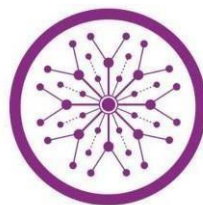


Synthesis And Characterization Of Mof-Ldh For Adsorptive Properties



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Requirement for the Degree of

Master of Philosophy in Chemistry

By

KASHISH ZAHRA

Roll No. SU92-MSCHW-F22-008

Session: 2022-2024

Faculty of Sciences

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Designation: Assistant Professor

Signature:

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This is to certify that the research work presented in this thesis, titled **“Synthesis and characterization of mof-ldh for adsorptive properties”** was conducted by **“Kashish Zahra”** under the supervision of **“Dr. Lala Rukh Sidra”**

No part of this thesis has been submitted anywhere else for any other degree. This thesis is submitted to the Faculty of Sciences, The Superior University, Lahore in partial fulfillment of the requirements for the degree of Master of Philosophy in the field of **“Chemistry”** in Faculty of Sciences at The Superior University, Lahore.

Student Name: Kashish Zahra

Signature: _____

Examination Committee:

Session Chair:

Signature: _____

a) External Examiner:

Signature: _____

b) Internal Examiner:

Signature: _____

c) Supervisor Name: Dr. Lala Rukh Sidra Signature: _____

d) Co Supervisor Name: Dr Sadaf Mutahir Signature: _____

e) Name of HOD: Prof. Dr. Uqba Mehmood Signature: _____

f) Name of Dean: Prof Dr. Naveed Babar Signature: _____

g) Controller Examination:

Signature: _____

DEDICATION

I dedicate this thesis to all those who dare to dream and persevere through adversity. To the next generation of researchers, may this thesis inspire innovation and progress.

Dedicated to the pursuit of excellence and the advancement of human knowledge. To my incredible mother, whose unwavering love and belief in me have been the light in my darkest moments, inspiring me to keep pushing forward.

To my father, whose quiet strength and wisdom have always guided me to believe in my own potential. Finally, to my supervisor, whose encouragement, mentorship, and insightful guidance have nurtured my growth as a scholar and motivated me to strive for excellence.

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ABSTRACT

A wastewater contaminated with heavy metals is tremendously unsafe for both the atmosphere and human health. A novel composite material, MOF-5-NiFe-LDH, was successfully synthesized and characterized to study their potential to remove heavy metals from contaminated waste water. Since of their high surface areas and flexible structures, metal organic framework (MOF) and layered double hydroxide (LDH) had become latent adsorbents for the elimination of heavy metals. MOF5-NiFe-LDH was synthesized using coprecipitation and solvothermal techniques method, with controlled composition. It was characterized by X-ray diffraction, Scanning Electron Microscopy and Fourier Transform Infrared Radiation. The synthesis process and characterization techniques revealed the material's unique structure and properties. The impact of initial concentration, pH, and contact time on the adsorption process were investigated. The results showed that MOF5-NiFe-LDH effectively removed 83% of copper and 81% of lead ions from waste water at concentration of 50mg/L, with an optimal pH of 6 for both copper and lead ion adsorption. The majority of ions were removed by MOF5-NiFe-LDH within 50 minutes were also observed. MOF5-NiFe-LDH demonstrated the adsorption capacity of copper were 80mg/g and 78.5mg/g for lead at 50mg/L concentration. The experimental data for kinetics model, were best fit in second order of kinetics. This study hold the potential to develop novel MOF-LDH adsorbents with superior selectivity and efficiency for the elimination of heavy metals, contributing to clean water resources.

CHAPTER 1

INTRODUCTION

1.1 Water Pollutants

Over one million people worldwide lack access to clean drinking water, which leads to a high rate of waterborne infections and two to five million deaths each year. Heavy metal accumulation in freshwater has been accelerated by fast industrialization, urbanization, and increased usage of these elements, the metals like mercury, lead, cadmium, silver, and copper pose the greatest risks. Because these trace heavy metal cations have significant effects on human health and ecosystems, decontamination must occur immediately [1].

The adsorption method stands out compared to other techniques due to its flexibility in both function and design approaches. Additionally, it indicates to have a substantial impact on the toxicity, organic accessibility, and movement of heavy metals in waste water [2].

Examples of conventional adsorption material incorporate metal oxides, zeolite molecular sieves, activated carbon nanotubes, nano zero-valent iron, and organic resins. Generally of these conventional adsorbents are porous, whether organics or inorganics, and they had specific limitations when it comes to absorbing heavy metals. For example, organic resins tend to have low reusability, activated carbon features minute aperture sizes, and metal oxides often demonstrate time-consuming adsorption kinetics and partial selectivity [3].

To prevail over the shortcomings of conventional adsorption materials, it is essential to explore more effective porous substances [4].

A highly effective approach to transform extremely toxic heavy metal ions in a high-valence state into low-valence state ions that are either low-toxic or non-toxic is through photocatalytic reduction. Thus, combining adsorption with photocatalysis technology is an excellent strategy for removing these heavy metal ions as well as reducing their toxicity. Here in this context,

(MOFs) have great potential as multifunctional materials, making them ideal candidates for both photocatalytic reduction and heavy metal adsorption [5].

1.2 Metal Organic Framework

The high MOF adsorption capacity alongside their simple operation and ease of regeneration makes MOFs attractive. Their adjustable porosity alongside high adsorption properties makes MOFs promising materials for treatment of water [6].

MOFs, or metal-organic frameworks, are considered a new class of crystalline porous materials consisting of organic ligands and inorganic metal ions that are linked together [7].

MOFs have been previously reported to have unique characteristics such as high specific surface area, porosity, and the existence of open metal sites. MOFs have structural and functional diversity because of their ability to change organic ligands and metal center [8].

MOFs or metal-organic frameworks are a type of hybrid material formed by the self-assembly of organic ligands and metal ions or clusters, which is held together by coordination bonds [9].

1.2.1 APPLICATION OF METAL ORGANIC FRAMEWORK:

MOFs have been studied for many purposes like, chemical sensing, drug delivery, catalysis, gas storage, etc, there is limited literature committed to their application in heavy metal ions extraction from waste water [10].

The stability of MOFs depends on the metal used, linker design, and cluster coordination. Low-valent metals like Cu, Zn, and Ni can lead to instability, while high-charge metals like Fe, Cr, and Zr provide greater stability. Strong Lewis bases and electropositive metals can enhance framework stability, as seen in carboxylate-based MOFs. such as MIL-100(Fe), MIL-53, and UiO-66 in various conditions, including water, acids, and bases [11].

MIL-100(Fe)

It offers excellent hydrothermal and thermal stability, making it ideal for applications like drug delivery and catalysis. However, its pores are smaller

than those of MOF-5, which means that certain molecules cannot pass through it [12].

MIL-53

It serves as an alternative option with robust hydrothermal stability. Its functional groups can interact with specific molecules, making it particularly useful for separation processes.

UiO-66

Because of its quick drug adsorption, it shows strong chemical stability and outstanding efficiency in drug delivery applications. However, its pores are smaller when compared to MOF-5 [13].

MOF-5

MOF-5 is recognized for its large pores and thermal stability, making it ideal for gas storage and separation applications. In water remediation, combining powdered MOF adsorbents with larger LDH sheets enhances separation, recovery, and regeneration effectiveness. LDHs, which are two-dimensional clays, have a structure of $[M_{1-x}^{2+} M_x^{3+} (OH)_2]^{x+} (A^{n-})_{\frac{x}{n}} \cdot mH_2O$. They excel at removing heavy metals through processes like mineralization, anion exchange, -OH binding sites, and functional group coordination. The flexible structures of LDHs facilitate efficient adsorption, leading to improvements in water treatment techniques for more effective pollutant removal [14].

1.3 Layered Double Hydroxides (LDH)

Layered double hydroxides (LDHs) are often referred to as synthetic anionic clays or minerals that resemble hydrotalcite. These compounds are classified mainly as ionic layered materials due to their positive charged brucite-like layers and the non-framework anions that compensate for the charge in the interlayer spaces. Specifically, in the brucite (magnesium hydroxide) like layers, some divalent metal cations are substituted by trivalent metal cations, resulting in positively charged sheets. The anions intercalated within the LDH layers counterbalance this positive charge. Common interlayer anions, which can be exchangeable or host anions, include, OH^- , ClO_4^- , SO_4^{2-} , and NO_3^- as noted in previous studies. The universal formula for Layered double

hydroxides expresses as $[M_{1-x}^{2+} M_x^{3+} (\text{OH})_2]^{x+} (A^{n-})_{\frac{x}{n}} \cdot n\text{H}_2\text{O}$, where's M^{2+} represents divalent metal cation and M^{3+} denotes trivalent metal cations [16].

Layered double hydroxides (LDHs) are a sort of anionic soil resembling hydrotalcite. They consist of stack positive layer that is neutralized and separated by transferable anions located within the interlamellary spaces. The positively charged main layers of LDHs are made up of water molecules, divalents or trivalents cations, and non-structural sandwich layer anions. LDHs are formed through non-covalent bonding.

What makes LDHs particularly unique is their potential use in composite materials, attributed to several intriguing properties. These include easy synthesis, a evenly dispersed covered structure, the existence of facade hydroxyl group, flexibility, and high chemical and thermal stability. They also exhibit a high capacity for intercalating various inorganics, organics, biomolecules, and homogeneous genes. Due to these special characteristics, LDHs may be utilized in diverse applications, such as pollutant elimination, electrocatalytic oxygen evolution, carbon dioxide reduction, and photocatalytic hydrogen synthesis. Additionally, owing to the scenery of metal cations and metal-oxygen bond, Layered double hydroxides is alkaline and positive charged, which facilitates electrostatic exchanges with anionic contaminants, effectively addressing the limitations of bioregion. In contrast, LDHs can also form a compact multilayer stacked configuration [17].

Brucite consists of non-polar layers with Magnesium cation situated at the core of octahedral, surrounded by 6 hydroxyl group at corner. When magnesium within layered double hydroxides (LDHs) is substituted by trivalent metal ions, the layers develop a net positive charge, which is compensated by anions situated in the interlayer region. The universal formula for LDHs is $[M_{1-x}^{2+} M_x^{3+} (\text{OH})_2]^{x+} (A^{n-})_{\frac{x}{n}} \cdot n\text{H}_2\text{O}$ where 'x' typically ranges from 0.20 to 0.33, equivalent to an $\text{Mn}^{2+}/\text{Mn}^{3+}$ molar ratio spanning 2.0 to 4.0. This configuration comprises brucite-like layers containing a mixture of divalent and trivalent metal ions, forming a positively charged lattice that is stabilized by exchangeable anions and hydrated molecules.

A range of cations may be used to synthesized diversely LDHs, including magnesium, iron, cobalt ,copper , for Mn^{2+} , and aluminium, chromium, manganese, for Mn^{3+} . Both unmodified LDHs and their oxides produced through calcination have diverse applications in fields such as catalysis, pharmaceuticals, photochemistry, electrochemistry, and adsorption [18].

Since then, numerous layered double hydroxides have been synthesize, and these materials has been employed for removing a variety of organic and inorganic hazardous. These include CO_2 , metallic ion, organic dyes, pharmaceuticals, as well as pesticides [19].

The basic structure of layered double hydroxides (LDHs) can be represented by the formula, $[M_{1-x}^{2+} M_x^{3+} (OH)_2]^{x+} (A^{n-})_{\frac{x}{n}} \cdot mH_2O$ where M includes divalent cations such as calcium, magnesium, zinc, cobalt, nickel, copper, manganese, and lithium; M consists of trivalent cations like aluminium, chromium, iron, cobalt, and manganese; and A represents various anions such as chloride, nitrate, perchlorate, carbonate, and sulfate. The layer charge is defined as x for divalent cations and $x=2x^{-1}$ for monovalent cations. Typically, the MII/MIII ratio ranges from 1 to 5. LDHs, which are synthesized through coprecipitation, display varying interlayer spacing's that dependent on the dimensions and configuration of the anions, as well as considerable specific surface areas (0.02–0.12 km^2/kg) and exceptional anion exchange capacities (200–500 mol/kg) [20].

1.4 Combination Of MOF-LDH

Metal-organic frameworks (MOFs) and layered double hydroxides (LDHs) have shown remarkable efficiency in eliminating heavy metals from water, owing to their distinctive morphological attributes and substantial specific surface areas. It is well-suited for environmental remediation efforts [21].

Integrating MOFs with LDH takes advantage of the layered structure, surface area, and anion exchange capacity of EDHs as well as the tunable porosity and different functional groups within the LDHs. This integration greatly enhances the efficiency and selectivity of adsorption of toxic heavy metal ions like lead, chromium, cadmium, and others [22].

For example, a hierarchical MOF/LDH nano-composite manifests remarkable sorption capacities for organic dyes and chromium, 1173 mg/g and 733 mg/g respectively, which demonstrates its multi pollutant or synergistic effect. Moreover, these materials can be put to use in other more hazardous environments where heavy metals are poses a danger to human and ecological well being such as air and soil. Because of their efficiency and wide applicability, MOF/LDH composites are perfect for these uses [23].

While it is clear that there is a lot of promise with the application of the composites, as with any emerging products, there are challenges that need to be solved. The main difficulty lies in the expense of bulk purchased and deployed MOF/LDH composites. More work needs to be done to increase the stability, reusability and responsiveness of the composites straddling multiple environmental conditions [24].

Various applications have been required using this combination such as the capture of gases such as methane or CO₂ for fuel [25]

This thesis aimed to synthesis MOF5-NiFe-LDH for the removal of heavy metal and this research will cover environmental remediations. It will involve the fabrication of MOF/LDH composites with adjustable properties for the adsorption of heavy metals, toxic metal analysis and identification. Additionally, the focus will be on removing specific heavy metals from wastewater, including lead, and copper [26].

Improving the synthesis method to prepare MOF/LDH composites with the desired metal ion exchange capacity, high surface area, and porosity. We employed analytical techniques, to investigate the physicochemical properties of the synthesized composites. We conduct batch adsorption tests to evaluate the sorption capacity of the MOF/LDH composites for the targeted heavy metal. To investigate how factors like pH, initial concentration of metals, and contact time influence the efficiency and sorption capacity. And understand the mechanism, such as ion substitute and chelation, through which MOF/LDH composites eliminate heavy metals.

On the other hand, since last ten years considerable advancements have been made in MOF/LDH nano-composites to investigate the reusability and

regeneration strategies for the MOF/LDH composite. And evaluate how various MOF and LDH precursors affect the performance of the finished composite.

The environment and human health are seriously threatened by the existence of heavy metals in contaminated water. These toxins have the ability to bioaccumulate in living things, leading to a variety of health issues. These contaminants are frequently difficult for conventional wastewater treatment techniques to eliminate completely.

MOFs are perfect for adsorbing heavy metals due to their vast surface area and highly spongy structure. LDHs use ion exchange processes to provide more metal binding sites. A synergistic effect is produced when several materials are combined, increasing the overall capacity to remove heavy metals. The structural diversity provided by MOFs and LDHs enables researchers to customise the composite's pore size, surface functioning, and metal binding sites to target heavy metals of concern.

MOF/LDH composites for heavy metal removal are a rapidly expanding field. The following areas have been the focus of recent research by designing innovative MOF/LDH structures with improved morphologies, porosities, and functions for increased selectivity and adsorption capacity. Elucidation of Mechanism, acquiring a more profound comprehension of the adsorption mechanisms related to ion exchange, complexation, and electrostatic interactions. Real-World Applications, investigating scalable synthesis techniques and assessing MOF/LDH composites' performance in actual wastewater matrices [26].

This thesis manuscript include a detailed literature review that delves deeper into the following areas. The extent of heavy metals contamination address about the harmful effects that heavy metal pollution has on the environment and human health, as well as how common it is in wastewater sources. Provide pertinent reports from academic studies and governmental agencies (such as the USEPA and WHO) to demonstrate the seriousness of the issue. Limitations of conventional methods consider the drawbacks, such as costly maintenance or restricted efficacy for certain metals, of conventional

treatment of wastewater technologies for the removal of toxic heavy metal. Cite studies that contrast various therapeutic approaches. Give an extensive explanation of how MOF/LDHs' special characteristics make them ideal for heavy metal adsorption. It provide studies that illustrate their great capacity for adsorption, tunability, and possible reusability.

1.5 Importance Of MOF/LDH

Importance of MOF/LDH Research MOF/LDH composites present a viable way around these restrictions. This study is crucial because MOFs' adjustable pore structures and large surface area enable effective heavy metal adsorption. LDHs provide anion exchange characteristics and active metal sites, which may improve selectivity for particular metals. The LDH and MOF components can be modified in order to achieve the ideal composite for the removal of specific heavy metals. The cost of some reusable MOF/LDH composites would be affordable and inexpensive, owing to the fact that these composites are easily synthesized and environmentally friendly.

The contamination of wastewater with heavy metals is an important issue and this research study tries to solve it. With the development of efficient and selective MOF/LDH composites, researchers hope to fulfill the following objectives. Subsequently, more sophisticated water treatment technologies can be developed that can significantly improve water quality by decreasing the concentration of heavy metals in wastewater and ensuring the water is safe to drink and safe for the environment.

In short, with the work on the MOF and LDH composites for the removal of heavy metals, this research promises to make significant strides in solving an important environmental problem. Effective and durable solutions for cleaner water and a healthier environment can be greatly provided with this study.

The most recent advances in water treatment processes and the potential use of the MOF5 Ni-FeLDH based composite as a heterogeneous catalyst are described together with the directions for further development of the new material. Adsorption, electrostatic interaction, complexation and degradation are the mechanisms under consideration [27].

AIMS AND OBJECTIVES

Aim

- To develop MOF5 Ni-Fe LDH composites that can remove heavy metals from waste water.

Objectives

- Combine Metal-Organic Frameworks (MOFs) with Layered Double Hydroxides (LDHs) to create a hybrid material.
- Design and synthesize novel MOF5-Ni-Fe-LDH composites with surface functionalities for targeted heavy metal adsorption.
- Analyze the structural properties using techniques like Scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR).
- Assess the potency of Ni-Fe LDH-based MOF5 in waste water samples.

CHAPTER 2

LITERATURE REVIEW

Water restoration techniques require improvement because of the global water crisis that affects more than one billion individuals. Fe-MOFs demonstrate potential for water decontamination through visible light photocatalysis and Fenton-like catalysis. However, issues with structural stability and limitations in practical applications highlight the need for additional research into diverse ligands and affordable alternatives [28].

2.1 Materials used for removal of heavy metals

Advanced materials designated as metal-organic coordination polymers (MOCPs) hold excellent potential to removing cadmium ions from water. Their unique structure, characterized by large pores and active metal sites, makes them highly effective at adsorbing these contaminants. Researchers are investigating the kinetics (the rate at which MOFs adsorb cadmium), isotherms (the capacity for storage), and mechanisms (the processes involved in capturing cadmium). This research contributes to the development of even more efficient MOFs for water treatment.

Industrial activities often lead to the contamination of water with dangerously high levels of heavy metals like cadmium. While there are various methods for cadmium removal, MOFs offer advantages such as high selectivity and cost-effectiveness [29].

Layered double hydroxides (LDHs) exhibit high latent of removing heavy metals from soil and wastewater. Due to their long layered topology they are perfect for trapping these contaminants. In this article, the benefits of employing LDHs for the removal of heavy metals are explained in detail, focusing on their stability and preparative simplicity. However, it also raises some issues that need to be considered, i.e., possible environmental toxicity and the need for further study of particular removals. These complexes are particularly attractive due to the beneficial properties of LDHs, including their unique layered structure and extensive surface area [30].

Researchers studied the modification of layered double hydroxide (LDH) via incorporation 3-amino-1H-1,2,4-triazole (MLDH) units into its molecular framework to enable extraction of copper and cadmium from water. According to the study, the adsorption of 326 mg/g of cadmium and 593 mg/g of copper was achieved. Furthermore, 639 and 457 mg/g of copper and cadmium, respectively, were observed after the completion of 3 h at 25°C with 0.4 g/L MLDH in slightly basic water (pH 9). The adsorption process occurs in two stages, following the sorption kinetics followed a pseudo-second-order rate equation, aligning with the Freundlich isotherm [31].

The study titled "Assessment of 3-amino-1H-1,2,4-triazole modified layered double hydroxide in effective remediation of heavy metal ions from aqueous environment" published in the Journal. It highlights the growing interest in developing cost-effective methods for treating industrial wastewater, particularly through adsorption. This research focuses on Co-Cu LDH as a promising candidate for methyl orange (MO) adsorption, owing to its expansive pore structure and elevated surface area."

The findings align well with the Freundlich isotherm model, and the analysis shows that sorption process follows a non-linear second order. Notably, Co-Cu LDH demonstrates significant adsorption capacity, post 5 cycle testing of MO adsorption, exhibiting promising characteristics as a competitive and economical solution for removing anionic dyes from industrial wastewater [32].

Scientists have developed a novel magnesium-aluminium Anionic Clay (MgAl-AC) using a unique technique to effectively remove heavy metals from water. This innovative material features a distinct structure with extremely thin flakes, allowing it to capture significantly more metal than previous versions up to 1422 mg/g of cadmium. The study indicates that this material removes metals through two mechanisms: forming a surface layer of trapped metals and substituting magnesium ions with the metal contaminants. The newly created magnesium-aluminium oxide (MgAl-LDO) appears to be quite durable and shows great potential for addressing heavy metal pollution in water [33].

Although the effectiveness of sulfur-based compounds for different metals is still unclear, researchers are excited about their potential to eliminate heavy metals through wastewater. It was explored from this research a novel material (MgAl-LDO@S) and determined that lead was the most readily adsorbed element, followed by cadmium and nickel. Lead was primarily captured ion exchange, whereas cadmium and nickel were complexed adsorbed by complexing, formation with sulfate groups. This difference in adsorption behaviour is associated with material properties but also parameters such as the charge, and size of the metal ions [34].

According to UN, by 2050, clean water will be out of reach of 6 billion people. This problem is being addressed by researchers based on LDH-[Sn₂S₆], an inexpensive material that exceeds WHO recommendations and exhibits high performance in the removal of heavy metals (eg., copper, silver, lead, and mercury). LDH-[Sn₂S₆] serves as an excellent adsorbent for wastewater purification due to its effective removal capabilities, high sorption capacities, and tolerance to various ions [35].

Researchers have produced a new environmentally friendly agent (Ca-Fe/LDH) for removal of lead and nickel from water. This material showed high efficiency with rates of greater than 60 mg/g in lead and greater than 2 mg/g in nickel removal. The optimal removal occurred within 30 minutes at a neutral pH of 7. With such efficacy and simplicity of use, scientists feel that this compound is a great solution to a real world us [36].

The preparation of a high-performance adsorbent material (ZIF-67/LDH-C) for the intended degradation of Pb²⁺ ions and toxic organic dyes (malachite green and Congo red) in water has been investigated. A detailed analysis of the structure and chemical composition of the material was carried out using advanced techniques. Such as nitrogen adsorption/desorption, XRD, FT-IR, SEM, TEM, TGA, and XPS, revealing two-dimensional nano sized LDH layers and a three-dimensional hollow MOF structure. ZIF-67/LDH-C demonstrated significant complexity, excellent stability, and chemisorption properties, with a highest sorption capacity of 662.25 mg/g for Pb²⁺. These attributes make it a suitable option for wastewater purification [37].

The previous study presents a multifunctional MOF-5/Ni-Co-LDH composite material embedded with zinc nickel cobalt oxide quantum dots (ZNCQD) and

is prepared using ultrasonication for the efficient photocatalytic degradation of thiazine, xanthene, and triarylmethane dyes in wastewater. This composite achieved a remarkable decomposition rate of 99.6% for Malachite Green, showcasing exceptional photoactivity. The photocatalyst demonstrates significant potential for wastewater treatment, exhibiting pseudo-first-order reaction kinetics and consistent performance over six cycles. Ultrasonic irradiation proved pivotal in tailoring the dimensions, architecture, and porous texture of the materials, highlighting ZNCQD's potential for eco-friendly extraction of organic contaminants from aquatic environments [38].

$\text{CuFe}_2\text{O}_4/\text{NiMgAl-LDH}$ composite demonstrated exceptional OTC removal efficiency from drinking water. Characterization analysis such as XRD, SEM, FTIR, and XPS revealed that this composite exhibited superior OTC adsorption compared to the individual components of CuFe_2O_4 and Ni-Mg-Al. The composite material demonstrated high efficacy in OTC removal from wastewater, achieving 192 mg/g adsorption capacity at 323 K, facilitated by anionic exchange, hydrogen bonding, and electrostatic attraction [39].

Zinc-based metal-organic framework (ZIF-8) were used to synthesize nitrogen-doped ZnO/carbon nanoparticles, which demonstrated effective adsorption of RBBR dye, achieving an impressive efficiency of 49.3 mg/g. Materials exhibited a surface area of 609.2 m^2/g and were analyzed by a rhombic dodecahedron shape. They displayed pseudo 1st order as well as pseudo 2nd order kinetics at different temperatures, aligning with Langmuir adsorption models. A thermodynamic analysis underscored the potential for environmental remediation through RBBR dye adsorption, revealing that the process was non-spontaneous and exothermic [40].

A novel sulfur-functionalized porous metal-organic composite ($\text{MoS}_4\text{-MOF}$) was synthesized using copper and benzene-1,3,5-tricarboxylic acid, along with immobilized tetrathiomolybdate (MoS_4^{2-}). This MOF formed M-S bonds in wastewater and exhibited excellent selectivity for heavy metal ions. The adsorbent was assessed through various methods, demonstrating good recyclability, chemical stability, and impressive sorption capacities ranging from 714.3 to 1000.0 mg/g, with favorable partition coefficients between 6.0

$\times 10^3$ and 5.5×10^4 mL/g. These findings position the sorbent as a promising option for water remediation. Additionally, the immobilization of $(\text{NH}_4)_2\text{MoS}_4$ on the Copper BTC MOF enhances stability and simplifies storage, further boosting its sorption capabilities [41].

Sorption-based thallium desorption during the water treatment process was also predicted using a mixture of MOF-LDH (LDH). In this research employed an inventive machine learning advance to forecast the elimination of thallium during adsorption. The chosen composite, Ni₅₀Co₅₀-LDH/UiO-66-NH₂, have a high surface area of 900 m²/g. The ability of artificial neural network model to remove pollutants was highlighted by its high accuracy (R^2 0.99) in predicting the adsorption process [42].

Researchers prepared Mo₃S₁₃-LDH, which could be effectively used to detoxify heavy metals (Ag, Hg) and toxic ions (Cr, As) in water. It retains hundreds of milligrams of contaminants per gram, and reaches equilibrium within an hour. The presence of impurity after absorbing in Mo₃S₁₃-LDH provides its reusability [43].

Alg-DOX-Cu MOF/LDH were prepared based on pH-controlled drug-release strategy tailored for releasing doxorubicin to breast cancer cells. The beads showed increased cytotoxicity towards MCF-7 cells, pH responsiveness and drug release control, which all suggested that the beads could be an efficient delivery method for cancer therapy [44].

Additionally, a three-dimensional porous carbon nanofiber platform were create by utilizing iron-manganese (MnFe-LDH) and MnFe₂O₄ which effectively adsorbed Chromium, Lead, and Arsenide ions from water. MnFe-LDH/MnFe₂O₃@3DNF displayed excellent sorption performance, and the treated water is at or above the international standard for potable water quality. The adsorption mechanisms included surface complexation, isomorphic substitution, precipitation, and electrostatic attraction. This material also demonstrated good durability and long-term performance without generating any secondary pollutants [45].

The distinctive properties of Metal-Organic Frameworks (MOF) and also its increasing application in membrane-based separation processes are

demonstrated. Specifically, it addresses the topics of MOF selection, membrane fabrication processes, and water treatment applications. The paper also discusses the potential and the problems for the use of MOF membranes industries [46].

Researchers fabricated a new hybrid material, PANI/LDH@CNT, showing efficient removal of toxic iodine from aqueous solutions (303 mg/g in 9 h) and metal ion detection in water. The efficiency of the material is maintained at 91% after repeated applications and shows fluorescence quenching or enhancement to certain metal ions. It is a multifunctional material and therefore, it is promising in water purification and pollution monitoring fields [47].

The review discusses an emerging approach to the functional materials' synthesis by grafting (LDHs) and (MOFs). LDHs function as a substrate, which promotes the production of MOFs as a source of metal and prevents aggregation. On the other hand, MOFs increase the material's porosity and surface area, which in turn improve the material's economy. The review describes five different strategies for the assembly of these MOF/LDH complex. Lastly, it describes the advantages of this approach, especially in applications related to energy production and storage, such as water splitting and battery technology [48].

The latest research have developed a novel material, NiCo-LDH/F-HNTs, towards the fast detection of the toxic insecticide parathion in environmental/food samples. This material consists of intercalated functionalized halloysite nanotubes being intercalated with nickel cobalt-layered double hydroxide (NiCo-LDH). Testing has demonstrated this novel compound has a very high specificity in the determination of very low concentrations of parathion. Its large surface area, high conductivity, and many active sites, which together are responsible for good efficiency [49].

The synthesized NiZnAl-LDH nanostructures, can be used for the removal of MO and Rh-B dye from water. The material showed optimal removal under specific pH conditions, with a high sorption capacity of 100 mg/g. The adsorption process suggested a single-layer accommodation of dye

molecules, and the material can be reused multiple times, making it a promising solution for treating dye-contaminated wastewater [50].

Materials have been created which are anionic and can extract zinc via water. This material has also been shown to have good efficiency up to 154 mg of zinc per gram. The optimal conditions for extraction process was determined to be room temperature and slightly acidic pH 5. The testing of the novel material indicated this material is stable enough to use more than once. In general, this work proposes that CuMgAl-LDH/MMt is possible for the remediation of water pollution arising from zinc [51].

The removal of toxic heavy metal cadmium aqueous by a new type of material called MgFe LDH/GO has been reported by researchers. This compound has been demonstrably effective in removing cadmium, especially at low levels, which are present in natural water resources. The findings reveal that the large surface area of MgFe LDH/GO enhances its ability to capture cadmium. Optimal cadmium removal conditions are room temperature and neutral pH. The effectiveness of MgFe LDH/GO remains intact even after repeated use. Overall, this research suggests that MgFe LDH/GO is a promising material for treating water contaminated with low levels of cadmium [52].

To improve MOF to the execution of lead (Pb) ions through water, researchers investigated a two-step process. They used a specially designed LDH within amino groups to decorate the MOF. Various methods confirmed the successful attachment of the LDH to the MOF. The modified MOF demonstrated stability up to 400°C.

The most notable finding was that this method effectively captured lead, achieving a capacity of 34.58 milligrams of lead per gram of modified MOF, which accounts for nearly 87% of the lead that the MOF could potentially adsorb. Further analysis revealed that lead adsorption followed specific patterns. The symmetry data was excellent described through the Temkin model, indicating a moderate interaction between lead and the MOF. Additionally, the kinetics were best explained by a pseudo 2nd order model, suggested chemical interaction between lead and the MOF surface. Finally,

the rate of lead uptake was limited by diffusion through a thin layer of water surrounding the MOF [53].

MOF has extensively study to their ability to remove contaminants from wastewater. In this research, eggshells were combined with a specific MOF structure known as ZIF-67 to create a new magnetic material. The team developed a straight forward and eco-friendly method that utilizes ultrasound to attach ZIF-67 crystals to a magnetic eggshell membrane. This innovative composite material, referred to as ZIF-67@Fe₃O₄@ESM, boasts a very high surface area, making it highly effective for absorbing pollutants [54].

The review also examines the composition, structure, and various research techniques related to layered double hydroxides (LDH). Exhibiting economical production costs and simplified manufacturing protocols. LDH is considered a features tailored surface chemistry for optimized heavy metal capture. However, standard LDH has limitations in efficiency. This literature review highlights how researchers are incorporating functional groups or structures referred to as functionalized LDH to enhance its performance. These modifications improve the stability of LDH, increase its selectivity for specific metals, and facilitate easier separation after use. Finally, the review identifies areas that require further investigation, particularly focusing on designing cost-effective and environmentally benign LDH water treatment protocols [55].

Researchers have developed a new composite material called MgAl-LDH@RHB by combining MgAl-LDH within biochar derived from rice husks (RHB). They then investigated the material's ability to remove Cu and Cd through water.

Findings showed that MgAl-LDH@RHB effectively extracted both Copper and Cadmium from water, within maximum metal up taken efficiencies of 125.34 mg/g of Cd and 104.34 mg/g for Cu. The removal process appears to involve a single layer of chemically adsorptions on the tophology of the material, likely driven by a combination of surface precipitation and ion exchange mechanisms. This research provides valuable insights into the processes involved in heavy metal removal using this innovative composite

material and underscores the latent of repurposing farming waste, such as rice husks, for water handling applications [56].

Researchers have created an innovative magnetic nano adsorbent designed to extract lead (Pb^{2+}) and mercury (Hg^{2+}) from water. This material is composed for thioglycolic acid TGA ZnFe -LDH and iron oxide nanoparticles (Fe_3O_4). The nano adsorbent demonstrated effective removal of Hg^{2+} and Pb^{2+} from water, achieving optimal results within 30 minutes at a pH at 5.5, using a specific 9 mg quantity.

The study indicates the sorption processes is energetically favorabled, characterized as endothermics, feasible, and spontaneous, and it occurs in two phases following pseudo-second-order kinetics. Among the various metals tested including Pb^{2+} , Fe^{2+} , Cu^{2+} , Zn^{2+} , and Cd^{2+} the nano adsorbent showed a strong preference for capturing Hg^{2+} . Remarkably, even after being reused three times, the nano-adsorbent maintained over 90% efficiency. This research highlights the potential of the novel magnetic nano adsorbent for effectively removing specific heavy metals from water, while its magnetic properties facilitate easy separation [57].

A magnetic adsorbent from industrial waste which is capable of removing methyl orange dye and heavy metals (Fe, Cr, Zn) from water. The adsorbent's absorption capacity is impressively high at 240mg/g, and can easily be separated and regenerated. This study emphasizes effective waste valorization for wastewater treatment and further sheds light on the extractive reusability of the adsorbent in heavy metal and dye elimination [58].

Researchers have developed a novel and effective nanocomposite that incorporates layered double hydroxide (LDH) within a tailored polymer matrix for the elimination of MB from water. This advanced material has increased affinity towards MB at higher ranges of pH, especially when it is around 11 and at elevated temperatures around 35 degrees celsius. The process of adsorption is a favorable one, as suggested with negative ΔG values. Even after 4 uses, the nanocomposite retained activity for methylene blue adsorption, making it an efficient multifunctional and economical sorbent for wastewater treatment [59].

Scientists deal with the problem of drinking water acquirement by investigating different approaches to desalinate water, especially focusing on capacitive deionization (CDI). By using one of the new materials Co-Fe-LDH which possesses a novel hollow core-shell structure. Their data revealed that this material have a lot of unique properties like tunable morphology ,large surface area, anion exchangeable, high adsorption capacity [60].

Researchers investigated a two-step process to improve a MOF, the removal of lead (Pb) ions by water.

1. Starting with a basic MOF known as Co-MOF.
2. Chemically attaching a specially designed layered double hydroxide (LDH) containing amino groups to the surface of the MOF.

Various methods confirmed the successful attachment of the LDH to the MOF, and the modified MOF demonstrated stability even at high temperatures (up to 400°C). Key findings regarding lead capture indicated that the modified MOF (PSM Co-MOF) was highly effective, with a lead adsorption capacity of 34.58 milligrams of lead per gram of MOF, which accounts for nearly 87% of the MOF's potential lead capture. Analysis suggests that the lead adsorption process follows specific patterns [61].

Green LDH Synthesis: This study developed a new, eco-friendly method for producing layered double hydroxides (LDH) using readily available magnesium oxide and industrial waste (ground blast furnace slag). The researchers compared two types of LDH: LDHa, which was made entirely from waste, and LDHb, which included magnesium oxide. Tests showed that LDHb exhibited greater stability. Both LDH variants were effective in completely removing cadmium (Cd) from water within a neutral pH range of 6–9. Additionally, LDHb demonstrated superior performance in removing arsenic (As) across various pH levels. In contaminated soil, both LDH types helped immobilize (trap) As and Cd. Notably, LDHa was highly effective, immobilizing over 80% of the arsenic found in industrial and agricultural soil [62].

Previous study described a novel Mg/Al/Fe-CLDH-type LDH that can effectively adsorb arsenic from water over a wide pH range (2-12). It outperforms traditional LDH with good efficiency even in the presence of the other contaminants. Its distinctive flower-shaped structure and iron loading increased the number of binding sites for arsenic, thus it is an environmentally friendly option for arsenic pollution prevention [63].

Researchers further prepared a material, MgAlDHBDC-LDH, which can absorb uranium from water. It can provide better stability, water solubility, and uranium removal over a wider pH range. The reaction is endothermic, spontaneous and recyclable, therefore is a potential and cheap method for the removal of such high level radioactive uranium waste from water [64].

CHAPTER 3

METHODOLOGY

3.1 Material Used

Zinc Nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Nickel Nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and Iron Nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$) (SRL, 99%) were purchased from Sinopharm chemical reagents. 1,4-Benzenedicarboxylic acid (BDC) (Sigma Aldrich 99.9%) were purchase from Madina Scientific Chemicals (Abkari,Lahore). Ammonium Chloride (NH_4Cl), Sodium bicarbonate (NaHCO_3), Dimethylformamide (DMF) and absolute alcohol (Sigma Aldrich, 99.9%) were purchased by Abkari Market Lahore. The metallic ion precursors ($\text{PbCl}_2, \text{CuCl}_2$) were purchased chemicals of high analytical purity. The stock solutions were precisely standrized to fabricate the functional standard solution (1000 mgL^{-1}). Deionized water was employed. All the reagents were used without further purification.

3.2 Methodology

3.2.1 Synthesis Of Ni-Fe-LDH:

The Ni-Fe-LDH was fabricated by facile co-precipitation technique reported by Bhuyan, A. and M. Ahmaruzzaman with minor modifications [65]. In the first step prepared the solutions of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3mM), $\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2mM), and NH_4Cl (10 mM) with 50ml distilled water in measuring flask and stir to completely solubilize the salt. And labelled this beaker as ‘A’. Then a blended solution of NaOH and NaHCO_3 was prepared in a separate beaker, with the sodium ion concentration held at 0.5 M and NaHCO_3 representing 5% of the total sodium mole and labelled as solution B. After that take 20mL of solution ‘B’ and introduced dropwise with the help of burette into a solution ‘A’ under high shear mixing. The mixture was stirred at 25°C for 24 hours to facilitate reaction kinetics on magnetic hot plate. Centrifugation was used to collect the synthesized LDH sample, and rinsed with ethanol and deionized water 3-4 times. The light-yellow sample therefore demonstrated were labelled as Ni-Fe-LDH.

3.2.2 Synthesis Of MOF-5/Ni-Fe-LDH Composite:

Firstly, make 2mM solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ into 50ml distilled water and take 10ml of this sol in separate beaker then add 1M NaOH solution slowly to it to precipitate $\text{Zn}(\text{OH})_2$ completely. After that, prepared 2mM solution of BDC (linker) in 50 ml DMF solvent. Then, mixed both the solution into a separate beaker and labelled the solution as C. In the next step, a volumetric flask was loaded with 150 mg of the already made Ni-Fe-LDH and 20ml of solution C was introduced drop by drop. After mixing the mixture was agitated for four hours and labelled as solution D. Then the solution was placed into the solvothermal reactor at 250°C temperature in drying oven for 24 hours, to synthesize the advanced MOF5-NiFe-LDH composite. Solvothermal technique enables the chemical reactions and synthesis under high temperature and pressure conditions using a solvent which is DMF in this case to dissolve and react with the reactants. Finally, centrifugation was done to collect the yellow sample, and rinsed with DMF and ethanol for 2 -3 times and then dry for 24hrs in drying oven. The obtained product was marked as MOF-5/Ni-Fe-LDH composite.

3.3 Characterization

To analyze the surface functionalities and structural properties using techniques like SEM (Scanning Electron Microscopy) of Zesis (model EVO LS10), XRD (X-ray diffraction) and FTIR (Fourier-transform infrared spectroscopy). SEM is usually use to analyze the surface morphology of the composite. X-ray diffraction is mostly used to detect the crystalline phases and molecular arrangement of the composite. While FTIR is used to detect and identify the functional groups present in the composite.

3.4 Adsorption Experiments

3.4.1 Effect Of Initial Concentration:

The prepared MOF5-NiFe LDH that was tested as an adsorbent material for Cu^{2+} and Pb^{2+} heavy metals from waste water. 1000mg/L stock solutions of Cu^{2+} and Pb^{2+} ions were prepared by adding precise amount of copper chloride (CuCl_2) and lead chloride (PbCl_2)) in distilled water. From the above

stock solutions different concentrations ranging from (25, 50, 75, 100, 125mg/L) for both metals were prepared.

For a range of concentrations (25-125 mg/L), 25 mg of MOF5-NiFe-LDH adsorbent was mixed with 30 mL of Cu^{2+} and Pb^{2+} ion solutions. The suspensions were then rotated at 60 rpm on the magnetic hot plate at 25°C for 1 hour. HALO DB-20 UV-Vis spectroscopy was employed to assess the removal efficiency of cations.

To evaluate the removal and adsorption efficiency of the MOF-LDH towards ions, the percentage of removal was calculated by applying following formula:

$$\text{Removal Efficiency} = \frac{C_0 - C_e}{C_0} \times 100$$

The adsorption kinetics were assessed by tracking the concentration changes (ΔC) between initial (C_0) mg/L and equilibrium (C_e) mg/L states, while maintaining constant solution volume and adsorbent mass.

3.4.2 Effect Of pH:

The stock solutions containing 50 mg/L of Cu^{2+} and Pb^{2+} were prepared in separate flasks to investigate the effect of pH on the adsorption capacity of MOF5-NiFe-LDH, exploring how varying pH levels influence its ability to remove contaminants. Solutions with pH ranging from 2 to 10 were created by accurately mixing HNO_3 , NaOH, and distilled water. pH indicator test strips were used to determine the pH of the solutions. The process of sorption were initiated by adding 25 mg of sorbent to 30 mL of prepared solution. The resulting mixture was then placed on a magnetic hot plate stirrer set at 25°C and rotated at a constant 60 rpm for 1 hour to ensure homogeneous mixing.

After 1 hour, the amount of removed cations were analyzed using UV and quantified using Equation (1).

$$\text{Removal Efficiency} = \frac{C_0 - C_e}{C_0} \times 100 \quad 1)$$

3.4.3 Effect Of Contact Time:

To investigate the contact time it was observed that maximum removal of copper and lead reached at 50 minutes, in the adsorption process of MOF5-NiFe-LDH. 25mg of MOF5-NiFe-LDH composite was added into 30ml of copper and lead solutions with concentration of 50 mg/L. Then the solution were placed at magnetic rotator at room temperature (25°C). Sample were collected at interval of 10, 20, 30 to so on 60min. And after 60min sample were taken with the interval of 40min for 2 hours. The quantity of cation removed at each time point was determined by using UV spectroscopy.

3.4.4 Adsorption Kinetics:

Adsorption capacity of MOF5-NiFe-LDH with the effect of contact time were studied. 25mg of sorbent composite were added into 30 ml of copper and lead solutions. Then the mixture were placed on magnetic hot plate for an hour. Sample were taken after increment of 10 minute, 30 minutes 1hour, 2 hours, and 3 hours of interval time. The removal of cations at each time of interval were determine by using UV spectroscopy.

The removed amount of cations of copper and lead from solution on MOF5-NiFe-LDH per unit weight of adsorbent were calculated by [66].

$$q_e = \frac{C_0 - C_e}{m} \times V \quad 2)$$

Here the capacity of adsorption (mg/g) is “ q_e ”, initial concentration (50mg/L) of copper and lead solution is “ C_0 ”, final concentration (mg/L) of copper and lead solution is “ C_e ”. The another parameter which is mass of the sorbent (25mg) is “ m ” and Volume of the solution (30ml) is “ V ” was kept constant.

The obtained data from the experiments were used and the kinetic adsorption of copper and lead ions onto the surface of MOF5-NiFe-LDH was evaluated by the pseudo first and 2nd order models.

The 1st order of pseudo model were introduced by Lagergren (1898) is showing below [67].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad 3)$$

The 2nd order of pseudo model were introduced by Ho (1995) is as follows [68].

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad 4)$$

where the adsorption capacity at equilibrium (mg/g) is “ q_e ”, at the time “ t ” (min) of equilibrium ,the adsorbed amount of solute is “ qt ” and “ k_1 ” and “ k_2 ” are the rate constant of pseudo 1st and 2nd order adsorption respectively (g/mg/min).

CHAPTER 4

RESULTS & DISSCUSION

4.1 Characterization

4.1.1 Scanning Electron Microscopy (SEM)

To investigate the surface morphology of the MOF5-NiFe-LDH composite, It is characterized by Scanning Electron Microscopy (SEM) at varying resolution. At high resolution of 5KX and 8KX for detailed surface feature and at lower resolution at 2KX for overall morphology as shown in figures (4.1) .

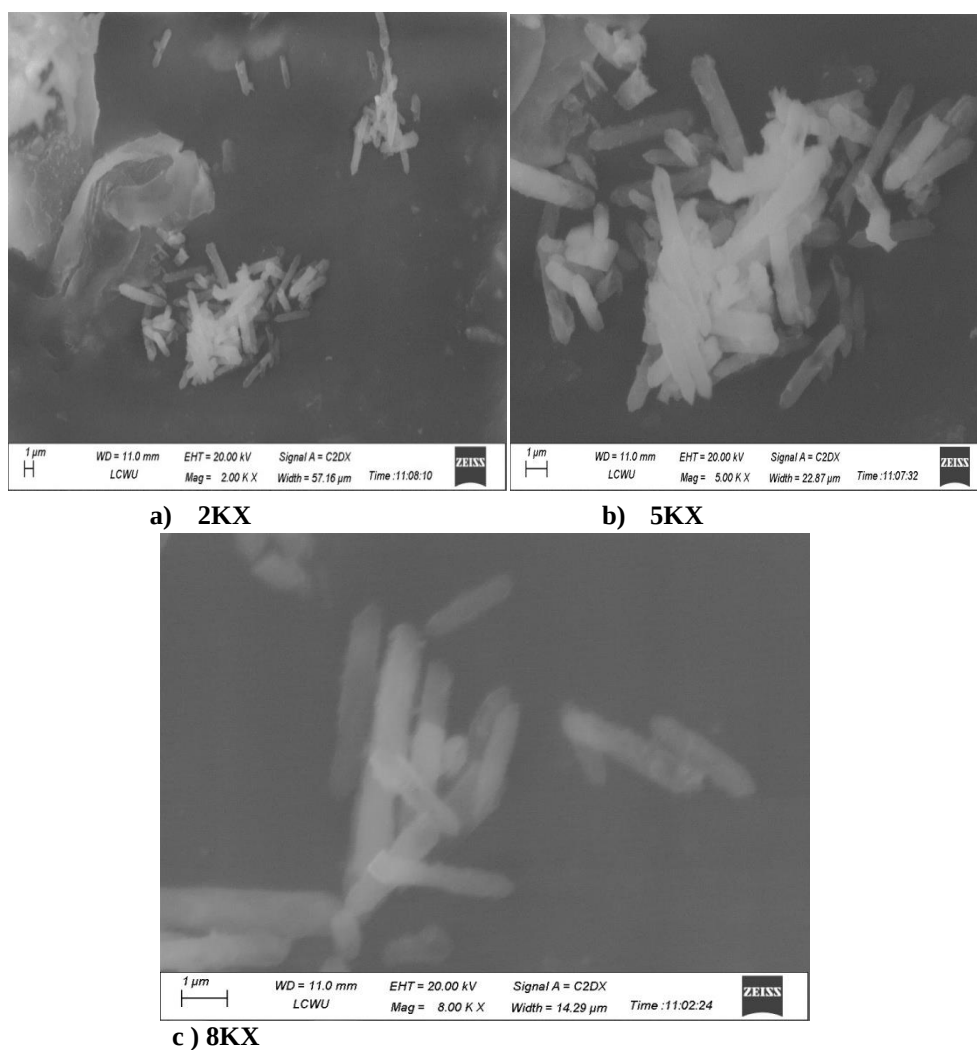
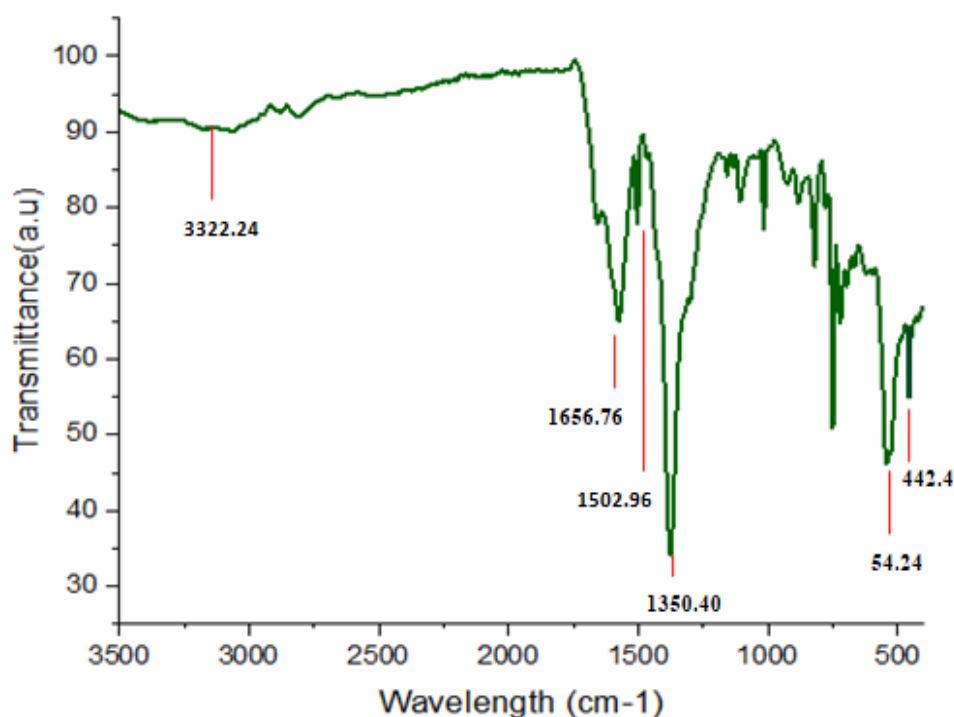


Figure (4.1) SEM images of MOF5-NiFe-LDH

The images of SEM revealed a highly interconnected and spindle like crystal structure with which NiFe-LDH nano sheets uniformly dispersed throughout the framework of MOF5. The confidential contact between these two components is likely enable interactions, optimizing the composites's efficiency for removal of heavy metals. These insights coherent with previously studies on similar composite materials, offering that the composite MOF5-NiFe-LDH design is promoting the sorption of heavy metals from the waste water [69, 70].

4.1.2 Fourier Transform Infrared (FTIR)

The novel MOF5-NiFe-LDH composite shows the Fourier-Transnsform Infrared (FTIR) spectrum which reveals that important functional groups and metal oxides present within the structure which enhance the adsorption properties of metals. Corresponding to organic groups such as (**O-H,C-C,C=C**) as well as metal oxides (**NiO,ZnO,FeO**) was identified the specific characteristics peaks. To confirming the presence of these functional groups or materials and their corresponding vibrational modes as shown in figure (4.2), compared the observed peaks with the established literature values.



Figurer (4.2) FTIR Graph of MOF5-NiFe-LDH

The observed peak at **542.24 cm⁻¹** reveal the presence of stretching vibration of NiO whose typical range fall at **500–600 cm** [71].

This peak can be attributed, to the stretching motion of nickel and oxygen bonds in the MOF5-NiFe-LDH composite. This peak also indicate the presence of ZnO, although ZnO stretching typically observed slightly lower around **430–500 cm⁻¹**. This overlap is common in FTIR spectrum where multiple oxides are present. The peak at **665.76 cm⁻¹** corresponds to the stretching vibration of **Fe-O** bonds, a characteristic feature of iron oxides. FeO typically exhibits peaks between **570–660 cm⁻¹**, as reported in literature [72, 73].

This peak confirms the presence of metal oxides in the composite which indicate that there is highly bonding occur between NiFe-LDH, contributing to its overall structural integrity and adsorptive properties.

FTIR spectrum of MOF5-NiFe-LDH also identified the organic functional groups which are typically present in the composition of MOF-LDH. The broad peak at **1175.12 cm⁻¹** were identified the presence of C-C stretching, typically observed in the range of **1200–1300 cm⁻¹**. Identification of this indicate the presence of aliphatic carbon-carbon single bonds in the structure from the organic linker used in this MOF framework [74, 75].

The C=C at **1600–1700 cm⁻¹** is typically range is seen as in this spectrum at **1502.96 cm⁻¹** which indicate the unsaturated organic linker used in the framework of MOF. The broad band around **3322.24 cm⁻¹** suggests the presence of **O-H stretching**, typical for hydroxyl groups or adsorbed water molecules. **O-H stretching** vibrations are generally found between **3200–3600 cm⁻¹**, which aligns with this observed band. This peak can be attributed to the surface hydroxyl groups or water molecules associated with the metal oxides [76].

Overall, the successful synthesis of MOF5-NiFe-LDH were confirmed by the FTIR analysis ,by comparing with literature reported values which align well in this spectrum of FTIR, with clear identification of metal oxides and organic functional groups. It giving the strong foundation, for the MOF5-NiFe-LDH composite's application in heavy metal adsorption.

4.1.3 X-ray Diffraction (XRD)

A well-defined framework of MOF5-NiFe-LDH indicating the crystallographic plane, with the presence of prominent peaks for the MOF5 and NiFeLDH which is reported in literature. The positions of these important peaks at approximately 6.56° , 11.34° , 13.82° , 15.22° , 22.1° , 33.94° , 39.45° , 46.8° , and 53.4° which indicate the successful formation of structure of mof5 [77].

The additional peaks which is approximately at 11.34° , 22.1° , 33.94° , 39.45° , and 53.4° suggested the presence of NiFeLDH . Due to the overlapping of some peaks which is between the MOF5 and NiFe-LDH, indicated a potential interpenetration between these two components of composite and it is also consistent with previously studies on MOF-LDH composite [78]. Which is shown as in below figure (4.3)

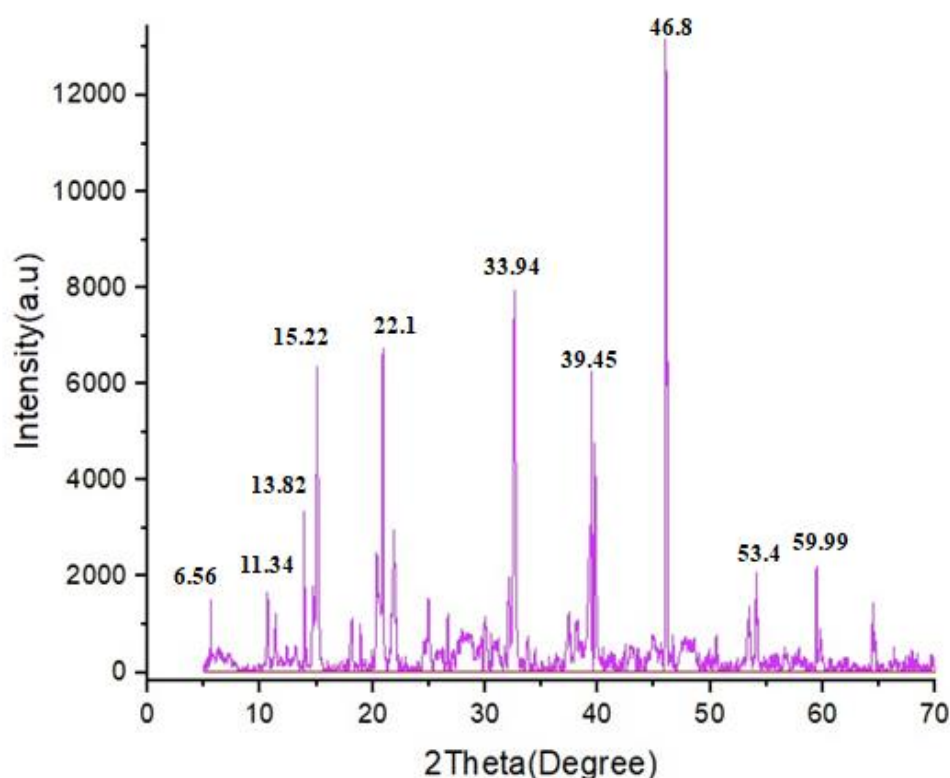


Figure (4.3) XRD Graph of MOF5-NiFe-LDH

The coexistence of these both MOF5 and NiFe-LDH components, is clearly demonstrated by the x-ray diffraction pattern of MOF5-NiFe-LDH. The successful synthesis of desired material of composite is suggested due to the presence of important characteristics peaks for each components, which influences the overall properties of the composite which able to perform highly adsorption of heavy metals.

4.2 Adsorption Analysis

4.2.1 Initial Concentration:

The MOF5-NiFe-LDH showed varying removal percentages of Cu^{2+} and Pb^{2+} ions in solution as the initial ion concentration was changed from 25-125mg/L over a 1hour contact time as shown in figure (4.4) for copper and figure (4.5) for lead.

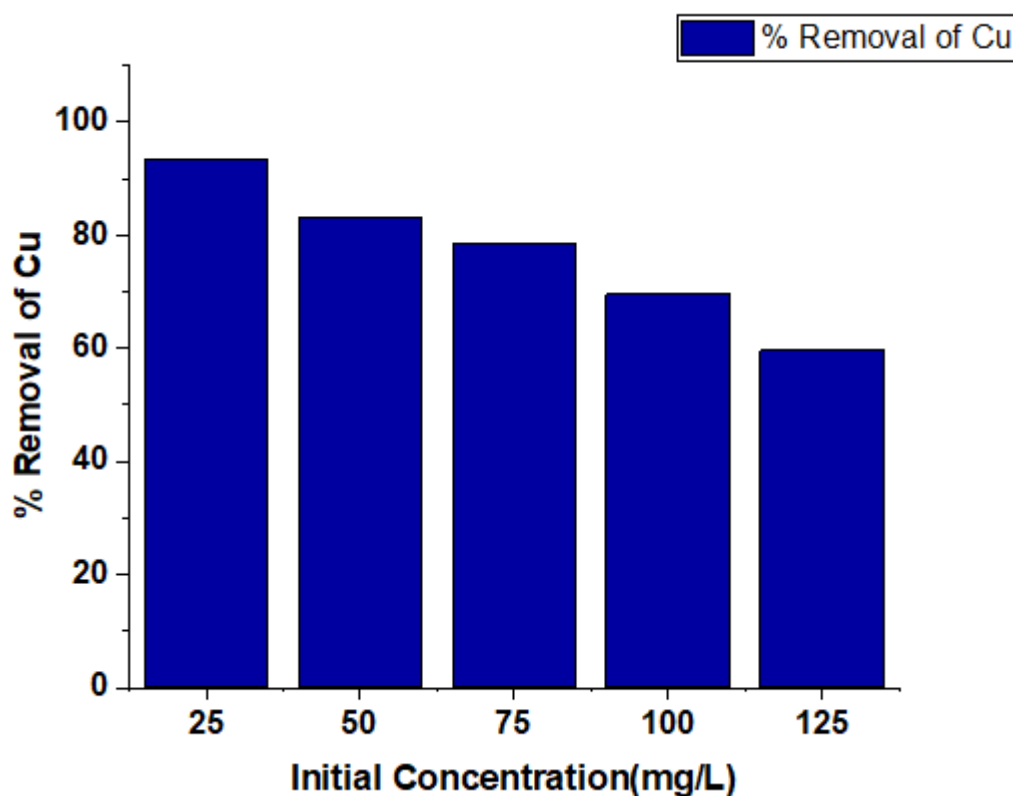


Figure (4.4) % Removal of Cu^{2+} varying with initial concentration

The adsorbent could eliminate over 90% of Cu^{2+} ions at a 25 mg/L concentration as show in figure (4.4). At lower concentrations of 25 mg/L, with the highest removal rate reaching 93%. However, as the copper (II) ion concentration increased, the removal efficiency decreased, with only 59%

removal at 125 mg/L. This decrease in effectiveness at higher concentrations is attributed to the limited available adsorption sites on the composite due to the fixed amount of adsorbent in each solution [79].

Similarly it was observed that the removal percentage of lead (II) ions decreased notably as the concentration of lead ions increased as shown in figure (4.5):

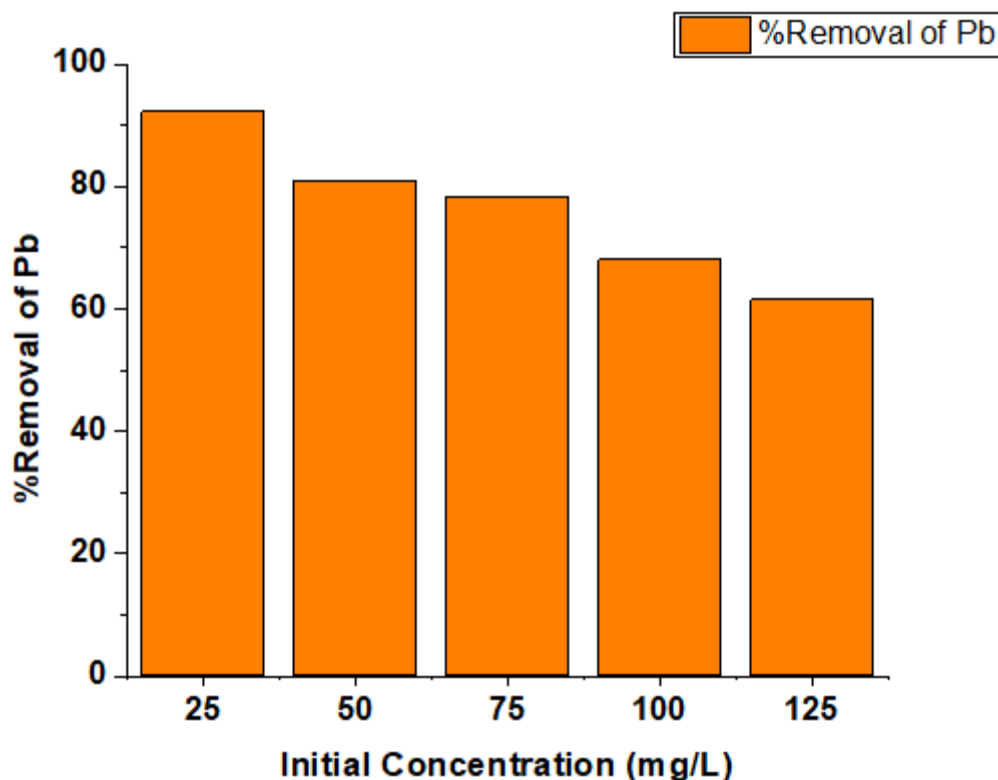


Figure (4.5) % Removal of Pb^{2+} varying with initial concentration

At 25 mg/L, the MOF-LDH could eliminate 92.25% of Pb^{2+} ions in solutions as shown in figure (4.5). However, at 50mg/L lead (II) concentration, the removal percentage is 81. At the highest concentration of 125 mg/L, only 61% of Pb^{2+} ions were removed by the MOF-LDH, possibly due to fewer available adsorption sites relative to the lead (II) ion ratio.

In literature it was published that alumina fiber removed only 50% lead ions at concentration of 125mg/L while by using MOF5-NiFe-LDH lead removal was 61% at 125mg/L concentration, so MOF5-NiFe-LDH is more efficient than that of alumina nanofiber [80].

Activated POP (Plaster of Paris) were removed 60% copper ions at 125mg/L concentration of by MOF5-NiFe-LDH removed at 59.9% [81].

4.2.2 pH Effect:

The adsorption of heavy metals like copper (Cu^{2+}) and lead (Pb^{2+}) by the MOF5-NiFe-LDH composite is highly dependent on the pH of the solution. The observed behaviour, 83% removal of copper ions Cu^{2+} and 81% removal of Lead Pb^{2+} ions at pH 6, with lower removal efficiencies at pH levels both below and above 6 show in figure (4.6):

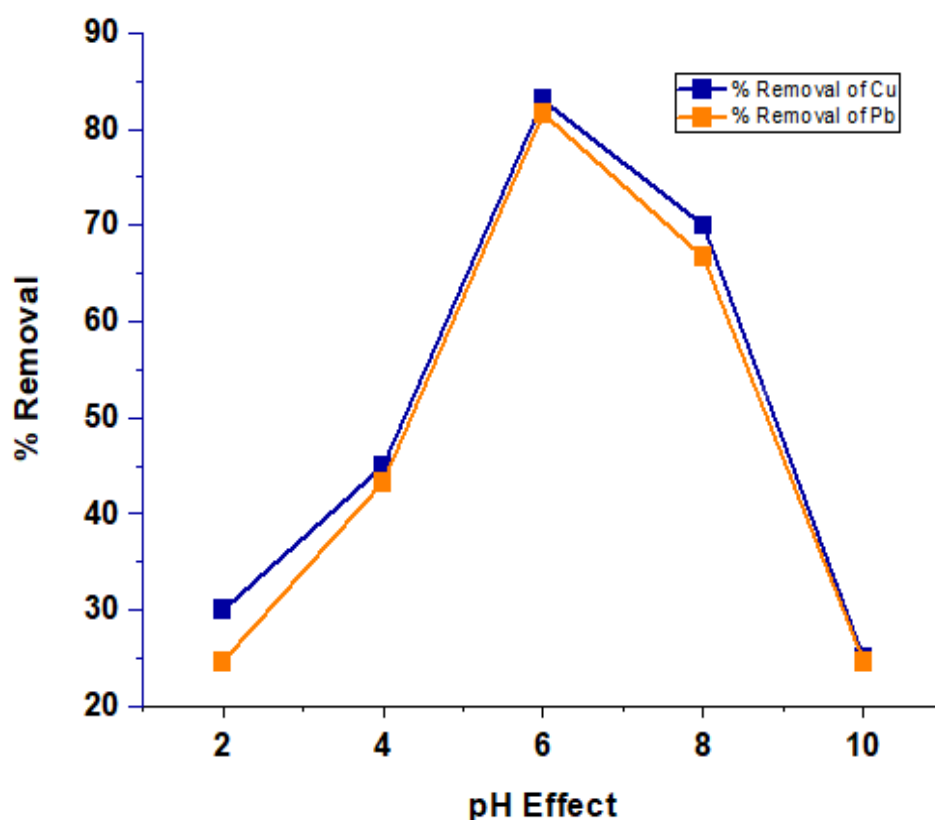


Figure (4.6) % Removal of Cu^{2+} and Pb^{2+} with change in pH

The study on the adsorption of copper and lead ions by the MOF5-NiFeLDH revealed that the most effective pH for metal ion adsorption is around 6. At this pH, approximately 83% of Cu^{2+} ions and 81% of Pb^{2+} ions were successfully removed from the solution. This aligns with previous findings, considering the pH of the deionized water used was also around 6 [82].

Surface Charge of the Adsorbent at pH 6 the MOF5NiFeLDH composite likely has an optimal surface charge at this pH, maximizing electrostatic attraction between the positively charged Cu^{2+} and Pb^{2+} ions and the negatively charged sites on the composite. This strong attraction leads to high adsorption efficiency.

As the pH decreases from 6, the solution becomes more acidic, increasing the concentration of H^+ ions. These H^+ ions can compete with Cu^{2+} and Pb^{2+} for adsorption sites on the composite, reducing the overall adsorption efficiency. Additionally, the composite itself might become less negatively charged or even positively charged at very low pH, further reducing its ability to attract and adsorb cations [83].

At higher pH levels, more than 6 the surface of the MOF5-NiFe-LDH composite might become more negatively charged, but the metal ions can begin to precipitate as metal hydroxides (e.g., $\text{Pb}(\text{OH})_2$). Once precipitated, these hydroxides are no longer in their ionic form and therefore are not adsorbed by the composite, resulting in a decrease in adsorption efficiency. Metal ion speciation at pH 6, the metal ions (Pb^{2+} and Cu^{2+}) are primarily in their free ionic forms, which are readily adsorbed by the composite. This results in the highest removal efficiency. At pH less than 6 is more acidic conditions, the metal ions remain in their ionic forms, but the competition with H^+ ions reduces adsorption efficiency. As pH increases, Pb^{2+} and Hg^{2+} ions may begin to form insoluble hydroxides (e.g., $\text{Pb}(\text{OH})_2$, $\text{Cu}(\text{OH})_2$). These hydroxides precipitate out of solution, meaning they are not available to be adsorbed by the MOF5-NiFe-LDH composite. This reduces the apparent removal efficiency, as the metals are no longer in a form that can be captured by the adsorbent.

Overall pH 6 offers the optimal balance where the metal ions remain in a form that is highly adsorbable, the surface charge of the composite is optimal, and no significant precipitation occurs. $\text{pH} < 6$ results in competition from H^+ ions, reducing adsorption efficiency. $\text{pH} > 6$ can lead to the precipitation of metal hydroxides, which are not adsorbed by the composite, reducing the apparent removal efficiency.

This pH-sensitive behaviour highlights the importance of optimizing pH conditions to achieve maximum heavy metal removal efficiency using MOF-5NiFe-LDH.

4.2.3 Contact Time:

The impact of the duration of contact on the adsorption capacity of the MOF5-NiFe-LDH was investigated. The results show that the majority of copper and lead ions were adsorbed within initial 30 minutes as shown in figure (4.7, 4.8):

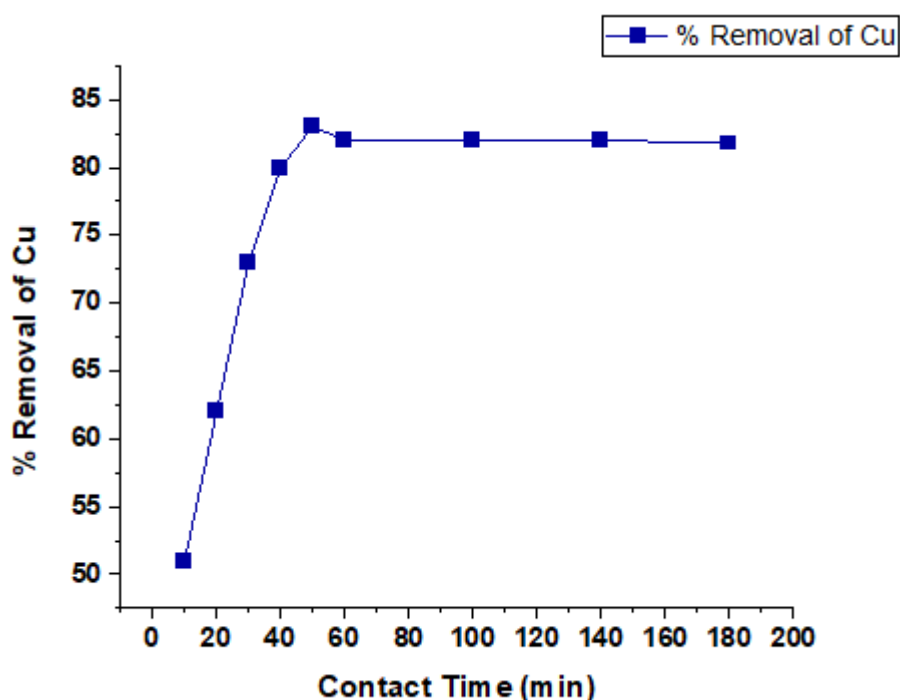


Figure (4.7) Adsorption capacity of MOF5NiFeLDH to Cu^{2+} with change in time

At initial 30 minutes 70 percent of both copper and lead ions were removed as shown in figure (4.7) for copper and (4.8) for lead. After 50 minutes, the adsorption rate stabilized, reaching equilibrium, and the trend line leveled off. Specifically, the composite removed 83% of copper and 81% of lead ions at 50 minutes. After 50 minutes, there is no increase in the removal percentage, for 2 more hours may be due to saturation of adsorbent material.

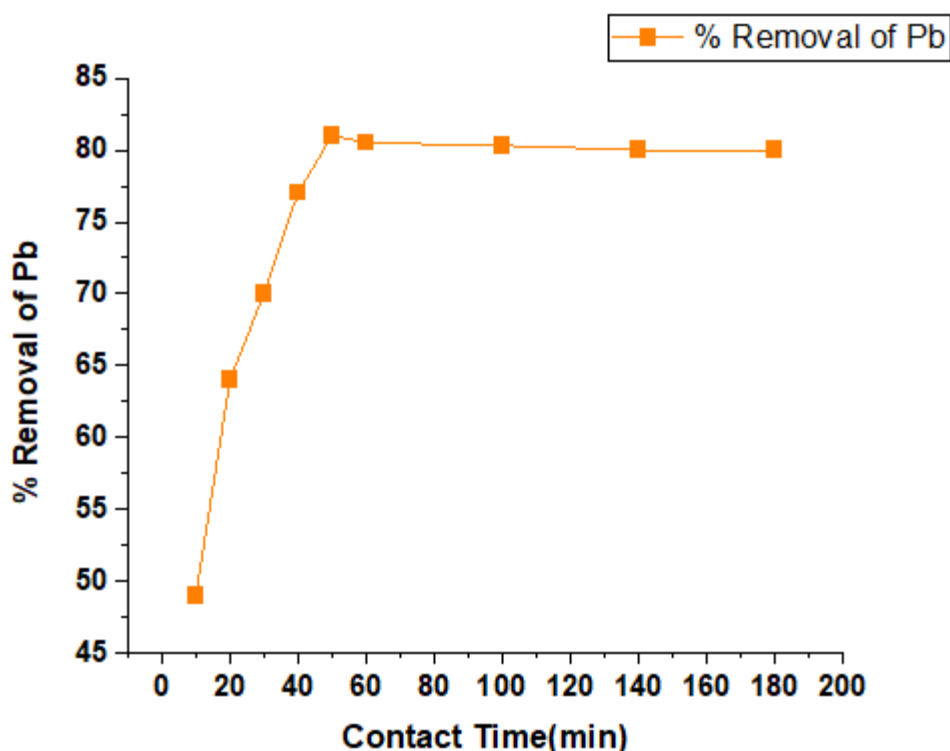


Figure (4.8) Adsorption capacity of MOF5NiFeLDH to Pb^{2+} with change in time

The data indicate that, the time variation curve is single, smooth and continuous and it shows the formation of monolayer coverage on the outer interface of the MOF-LDH [84].

4.2.4 Adsorption Studies:

By applying kinetics data of pseudo 1st and 2nd order model, the sorption onto MOF5-NiFe-LDH of copper and lead were examined.

4.2.4.1 Pseudo 1st Order Of Kinetics

1st order of pseudo model explains the physical process of adsorption. In which the adsorbate attach to the surface of adsorbent through Vander Waal's forces. [85]

For the adsorption of copper and lead onto MOF5-NiFe-LDH, plot pseudo 1st order by putting kinetic data into equation (3) as shown in figure (4.9)(a,b):

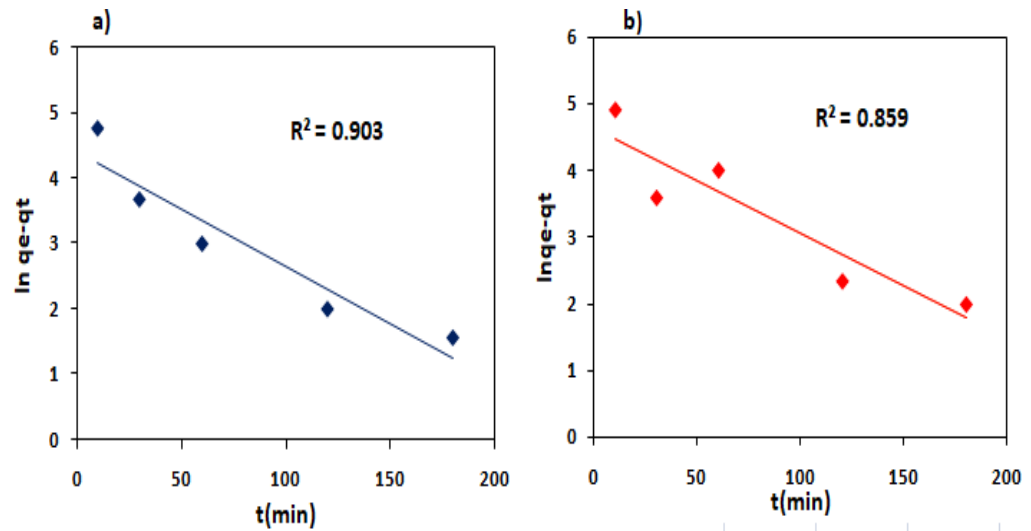


Figure (4.9) Pseudo 1st order kinetics for (a) Cu^{2+} and (b) Pb^{2+} adsorption

4.2.4.2 Pseudo 2nd Order Of Kinetics

The 2nd order of pseudo explain the chemisorption process. In which the process of adsorption is rate limiting step. It describes that the concentration of adsorbate in solution is not depend on adsorption rate while adsorption capacity of adsorbate is depend on adsorption rate [86].

By putting kinetic data into equation (4), 2nd order of pseudo were explore, it shows a linear graph between t/q_t on x-axis and time on y-axis as shown in figure (4.10)(a,b):

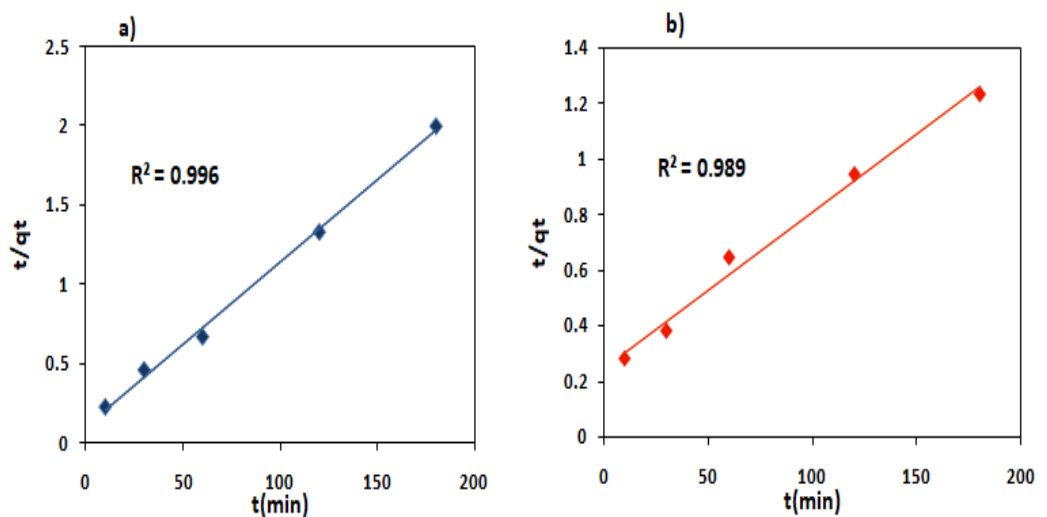


Figure (4.10) Pseudo 2nd order kinetics for (a) Cu^{2+} and (b) Pb^{2+} adsorption

All experimental and calculated parameters of kinetic data from 1st and 2nd order of pseudo were shown in table (4.1). The graph of 1st and 2nd pseudo order is shown in figure (4.9(a,b)) and (4.10(a,b)). The linear regression correlation coefficient (R^2) values for the 2nd order of pseudo is high with the range of **0.903-0.996** as compared to pseudo 1st order with the range of **0.859-0.986**. The calculated "q_e" values fit the experimental "q_e" better for 2nd order rather than 1st order of pseudo kinetics for copper(II) and lead(II) adsorption. These values explore that 2nd order is more fit than 1st order of pseudo kinetic model.

Table (4.1) Pseudo 1st and 2nd order kinetics parameters of Cu⁺² and Pb⁺² adsorption

Metals	Initial Conc. (mg/L)	q _e Exp (mg/g)	Pseudo 1 st Order			Pseudo 2 nd Order		
			k_1 (1/min)	R^2	q _e Cal (mg/g)	k_2 (1/min)	R^2	q _e Cal (mg/g)
Cu²⁺	50	80	1.8×10^{-3}	0.903	56.6	4.1×10^{-2}	0.996	83.33
Pb²⁺	50	75.75	1.9×10^{-1}	0.859	61.93	4.4×10^{-4}	0.989	78.51

CHAPTER 5

CONCLUSION

The results of this research demonstrate the successful synthesis of the MOF5-NiFe-LDH composite, which exhibited exceptional capabilities in the adsorption of heavy metals, specifically Cu^{2+} and Pb^{2+} ions, from aqueous solutions. Through SEM, FTIR, and XRD analysis, the structural and chemical integrity of the composite was confirmed, revealing a highly interconnected framework that optimized interactions between the MOF5 and NiFe-LDH components. This unique structure contributed to the composite's efficiency in removing heavy metals, with adsorption efficiency strongly influenced by initial ion concentration, pH, and contact time. Optimal conditions for maximum removal were identified at a pH of 6, where over 80% of both Cu^{2+} and Pb^{2+} ions were adsorbed within the first 50 minutes. Kinetic analysis revealed that the adsorption process followed pseudo-second-order kinetics, indicating a chemisorption mechanism. The adsorbent capacity of activated pop is 93 (mg/g) with 93% removal and MOF5-NiFeLDH have 83.33(mg/g) with 83% removal for Cu at (50mg/L) concentration. On the other hand the adsorbent capacity of alumina fiber is 23.75(mg/g) with 52% removal and MOF5NiFe-LDH have 78.5(mg/g) with 81% removal for Pb. The superior performance of MOF5-NiFe-LDH, compared to other adsorbents like alumina nanofibers and activated pop, highlights its potential for practical applications in wastewater treatment and environmental remediation.

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