiment, adsorbent is added (1 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, Arsenite, Lead are measured by ICP-OES instrument.

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

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.

Qe= $(Ce-Ci)/\ Dosage\ of\ adsorbent$

Chapter 5

5.1 Result and Discussion:

5.1.1 TGA Analysis:

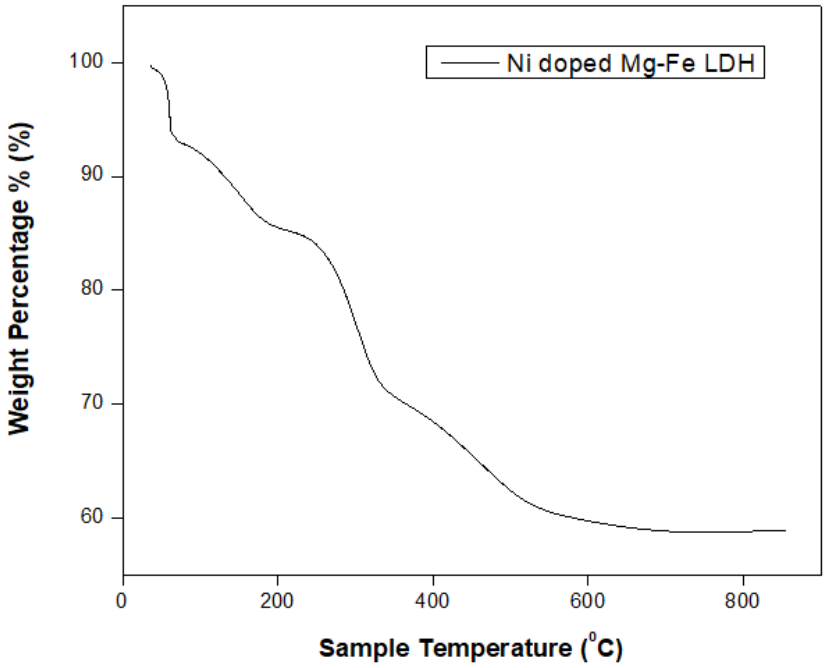


Fig14: TGA data analysis for Ni doped Mg Fe

The thermogravimetric analysis of Ni doped Mg Fe is comparable with the previous TGA data of LDH like material. The curve suggests an initial weight reduction between initial temperature and 200ºC which is caused by evaporation of water molecule which exists in the interlayer region by physisorption. Between 200ºC and 450ºC, 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 450ºC. Further increase in temperature from 450ºC to 950ºC causes complete dihydroxylation of Ni doped Mg Fe hydroxide layers and decomposition of nitrates. At a temperature beyond 600ºC the layered structure of LDH collapses and forms of new crystalline phase.

5.1. 2 FTIR Analysis:

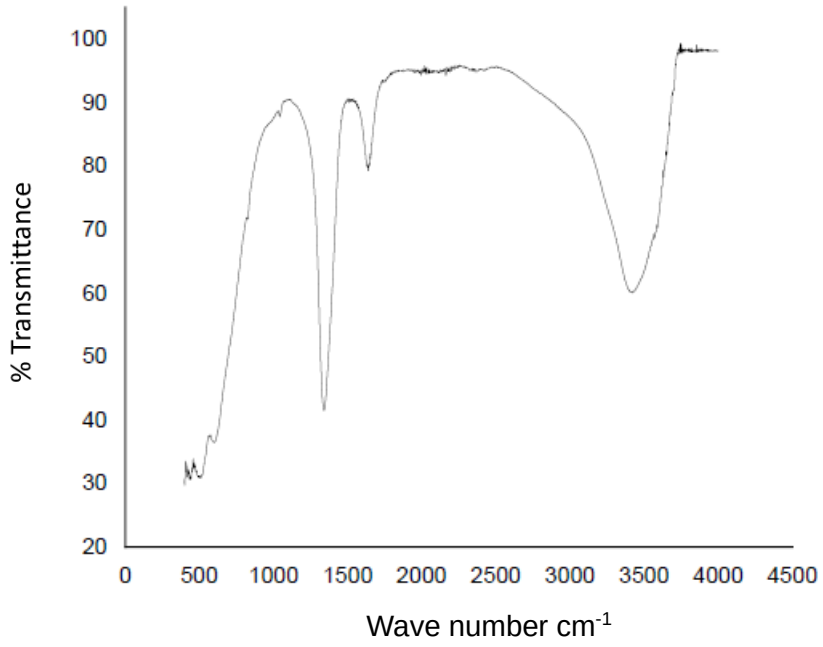


Fig15: FTIR data for Ni doped Mg Fe LDH material

The characteristic absorption band around 1400 cm^{-1} noticed in the IR spectrum due to the presence of $NO-$ 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 (<800ºC) suggests the vibration of lattice i.e., O-M-O vibration at 571cm^{-1} and M-O-H vibration at around 450cm^{-1}.

5.1.3 SEM Analysis:

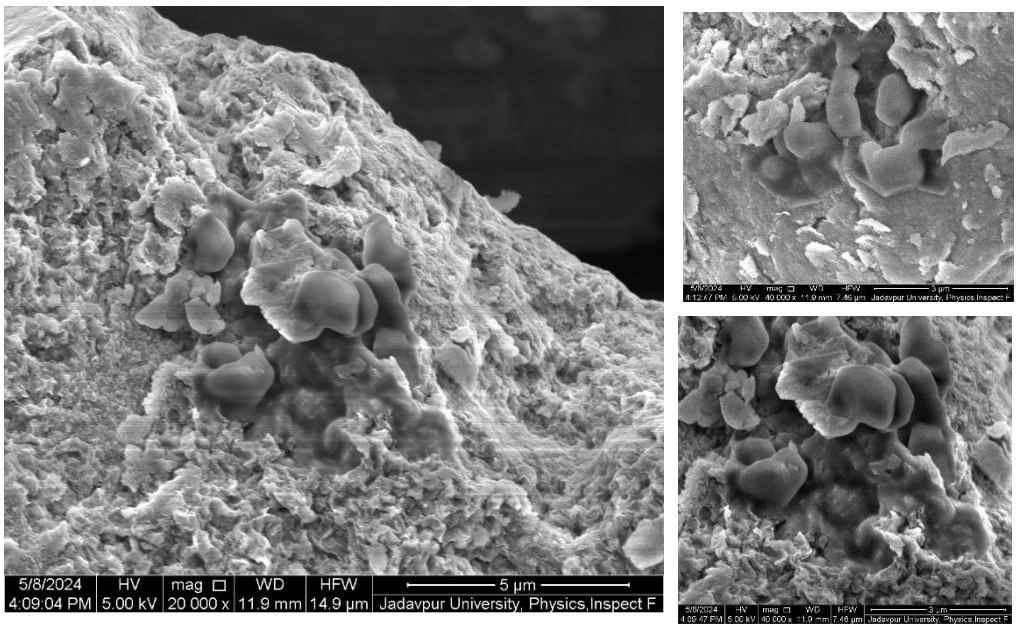


Fig16: Sem image of Ni doped Mg Fe LDH

Scanning electron micrographic images are shown here. LDH has hexagonal platelike 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.

5.1.4 XRD Analysis:

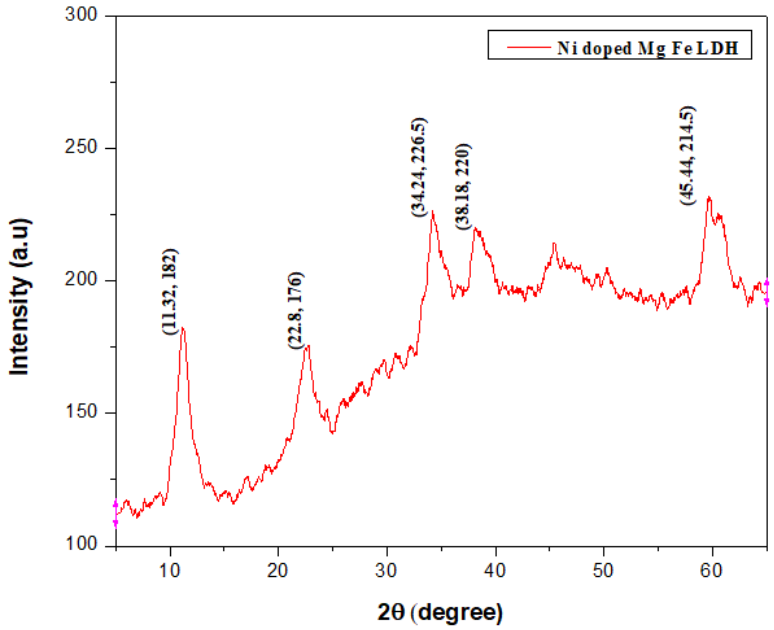


Fig17: XRD Pattern for Ni doped Mg Fe LDH (Mg: Ni: Fe = 2:2:1)

Diffraction patterns exhibited at 2Θ=11.32, 22.8, 34.24, 38.18, 45.44, 60 suggests the formation of layered double hydroxide structure of Ni doped Mg Fe. The sharp peaks confirm the crystalline structure in LDH. At 2Θ=60º there exists a peak which denotes the layered hexagonal plate like structure of LDH. This XRD plot confirms the formation of Ni doped Mg Fe nanocomposite having a highly crystalline hexagonal structure.

5.2 Adsorption studies:

Four different Ni doped Mg Fe LDH was prepared with four different metal ratios. A primary adsorption test (scanning experiment) was conducted to compare the adsorption capacity of Mg/Ni/Fe-LDH samples (prepared at four different molar ratios of (Mg/Ni/Fe) with As(V) and Pb(II) solution. The adsorption conditions were fixed at 0.5 g/L of adsorbent dose, 24 h, 25 °C, pH = 7.0, and 0.35 mg/L As (V) and Pb (II). The results (Figure:18) demonstrate that the Mg/Ni/Fe-LDH adsorbent prepared at the 2/2/1 ratio exhibited an efficiency in removing As ions similar to that prepared at the 1/2/1 ratio and higher than that prepared at 1/1/1 and 2/1/1. Therefore, Mn/Mg/Fe-LDH adsorbent (prepared at a ratio of 2/1/1) was selected in the subsequent batch adsorption experiments and material characterization.

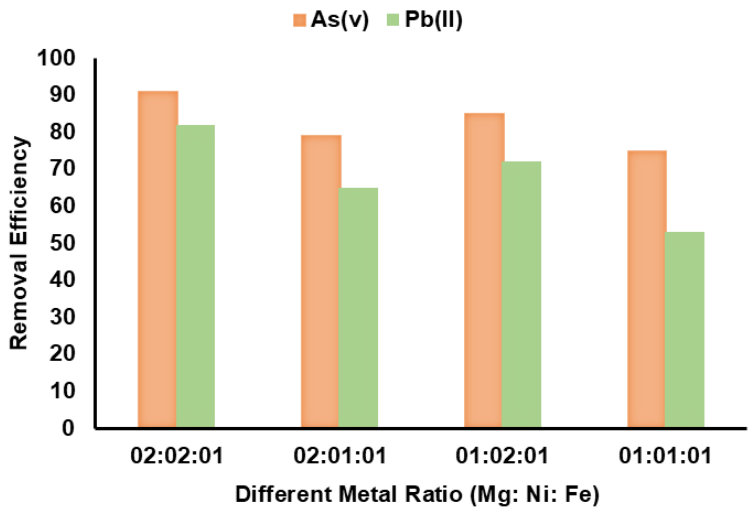


Fig18: Effect of molar ratio of metals (Mn, Mg, and Fe) on the adsorption capacity of resultant Mn/Mg/Fe-LDH samples towards As(V)and Lead (II)

5.2.1 Comparative Adsorption studies for Arsenic removal:

Comparative adsorption studies Ni doped Mg Fe (2:2:1) and Ni doped Mg Fe (1:2:1) was carried out for As(V).

Experiment No	Ci (ppb)	Ce° (ppb)	Ce (ppb)
1	1000	530.4	640.5
2	750	315.2	392.32
3	500	150.6	189.2
5	250	50.5	75.75
6	100	9.2	27.15

Table No 3: Comparative Arsenic adsorption data in higher conc. of LDH with different synthesis ratio

Where Ci is initial Arsenate Concentration, Ce° = final concentration after treating with Ni doped Mg-Fe (2:2:1), Ce = final concentration after treating with Ni doped Mg-Fe (1:2:1)

Experiment No	Ci (ppb)	Removal % (Mg:Ni:Fe= 2:2:1)	Removal % (Mg:Ni:Fe= 1:2:1)
1	1000	47.20	35.95
2	750	58.60	47.69
3	500	70.32	62.20
5	250	80.22	69.70
6	100	90.80	72.85

Table No 4: Comparative Arsenic removal data in higher conc. of LDH with different synthesis ratio.

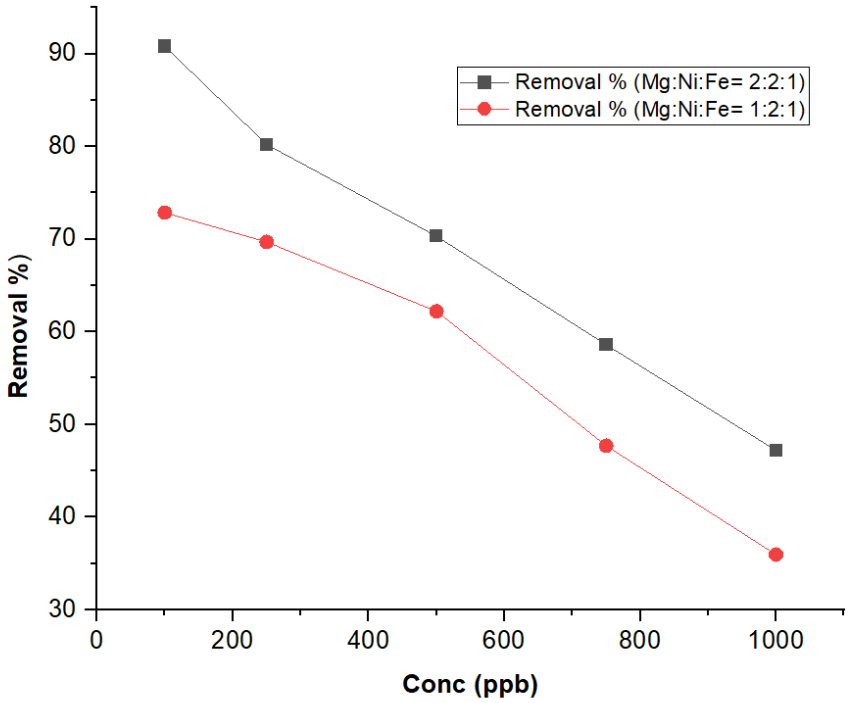


Fig 19: As removal % comparison between two Ni doped LDH with different synthesis ratio.

Experiment No	Ci (ppb)	Ce° (ppb)	Ce (ppb)
1	60	20.76	27.66
2	50	20.15	26.4
3	40	17.92	22.8
4	30	15.24	17.7
5	20	10.94	12.9
6	10	6.43	7.02

Table No 5: Comparative Arsenic adsorption data in lower conc. of LDH with different synthesis ratio

Experiment No	Ci (ppb)	Removal % (Mg:Ni:Fe= 2:2:1)	Removal % (Mg:Ni:Fe= 1:2:1)
1	60	65.40	53.9
2	50	59.7	47.2
3	40	55.2	43.0
4	30	49.2	41
5	20	45.3	35.5
6	10	35.7	29.8

Table No 6: Comparative Arsenic removal data in lower conc. of LDH with different synthesis ratio.

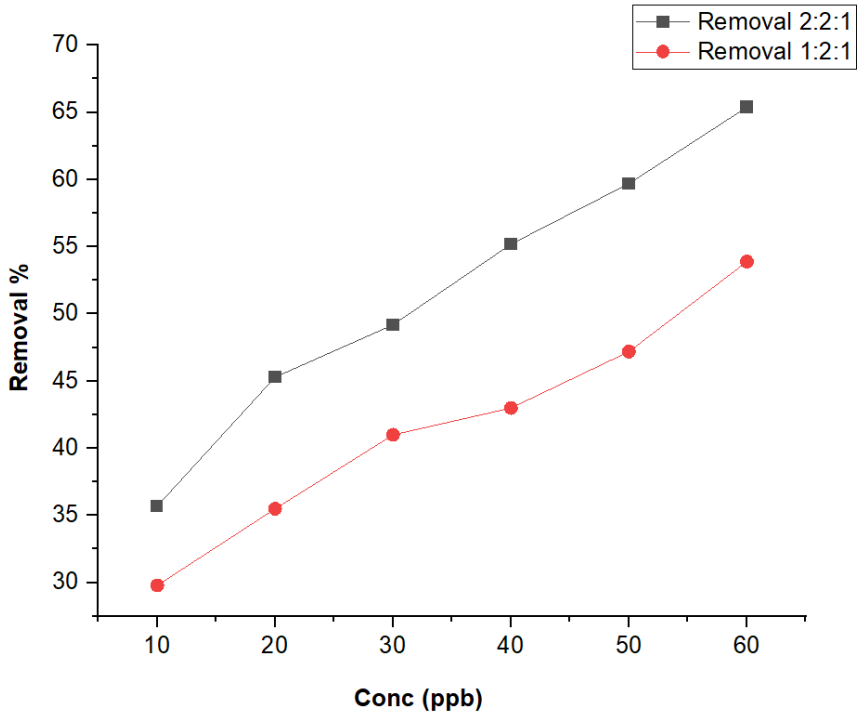


Fig 20: As removal % comparison between two Ni doped LDH with different synthesis ratio.

5.2.2 Comparative Adsorption studies for Lead removal:

Comparative adsorption studies Ni doped Mg Fe (2:2:1) and Ni doped Mg Fe (1:2:1) was carried out for Lead (II).

Experiment No	Ci (ppb)	Ce° (ppb)	Ce (ppb)
1	1000	608	694
2	750	391.95	465.62
3	500	172.5	213
5	250	74.87	94.25
6	100	26.92	35.90

Table No 7: Comparative Lead adsorption data in higher conc. of LDH with different synthesis ratio

Where Ci is initial Lead Concentration, Ce° = final concentration after treating with Ni doped Mg-Fe (2:2:1), Ce = final concentration after treating with Ni doped Mg-Fe (1:2:1)

Experiment No	Ci (ppb)	Removal % (Mg:Ni:Fe= 2:2:1)	Removal % (Mg:Ni:Fe= 1:2:1)
1	1000	39.20	30.60
2	750	47.74	38.45
3	500	65.5	57.40
5	250	70.05	62.30
6	100	73.08	64.10

Table No 8: Comparative Lead removal data in higher conc of LDH with different synthesis ratio.

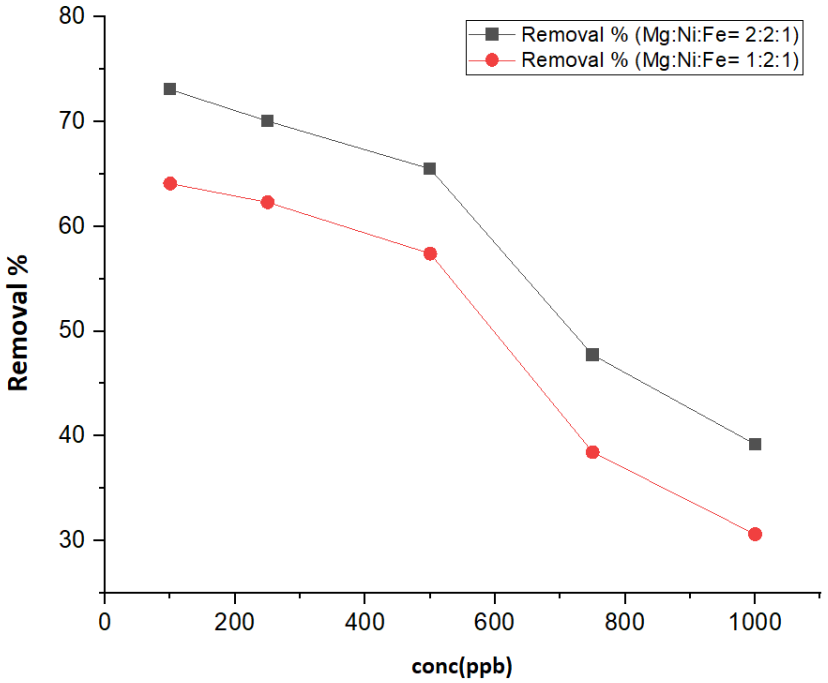


Fig 21: Lead removal % comparison between two Ni doped LDH with different synthesis ratio.

Experiment No	Ci (ppb)	Ce° (ppb)	Ce (ppb)
1	60	26.88	36.48
2	50	23.95	32.3
3	40	21.68	27.88
4	30	17.31	21.6
5	20	12.78	14.66
6	10	6.8	7.48

Table No 9: Comparative Lead adsorption data in lower conc. of LDH with different synthesis ratio.

Experiment No	Ci (ppb)	Removal % (Mg:Ni:Fe= 2:2:1)	Removal % (Mg:Ni:Fe= 1:2:1)
1	60	55.2	39.20
2	50	52.1	35.4
3	40	45.8	30.3
4	30	42.3	28.0
5	20	36.1	26.7
6	10	32.0	25.2

Table No 10: Comparative Lead removal data in lower conc. of LDH with different synthesis ratio.

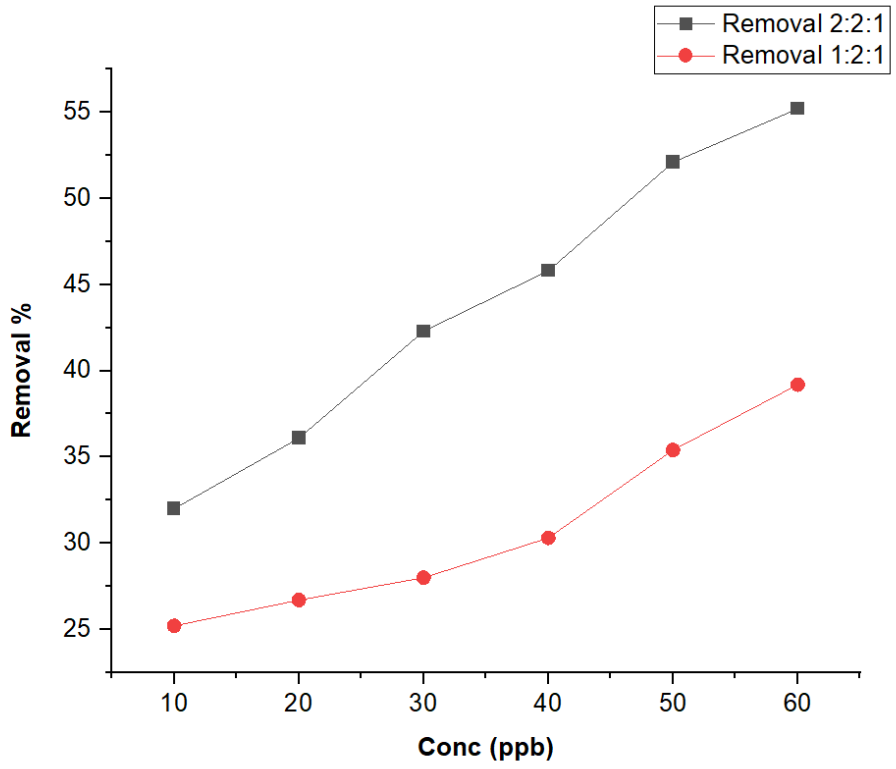


Fig 22: Lead removal % comparison between two Ni doped LDH with different synthesis ratio.

5.3 Adsorption Isotherm:

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 characterizing 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.[59]

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. [60]

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 favorability and capacity of the adsorbent/adsorbate system are related to the magnitude of 1/n. The n value between 1 and 10, indicating favorable adsorption. [61]

Langmuir Model:

$$\frac{1}{q_e} = \frac{1}{K_L} \times \frac{1}{C_e} + \frac{1}{q_{max}} \qquad K_L = \frac{1}{slope * q_{max}}$$

Freundlich Model:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

K_f = Inverse log intercept, $\frac{1}{n} = slope$

5.3.1 Adsorption Isotherm plot:

Maximum adsorption of Arsenic(V) and Lead(II) is shown in case of Ni doped Mg Fe LDH with Mg:Ni:Fe = 2:2:1 Adsorption isotherm data is plotted for both higher and lower conc. case.

Experiment No	Ci	C_e	$1/C_e$	Log C_e	q_e (mg/g)	$1/q_e$	Log q_e
1	1000	530.4	0.001887	2.724276	470	0.002128	2.672098
2	750	315.2	0.003175	2.498311	435	0.002299	2.638489
3	500	150.6	0.006667	2.176091	350	0.002857	2.544068
4	250	50.5	0.02	1.69897	200	0.005	2.30103
5	100	9.2	0.111111	0.954243	93	0.010753	1.968483

Table No 11: Adsorption data for Arsenic in higher Conc

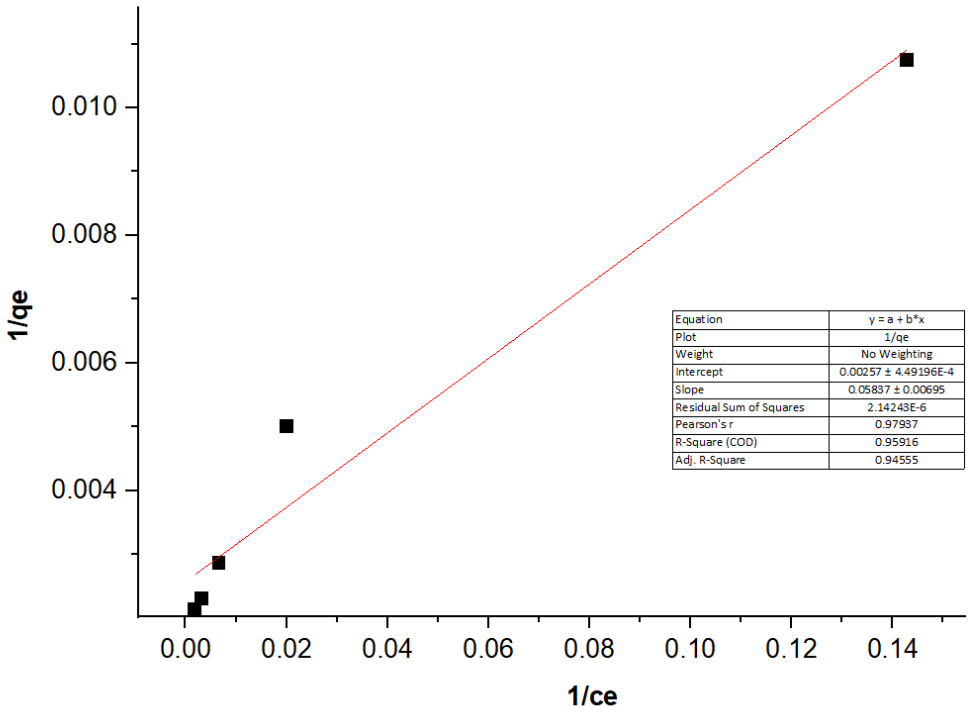


Fig 23: Langmuir Isotherm for Arsenic adsorption

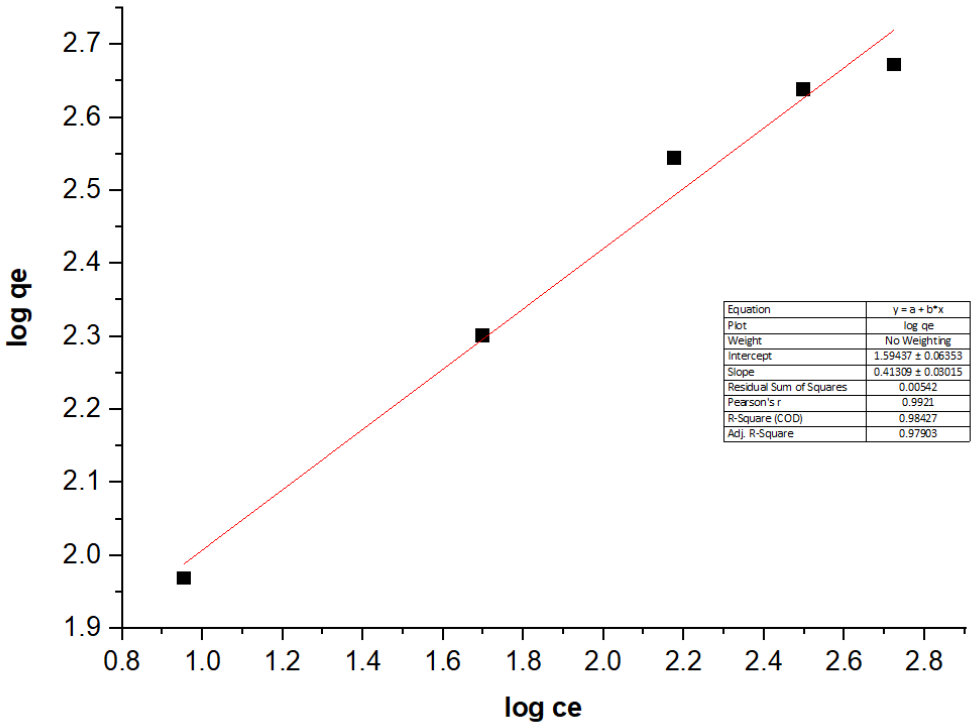


Fig 24: Freundlich isotherm for Arsenic adsorption

Langmuir Data:

Intercept	**Slope**	**R^2**
0.00257	0.05837	0.94555

Freundlich Data:

Intercept	**Slope**	**R^2**
1.59437	0.41309	0.9803

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

Experiment No	Ci	C_e	$1/C_e$	Log C_e	q_e (mg/g)	$1/q_e$	Log q_e
1	1000	608	0.001887	2.724276	470	0.002128	2.672098
2	750	391.95	0.003175	2.498311	435	0.002299	2.638489
3	500	172.5	0.006667	2.176091	350	0.002857	2.544068
4	250	74.87	0.02	1.69897	200	0.005	2.30103
5	100	26.92	0.111111	0.954243	93	0.010753	1.968483

Table No 12: Adsorption data for Lead in higher Conc.

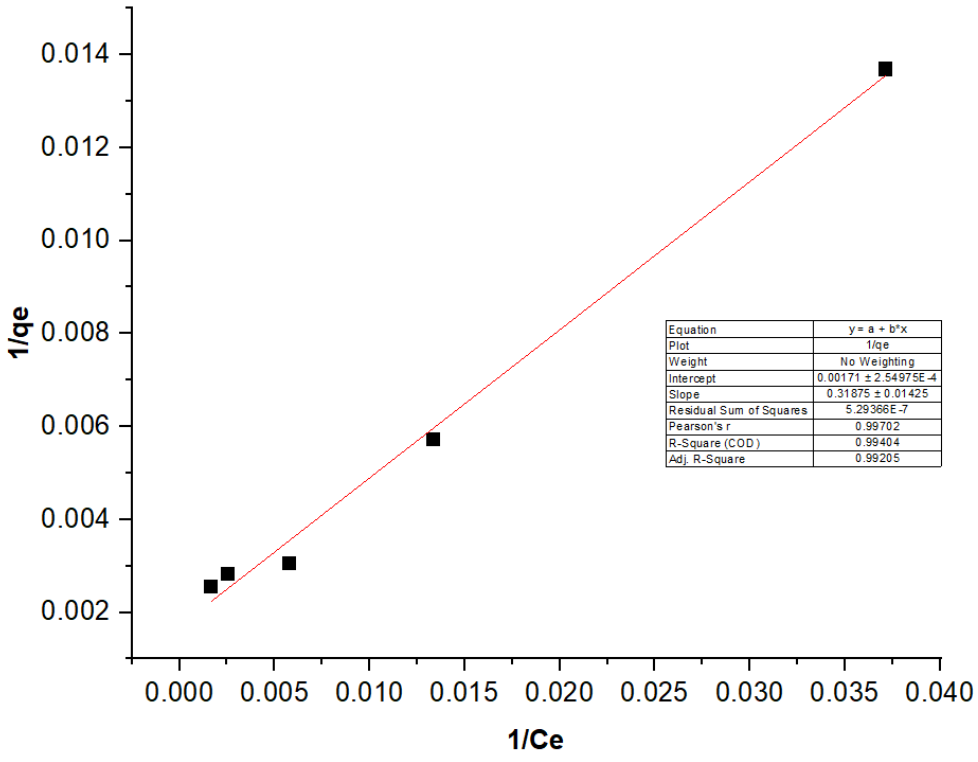


Fig 25: Langmuir Isotherm for Lead removal

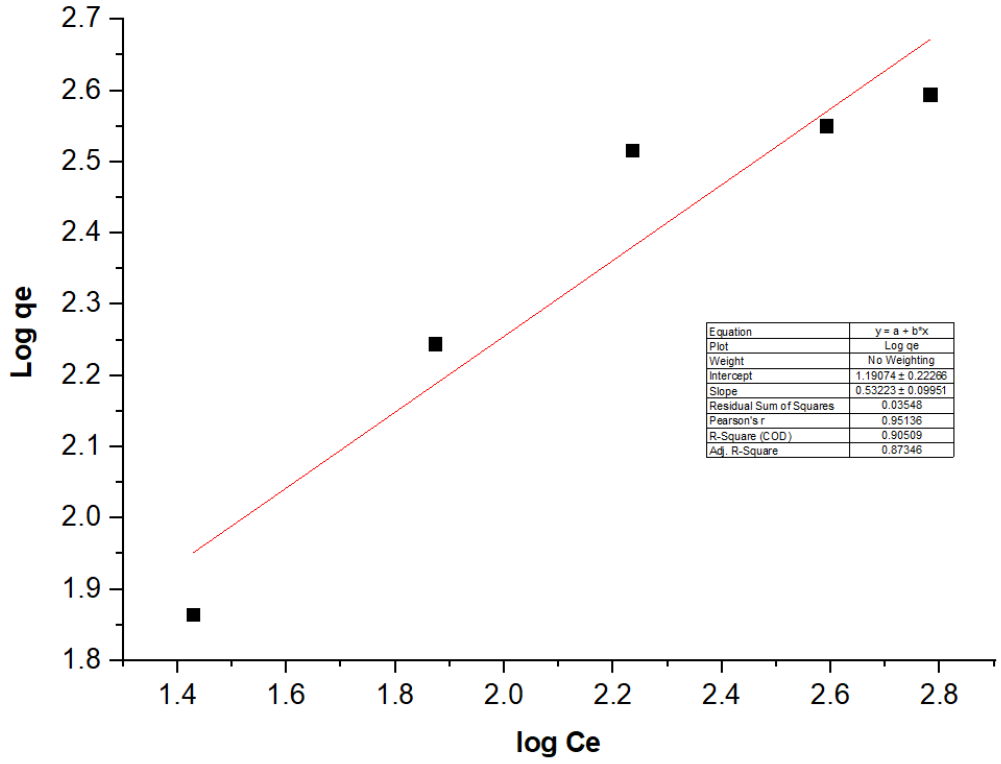


Fig 26: Freundlich isotherm for Lead removal

Langmuir Data:

Intercept	**Slope**	**R^2**
0.00171	0.31875	0.99205

Freundlich Data:

Intercept	**Slope**	**R^2**
0.19074	0.53223	0.8734

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

5.3.2 Adsorption data for As(V) and Lead (II) in lower Concentration:

Experiment No	Ci	C_e	$1/C_e$	Ln Ce	qe (mg/g)	1/qe	Log qe
1	60	20.76	0.048	3.03	78.48	0.012	2.59
2	50	20.15	0.049	3.00	59.7	0.016	2.55
3	40	17.92	0.055	2.88	44.16	0.022	2.51
4	30	15.24	0.065	2.72	29.52	0.033	2.46
5	20	10.94	0.091	2.39	18.12	0.055	2.24
6	10	6.43	0.155	1.86	7.12	0.14	1.78

Table No 13: Adsorption data for Arsenic in lower Conc.

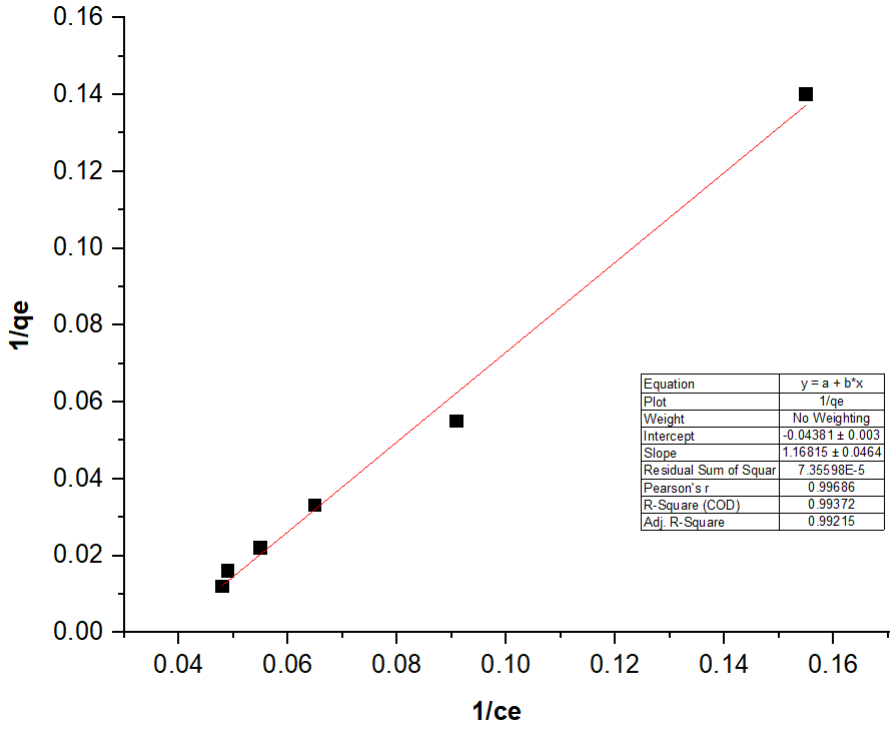


Fig 27: Langmuir isotherm for Arsenic adsorption

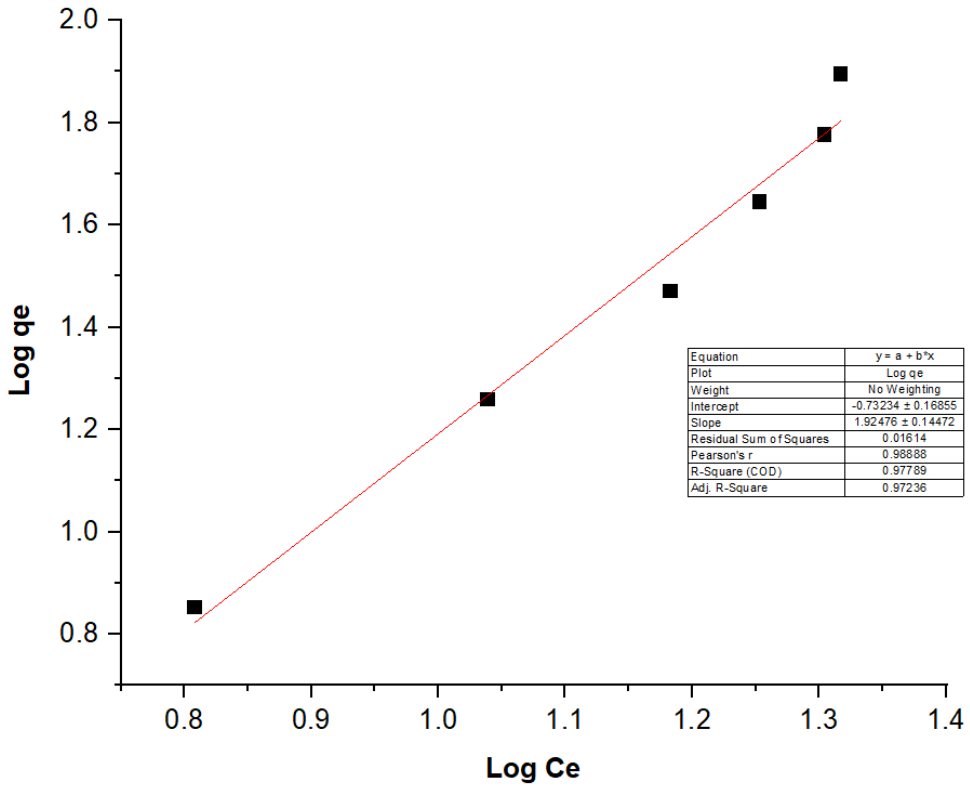


Fig 28: Freundlich isotherm for Arsenic adsorption

Langmuir Data:

Intercept	**Slope**	**R^2**
-0.043	1.16	0.99215

Freundlich Data:

Intercept	**Slope**	**R^2**
-0.732	1.92	0.972

Looking at the R square value it can be said that Langmuir isotherm model is better fitted here. So, it can be confirmed that mono layer adsorption is happening here.

Experiment No	Ci	C_e	$1/C_e$	Ln Ce	qe (mg/g)	1/qe	Log qe	Log Ce
1	60	26.88	0.037202	3.291383	66.24	0.015097	1.82112	1.429429
2	50	23.95	0.041754	3.175968	52.1	0.019194	1.716838	1.379306
3	40	21.68	0.046125	3.07639	36.64	0.027293	1.563955	1.336059
4	30	17.31	0.05777	2.851284	25.38	0.039401	1.404492	1.238297
5	20	12.78	0.078247	2.547881	14.44	0.069252	1.159567	1.106531
6	10	6.8	0.147059	1.916923	6.4	0.15625	0.80618	0.832509

Table No 14: Adsorption data of Lead in lower conc.

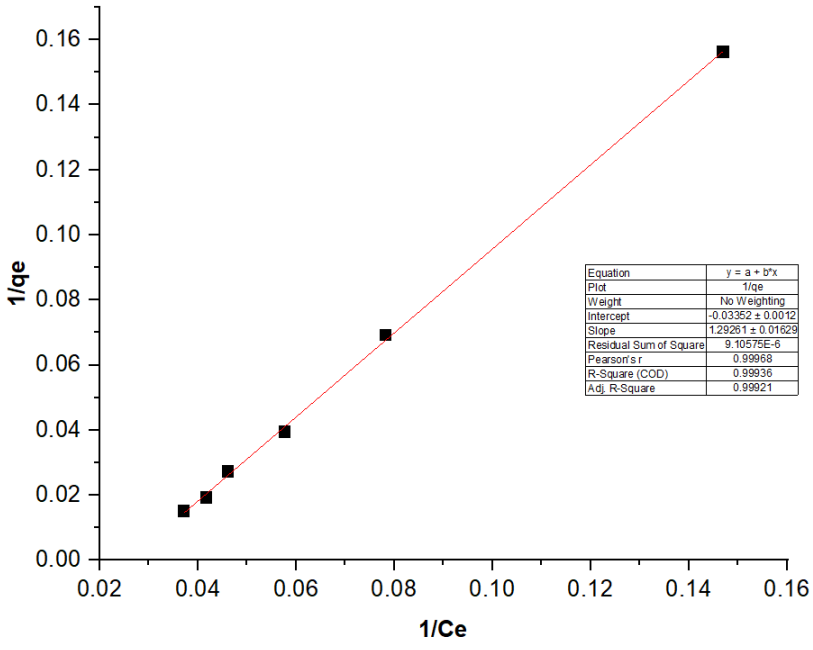


Fig 29: Langmuir isotherm for Lead adsorption

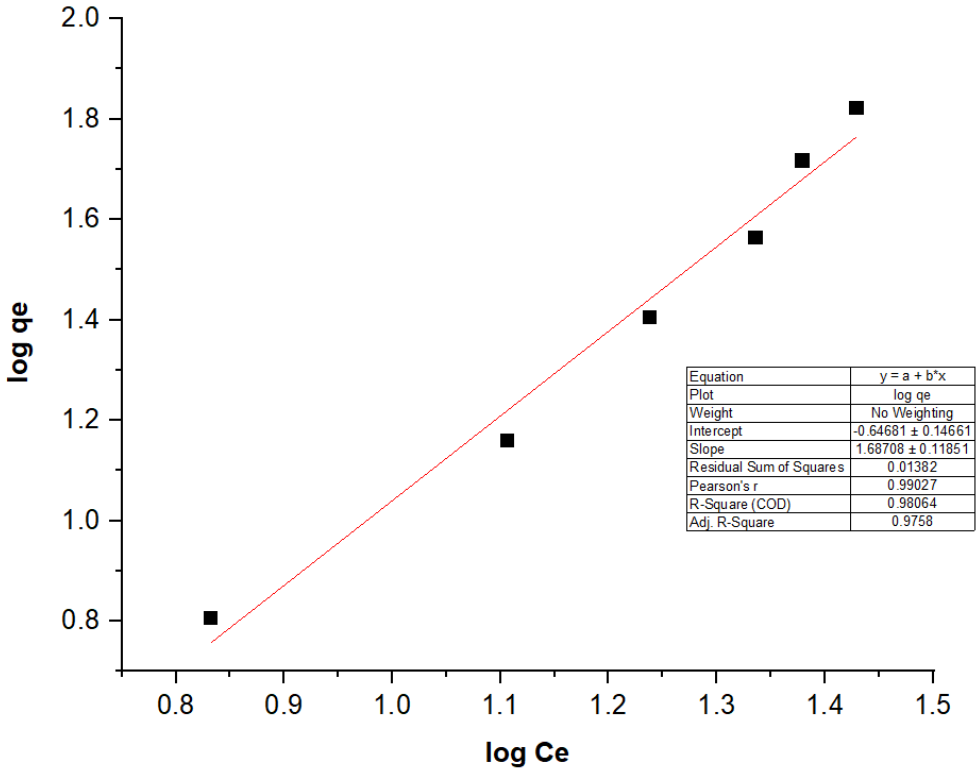


Fig 30: Freundlich isotherm for Lead adsorption

Langmuir Data:

Intercept	**Slope**	**R^2**
-0.035	1.29	0.99921

Freundlich Data:

Intercept	**Slope**	**R^2**
-0.64	1.68	0.9758

Looking at the R square value it can be said that Langmuir isotherm model is better fitted here. So, it can be confirmed that mono layer adsorption is happening here.

5.4 Effect of Contact time:

Adsorption phenomenon Ni doped Mg Fe LDH is performed with different contact time (60min, 120 min, 180 min, 240 min, 300 min) for 100 ppb Arsenate solution.

Concentration in ppb	Contact Time in min	Removal %
100	60	59
100	120	68
100	180	75
100	240	91
100	300	91

Table No 15: Effect of Contact time for Arsenic removal

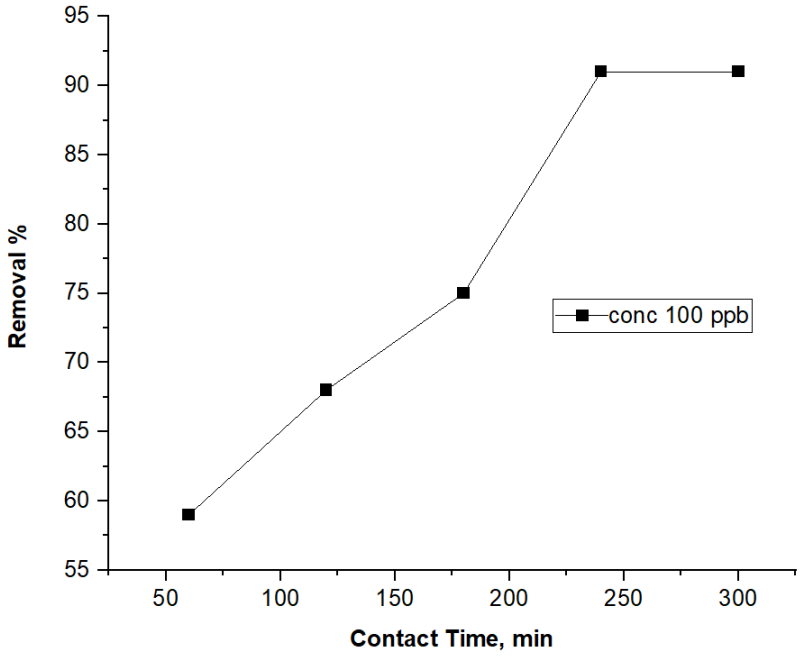


Fig 31: Effect of Contact time for Arsenic removal

From the fig 31, it is obvious that with increasing contact time arsenic removal increases till 240 min then it reaches equilibrium.

5.5 Effect of pH:

Adsorption phenomenon Ni doped Mg Fe LDH is performed with different pH values (12,10,8,6,4) for 100 ppb Arsenate solution. Adsorption time was 200min. Ph of the Arsenic solution is adjusted with mixing with diluted H_2SO_4 and NaOH.

Concentration in ppb	pH	Removal %
100	12	67
100	10	75
100	8	82
100	6	86
100	4	86

Table No 16: Effect of pH for Arsenic removal

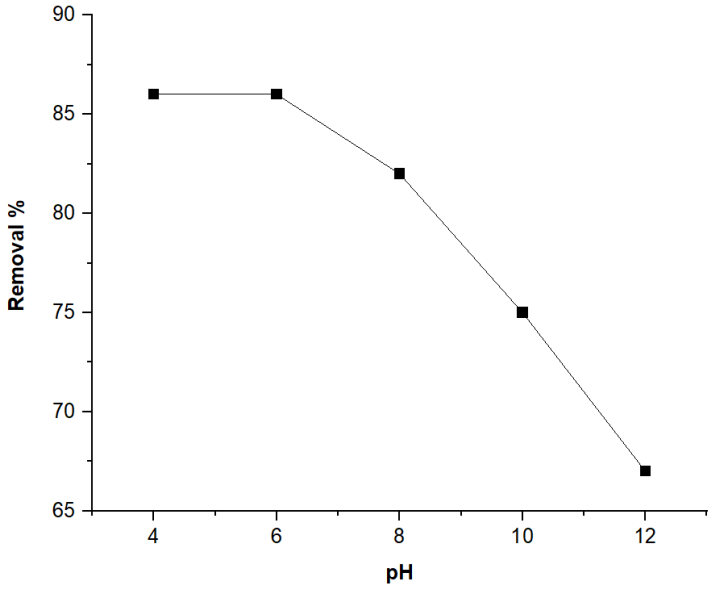


Fig No 32: Effect of pH for Arsenic removal

Maximum arsenic removal is achieved at pH value of 6 from fig 30. Furthermore, in acidic medium it reaches equilibrium.

Chapter 6

6.1 Conclusion:

Ni doped Mg Fe LDH can be efficient adsorbent for simultaneous removal of As(V) and Pb (II). In this study, Ni doped Mg- Fe LDH with four different Mg/Ni/Fe (2:2:1, 2:1:1, 1:2:1, 1:1:1) have been synthesized via typical co precipitation method. The results are summarized as follows (1) the experimental results demonstrated that Ni doped Mg Fe shows maximum arsenic and lead removal 91% and 81.5% at value in neutral medium. (2) For higher concentration, Arsenic adsorption model can be well described by Freundlich isotherm it can be confirmed that double layer adsorption is happening here. (3) Diffraction patterns exhibited at 2Ɵ=11.32, 22.8, 34.24, 38.18, 45.44, 60 suggests the formation of layered double hydroxide structure of Ni doped Mg Fe. The sharp peaks confirm the crystalline structure in LDH. At 2Ɵ=60º there exists a peak which denotes the layered hexagonal plate like structure of LDH. (4) From SEM analysis it is confirmed Ni doped Mg/Fe-LDH adsorbent showed characteristics of plate-like morphology and hexagonal crystallite. (5) TGA data confirms that Ni doped Mg/ Fe has higher thermal stability. (6) The characteristic absorption band around 1400 cm^{-1} noticed in the IR spectrum due to the presence of $NO-$ 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. From above experimental result Ni doped Mg/Fe can use used as a novel adsorbent in corporation with mixed matrix membrane for application purposes.

6.2 Reference:

1. Kumar, P. R., Gowd, S. S., & Krupavathi, C. (2024). Groundwater quality evaluation using water quality index and geospatial techniques in parts of Anantapur District, Andhra Pradesh, South India. In HydroResearch (Vol. 7, pp. 86–98). Elsevier BV. https://doi.org/10.1016/j.hydres.2024.01.001

2. Adimalla N, Wu J (2019) Groundwater quality and associated health risks in a semi-arid region of south India: implication to sustainable 1136 Page 18 of 20 Arab J Geosci (2022) 15: 1136 1 3 groundwater management. Hum Ecol Risk Assess Int J 25(1–2):191– 216. https://doi.org/10.1080/10807039.2018.1546550

3. Ground water year book 2017-18 MINISTRY OF WATER RESOURCES, RIVER DEVELOPMENT AND GANGA REJUVENATION

4. Sharma, P. K., Mayank, M., Ojha, C. S. P., & Shukla, S. K. (2018). A review on groundwater contaminant transport and remediation. In ISH Journal of Hydraulic Engineering (pp. 1–10). Informa UK Limited. https://doi.org/10.1080/09715010.2018.1438213

5. Christensen, T. H., Bjerg, P. L., Banwart, S. A., Jakobsen, R., Heron, G., & Albrechtsen, H.-J. (2000). Characterization of redox conditions in groundwater contaminant plumes. In Journal of Contaminant Hydrology (Vol. 45, Issues 3–4, pp. 165–241). Elsevier BV. https://doi.org/10.1016/s0169-7722(00)00109-1

6. Shankar, S., Shanker, U., & Shikha. (2014). Arsenic Contamination of Groundwater: A Review of Sources, Prevalence, Health Risks, and Strategies for Mitigation. In The Scientific World Journal (Vol. 2014, pp. 1–18). Hindawi Limited. https://doi.org/10.1155/2014/304524

7. Shen, S., Li, X.-F., Cullen, W. R., Weinfeld, M., & Le, X. C. (2013). Arsenic Binding to Proteins. In Chemical Reviews (Vol. 113, Issue 10, pp. 7769–7792). American Chemical Society (ACS). https://doi.org/10.1021/cr300015c

8. Shukla, D. P., Dubey, C. S., Singh, N. P., Tajbakhsh, M., & Chaudhry, M. (2010). Sources and controls of Arsenic contamination in groundwater of Rajnandgaon and Kanker District, Chattisgarh Central India. In Journal of Hydrology (Vol. 395, Issues 1–2, pp. 49–66). Elsevier BV. https://doi.org/10.1016/j.jhydrol.2010.10.011

9. Zhou, Q., Yang, N., Li, Y., Ren, B., Ding, X., Bian, H., & Yao, X. (2020). Total concentrations and sources of heavy metal pollution in global river and lake water bodies from 1972 to 2017. In Global Ecology and Conservation (Vol. 22, p. e00925). Elsevier BV. https://doi.org/10.1016/j.gecco.2020.e00925

10. QU, J. (2008). Research progress of novel adsorption processes in water purification: A review. In Journal of Environmental Sciences (Vol. 20, Issue 1, pp. 1–13). Elsevier BV. https://doi.org/10.1016/s1001-0742(08)60001-7

11. Wang, J., & Guo, X. (2020). Adsorption isotherm models: Classification, physical meaning, application and solving method. In Chemosphere (Vol. 258, p. 127279). Elsevier BV. https://doi.org/10.1016/j.chemosphere.2020.127279

12. Xie, Y., Yuan, X., Wu, Z., Zeng, G., Jiang, L., Peng, X., & Li, H. (2019). Adsorption behavior and mechanism of Mg/Fe layered double hydroxide with Fe3O4-carbon spheres on the removal of Pb(II) and Cu(II). In Journal of Colloid and Interface Science (Vol. 536, pp. 440–455). Elsevier BV. https://doi.org/10.1016/j.jcis.2018.10.066

13. Stamate, A.-E., Pavel, O. D., Zavoianu, R., & Marcu, I.-C. (2020). Highlights on the Catalytic Properties of Polyoxometalate-Intercalated Layered Double Hydroxides: A Review. In Catalysts (Vol. 10, Issue 1, p. 57). MDPI AG. https://doi.org/10.3390/catal10010057

14. Boumeriame, H., Da Silva, E. S., Cherevan, A. S., Chafik, T., Faria, J. L., & Eder, D. (2022). Layered double hydroxide (LDH)-based materials: A mini-review on strategies to improve the performance for photocatalytic water splitting. In Journal of Energy Chemistry (Vol. 64, pp. 406–431). Elsevier BV. https://doi.org/10.1016/j.jechem.2021.04.050

15. He, X., Qiu, X., Hu, C., & Liu, Y. (2017). Treatment of heavy metal ions in wastewater using layered double hydroxides: A review. In Journal of Dispersion Science and Technology (Vol. 39, Issue 6, pp. 792–801). Informa UK Limited. https://doi.org/10.1080/01932691.2017.1392318

16. Johnston, A.-L., Lester, E., Williams, O., & Gomes, R. L. (2021). Understanding Layered Double Hydroxide properties as sorbent materials for removing organic pollutants from environmental waters. In Journal of Environmental Chemical Engineering (Vol. 9, Issue 4, p. 105197). Elsevier BV. https://doi.org/10.1016/j.jece.2021.105197

17. Bugaenko, L. T., Ryabykh, S. M., & Bugaenko, A. L. (2008). A nearly complete system of average crystallographic ionic radii and its use for determining ionization potentials. In Moscow University Chemistry Bulletin (Vol. 63, Issue 6, pp. 303–317). Allerton Press. https://doi.org/10.3103/s0027131408060011

18. Sebri, N. J. M., Latip, A. F. A., Adnan, R., & Hussin, M. H. (2022). Layered double hydroxides (LDHs) as green nanofillers in composites. In Green Sustainable Process for Chemical and Environmental Engineering and Science (pp. 23–42). Elsevier. https://doi.org/10.1016/b978-0-323-99643-3.00004-8

19. Cavani, F., Trifirò, F., & Vaccari, A. (1991). Hydrotalcite-type anionic clays: Preparation, properties and applications. In Catalysis Today (Vol. 11, Issue 2, pp. 173–301). Elsevier BV. https://doi.org/10.1016/0920-5861(91)80068-k

20. Johnston, A.-L., Lester, E., Williams, O., & Gomes, R. L. (2021). Understanding Layered Double Hydroxide properties as sorbent materials for removing organic pollutants from environmental waters. In Journal of Environmental Chemical Engineering (Vol. 9, Issue 4, p. 105197). Elsevier BV. https://doi.org/10.1016/j.jece.2021.105197

21. VACCARI, A. (2002). Layered double hydroxides: present and futureV. Rives (Ed.), Nova Science Publishers, Inc., New York, 2001, IX+439 pp., ISBN 1-59033-060-9. In Applied Clay Science (Vol. 22, Issues 1–2, pp. 75–76). Elsevier BV. https://doi.org/10.1016/s0169-1317(02)00112-6

22. Hadipour, H., & Akhavan, M. (2010). Effect of electron correlation in Sr(Ca)Ru1−xCrxO3: Density functional calculation. In Journal of Solid State Chemistry (Vol. 183, Issue 7, pp. 1678–1690). Elsevier BV. https://doi.org/10.1016/j.jssc.2010.05.013

23. Xie, S., Liu, M., Zhang, X., Yang, C., Zhang, Y., Qin, Y., He, C., Dou, Y., Gao, C., & Yuan, Y. (2022). Zeolite/ZnAl-layer double hydroxides with different Zn/Al ratios and intercalated anions as the substrate of constructed wetlands: synthesis, characterization and purification effect of Hexavalent chromium. In Environmental Science and Pollution Research (Vol. 30, Issue 8, pp. 19814–19827). Springer Science and Business Media LLC. https://doi.org/10.1007/s11356-022-23594-5

24. Zhang, T., Steenhaut, T., Li, X., Devred, F., Devillers, M., & Filinchuk, Y. (2023). Aluminum methylamidoborane complexes: mechanochemical synthesis, structure, stability, and reactive hydride composites. In Sustainable Energy & Fuels (Vol. 7, Issue 4, pp. 1119–1126). Royal Society of Chemistry (RSC). https://doi.org/10.1039/d2se01558g

25. Miyata, S., & Okada, A. (1977). Synthesis of Hydrotalcite-Like Compounds and their Physico-Chemical Properties—The Systems Mg2+-Al3+-SO42− and Mg2+-Al3+-CrO42−. In Clays and Clay Minerals (Vol. 25, Issue 1, pp. 14–18). Cambridge University Press (CUP). https://doi.org/10.1346/ccmn.1977.0250103

26. Johnston, A.-L., Lester, E., Williams, O., & Gomes, R. L. (2021). Understanding Layered Double Hydroxide properties as sorbent materials for removing organic pollutants from environmental waters. In Journal of Environmental Chemical Engineering (Vol. 9, Issue 4, p. 105197). Elsevier BV. https://doi.org/10.1016/j.jece.2021.105197

27. Daniel, S., & Thomas, S. (2020). Layered double hydroxides: fundamentals to applications. In Layered Double Hydroxide Polymer Nanocomposites (pp. 1–76). Elsevier. https://doi.org/10.1016/b978-0-08-101903-0.00001-5

28. . Lehmann, M., Zouboulis, A. I., & Matis, K. A. (1999). Removal of metal Ions from dilute aqueous solutions: A comparative study of inorganic sorbent materials. In Chemosphere (Vol. 39, Issue 6, pp. 881–892). Elsevier BV. https://doi.org/10.1016/s0045- 6535(99)00031-4

29. Dong, Y., Kong, X., Luo, X., & Wang, H. (2022). Adsorptive removal of heavy metal anions from water by layered double hydroxide: A review. In Chemosphere (Vol. 303, p. 134685). Elsevier BV. https://doi.org/10.1016/j.chemosphere.2022.134685

30. Behrens, P. (1993). Mesoporous inorganic solids. In Advanced Materials (Vol. 5, Issue 2, pp. 127–132). Wiley. https://doi.org/10.1002/adma.19930050212

31. Velu, S., Shah, N., Jyothi, T. M., & Sivasanker, S. (1999). Effect of manganese substitution on the physicochemical properties and catalytic toluene oxidation activities of Mg–Al layered double hydroxides. In Microporous and Mesoporous Materials (Vol. 33, Issues 1– 3, pp. 61–75). Elsevier BV. https://doi.org/10.1016/s1387-1811(99)00123-7

32. Zhou, M., Yan, L., Ling, H., Diao, Y., Pang, X., Wang, Y., & Gao, K. (2017). Design and fabrication of enhanced corrosion resistance Zn-Al layered double hydroxides films based anion-exchange mechanism on magnesium alloys. In Applied Surface Science (Vol. 404, pp. 246–253). Elsevier BV. https://doi.org/10.1016/j.apsusc.2017.01.161

33. Wang, J., Zhang, T., Li, M., Yang, Y., Lu, P., Ning, P., & Wang, Q. (2018). Arsenic removal from water/wastewater using layered double hydroxide derived adsorbents, a critical review. In RSC Advances (Vol. 8, Issue 40, pp. 22694–22709). Royal Society of Chemistry (RSC). https://doi.org/10.1039/c8ra03647k

34. HONGO, T., IEMURA, T., & YAMAZAKI, A. (2008). Adsorption ability for several harmful anions and thermal behavior of Zn-Fe layered double hydroxide. In Journal of the Ceramic Society of Japan (Vol. 116, Issue 1350, pp. 192–197). Ceramic Society of Japan. https://doi.org/10.2109/jcersj2.116.192

35. Xu, Y., Dai, Y., Zhou, J., Xu, Z. P., Qian, G., & Lu, G. Q. M. (2010). Removal efficiency of arsenate and phosphate from aqueous solution using layered double hydroxide materials: intercalation vs. precipitation. In Journal of Materials Chemistry (Vol. 20, Issue 22, p. 4684). Royal Society of Chemistry (RSC). https://doi.org/10.1039/b926239c

36. Liang, X., Hou, W., & Xu, J. (2009). Sorption of Pb(II) on Mg-Fe Layered Double Hydroxide. In Chinese Journal of Chemistry (Vol. 27, Issue 10, pp. 1981–1988). Wiley. https://doi.org/10.1002/cjoc.200990333

37. Saiah, F. B. D., Su, B.-L., & Bettahar, N. (2009). Nickel–iron layered double hydroxide (LDH): Textural properties upon hydrothermal treatments and application on dye sorption. In Journal of Hazardous Materials (Vol. 165, Issues 1–3, pp. 206–217). Elsevier BV. https://doi.org/10.1016/j.jhazmat.2008.09.125

38. Goh, K.-H., Lim, T.-T., Banas, A., & Dong, Z. (2010). Sorption characteristics and mechanisms of oxyanions and oxyhalides having different molecular properties on Mg/Al layered double hydroxide nanoparticles. In Journal of Hazardous Materials (Vol. 179, Issues 1–3, pp. 818–827). Elsevier BV. https://doi.org/10.1016/j.jhazmat.2010.03.077

39. . Wasewar, K. L., Singh, S., & Kansal, S. K. (2020). Process intensification of treatment of inorganic water pollutants. In Inorganic Pollutants in Water (pp. 245–271). Elsevier. https://doi.org/10.1016/b978-0-12-818965-8.00013-5

40. 6. Goh, K.-H., Lim, T.-T., & Dong, Z. (2008). Application of layered double hydroxides for removal of oxyanions: A review. In Water Research (Vol. 42, Issues 6–7, pp. 1343– 1368). Elsevier BV. https://doi.org/10.1016/j.watres.2007.10.043

41. WANG, S., LIU, C., WANG, M., CHUANG, Y., & CHIANG, P. (2009). Arsenate adsorption by Mg/Al–NO3 layered double hydroxides with varying the Mg/Al ratio. In Applied Clay Science (Vol. 43, Issue 1, pp. 79–85). Elsevier BV. https://doi.org/10.1016/j.clay.2008.07.005

42. . Kang, D., Yu, X., Tong, S., Ge, M., Zuo, J., Cao, C., & Song, W. (2013). Performance and mechanism of Mg/Fe layered double hydroxides for fluoride and arsenate removal from aqueous solution. In Chemical Engineering Journal (Vol. 228, pp. 731–740). Elsevier BV. https://doi.org/10.1016/j.cej.2013.05.041

43. Wen, T., Wu, X., Tan, X., Wang, X., & Xu, A. (2013). One-Pot Synthesis of WaterSwellable Mg–Al Layered Double Hydroxides and Graphene Oxide Nanocomposites for Efficient Removal of As(V) from Aqueous Solutions. In ACS Applied Materials & Interfaces (Vol. 5, Issue 8, pp. 3304–3311). American Chemical Society (ACS). https://doi.org/10.1021/am4003556

44. Cao, Y., Guo, Q., Liang, M., & Sun, W. (2020). Sb(III) and Sb(V) removal from water by a hydroxyl-intercalated, mechanochemically synthesized Mg-Fe-LDH. In Applied Clay Science (Vol. 196, p. 105766). Elsevier BV. https://doi.org/10.1016/j.clay.2020.105766

45. Balcik, C., Ozbey-Unal, B., Cifcioglu-Gozuacik, B., Keyikoglu, R., Karagunduz, A., & Khataee, A. (2022). Fabrication of PSf nanocomposite membranes incorporated with ZnFe layered double hydroxide for separation and antifouling aspects. In Separation and Purification Technology (Vol. 285, p. 120354). Elsevier BV. https://doi.org/10.1016/j.seppur.2021.120354

46. Zhao, Y., Li, N., & Xia, S. (2016). Polyamide nanofiltration membranes modified with Zn– Al layered double hydroxides for natural organic matter removal. In Composites Science and Technology (Vol. 132, pp. 84–92). Elsevier BV. https://doi.org/10.1016/j.compscitech.2016.06.016

47. Lee, S.-H., Choi, H., & Kim, K.-W. (2018). Removal of As(V) and Sb(V) in aqueous solution by Mg/Al-layered double hydroxide-incorporated polyethersulfone polymer beads (PES-LDH). In Environmental Geochemistry and Health (Vol. 40, Issue 5, pp. 2119– 2129). Springer Science and Business Media LLC. https://doi.org/10.1007/s10653-018- 0087-y

48. 24. Nakahira, A., Kubo, T., & Murase, H. (2007). Synthesis of LDH-Type Clay Substituted With Fe and Ni Ion for Arsenic Removal and Its Application to Magnetic Separation. In IEEE Transactions on Magnetics (Vol. 43, Issue 6, pp. 2442–2444). Institute of Electrical and Electronics Engineers (IEEE). https://doi.org/10.1109/tmag.2007.894359

49. 25. Tang, Z., Qiu, Z., Lu, S., & Shi, X. (2020). Functionalized layered double hydroxide applied to heavy metal ions absorption: A review. In Nanotechnology Reviews (Vol. 9, Issue 1, pp. 800–819). Walter de Gruyter GmbH. https://doi.org/10.1515/ntrev-2020-0065

50. Zaghloul, A., Abali, M., Benhiti, R., Ait ichou, A., Soudani, A., Chiban, M., Zerbet, M., & Sinan, F. (2019). Removal of methyl orange from aqueous solution using synthetic clay type MgAl-LDH: Characterization, Isotherm and thermodynamic studies. In Mediterranean Journal of Chemistry (Vol. 9, Issue 2, pp. 155–163). Mediterranean Journal of Chemistry. https://doi.org/10.13171/mjc92190925728fs

51. Lu, Y., Jiang, B., Fang, L., Ling, F., Gao, J., Wu, F., & Zhang, X. (2016). High performance NiFe layered double hydroxide for methyl orange dye and Cr(VI) adsorption. In Chemosphere (Vol. 152, pp. 415–422). Elsevier BV. https://doi.org/10.1016/j.chemosphere.2016.03.015

52. Eshaq, Gh., Rabie, A. M., Bakr, A. A., Mady, A. H., & ElMetwally, A. E. (2015). Cr(VI) adsorption from aqueous solutions onto Mg–Zn–Al LDH and its corresponding oxide. In Desalination and Water Treatment (Vol. 57, Issue 43, pp. 20377–20387). Elsevier BV. https://doi.org/10.1080/19443994.2015.1110840

53. Khitous, M., Salem, Z., & Halliche, D. (2016). Effect of interlayer anions on

chromium removal using Mg–Al layered double hydroxides: Kinetic, equilibrium and thermodynamic studies. In Chinese Journal of Chemical Engineering (Vol. 24, Issue 4, pp. 433–445). Elsevier BV. https://doi.org/10.1016/j.cjche.2015.11.018

54. Bagherifam, S., Komarneni, S., Lakzian, A., Fotovat, A., Khorasani, R., Huang, W., Ma, J., & Wang, Y. (2014). Evaluation of Zn-Al-SO_4 layered double hydroxide for the removal of arsenite and arsenate from a simulated soil solution: Isotherms and kinetics. *Applied Clay Science*, *95*, 119-125. https://doi.org/10.1016/j.clay.2014.02.028

55. Zhang, H., Huang, F., Liu, D.-L., & Shi, P. (2015). Highly efficient removal of Cr(VI) from wastewater via adsorption with novel magnetic Fe3O4@C@MgAl-layered double-hydroxide. In Chinese Chemical Letters (Vol. 26, Issue 9, pp. 1137–1143). Elsevier BV. https://doi.org/10.1016/j.cclet.2015.05.026

56. Li, Y., Gao, B., Wu, T., Sun, D., Li, X., Wang, B., & Lu, F. (2009). Hexavalent chromium removal from aqueous solution by adsorption on aluminum magnesium mixed hydroxide. In Water Research (Vol. 43, Issue 12, pp. 3067–3075). Elsevier BV. https://doi.org/10.1016/j.watres.2009.04.008

57. Babu, B. V., & Gupta, S. (2007). Adsorption of Cr(VI) using activated neem leaves: kinetic studies. In Adsorption (Vol. 14, Issue 1, pp. 85–92). Springer Science and Business Media LLC. https://doi.org/10.1007/s10450-007-9057-x

58. Baruah, A., Mondal, S., Sahoo, L., & Gautam, U. K. (2019). Ni-Fe-layered double hydroxide/N-doped graphene oxide nanocomposite for the highly efficient removal of Pb(II) and Cd(II) ions from water. In Journal of Solid State Chemistry (Vol. 280, p. 120963). Elsevier BV. https://doi.org/10.1016/j.jssc.2019.120963

59. Wang, J., & Guo, X. (2020). Adsorption isotherm models: Classification, physical meaning, application and solving method. In Chemosphere (Vol. 258, p. 127279). Elsevier BV. https://doi.org/10.1016/j.chemosphere.2020.127279

60. Brezesinski, G., & Möhwald, H. (2003). Langmuir monolayers to study interactions at model membrane surfaces. In Advances in Colloid and Interface Science (Vols. 100–102, pp. 563–584). Elsevier BV. https://doi.org/10.1016/s0001-8686(02)00071-4

61. Yang, C. (1998). Statistical Mechanical Study on the Freundlich Isotherm Equation. In Journal of Colloid and Interface Science (Vol. 208, Issue 2, pp. 379–387). Elsevier BV. https://doi.org/10.1006/jcis.1998.5843