

**REMOVAL OF HEAVY METALS FROM AQUEOUS
STREAMS USING ZEOLITIC IMIDAZOLATE
FRAMEWORK BASED MATERIAL**

BY

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Dedication

This work is dedicated to my parents, siblings, relatives, friends and all my well-wishers.

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LIST OF ABBREVIATIONS

AD	:	Adsorbent dosage
ANN	:	Artificial neural network
C	:	Initial concentration
CNTs	:	Carbon nanotubes
EPA	:	Environmental protection agency
FTIR	:	Fourier transform infrared spectroscopy
GO	:	Graphene oxide
MOF	:	Metal-organic framework
nZVI	:	Nanoscale zero-valent iron
RF	:	Random forest
rGO	:	Reduced graphene oxide
RMSE	:	Root mean square error
RSM	:	Response surface methodology
SVM	:	Support vector machine
T	:	Temperature
t	:	time
TGA	:	Thermogravimetric analysis
WHO	:	World health organization
XRD	:	X-ray diffraction analysis
ZIF	:	Zeolitic imidazolate framework
ZVI	:	Zero-valent iron

ABSTRACT

Full Name : Usman Muhammad Ismail

Thesis Title : Removal of Heavy Metals from Aqueous Streams using Zeolitic Imidazolate Framework Based Materials

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Water is a valuable resource and essential for life on Earth, however, water resources are polluted at an unprecedented rate. Heavy metals are one of the most toxic aqueous contaminants because many of them are carcinogenic, teratogenic and mutagenic at levels above the permissible limits, hence, human exposure to such contaminants should be avoided. Several methods have been used for the treatment of aqueous heavy metals, however, because of specific limitations, the search for low cost, time efficient and reliable treatment method still presents an interesting research area. Adsorption is considered a suitable method, and zeolitic imidazolate frameworks (ZIFs) based materials have emerged as suitable candidates for such application because of their superb characteristics like better chemical stability relative to other MOFs, high specific surface area, thermal stability and ability to host different kind of nanomaterials to produce an improved performance. However, most of the studies related to usage of ZIFs in water treatment applications have focused on ZIF-8, and to a lesser extent ZIF-67. As such, this work pioneered the use of ZIF-60 for water treatment application, using Pb(II) as the model contaminant. The response surface methodology experimental design technique was adopted as the tool for studying the effect of variation in process parameters on the performance of ZIF-60 towards decontamination of water polluted with Pb(II). Further, classical adsorption experiments including adsorption kinetics, isotherms and thermodynamic investigations were conducted. In addition, the generated

experimental data are collated and used to test the predictive prowess of several machine learning algorithms. The findings of the study have been published in the paper titled “Aqueous Pb(II) removal using ZIF-60: adsorption studies, response surface methodology and machine learning predictions”. The paper is attached as chapter 4 of this work. In addition to the published paper, a patent titled “ZIF-60 for aqueous Pb(II) treatment from contaminated waters” is being filed for. While conducting the experiments, a separate effort was made to write a comprehensive literature review that tracked the progress of several adsorbents with ZIFs and MOFs included in the removal of heavy metals from aqueous solutions. The findings are reported in the literature review of this work (chapter 2), and it is intended to be published in a reputable journal. In addition, the summary of other preliminary results is presented as chapter 5 of the report.

ملخص الرسالة

الاسم الكامل: عثمان إسماعيل محمد

عنوان الرسالة: إزالة المعادن الثقيلة من التيارات المائية باستخدام مواد أساسها هيكل زيوليت إيميدازولات

التخصص: الهندسة المدنية

تاريخ الدرجة العلمية: مايو 2023 م

الماء مورد قيم وضروري للحياة على الأرض، ومع ذلك، فإن موارد المياه ملوثة بمعدل غير مسبوق. تعتبر المعادن الثقيلة من أكثر الملوثات المائية سمية لأن العديد منها مسببة للسرطان وماسخة ومسببة للطفرات بمستويات أعلى من الحدود المسموح بها، وبالتالي يجب تجنب تعرض الإنسان لمثل هذه الملوثات. تم استخدام العديد من الطرق لمعالجة المعادن الثقيلة المائية، ومع ذلك، نظرًا لقيود معينة، لا يزال البحث عن طريقة معالجة منخفضة التكلفة وفعالة للوقت وموثوق بها يمثل مجال بحث مثيرًا للاهتمام. يعتبر الامتزاز طريقة مناسبة، وقد ظهرت المواد القائمة على أطر الزيوليت إيميدازولات (ZIFs) كمرشحين مناسبين لمثل هذا التطبيق بسبب خصائصها الرائعة مثل الاستقرار الكيميائي الأفضل بالنسبة للأطر العضوية المعدنية الأخرى، ومساحة السطح المحددة العالية، والاستقرار الحراري والقدرة على استضافة مختلفة نوع من المواد النانوية لإنتاج أداء محسن. ومع ذلك، فإن معظم الدراسات المتعلقة باستخدام ZIFs في تطبيقات معالجة المياه قد ركزت على ZIF-8، وبدرجة أقل ZIF-67. على هذا النحو، كان هذا العمل رائدًا في استخدام ZIF-60 لتطبيق معالجة المياه، باستخدام Pb (II) باعتباره الملوث النموذجي. تم اعتماد تقنية التصميم التجريبي لمنهجية سطح الاستجابة كأداة لدراسة تأثير التباين في معامل العملية على أداء ZIF-60 تجاه إزالة تلوث المياه الملوثة بالرصاص (II). علاوة على ذلك، أجريت تجارب الامتزاز الكلاسيكية بما في ذلك حركية الامتزاز، متساوي الحرارة والتحقيقات الديناميكية الحرارية. بالإضافة إلى ذلك، يتم تجميع البيانات التجريبية الناتجة واستخدامها لاختبار البراعة التنبؤية للعديد من خوارزميات التعلم الآلي. تم نشر نتائج الدراسة في ورقة بعنوان "إزالة الرصاص المائي (II) باستخدام ZIF-60: دراسات الامتزاز، ومنهجية سطح الاستجابة وتنبؤات التعلم الآلي". الورقة مرفقة كفصل 4 من هذا العمل. بالإضافة إلى الورقة المنشورة، تم تقديم براءة اختراع بعنوان "ZIF-60 للمعالجة المائية للرصاص (II) من المياه الملوثة". أثناء إجراء التجارب، تم بذل جهد منفصل لكتابة مراجعة شاملة للأدبيات التي تتبع تقدم العديد من المميزات باستخدام ZIFs و MOFs المضمنة في إزالة المعادن الثقيلة من المحاليل المائية. تم الإبلاغ عن النتائج في مراجعة الأدبيات لهذا العمل (الفصل 2)، ومن المقرر نشرها في مجلة مرموقة. بالإضافة إلى ذلك، يتم تقديم ملخص النتائج الأولية الأخرى في الفصل الخامس من التقرير.

CHAPTER 1

INTRODUCTION

1.1 Background

Water is an important natural resource and demand for water is increasing across the globe because of industrial growth and increase in human population. WHO projections are that by 2025, about 50% of the world's population will suffer from water crisis (Ighalo et al., 2022). Thus, it is essential to treat water as a valuable resource. However, the rate at which water bodies are contaminated endangers human health (Shannon et al., 2008). Contaminants in water are classified as either organic or inorganic based on their chemical class, and heavy metals are described as one of the most influential inorganic pollutants that are found in water and wastewater (M. Verma et al., 2022). Common heavy metals include mercury, lead, chromium, copper, cadmium and arsenic. Because of their widespread use in many industrial processes, they are released into the aquatic environment as part of industrial wastewater. Many heavy metals are considered as hazardous substances that are mutagenic, carcinogenic and teratogenic that can migrate with water flow as such presenting multiple routes for human exposure. Further, they can be taken up by plants and animals resulting in bioaccumulation and biomagnification (Rehman et al., 2018; Sankhla et al., 2016). Thus, is important to find innovative ways for control and treatment of polluted water systems.

Many technologies including electrolysis, chemical reduction, ion-exchange, chemical precipitation, coagulation, phytoremediation, membrane filtration, and adsorption have been applied and improved for treatment of contaminated water (Mo et al., 2022). While no one method has shown complete dominance over the others in the field of application, adsorption has emerged as a suitable treatment method due to its simple nature in terms of application, time efficiency, low cost and ability to remove multiple pollutants from waste streams. Traditional adsorbents such as activated carbon, chitosan, biomass, molecular sieves and polymers have been used. However, their adsorption capacity is not high, they show poor selectivity towards many contaminants and are often needed to be disposed of after use (Chairunnisa et al., 2021) making the field of developing novel adsorbents an interesting area of research.

Zeolitic imidazolate frameworks (ZIFs) are a category under the metal organic frameworks (MOFs) that were first synthesized in 2006. In addition to their thermal and chemical stability, they have shown many interesting characteristics that makes them good candidates for use in water treatment domain, they have high specific surface area which may reach up to 10000 m²/g and have permanent porosity which allows for easy introduction of functional groups which can help increase active site adsorption (Y. Liu et al., 2021). Further, they can easily be modified because of their tailorable structures and pore sizes. ZIFs documented heavy metal removal mechanisms including ion-exchange, pore diffusion, coordination and many others make them promising adsorbent for heavy metals in aqueous streams. Even though, ZIF materials have some certain drawbacks when applied in the field of adsorptive removal of aqueous contaminants including agglomeration and poor dispersibility in aqueous solution, their remarkable uptake towards heavy metals make research in their domain worth exploring.

Hence, this study focused on developing zeolitic imidazolate framework-60 (ZIF-60) and using it for decontamination of water polluted with lead. The response surface methodology (RSM) technique was adopted as the experimental design technique while machine learning approach was used for the prediction of aqueous lead removal from the contaminated aqueous system. The result of this experiment study have been published with the title “Aqueous Pb(II) removal using ZIF-60: Adsorption studies, response surface methodology and machine learning predictions”. In addition, the results from the experimental section were interesting and has resulted in filing the patent titled “ZIF-60 for aqueous Pb(II) treatment from contaminated waters”. The process of the patent filing is still ongoing.

Further, a comprehensive literature review on the removal of aqueous heavy metals by adsorbents that are based on activated carbon, natural adsorbents, biosorbents, clay minerals, layered double hydroxides (LDHs), zero-valent iron (ZVI), graphene, carbon nanotubes (CNTs), metal-organic frameworks and zeolitic imidazolate frameworks (ZIFs). The findings are attached in the literature review section of this work. The comprehensive literature review was done to find out the suitability and challenges encountered when the several classes of the materials are used for aqueous heavy metal treatment. Further, the review provided room for comparison between the performance of materials that are ZIF based and other materials, this indicated why ZIFs have a role to play in decontamination of water polluted by heavy metals.

The thesis report is divided into five chapters with the first being the introduction. **Chapter 2** is a comprehensive literature review titled “Adsorptive removal of heavy metals from aqueous solutions: A review on the progress of adsorbents development and their effectiveness”. It discusses ZIF-based materials as adsorbents, however, prior to ZIFs discussion, other adsorbents were also discussed to understand why ZIFs may have a major role to play in decontamination of

water. This review article is intended to be published in a high-impact factor journal as soon as possible. **Chapter 3** itemizes the objectives of the study while **Chapter 4** is the experimental section of the work. The findings have been published in the paper titled “Aqueous Pb(II) removal using ZIF-60: Adsorption studies, response surface methodology and machine learning predictions”. The paper is attached as published in chapter 4. **Chapter 5** gives the summary of preliminary results and screening exercise that was conducted using various contaminants prior to starting the full scale study on Pb(II) removal from contaminated aqueous system. **Chapter 6** is the last chapter and gives the conclusions and recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

Adsorptive removal of heavy metals from aqueous solutions: A review on the progress of adsorbents development and their effectiveness

2.1 Introduction

Water is the most important natural resource and it is essential for the sustainability of living organisms on Earth (J. Xu et al., 2018). However, access to safe and clean drinking water is increasingly becoming more difficult due to the continuous discharge of contaminants as effluents from industries and domestic activities. This is especially true for emerging and developing countries because of the high rate of industrialization, negative consequences of climate change and unplanned civilization among a host of other factors (Sheth et al., 2021; Vardhan et al., 2019). The UN World Water Development Report published by UNESCO in 2018 postulates that close to 50% of the global population experience difficulties at least once a month in accessing reliable and clean water. Further, projections were made that by 2050, the percentage will increase by approximately 10%, which is significant considering that the world population is also expected to grow (Bilal et al., 2022; UNESCO, 2018). Consumption of contaminated water can lead to several acute and chronic diseases such as the Minamata disease that happened in Japan due to the consumption of water and aquatic biota that have been contaminated with methylmercury. The

‘Itai-Itai’ disease is another example of a disaster caused by the consumption of water contaminated by cadmium (R. Chakraborty et al., 2022; Sud et al., 2008).

Exposure to heavy metals poses both acute and chronic toxicity which make them a serious class of aqueous inorganic contaminants. They are considered as non-biodegradable and persistent; this results in their accumulation in the environment for a very long time, presenting a continuous serious risk (Rao & Kashifuddin, 2014; Uddin, 2017; M. Verma et al., 2022). Further, several heavy metals are carcinogenic, teratogenic, mutagenic and toxic even at trace levels (R. Chakraborty et al., 2022). Although some of the heavy metals are necessary for the proper functioning of the human metabolic system, all of them are toxic above their permissible limit (Uddin, 2017). Hence, keeping them well below their permissible limits is imperative for the protection of the public health.

To address these concerns, several conventional and advanced treatment methods have been applied for the removal of hazardous heavy metals from aqueous streams including chemical precipitation, ion exchange, adsorption, membrane separation, electrochemical precipitation, photocatalysis and reduction (Bilal et al., 2022). While each of these methods offers its own advantages, many of them suffer from certain drawbacks such as high cost, long treatment time or/and the inability to remove trace levels of contaminants. A summary of the merits and demerits of some of the methods used to remove heavy metals from aqueous media is given in Figure 2.1.

Adsorption has emerged as one of the most attractive wastewater treatment methods due to the various advantages it offers including simplicity of operation, low cost, short treatment time, high efficiency and eco-friendliness (Liang et al., 2022). As such, development of novel adsorbents and the modification of existing ones to enhance their performance and selectivity towards individual

or group of heavy metals (contaminants) have attracted great research and industrial interests. Several classes of materials have been used as adsorbents for the treatment of contaminated water including activated carbon, natural adsorbents, bio-based adsorbents, clay minerals, zero-valent iron, LDH-based, CNT-based, graphene-based, MOFs-based and more recently ZIFs-based materials. Some of these adsorbents like activate carbon, clay minerals and some natural adsorbents are already in use for large-scale and commercial applications, while many of the others with a great application potential are still being explored on lab-scale, aiming to pave the way for their deployment on a commercial-scale. As such there is a plethora of articles available on this subject matter. While there are individual review articles on each class of the above-mentioned materials, this review article aims to provide readers with a succinct but comprehensive advances in the field of application of all these commonly used adsorbents. Each of these materials have certain properties that make it function as suitable adsorbent for heavy metals in aqueous stream and through this article, the several advantages and areas of deficiency for each class of materials would be highlighted.

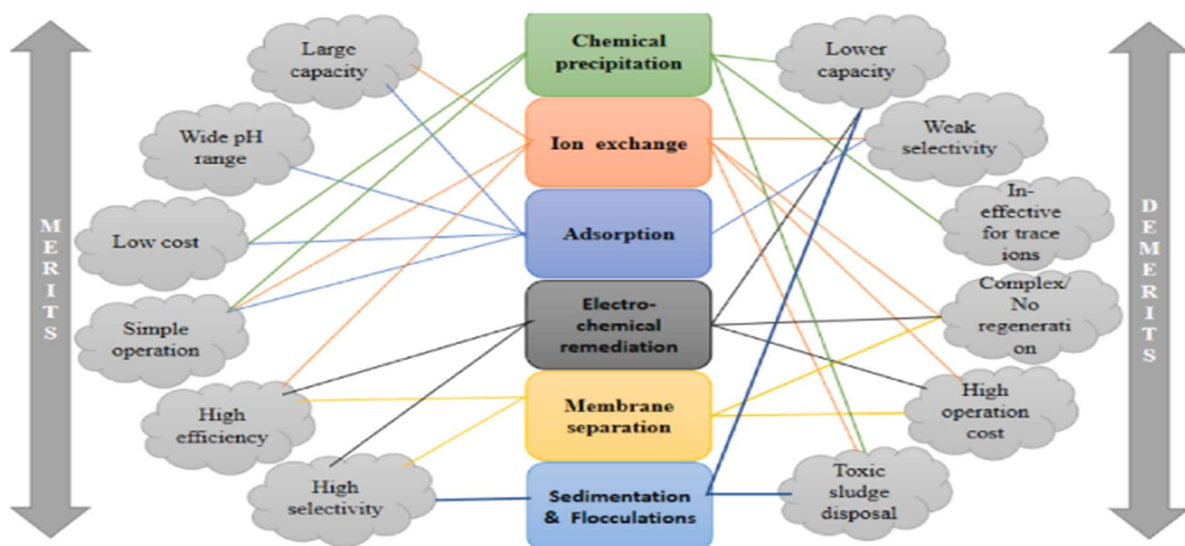


Figure 2.1. Merits and demerits of common techniques used for aqueous heavy metal treatment (Bilal et al., 2022)

2.2 Sources and toxicity of heavy metals

Heavy metals are a class of metal ions that are identified by their atomic weight which ranges between 63.5 and 200.6 g/mol and/or having a relative density (with respect to water) that is greater than 5.0 (X. Feng et al., 2022). Some commonly found heavy metals in the Earth's crust include mercury (Hg), cadmium (Cd), lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), and copper (Cu). Heavy metals are found naturally in Earth's crust; however, the recent increase in anthropogenic activities has resulted in significant changes in their geochemical cycling (Rehman et al., 2018). Industrial activities such as metal processing, electroplating, mining and batteries manufacturing have resulted in the discharge of significant quantities of water contaminated with heavy metals into the environment. Once present in the environment, heavy metals are difficult to degrade into non-toxic compounds. This leads to their accumulation in the environment, which represents a great and long-term threat to the ecological environment and the public health (V. Kumar et al., 2019). Figure 2.2 gives a schematic interaction between the environment and anthropogenic sources of heavy metals. While some heavy metals like zinc, manganese, copper, iron and cobalt are essential for the functioning of the human body, they are considered as deleterious if ingested at more than the recommended concentrations (Chronopoulos et al., 1997; Hashim et al., 2011; Lane & Morel, 2000; L. Xu et al., 2017).

Table 2.1 presents a list of some heavy metals along with their sources and respective permissible limits as set by various organizations along with significant health concerns which they pose.

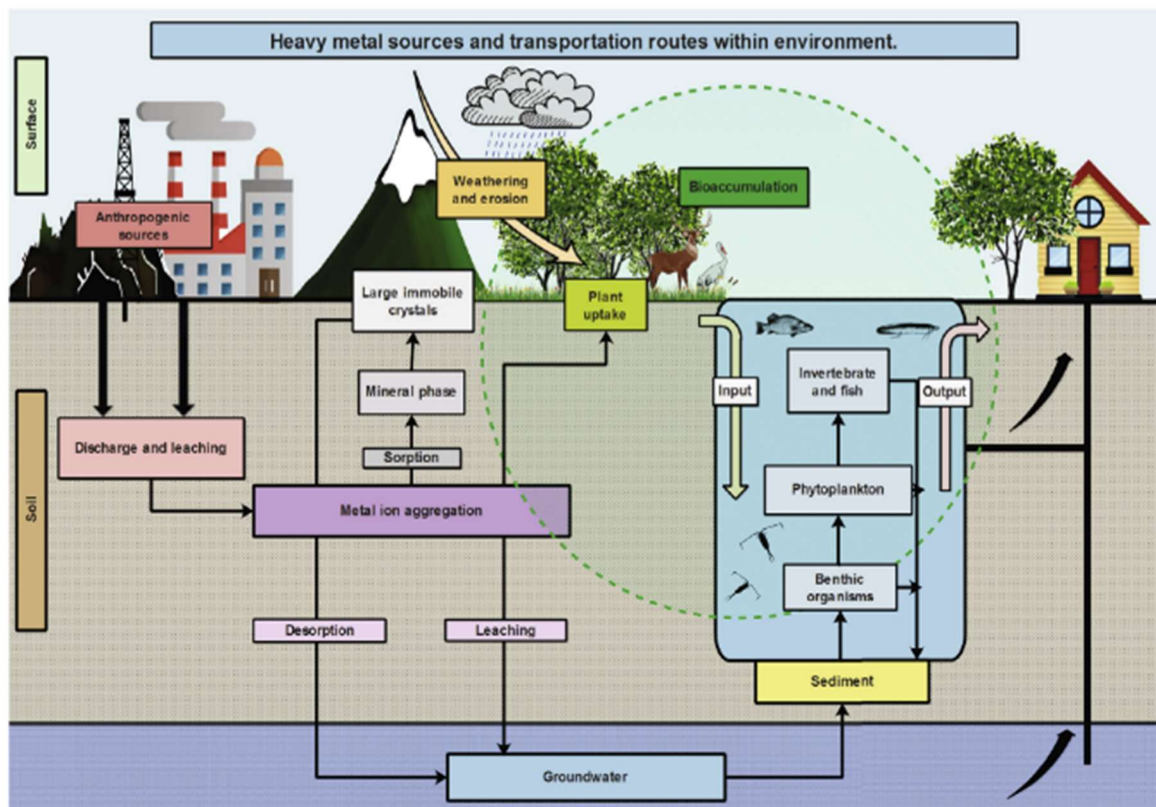


Figure 2.2. Interaction between the environment and anthropogenic sources of heavy metals (Kobielska et al., 2018).

Table 2.1 Common heavy metals, their sources and characteristics along with regulatory limits. Adapted from (Bilal et al., 2022; Kobielska et al., 2018; Mariana et al., 2021; Uddin, 2017).

Heavy metal	Atomic mass	Density (g/cm ³)	Sources	Health effects	Permissible limits (mg/L)				
					WHO	USEPA	EU Standard	CDW, Canada	IS 10500
Arsenic	74.9	5.72	Waste from electronics production, orchards runoff, erosion of natural deposits	Increased cancer risk, skin damage and circulatory system problems	0.01	0.01	0.01	0.01	0.01
Cadmium	112.4	6.65	Discharge containing metals from refineries, leaching of natural deposit, batteries and paints runoff, corrosion of galvanized pipes	Kidney damage	0.003	0.005	0.005	0.005	0.003
Chromium	52	7.19	Steel industry discharges, pulp mills discharges, natural deposits erosion	Allergic dermatitis	0.05	0.1	0.05	0.05	0.05
Copper	63.5	8.96	Household plumbing systems corrosion, natural deposits erosion	Gastrointestinal distress, kidney or liver damage	2	1.3	2	1	0.05
Lead	207.2	11.35	Household plumbing systems corrosion, erosion of natural deposit	High blood pressure and kidney problems in adults, physical and mental development problems in children	0.01	0.015	0.01	0.01	0.01
Mercury	200.6	13.55	Landfills and croplands runoff, factories and refineries and erosion of natural deposits	Kidney damage	0.001	0.002	0.001	0.001	0.001
Nickel	58.7	8.9	Alloy from steel industries, electroplating industry and nickel-cadmium batteries factories.	Chronic respiratory infections and contact dermatitis	0.02	0.1	0.02		0.02
Zinc	65.4	7.13	Gold precipitation from cyanide solution, pharmaceutical discharges, discharges from rubber industry and Zn alloys.	Human cholesterol metabolism affected may be at high dose	3	5		5	5

2.3 Progress in the adsorptive removal of heavy metals using various adsorbents.

The presence of heavy metals in the aqueous environment at concentrations significantly above the baseline level has led to abundance of research in the field of their removal using several techniques as mentioned earlier. The advantages offered by adsorption as a removal technique are numerous and were also highlighted. One important factor when dealing with adsorption is the choice of the adsorbent, however, the operating conditions including pH, temperature, dose, and concentration etc., will significantly dictate the performance of the selected adsorbent. Factors inherent to the adsorbent type include pore structure, pore volume, specific surface area, surface cation exchange capacity, abundance and type of functional groups (Bilal et al., 2022). Several adsorbents are naturally available, and others are synthesized at the lab, with many of them tested under different environmental conditions with them aim of ascertaining optimum conditions for specific contaminant(s) removal often in a batch reactor system. To improve adsorbent performance, several modifications and functionalization are carried out and the overall aim is to synthesize an adsorbent that is of affordable cost, recyclable, environmentally friendly and of excellent environmental adaptability. This section is intended to provide a discussion on several classes of adsorbents that have shown promising performance in the field of heavy metal removal. A special emphasis is placed on materials that have been recently developed, synthesized, modified or functionalized for heavy metal treatment applications. These materials include graphene-based adsorbents, CNTs-based adsorbent, MOFs-based adsorbents and ZIFs-based adsorbent as a special class of MOFs.

2.3.1 Activated carbon-based adsorbents

Activated carbon has gained significant attention in both the research and industrial world because of its performance as an adsorbent for several classes of pollutants. Several of its characteristics

including high porosity, large specific surface area, high pore volume and tunable surface properties in addition to its ability to accommodate surface functional groups makes it function as a remarkable adsorbent for heavy metals (Mariana et al., 2021; Y. Zhou et al., 2021). The synthesis of activated carbon begins with a carbon source, which can be broadly classified as degradable and non-degradable. The classes of materials that have been used to synthesize activated carbon are highlighted in Figure 2.3. The choice of the precursor is an important step in the synthesis of activated carbon and it is desirable to select resources that are abundant in nature, having a low cost and endowed with non-toxic properties (A. Gul et al., 2022). Further, material with high fixed carbon content and low amount of ash are more suitable for the production of activated carbon. These makes plant-based materials one of the most suitable for the fabrication of activated carbon (González-García, 2018; A. Gul et al., 2022). The production process starts with pyrolysis, which is the thermal decomposition of carbon containing material in an inert atmosphere, resulting in the formation of biochar. The pyrolysis is done to decompose volatile matter, improve the structural stability of the base material and enhance its porosity (Hoang, Kumar, et al., 2022; Osman et al., 2016). For an effective pyrolysis, several factors including heating rate, temperature, flow rate of nitrogen gas, and residence time should be optimized. The activation stage follows the pyrolysis, it is done to improve the porosity and the number of oxygen-containing functional groups on the surface of the carbonaceous material (González-García, 2018; Mariana et al., 2021). Primarily, physical and chemical methods are used for the activation of biochar. In the physical activation, gases with oxidizing capabilities such as nitrogen, carbon dioxide, water steam or air mixture are injected into a controlled environment containing the biochar. The process is carried out at elevated temperature (exceeding 800 °C) and it is considered as green technique because it does not involve the use of harmful chemicals. Further, it is inexpensive and hence adopted by industries for the

fabrication of activated carbon (González-García, 2018; A. Gul et al., 2022). In the chemical activation method, the process of pyrolysis and activation happens concurrently. As the name implies, chemicals that can serve as dehydrating agents are introduced to the precursor material. A variety of chemicals including alkaline compounds like potassium hydroxide, intermediate metal salts like zinc chloride, and acidic compounds like phosphoric acid have been used (González-García, 2018; A. Gul et al., 2022). While the chemical method is less environmentally friendly, it produces more activated carbon yield, enhances the porosity of activated carbon and offers more savings on energy cost, hence less CO₂ emission (Yahya et al., 2015). However, a washing step is often necessary after treatment when chemical activation is used. More recently, a combination of both physical and chemical activation is used. Further, microwave assisted synthesis is being explored because it can offer heating at the molecular level (Hoang, Kumar, et al., 2022; Xin-hui et al., 2012). Figure 2.3 (a,b) gives a summary of the processes involved in the fabrication of activated carbon along with different choices of raw materials for activated carbon production. The final product obtained (activated carbon) has been tested extensively for the removal of several heavy metals from the aqueous environment. Even though promising performance and suitability in terms application have been noted when activated carbon is used for adsorptive removal of contaminants, there is still room to improve its performance especially with respect to regeneration, adsorption capacity and enhancing its selectivity towards specific contaminants. Hence, surface modification and functionalizing are carried out on the produced activated carbon to enhance its heavy metal adsorption performance in aqueous system. Table 2.2 gives a summary of recent studies that have been conducted for the removal of heavy metals from contaminated water using activated carbon and activated carbon-based materials.

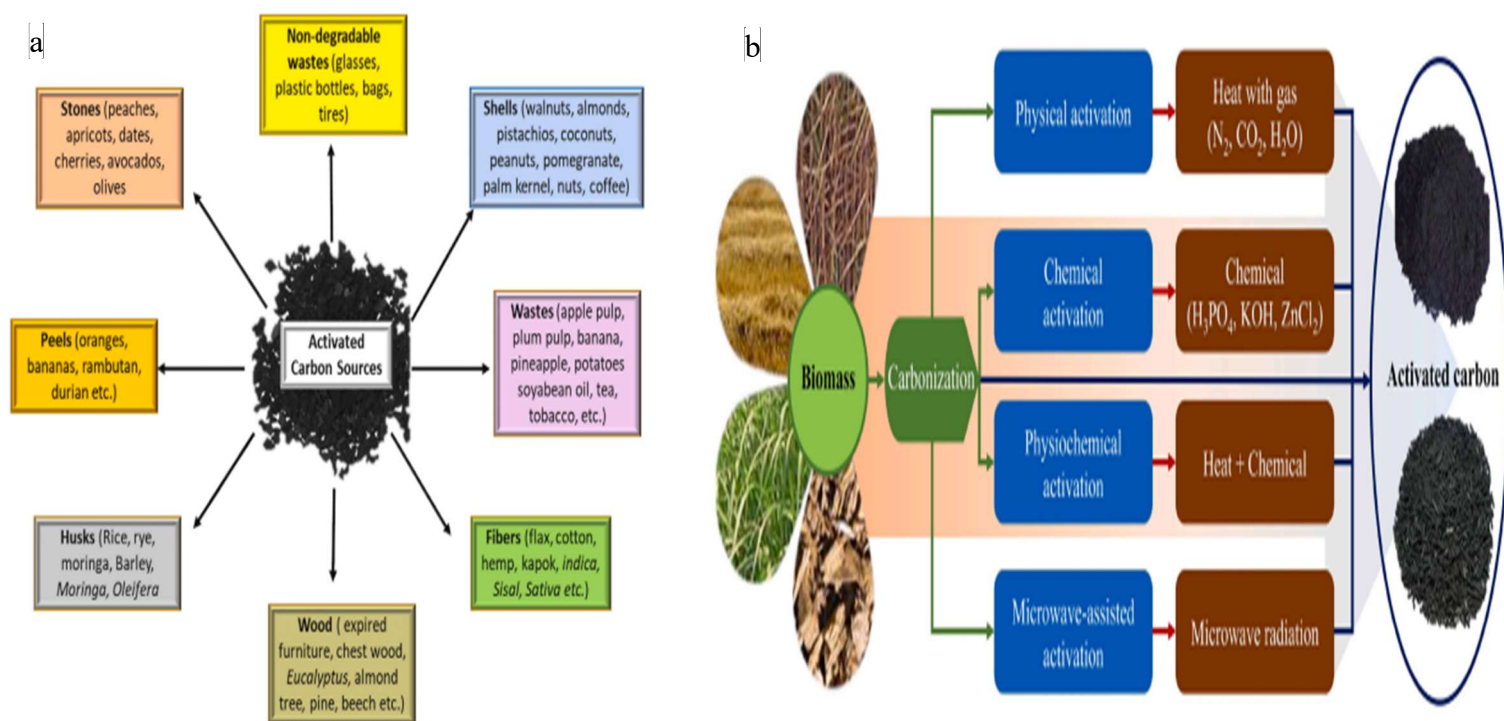


Figure 2.3. a) Different Carbon sources for production of activated carbon (A. Gul et al., 2022)
b) methods for fabrication of activated carbon from biomass (Hoang, Kumar, et al., 2022).

Table 2.2 Adsorptive removal of Heavy metals using activated carbon-based adsorbents.

Carbon source	Activation method	Modification	Textural properties	Heavy metal	Experimental conditions	Adsorption capacity (Q _{max} in mg/g)	Removal efficiency	Kinetics	Isotherm	Proposed mechanism	Reference
Bermuda grass	KOH	Nil	BET SSA = 1833.69 m ² /g, V _t = 0.7346 cm ³ /g, pore size = 1.6024 nm	Cr(VI)	pH = 2.0, AD = 0.5 g/L, C = 50 - 400 mg/L, T = 298 K, pH = 3.5, AD = 0.05 g in 25 mL, t = 25 min, C = 75 mg/L	403.23	–	PSO	Langmuir model	Adsorption, reduction, precipitation	(Tu et al., 2020)
Bombax ceiba fruit shell	ZnCl ₂	Nil	–	Fe(III)	pH = 7, AD = 20 mg/L, C = 60 ug/L, T = 2 h, T = 298 K	37.16	99.1	–	Temkin model	–	(Brishti et al., 2023)
Corn corb	KOH	Nil	BET SSA = 1054.2 m ² /g, pore size = 2.41 nm,	Hg(II)	pH = 5.5, t = 60 min, C = 50 mg/L, AD = 0.01 g/10 ml, T = 298 K	2.39	97.2	PSO	Langmuir model	Chemisorption	(Z. Liu et al., 2020)
Water hyacinth	H ₃ PO ₄	2-aminothiazole chelating legend	–	Pb(II)	pH = 5.5, t = 60 min, C = 50 mg/L, 0.1 g/10 ml, T = 298 k	310	100	PSO	Langmuir model	Complexation, chemisorption	(Waly et al., 2021)
Water hyacinth	H ₃ PO ₄	2-aminothiazole chelating legend	–	Hg(II)		252.2	100	PSO	Langmuir model	Complexation, chemisorption	(Waly et al., 2021)

Datestone seeds	HNO ₃	ZrO ₂	BET SSA = 153.4 m ² /g, Vt = 0.04 cm ³ /g, pore size = 8.8 nm	Cd(II)	pH = 6, AD = 100 mg in 250 mL, C = 20 mg/L, T = 298 K, t = 240 min,	166.7	—	PFO	Langmuir model	—	(Shar ma & Naush ad, 2020)
Enteromorph prolifer	KOH	Nil	BET SSA = 1684 m ² /g, Vt = 0.92 cm ³ /g, pore size = 2.19 nm	Cd(II)	pH = 7, C = 5 -100 mg/l, AD = 0.02 - 0.16 g in 25 mL. T = 298 K	5.84	98.8	PSO	Langmuir model	Electrostatic attraction	(C. Wang et al., 2021)
Moringa oleifera	Furnace (500 °C, rate 5 °C/min)	Chitosan and iron oxide nanoparticles	—	Cr(VI)	pH = 2, C = 20 mg/L, adsorbent AD = 1 g/L, T = 298K, t = 50 min	130.8	—	PSO	Freundlich model	— Physical interaction including electrostatic attraction, van der waals force. Chemical bonding including surface complexation, hydrogen bond and reduction.	(Bahador et al., 2021)
Commercial Activated Carbon	— H ₃ PO ₄ impregnation followed by heating at 650 °C for 2h at a rate of 10 °C/min	HA acid addition to Cr(VI)	—	Cr(VI)	pH = 3, AD = 20 mg/50 mL, C = 80 mg/L, t = 24 h, T = 298 K. pH = 5, AD = 0.05 - 0.25 g in 100 mL, C = 50 - 250 mg/L, T = 303 K, t = 120 min	—	99.1	—	—	—	(Y. Chen et al., 2022)
Banana leaves	—	—	—	Cu(II)	—	66.2	—	PSO	Langmuir model	—	(Darweesh et al., 2022)

Tire	KOH followed by heating at 30 °C /min to 750 °C	–	BET SSA 82 m ² /g, total Vt = 0.30 cm ³ /g, pore size 19.76 nm	Pb(II)	pH =7, AD = 0.2 g in 50 mL, t = 24 h, C = 500 mg/L,	322.50	–	PSO	Langmuir model	Physical sorption, ion exchange, electrostatic attraction, coordination through complexation	(Shahokhi-Shahaki et al., 2021)
Tire	KOH followed by heating at 30 °C /min to 750 °C	–	BET SSA 82 m ² /g, total Vt = 0.30 cm ³ /g, pore size 19.76 nm	Cu(II)	pH =7, AD = 0.2g in 50 mL, t = 24 h, C = 500 mg/L,	185.20	–	PSO	Langmuir model	Physical sorption, ion exchange, electrostatic attraction, coordination through complexation	(Shahokhi-Shahaki et al., 2021)
Tire	KOH followed by heating at 30 °C /min to 750 °C	–	BET SSA 82 m ² /g, total Vt = 0.30 cm ³ /g, pore size 19.76 nm	Zn(II)	pH =7, AD = 0.2 g in 50 mL, t = 24 h, C = 500 mg/L,	71.90	–	PSO	Langmuir model	Physical sorption, ion exchange, electrostatic attraction, coordination through complexation	(Shahokhi-Shahaki et al., 2021)
Rape straw powder	H ₃ PO ₄	MnFe ₂ O ₄ magnetic particles	BET SSA =553.3 m ² /g, Vt = 0.374 cm ³ /g, pore size =2.69 nm	Pb(II)	pH = 6.0, AD = 0.25 g/L, t = 12 h, temp, 298 K	253.2	–	PSO	Freundlich model	Electrostatic attraction, surface complexation, co-precipitation	(Z. Zhang et al., 2021)

Rape straw powder	H ₃ PO ₄	MnFe ₂ O ₄ magnetic particles	BET SSA = 553.3 m ² /g, Vt = 0.374 cm ³ /g, pore size = 2.69 nm	Cd(II)	pH = 6.0, AD = 0.25 g/L, t = 12 h, temp, 298 K	73.3	–	PSO	Freundlich model	Electrostatic attraction, surface complexation, co-precipitation	(Z. Zhang et al., 2021) (Ramutshatsha-Makhwedzha et al., 2023) (Ramutshatsha-Makhwedzha et al., 2023) (Ramutshatsha-Makhwedzha et al., 2023)
Waste orange and lemons	H ₃ PO ₄	–	BET SSA 168.29 m ² /g, pore size = 5.18 nm	Cd(II)	–	60	–	PSO	Langmuir model	–	
Waste orange and lemons	H ₃ PO ₄	–	BET SSA 168.29 m ² /g, pore size = 5.18 nm	Pb(II)	–	50.2	–	PSO	Langmuir model	–	
Waste orange and lemons	H ₃ PO ₄	–	BET SSA 168.29 m ² /g, pore size = 5.18 nm	Fe(II)	–	35	–	PSO	Langmuir model	–	
Rice husk	ZnCl ₂ impregnation followed by microwave and electrical heating with T = peaked at 600 °C, rate 15 °C/min	–	BET SSA = 1719.32 m ² /g, Vt = 1.05 cm ³ /g, pore size = 2.44 nm	Cr(VI)	pH = 3, AD = 2 g/L, t = 120 min, C = 28 - 145 mg/L, T = 318 K	56.82	–	PSO	Freundlich model	–	(X. Zhang et al., 2023)

Date palm	Na ₂ CO ₃ , K ₂ CO ₃ , Cs ₂ CO ₃ and CaCO ₃	Nitrogen doping	BET SSA = 1467 m ² /g, V _t = 0.921 cm ³ /g, 2.4 nm	Pb(II)	pH 7, AD = 10 g/L, C = = 10 mg/L	4.112	>99.9	PSO	Langmuir model	–	(Buma jedad & Hasila, 2023)
Date palm	Na ₂ CO ₃ , K ₂ CO ₃ , Cs ₂ CO ₃ and CaCO ₃	Nitrogen doping	BET SSA = 1467 m ² /g, V _t = 0.921 cm ³ /g, 2.4 nm	Cr(VI)	pH = 2, AD = 10 g/L, C = = 10 mg/L PH = 6, AD = 0.05 g in 40 mL, Concentration = 50 mg/L, T = 308 K, t =	0.004	>99.9	PSO	Freundlic h model	–	(Buma jedad & Hasila, 2023)
Banana penduncle	H ₃ PO ₄	iron metal impregnation	BET SSA = 369.7 m ² /g, V _t = 0.455 cm ³ /g, pore size = 1.92 nm	As(V)	90 min	9.066	–	PSO	Langmuir model	–	(Razzaq et al., 2022)

2.3.2 Natural adsorbents

The word “natural adsorbents” is a broad terminology, as such, in the context of this article, it refers to low-cost material that are found naturally and in abundance on the crust which has been tested for decontamination of water. Several classes of materials fit into these criteria including natural waste materials, siliceous materials, zeolites, natural polymeric materials and clays. However, because of the extensive use of clay-based materials for the removal of pollutants from contaminated water, it will be discussed in a different section. Factors including prevalence in nature, environmental friendliness, biodegradability, minimal processing cost and possibility for modification enhance the appeal for natural adsorbents in water treatment applications (Khalifa et al., 2019; Tamer et al., 2018). Various agricultural, forest and animal waste including nutshells, straws, husks, bark, leaves, eggshells and chicken feathers all fall under the class of natural waste materials (R. Chakraborty et al., 2022). Silica is found in abundance as a major component of sand and has demonstrated significant adsorptive capability especially if modified because of its significant pore size, thick silica wall and available micropores which are favourable for mass transfer (Corda & Kini, 2020; Shahbazi et al., 2013). Zeolites are crystalline materials having a three-dimensional structure consisting of tetrahedral combination of AlO_4 and SiO_4 . The nature of combination between AlO_4 and SiO_4 results in a framework that is negatively charged. Hence, the framework is neutralized by cations that can be exchanged. These properties along with relatively high surface area results in zeolite being a suitable material for aqueous heavy metal treatment (Corda & Kini, 2020; Shavandi et al., 2012). Chitin, which is used to produce chitosan is the second most abundant biopolymer in nature after cellulose. It is found on the exoskeleton of crustacean shells and cell walls of fungi. Chitosan is endowed with properties like biocompatibility, adhesion properties, polyelectrolyte properties, hydrophilicity, high reactivity and availability of surface amine functional groups results in its good adsorptive performance towards several aqueous

contaminants (Omer et al., 2021). Despite the suitable characteristics of natural adsorbents, they tend to suffer from relatively low adsorption capacity towards several heavy metals, poor selectivity and poor recovery in aqueous medium (Karimi-Maleh et al., 2021; Omer et al., 2022). Hence, attempts to counter these deficiencies are made by scientists through surface functionalization, modification and incorporation of other materials into the structure of natural materials. A summary of usage of natural materials and modified natural materials for heavy material removal in water is presented in Table 2.3. Further, Figure 2.4 gives a summary of the advantages and drawbacks of several natural adsorbents in terms of adsorptive performance in aqueous medium.

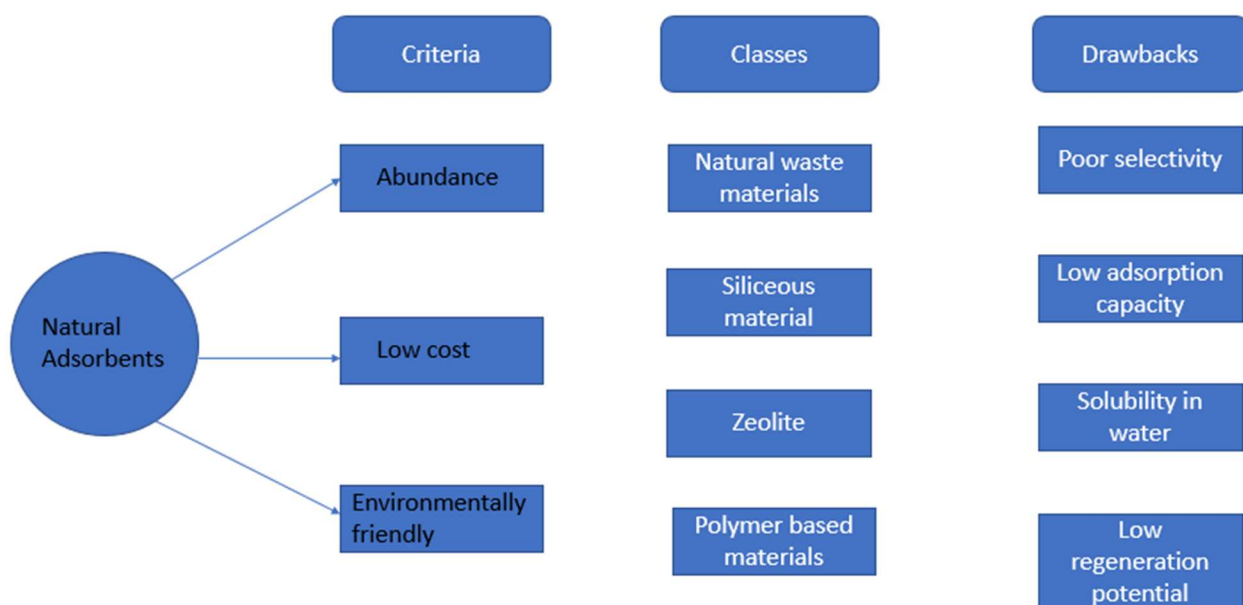


Figure 2.4. Types of natural adsorbents and criteria for selection.

Table 2.3 Adsorptive removal of heavy metals from aqueous system using natural adsorbents.

Natural adsorbent	Class	Modification	Textural Properties	Heavy metal	Experimental conditions	Adsorption capacity (Q _{max} in mg/g)	Removal efficiency (%)	Kinetics	Isotherm	Proposed mechanism	Reference
Chitosan	Polymeric materials	Tetracarboxylic functionalized magnetic nanoparticles	BET SSA = 45.4 m ² /g, V _t = 0.011 cm ³ /g, Pore size = 30 nm	Pb(II)	pH = 5.5, T = 298K, AD = 0.015 g in 25 mL, t = 180 min, C = 20 mg/L	204.92	–	PFO	Freundlich Model	Electrostatic attraction, coordination interaction, Ion exchange, surface complexation,	(Alga mdi et al., 2023)
Rice straw biochar	Agricultural waste	Chitosan Schiff base and MnFe ₂ O ₄	–	Cr(VI)	pH = 2.0, t = 360 min, AD = 10 mg in 100 mL, C = 40 mg/L, T = 308 K	125.34	–	PSO	Freundlich Model	electrostatic attraction and pore adsorption	(L. Yan et al., 2023)
Rice husk and orange peel	Agricultural waste	Mixed together	–	Cu(II) and Ni(II)	AD = 9 g in 100 mL, t = 120 min	–	99.1 and 99.36	–	Redlich-Peterson Model	–	(Lakshmana Naik et al., 2023)
Date pits and olive stone	Agricultural waste	Epichlorohydrin and diethylenetriamine(EDTA) modification	–	Cr(VI)	pH = 2, AD = 2.5 g/L, t = 3 days, T = 298 K	82.63 and 53.31	–	PSO	Freundlich Model	–	(Mangwandi et al., 2020)
Date palm empty fruit bunch	Agricultural waste	–	BET SSA = 6.126 m ² /g, V _t = 1.495 * 10 ⁻³ cm ³ /g, pore size = 0.124 nm	Cr(VI)	pH = 2, C = 50 mg/L, t = 120 min, T = 303 K	70.49	58.02	PSO	Temkin Model	cationic and anionic adsorption coupled with reduction and surface complexation	(Rambabu et al., 2020)

Fish scale	Agricultural waste/animal	–	BET SSA = 21.0 m ² /g, Pore size = 12.0 nm	Cr(III)	pH = 5, C = 150 mg/L, t = 90 min, AD = 0.8 g in 100 mL	18.25	99.75	PSO and PFO	Langmuir Model	–	(Teshale et al., 2020)
Soybeans cake	Agricultural waste	Heating to form biochar		Pb(II)	pH = 5, AD = 0.3 g in 40 mL, t = 30 min, C = 60 mg/L	133.69	–	PSO	–	–	(W. Yin et al., 2019)
Sugarcane bagasse	Agro industrial waste	Thermal treatment	BET SSA = 182.92 m ² /g, Pore size = 0.079 nm	Hg(II)	pH = 6, AD = 0.01 g in 50 mL, C = 1 mg/L, t = 2 h, T = 298 K	11.47	85	PSO	Freundlich, Temkin and D-R Model	Complexation, electrostatic attraction	(Giraldo et al., 2020)
Sugarcane bagasse	Agro industrial waste	Chemical treatment (ZnCl ₂ and H ₃ PO ₄)	BET SSA = 182.69 m ² /g, Pore size = 0.081 nm	Hg(II)	pH = 6, AD = 0.01 g in 50 mL, C = 1 mg/L, t = 2 h, T = 298 K	13.6	95	PSO	Freundlich, Temkin and D-R Model	Complexation, electrostatic attraction	(Giraldo et al., 2020)
Java Plum and Amaltash Seed	Biomass	–	–	As(III)	pH = 8.8, AD = 80 mg in 50 mL C = 2.5 mg/L, t = 80 min	1.45 and 1.42	93 and 91	PFO	Freundlich Model	–	(Giri et al., 2021)
Oil palm bagasse	Biomass	Alumina nanoparticles	–	Cd(II) and Ni(II)	pH 6	17.4 and 16.2	87 and 81	–	–	–	(Herrera-Barros et al., 2020)

Silica Composite	Siliceous material	poly(catechol-tetraethylenepentamine)@aminopropyl modification	BET SSA = 10.9 m ² /g	Cr(VI)	pH = 2.5 AD = 0.05 g in x mL, C = 180 mg/L, T = 303K, t = 48 h	400.86	100	PSO	Langmuir Model	–	(Q. Zhang et al., 2020)
Polyacrylamide-modified chitosan	Polymeric material	Amixdioxine-functionalization	BET SSA = 247.4 m ² /g. Pore size = 3.82 nm	Cu(II) and Ni(II)	pH = 5, AD = 50 mg in 50 mL T = 298 K, t = 24 h	190.7 and 128.9	–	PSO	Sips Model	Chelation	(Y. He et al., 2021)
Chitosan	Polymeric material	Manganese oxide	BET SSA = 26.52 m ² /g	Cr(VI)	pH = 2.0, AD = 80 mg/L, t = 120 min	61.56	–	PSO	Sips Model	electrostatic attraction	(Dinh et al., 2020)
Chitosan microspheres	Polymeric material	Functional iron	–	As(V)	pH = 5.2, AD = 30 mg in 30 mL C = 0.3 mg/L, T = 298 K, t = 24 h	120.77	–	PSO	Langmuir Model	–	(Lobo et al., 2020)
Tripolyphosphate cross-linked chitosan	Polymeric material	–	–	Cd(II)	pH = 7, AD = 0.45 g/L, C = 50 mg/L, T = 298 K, t = 24 h	99.87	–	–	Langmuir Model	–	(Babakhani & Sartaj, 2020)
Chitosan-pectin gel beads	Polymeric material	–	BET SSA = 23.66 m ² /g	Cu(II), Cd(II), Hg(II) and Pb(II)	pH = 7, C = 100 mg/L, AD = 50 mg in 50 mL, T = 298 K.	169.4, 177.6, 208.5 and 266.5	–	PSO	Langmuir Model	Complexation	(Z. Shao et al., 2021)

Modified alginate aerogel with malamine/chitosan	Polymeric material	—	BET SSA = 776.8 m ² /g, Vt = 15.4 cm ³ /g, Pore size = 2.4 nm	Pb(II)	pH = 5.5, AD = 20 mg in 20 mL, C = 200 mg/L, T = 298 K	1331.6	—	PSO	Langmuir Model	Surface complexation, ion-exchange and regeneration with H ⁺	(C. Gao et al., 2021)
Silica nanospheres	Siliceous material	Polyaniline wrapping		Cr(VI)	pH = 6.9, AD = 50 mg in 100 mL,	212.8	—	PSO	Langmuir Model	Adsorption followed by reduction	(J. Li et al., 2020)

2.3.3 Microbial adsorbents

The use of biological species for decontamination of water is an exciting topic because of the various advantages offered by the process. The commonly used microbes for water treatment and remediation include algae, fungi and bacteria. These organisms have the capacity to not only bioaccumulate toxic contaminants but also degrade them into simple and non-toxic products. Further, the generation of by product in the form of sludge is minimized while at the same time the relative treatment cost and time of the technology are low and short, respectively, provided that the microbes are acclimatized to the environment. The versatility of the organisms and potential for reuse is another major merit of employing microbes as adsorbent for heavy metals (Razzak et al., 2022). The advantages offered by these species are attributed to the several removal mechanisms that are used by the species which can be broadly divided into metabolism dependent and non-metabolism dependent. The non-metabolism dependent processes are carried out by dead organisms and are rapid in nature. They are cell surface sorption processes and can occur in the form of complexation, precipitation, ion exchange and surface adsorption. Cellular energy is needed for the metabolic dependent processes and only occurs when the organisms are in a special biological state (alive). The mechanisms include internal accumulation of cells and surface microprecipitation (Janyasuthiwong et al., 2015; M. Liu et al., 2017). An illustration of the adsorptive removal of heavy metals by biological cells is given in Figure 2.5.

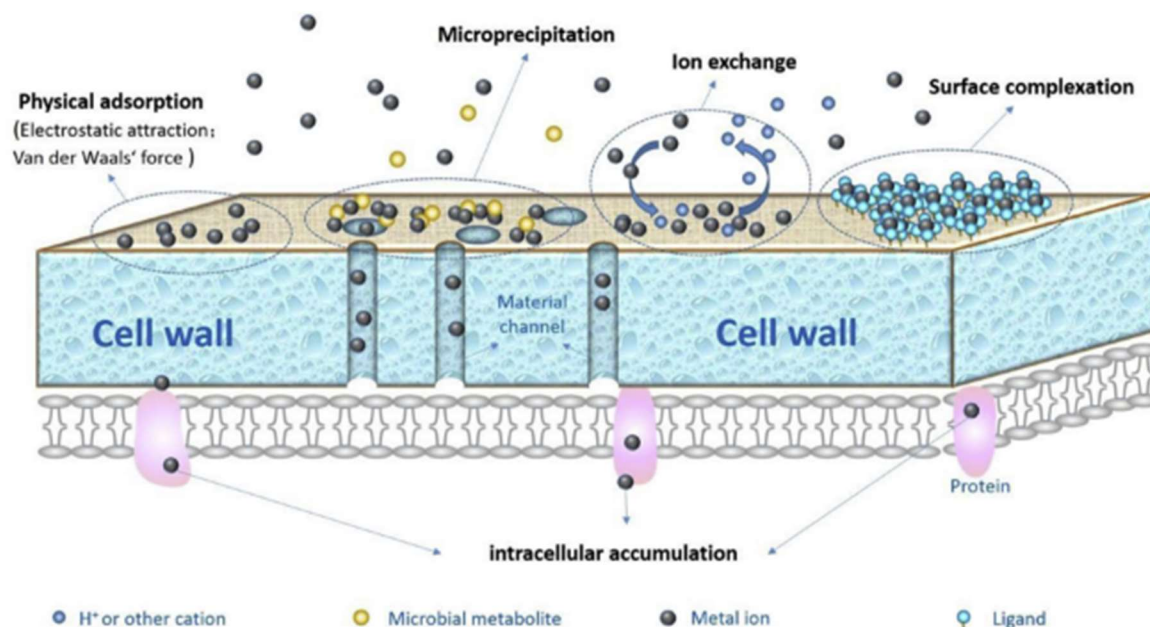


Figure 2.5. Heavy metals removal mechanism of microbial based adsorbents (Qin et al., 2020)

Nontoxic algal species are reportedly favoured for the biosorption of heavy metals because of their prevalence in nature, minimal nutrient requirement and high surface area to volume ratio. Further, their cell wall consists of diverse functional groups including sulfonate, carboxyl, amino and sulfhydryl which makes it possible for them to exchange ions or bind with metallic cations (Y. Geng et al., 2022; Y. Zhang et al., 2019). Polymers such as polysaccharides, peptidoglycans and protein are also found on the algae cell wall and are essential for heavy metal adsorption. Fungi have high yield and a cell wall that can form greater than 30% of their dry weight. The cell wall of fungi consists mainly of polysaccharides and has several other polymers including glucan, chitin, mannan and chitosan which makes the fungi function as a biosorbent with metal binding capabilities. Hydroxyl, carboxyl, phosphate and amine functional groups present in the fungal cell wall improves its metal binding capability (Mir-Tutusaus et al., 2018). Added advantage is the filamentous nature of fungi which makes their separation from aqueous media an easier task achievable through means such as filtration (Herath et al., 2014). Bacteria are often found in large

quantities post fermentation process as a waste by-product (H. L. Fan et al., 2017). The cell walls are made of peptidoglycan which contains several functional groups that are useful for the adsorption of heavy metals. Further, they have high surface area to volume ratio which is essential for surface adsorption (F. M. Hassan et al., 2016).

Despite the numerous merits offered by microbial adsorbents, they all do have drawbacks which include the possibility of producing intermediate products that are more deleterious than the parent compounds or molecules. Further, optimum environmental conditions are needed for the culture of microbes which proves to be challenging. Most of the work done in the field of microbial adsorbents is in the rudimentary stage, hence, translating the result to field application is a challenging task especially in complex systems. To overcome some of the inherent shortcomings, genetically engineering microorganisms to suit the need has been touted as a solution (Diep et al., 2018; García-García et al., 2016; L. Liu et al., 2019). However, genetic modification is an expensive solution and the risk it might present is relatively unknown at the moment. Hence, other simpler solutions have been implemented which include chemical modification of biosorbents and/or combining them with other chemical materials to enhance their properties. Chemical modification can be done through simple washing with acids, base, salts and organic materials or through more complex means such as modification of intracellular resistance to heavy metals and intracellular autogenous nanomaterials (Qin et al., 2020). Combining microbes with other chemical materials can be done through adsorption, entrapment, crosslinking, encapsulation, aggregation, electrostatic and covalent bonding (Bouabidi et al., 2018; L. Liu et al., 2019). This is done to immobilize the microbes so as to achieve the best fixing effect. Complex systems involving multiple biomass is also be explored with the aim of finding biomass that can complement each other in terms of treatment or provide a positive interaction in terms of biological association (Qin

et al., 2020). Table 2.4 presents recent studies that have employed the use of microbial based adsorbent for the removal of heavy metals from aqueous streams.

Table 2.4 Adsorptive removal of heavy metals from aqueous system using microbial adsorbents.

Microbe	Class	Modification	Textural properties	Heavy metal	Experimental conditions	Adsorption capacity (Q _{max} in mg/g)	Removal efficiency (%)	Kinetics	Isotherm	Proposed mechanism	Reference
			—								
Pseudomonas putida I3, Microbacterium sp. OLJ1 and Taloromyces amestolkia	Gram-negative bacteria, gram positive bacteria and mycelial fungus	One step method to synthesize X-PI3, X-OLJ1 and X-TPb	—	Pb(II)	pH = 5.0, C = 100 mg/L, AD = 0.2 g/L, t = 60 min	X-PI3=199.02, X-OLJ1 = 237.02 and X-TPb = 345.02	—	PSO	Langmuir Isotherm	Ion exchange, microprecipitation and surface complexation	(N. Wang et al., 2019)
Serratia rubidaea NCTC12971	Bacteria	Immobilized on Ca-alginate beads	—	Pb(II), Cd(II), Cu(II) and Zn(II)	pH = 7, t = 48 h, AD = 2g in 100 mL	32.14, 45.87, 0.06 and 3.01	92.07, 98.05, 95.57 and 88.39	—	Langmuir Model	—	(Moula et al., 2023)
			—								
Bacillus Subtilis	Bacteria	—	—	Pb(II)	pH = 4, T = 298 K, AD = 35 mg in 50 mL, C = 100 mg/L, t = 30 min	164.4	—	PFO	Langmuir Model	Complexation and chelation	(P. Zhao et al., 2020)

Klebsiella sp. And Bacillus sp,	Bacteria	Extracellular polymeric substances (EPS) extracted from the species (EPS-K and EPS-B)	—	Hg(II)	pH = 6.0, C = 100 mg/L, AD = 5 mL 50 mg/L EPS in x mL, t = 3.5 h, T = 298 K	2597.62 and 2617.23	—	PSO	Langmuir Model	Complexation and chelation	(Xia et al., 2020)
Comamonas testosteroni FJ17	Bacteria	Modified with rice husk	—	Cu(II)	pH = 7.0, C = 100 mg/L, T = 298 K, AD = 0.1 g in 100 mL, t = 4 h	28.4	27.40		Freundlich Model	Physical and chemical adsorption	(Xue et al., 2020)
Urease bacteria (UF1)	Bacteria	Immobilization onto scoria	—	Pb(II) and Cd(II)	AD = 0.2 g in 50 mL, C = 1 mmol/L, T = 298 K, t = 24 h, pH 6- 9	0.078 mmol/g and 0.054 mmol/g	—	PFO	Langmuir Model	Surface complexation, microprecipitation and biological fixation	(H. Song et al., 2021)
Pichia pastori	Fungi	—		Rh(III)	pH = 1.2, T = 303 K, AD = 0.25 g/L t = 2 h	110.1	55.59	PSO	Langmuir model	—	(M. Gao et al., 2022)

Pichia pastori GS-R	Fungi	Surface- displayed Rh metal peptides	—	Rh(III)	pH = 1.2, C = 50 mg/L, T = 303 K, AD = 0.25 g/L, t = 2h	142.11	75.03	PSO	Temkin Model	—	(M. Gao et al., 2022)
Parmotrena tinctorum	Fungi	—		Ni(II)	pH = 7, t = 120 min, C = 100 mg/L, AD = 2 g/L	33.92	—	PFO	Langmuir Model	—	(Gratia et al., 2021)
Microcystis aeruginosa	Cyanobacteria	—	BET SSA = 6.59 m ² /g, Vt = 0.023 cm ³ /g and Pore size = 3.145 nm	Cu(II)	pH = 8, T = 303 K, t = 5 h, C = 25 mg/L	—	83.24	—	—	—	(G. Zeng et al., 2022)
Microcystis aeruginosa	Cyanobacteria	—	BET SSA = 6.59 m ² /g, Vt = 0.023 cm ³ /g and pore size = 3.145 nm	Cd(II)	pH = 8, T = 308 K, t = 4 h, C = 5 mg/L	—	92	—	—	—	(G. Zeng et al., 2022)

Microcystis aeruginosa	Cyanobacteria	—	BET SSA = 6.59 m ² /g, Vt = 0.023 cm ³ /g and pore size = 3.145 nm —	Ni(II)	pH = 7, T = 308 K, t = 1 h, C = 15 mg/L	—	88.67	—	—	—	(G. Zeng et al., 2022)
Nannochloropsis oculate	Microalga	—	—	Pb(II)	pH = 5, C = 100 mg/L, AD = 0.05 g in x	1087.20	—	PSO	Langmuir Model	Surface complexation	(Nateras- Ramírez et al., 2022)
Nannochloropsis oculate	Microalga	—	—	Cd(II)	pH = 4, C = 100 mg/L, AD = 0.3 g in x	934.33	—	PSO	Langmuir Model	Surface complexation	(Nateras- Ramírez et al., 2022)

2.3.4 Clay minerals based adsorbents

Clays are minerals of phyllosilicate nature found in deposits, sediments and soils. They have a particle size that is less than 2 μm (Guggenheim & Martin, 1995). The structure of clay is made up of layered units having single or double tetrahedral silica sheets ($\text{Si}_2\text{O}_6(\text{OH})_4$) bonded to octahedral aluminum sheets ($\text{Al}_2(\text{OH})_6$) majorly in 2:1 or 1:1 proportion (Abu-Danso et al., 2020; Guggenheim & Martin, 1995). The chemical structure and composition of clays give them unique physical characteristics including plasticity, cohesion, surface that can easily be decorated among other characteristics thereby enhancing their suitability for various applications (Uddin, 2017). On the basis of adsorption, it is their abundance in nature, low-cost, non-toxic nature, good adsorption characteristics, large specific surface area and significant ion-exchange potential that makes them suitable for application in the field of adsorptive removal of heavy contaminants (Crini & Badot, 2010). Many clay minerals are negatively charged, hence, have affinity for cationic species of contaminants such as heavy metal ions (Churchman et al., 2006; Uddin, 2017). The uptake of contaminants by clays happens through a number of convoluted mechanisms which include surface complexation, surface bonding, electrostatic attraction and ion exchange among others (Churchman et al., 2006). However, it must be noted that the specific type of clay mineral and its composition will significantly affect its uptake behavior toward contaminants. The three most important types of clay minerals include montmorillonite, illite and kaolinite while other types include pyrophyllite, vermiculite, serpentine and sepiolite etc. (Shichi & Takagi, 2000). For example, kaolinite is very stable, however, it has low ion-exchange capacity because it does not undergo isomorphic substitution. Further it has low specific surface area ($2 - 5 \text{ m}^2/\text{g}$), hence, less appealing for uptake of cationic heavy metals and other contaminants in general (Miranda-Trevino & Coles, 2003). On the other hand, montmorillonite has a net negative charge ranging between -0.2 to 0.6 because of the replacement of lower valent atoms like Mg^{2+} and Al^{3+} by higher valent

atom like Al^{3+} and Si^{4+} , respectively. For charge neutralization purpose, exchangeable cations bond together with the clay minerals resulting in enhanced cation exchange performance (Frenkel, 1974). While clay minerals are considered as promising adsorbents, they are often required to be used in large quantities for effective performance. This approach can solve the problem of water contamination, however, it results in toxic solid waste accumulation. To reduce the magnitude of this issue, modifications are conducted on clays to enhance their adsorption capacity and uptake toward specific contaminants. Several approaches including thermal treatment, acid washing, inorganic pillaring and organic modifications are adopted. A summary of these approaches, suitable conditions and advantages are depicted in Figure 2.6.

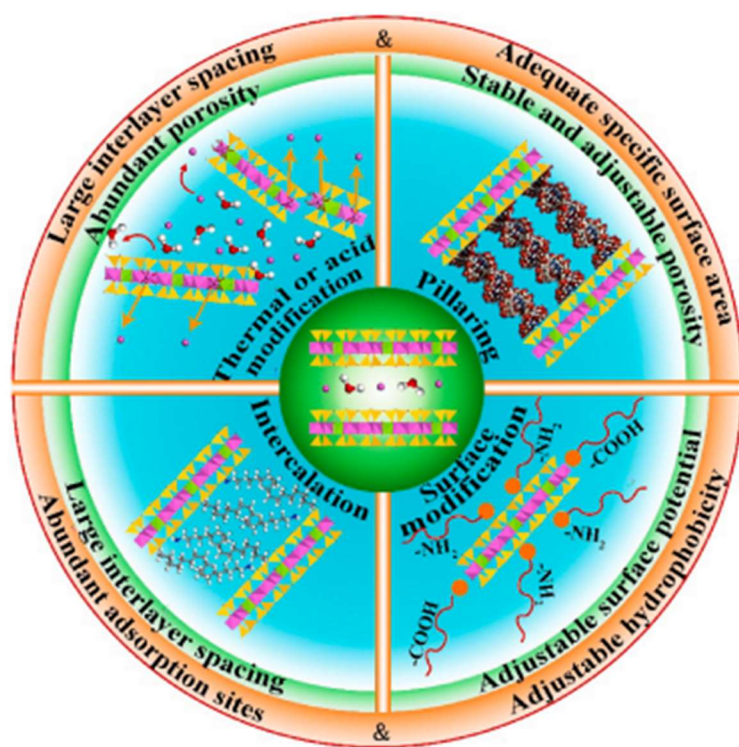


Figure 2.6. Several types of modifications that can be done clay minerals (T. Zhang et al., 2021). Furthermore, because of clay minerals' chemical stability, they can function as support for nanoparticles. Many nanoparticles are efficient adsorbents because of their reactivity, significantly improved surface area and nanoscale effect. However, their practical application is limited because

of their tendency to aggregate in water leading to lowered performance and their separation from water after treatment is also a difficult task (Ezzatahmadi et al., 2017). Hence, composites of clays and nanomaterials are synthesized for synergistic effects to remove contaminants. Apart from providing support, studies have revealed that clay minerals can enhance the performance of the precursor nanomaterials (S. Ahmad et al., 2019; Hamza et al., 2020; Mekewi et al., 2016; Yao et al., 2020). Table 2.5 gives a summary of recent studies that involved the use of clay-based materials and clay minerals composite for the removal of heavy metals from contaminated aqueous streams.

Table 2.5 Adsorptive removal of heavy metals from aqueous system using clay-based adsorbents.

Clay type	Modification	Textural properties	Heavy metal	Experimental conditions	Adsorption capacity (Q _{max} in mg/g)	Removal efficiency (%)	Kinetics	Isotherm	Proposed mechanism	Reference
Nano-clay	–	BET SSA = 43.39 m ² /g, V _t = 0.104 cm ³ /g, Pore size = 2.81 nm	Pb(II)	pH = 5.0, t = 90 min, AD = 0.83 g/L C = 4 mg/L, T = 298 K	11.95	99.60	PSO	Langmuir Model	Chemisorption	(Tarekegn et al., 2022)
Nano-clay	Iron impregnation	BET SSA = 73.11 m ² /g, V _t = 0.153 cm ³ /g, Pore size = 3.83 nm	Pb(II)	pH = 5.0, t = 90 min, AD = 0.67 g/L C = 6 mg/L, T = 298 K	11.96	99.70	PSO	Langmuir Model	Chemisorption	(Tarekegn et al., 2022)
Nano-clay	–	BET SSA = 43.39 m ² /g, V _t = 0.104 cm ³ /g, Pore size = 2.81 nm	Cu(II)	pH = 5.0, t = 180 min, AD = 1.0 g/L C = 2 mg/L, T = 298 K	11.9	99.20	PSO	Freundlich Model	Chemisorption	(Tarekegn et al., 2022)
Nano-clay	Iron impregnation	BET SSA = 73.11 m ² /g, V _t = 0.153 cm ³ /g, Pore size = 3.83 nm	Cu(II)	pH = 5.0, t = 150 min, AD = 0.83 g/L C = 4 mg/L, T = 298 K	11.97	99.80	PSO	Langmuir Model	Chemisorption	(Tarekegn et al., 2022)
Moroccan natural clay	–	–	Cu(II), Co(II), Ni(II) and Pb(II)	pH = 8.0, C = 120 mg/L, t = 60 min, AD =	6.21, 7.11, 5.79 and 6.93	–	–	Langmuir and Freundlich Model	Electrostatic interaction and ion exchange	(Es-sahbany et al., 2022)

				3 g in x L, T = 25						
Cosmetic clay powder	–	–	Cd(II)	pH = 7, AD = 0.1 g/L, T = 273 K, C = 11 - 157 mg/L	15.80	99	PSO	Langmuir Model	–	(Tonk et al., 2022)
Acid- modified kaolinite	Support for TiO ₂	BET SSA = 32.98 m ² /g, Pore size = 4.86 nm, Vt = 0.150 cm ³ /g	Mn(II), Fe(III), Pb(II) and Cu(II)	Mining wastewater, pH = 5.2, t = 120 min, C = 4.291, 20.013, 0.975 and 0.3113 mg/L, T = 343 K	0.678, 3.989, 0.169 and 0.002	–	PSO	Langmuir Model	Electrostatic interaction	(Ajala et al., 2022)
acid- activated bentonite	Rarasaponin aliginat bentonite composite	BET SSA = 17.5 m ² /g, Vt = 0.12 cm ³ /g	Cr(VI)	pH = 3, C = 1000 mg/L, AD = 0.5 g in 100 mL, T = 50, t = 8 h pH = 8, C = 5 mg/L, AD = 1 g/L, t = 90 min. T = 298 K	175.44	–	PFO	Freundlich Model	–	(Santoso et al., 2023)
Halloysite nanoclay	8-hydroxyquinoline modification	BET SSA = 72.5 m ² /g.	As(III)		8.67	82.40	PSO	Langmuir and Freundlich Model	–	(Aljohani et al., 2023)
Bentonite	–	BET SSA = 46 m ² /g, Vt = 0.17 cm ³ /g, Pore size = 14.78 nm BET SSA = 76 m ² /g, Vt = 0.19 cm ³ /g, Pore size =	Zn(II), Fe(II) and Ni(II)	Pharmaceutical effluent, pH = 8	0.75, 3.65 and 0.96	63.90, 59. 60 and 58.70	PSO	Freundlich Model	–	(Ibighami et al., 2022)
Activated bentonite	HNO ₃ activation	10.00 nm	Zn(II), Fe(II) and Ni(II)	Pharmaceutical effluent, pH = 10,	1.65, 0.48 and 0.44	88.90, 81.80 and 75.50	PSO	Freundlich Model	–	(Tarekegn et al., 2022)

Natural Clay	–	–	Cd(II)	pH = 10, AD = 2 g in 100 mL, C = 200 mg/L, T = 298 K	5.65	–	PSO	–	(Es-said et al., 2021)
Shanghai silty clay	–	–	Cd(II), Pb(II), As(V) and Cr(VI)	pH = 9.0, 6.0, 7.0 and 2.0, AD = 15, 6, 40 and 40 g/L, t = 1440 min., T = 298 K	8.90, 26.46, 2.80 and 1.85	–	PSO	Langmuir for Cd(II) and Pb(II), Freundlich for AS(V) and Cr(VI)	(J. Wang & Zhang, 2021)
Malangali kaolinite	HCL modifed	BET SSA = 107.27 m ² /g, Vt = 0.81 cm ³ /g, pore size = 3.60 nm	Cd(II) and Co(II)	pH = 6, AD = 0.6 g in 25 mL t = 120 min., T = 298, C = 5 - 25 mg/L	1.067 and 1.043	–	PSO	Langmuir Model	(Malima et al., 2021)
Bentonite	HTDMA-modification	BET SSA = 19.82 m ² /g BET SSA = 70.48 m ² /g, Pore size =	Pb(II)	pH = 5.0, t = 120 min, T = 303 K, AD = 0.2 g in 100 mL, C = 50 - 200 mg/L pH = 5.5, T = 298 K, AD = 1.0 g/L, C = 200 mg/L T = 24 h	25.8	–	PSO	Sips isotherm Inner sphere complexation	(Dinh et al., 2022)
Sepiolite	Polyethyleneimine/sodium alginate modification	12.01 nm	Pb(II)		1094.86	–	PSO	Langmuir Model	(X. Wu et al., 2022)

2.3.5 LDH based materials

Hydrotalcite, the layered double hydroxide (LDH) of magnesium and aluminium intercalated with carbonate has its origin traced back to Sweden where it was discovered in 1842 (M. Z. Bin Hussein et al., 2001; San Román et al., 2008). Currently, many more LDHs have been synthesized and the key to such synthesis is the chemical structure and properties of the LDH material. The LDHs are considered as anionic clays which are two-dimensional in nature consisting of brucite-like host layers that are positively charged, interlayer anion for charge neutralization and molecules of the solvent used for its synthesis (J. Feng et al., 2015; Q. Wang & Ohare, 2012; Y. Zhao et al., 2016). The LDHs have a well-known molecular formula which is denoted by $[M^{2+}_{1-x}M^{3+}_x(OH)_2][An^-]_{x/n} \cdot zH_2O$, where M^{3+} represents trivalent metallic cation and M^{2+} is the divalent metallic cation, An^- is the anion present in the interlayer space. For a true phase LDH, x should be between 0.2 to 0.33 (Y. Wang et al., 2018; Zubair et al., 2017). The schematic representation of the LDH structure is given in Figure 2.7.

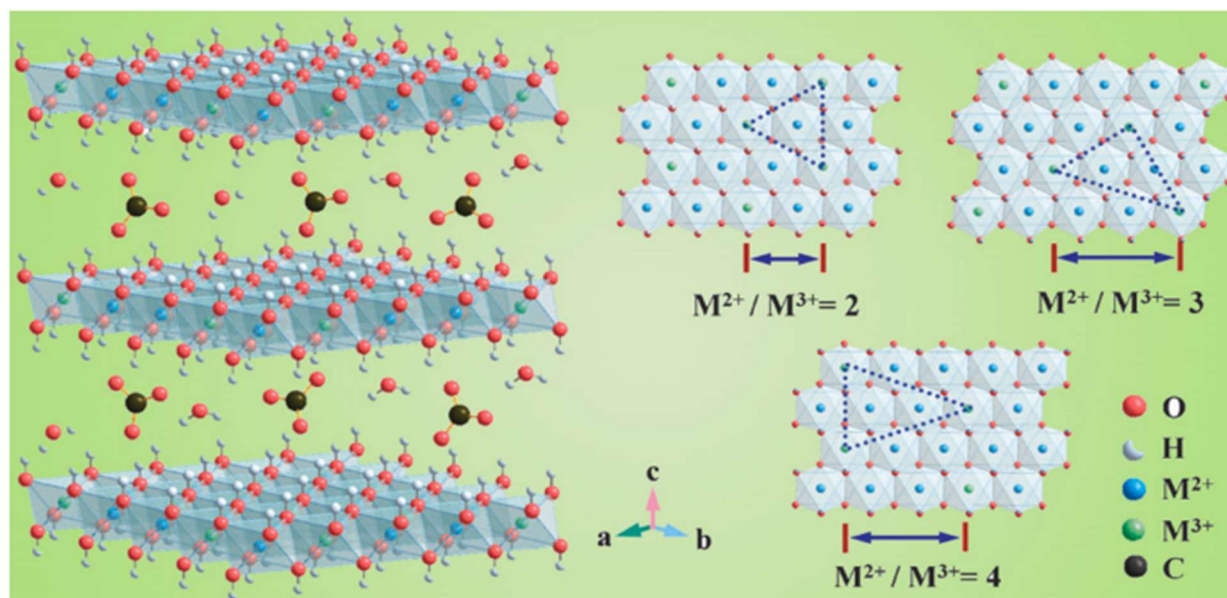


Figure 2.7. Typical LDH structure and the effect of varying the divalent to trivalent cation (X. Feng et al., 2022)

The tunable nature of the LDH structure endows it with many unique features, hence, suitable materials for numerous applications (Daud et al., 2019). The anions in the interlayer are exchangeable and the lack of crosslinking between the cation layers present room for contraction and expansion of the interlayer space, therefore can house a wide variety of interlayer anions (Theiss et al., 2016). Theoretically, provided that the anion does not cause distortion of the metal ions on the brucite-like sheet, then it can be intercalated into the LDH (M. Shao et al., 2015). Further, different cations can replace the metal ion on the brucite-like sheet provided that they are of similar radius. These features along with their non-toxicity and chemical multifunctionality allows for the LDHs to be applied in wide ranging fields including adsorption of contaminants, catalysis, drug delivery and supercapacitor applications (Daud et al., 2019; Rogez et al., 2011). Further, their high surface area and low cost make them a good candidate material for use as adsorbent in water treatment and remediation. The removal of heavy metals by LDHs can happen through a series of mechanisms including interlayer anion exchange, memory effect, isomorphic substitution, interlayer anion coordination and surface adsorption. The classical anions in the LDH gallery can be exchanged with heavy metal anions such as $\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_7^{2-}$ thereby effectively removing the aqueous contaminants (Sideris et al., 2008). Calcined LDH (bimetallic oxides) when inserted into aqueous environment containing heavy metal anions can regain their LDH structure by taking up heavy metal anions there by eliminating them from the contaminated water (Hermosin et al., 2008). Less toxic metals of LDH laminate such as Mg^{2+} and Ca^{2+} can be replaced by other toxic heavy metals like Cd^{2+} through isomorphic substitution if there is good match between the size of the heavy metal and the host metal ions in the LDH laminate (Kong et al., 2021). LDH may be intercalated with heavy metal chelating agents, hence, enhancing its activity toward heavy metal through interlayer coordination (T. He et al., 2023; L. Ma et al., 2017). The surface adsorption can

happen through multiple routes and the presence of abundant OH^- group on the LDH laminate enhances its coordination with heavy metals (T. He et al., 2023). Most of the LDHs used for water treatment are synthetic in nature, therefore, the synthesis method plays a significant role in the properties and characteristics of the synthesized material. Several methods are employed for the synthesis of LDHs including co-precipitation, ion exchange method, hydrothermal synthesis, alkaloxide solgel method, calcination and dry milling and ultrasonic irradiation etc. However, the most widely adopted is the co-precipitation method because of its simplicity (Dong et al., 2022; X. Feng et al., 2022; Ismail et al., 2023b). Variation in precursors ratio, reaction pH, crystallization temperature and time can result in material with different crystallinity, crystal grain size and crystal phase structure (X. Feng et al., 2022). Hence care needs to be taken when synthesizing the LDH material for specific purposes. It is worth noting that the traditional LDHs do not possess abundant functional groups, hence, their adsorption capacity and selectivity toward specific contaminants is often limited and combining them with other functional materials does greatly enhance its performance (X. Feng et al., 2022; T. Hou et al., 2020). Because of their thermal and chemical stability, they can serve as support materials for nanomaterials thereby enhancing the stability and separation of nanomaterials in aqueous media. Table 2.6 gives a summary of recent studies that involve the use of LDH materials for the removal of heavy metals from aqueous system.

Table 2.6 Adsorptive removal of heavy metals from aqueous system using LDH-based adsorbents.

LDH	LDH Synthesis method	Modification	Textural properties	Heavy metal	Experimental conditions	Adsorption capacity (Q _{max} in mg/g)	Removal efficiency (%)	Kinetics	Isotherm	Proposed mechanism	Reference
Zn ₂ [FeAl]-CO ₃	Co-precipitation	–	BET SSA= 54.48 m ² /g, V _t = 0.056 cm ³ /g, Pore size = 6.23 nm	Cu(II) and Pb(II)	pH = 7, AD = 1.75 g/L, T = 298 K, t = 3 h, C = 10 - 300 mg/L	98 and 87	–	PFO and PSO	Redlich-Peterson and Freundlich	–	(Ait Ichou et al., 2023)
CuMgAl-NO ₃ ²⁻	Co-precipitation	Montmorillonite nanocomposite	BET SSA= 77.6 m ² /g, V _t = 0.156 cm ³ /g, Pore size = 26.2 nm	Cd(II)	pH = 5, AD = 0.02 g/L, C = 50 mg/L, t = 120 min, T = 298 K	174.87	–	PSO	Langmuir and Freundlich Model	–	(Alnasrawi & Mohammed, 2023)
NiAl LDH	Urea decomposition process	Etidronic acid intercalation	–	Zn(II) and Fe(III)	pH = 5, C = 50 - 500 mg/L, t = 60, T = 298 K	281.36 and 206.03	–	PSO	Langmuir Model	Chelation	(S. Zhu et al., 2022)

MgAl-LDH	Co-precipitation	Polyethylene glycol modification	—	Cu(II), Pb(II) and Cd(II)	AD = 0.03 in 20 mL, t = 240 min, pH = 5.01 C = Cu(II) and Cd(II) = 10-800 mg/L, Pb(II) = 20 - 1000 mg/L T = 298 K	142.8, 125.9 and 69.11	—	PSO	Langmuir Model	Precipitation and complexation	(W. Song et al., 2023)
			BET SSA= 77.6 m ² /g, Vt = 0.156 cm ³ /g, Pore size = 26.2 nm		pH = 5, AD = 0.25 g in 100 mL, T = 298 K, C = 70 mg/L, t = 90 min						
CuMgAl-NO ₃ ²⁻	Co-precipitation	Montmorillonite nanocomposite		Zn(II)		154.21	95.10	PSO	Langmuir Model		(Alnasrawi et al., 2023)
			BET SSA= 72.82 m ² /g, Vt = 0.28 cm ³ /g, Pore size = 13.98 nm		pH = 7, T = 298 K, C = 50 -500 mg/L, t = 12 h, AD = 20 mg in 100 mL	266.16, 175.60 and 106.56					
NiFe-LDH	Solvothermal synthesis	2 mercaptoethance sulfonic acid (MS)		Cd(II), Mn(II) and Co(II)			—	PSO	Langmuir model	—	(Hong et al., 2023)

Zn-Al LDH	Co-precipitation	Ag decoration	BET SSA= 162 m ² /g, Pore size = 8.55 nm	Pb(II) and Cd(II)	pH = 8.0, C = 200 mg/L, t = 90 min, T = 303 K	537.63 and 401.62	98.90	PSO	Langmuir and Freundlich Model	–	(Asha et al., 2023)
Mg-Al LDH	Co-precipitation	–	BET SSA= 31.95 m ² /g	Cr(VI)	pH =2, C = 50 - 200 mg/L AD = 0.5 - 6 g/L, t = 90 minT = 323	25.5	–	PFO	Langmuir Model	Intercalation, ion-exchange, other sphere complexation, precipitation and substitution	(B. Zeng et al., 2022)
Mg-Al LDH	Co-precipitation	Calcination	BET SSA= 56.49 m ² /g	Cr(VI)	pH =2, C = 50 - 200 mg/L AD = 0.5 - 6 g/L, t = 90 minT = 324	37.7	–	PSO	Langmuir Model	Intercalation, ion-exchange, other sphere complexation, precipitation and substitution	(B. Zeng et al., 2022)
MgAl-LDH	Hydrothermal	Rice husk biochar modification	–	Cd(II) and Cu(II)	pH = 6.0, AD = 50 mg in 20 mL, t = 1440 min, T = 298 K, C = 10 - 500 mg/L	123.34 and 104.34	–	PSO	Langmuir- Freundlich Model	Surface precipitation and ion- exchange	(A. Li et al., 2022)

MgAl-LDH	Co-precipitation, ultrasonic assisted ion exchange	L-cysteine modification	BET SSA = 45.90 m ² /g	Pb(II) and Cd(II)	pH = 6, C = 10 - 1000 mg/L, AD = 1 g/L, t = 720 min, T = 298 K	279.58 and 135.68	–	PSO	Freundlich Model	Isomorphous replacement, precipitation, chelation	(D. Wang et al., 2022)
FeMg-LDH	Co-precipitation	Bentonite	BET SSA = 154.83 m ² /g, Vt = 0.333 cm ³ /g	Pb(II) and Cd(II)	pH = 7, AD = 5 mg in 20 mL, t = 1440 min, T = 298 K, C = Pb(II), Cd(II) = 100 - 350, 50 - 175 mg/L	1397.62 and 510.2	–	PSO	Langmuir Model	Ion-exchange, electrostatic attraction and surface complexation	(Guan et al., 2022)
NiFe-LDH	Co-precipitation	Sodium alginate gel ball encapsulation	–	Ni(II) and Cu(II)	pH = 7, AD = 0.05 g in 100 mL, C = 100 - 1500 mg/L, t = - 120 min T = 298 K	182.8 and 196.2	–	PFO and PSO	Langmuir Model	Precipitation, electrostatic adsorption, ion exchange and chelation	(R. Long et al., 2022)
MgAl-LDH	Co-precipitation	Sodium hexametaphosphate (SHMP) intercalation	–	Pb(II) and Cd(II)	pH = 5, AD = 0.1 g in 20 mL, t = 180 min, C = = 400 mg/L T = 298 K	45.66 and 24.34	–	PSO	Langmuir Model	Surface complexations, isomorphous substitution, precipitation and chelation	(HoBET SSA in et al., 2022)

FeCr-LDH	Co-precipitation	–	BET SSA = 17.75 m ² /g, Vt = 0.151 cm ³ /g Pore size = 34 nm	Hg(II)	pH = 5, T = 298 K, AD = 20 mg in 20 mL, C = 0 - 500 mg/L, t = 120 min	116	–	PSO	Langmuir Model	–	(Bahami et al., 2022)
MgCuCaAL-LDH	Co-precipitation	–	–	Pb(II)	pH = 5.5, T = 298 K, t = 5 h, AD = 0.1 g on 100 mL, C = 300 mg/L	245.77	–	PSO	Sips Model	Physisorption	(Mahmoudi et al., 2022)
CaAl-LDH	Co-precipitation, ion exchange reaction	[MoS ₄] ²⁻ intercalation	BET SSA = 12.83 m ² /g,	Pb(II) and Cd(II)	pH = 5, C = 50 - 1000 mg/L, AD = 1 g/L, T = 298 K, t = 1440 min	1202.1 and 678.3	–	PSO	Langmuir Model	Chelation and isomorphic substitution, complexation	(F. He et al., 2022)

2.3.6 Zero-valent iron-based adsorbents

Zero-valent iron (ZVI) is an Fe-based material that has been extensively used for environmental remediation purposes, it belongs to the zero-valent metals group that have gained momentum for such applications from around 1972 (Galdames et al., 2020). The ZVI is also referred to as metallic iron (Fe^0), it is considered as a non-toxic material that is inexpensive and can serve as a reducing agent because of its standard electrode potential (E^0) of -0.44 V (Galdames et al., 2020). The low cost of ZVI is due to the prevalence of iron in the earth's crust especially in igneous rocks, it is considered the second most abundant element next to aluminium (Tarekegn et al., 2021). The initial use of ZVI for water treatment applications was in the form of granular iron, iron filling and iron powder (Cantrell et al., 1995; Gould, 1982). However, recently, nanoscale zero-valent iron (nZVI) has gained prominence because of the advantages it offers including larger specific surface area (X. Zhao et al., 2016), higher reactivity and better performance under similar experimental conditions (Alazaiza et al., 2022; Cundy et al., 2008). Since the nZVI is not a naturally occurring material, several methods including liquid-phase reduction, gas-phase reduction, thermal decomposition method, ultrasound assisted method, precision milling method, electrochemical method and other green method do exist for its synthesis. Nevertheless, the methods are broadly classified into the top-down and bottom-up approach. In the top-down approach, bulk particles of iron are broken down into smaller nano-sized particles through mechanical and/or chemical means. Whereas the bottom-up approach, nZVI is synthesized through assembly of individual atoms and molecules (Tarekegn et al., 2021). The application of ZVI/nZVI in water treatment application is greatly encouraged because of the several interaction mechanisms between the nZVI and heavy metal contaminants (Zou et al., 2016). Heavy metals can be removed by pristine nZVI through surface interactions and formation of inner-sphere complexes (Zou et al., 2016). Further, heavy metal ions can be directly reduced by Fe^0 or heavy metals ions adsorbed on the core-shell of nZVI

may be slowly reduced by Fe^{2+} generated from the nZVI (Y. Li et al., 2015; M. Liu et al., 2015). While oxidation process is rare when the nZVI system is employed for environmental remediation process, it happens in special instance in which the nZVI leads to the generation of powerful oxidizing agents such as H_2O_2 , $\text{HO}^\bullet$, and $\text{O}_2^{\bullet-}$. As(III) was partially oxidized to less toxic As(V) in aqueous solution in the presence of Mt-nZVI (Bhowmick et al., 2014). Other special interaction mechanisms such as precipitation may occur especially when nZVI is coupled with other function materials (J. Li et al., 2016). The schematic representation of the interaction between nZVI and cationic heavy metals is given in Figure 2.8.

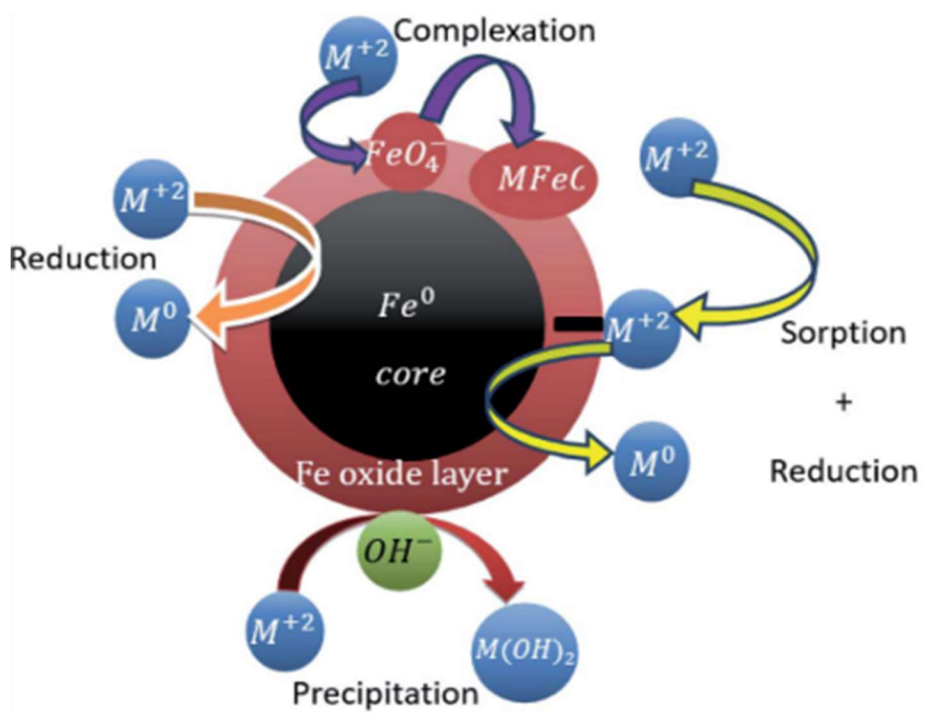


Figure 2.8. Postulated mechanisms for the removal of aqueous heavy metals using pristine nZVI (Tarekegn et al., 2021)

Despite the plethora of removal mechanism available to the pristine nZVI and the promise shown by the nZVI for use in water treatment and remediation, it suffers from certain drawbacks that significantly reduces its efficiency, hence, limiting its field scale application. First, the high surface energy, intrinsic magnetic interactions and weak van der Waals forces causes its rapid

agglomeration. This in turn results in reduced interaction between the contaminants and the nZVI, hence, lower treatment efficiency (Boparai et al., 2011; Phenrat et al., 2007). Secondly, it rapidly loses its reactivity because of several reactions with water due to its non-selectivity (Liang et al., 2022). As such several approaches including surface modification, providing porous support, metal doping and incorporation of another metal into the structure of nZVI are done to enhance its performance and limit its drawback (Galdames et al., 2020; L. Yang et al., 2023; Zou et al., 2016). However, caution must be taken when selecting materials for the creation of nZVI composites. Some stabilizers are capable of blocking nZVI active sites and also greatly reduce the electron transfer potential of the pristine nZVI. Furthermore, incorporating metals into the structure of nZVI could hasten its corrosion, resulting in secondary pollution (Liang et al., 2022). Table 2.7 gives a summary of the recent application of nZVI and its composites for the removal of heavy metals from aqueous stream.

Table 2.7 Adsorptive removal of heavy metals from aqueous system using nZVI based adsorbents.

ZVI	Modification	Textural properties	Heavy metal	Experimental conditions	Adsorption capacity (Q _{max} in mg/g)	Removal efficiency (%)	Kinetics	Isotherm	Proposed mechanism	Reference
sulfide nZVI	Hydrophilic activated carbon	BET SSA = 1229.8 m ² /g, V _t = 0.54 cm ³ /g	Pb(II)	pH = 5.0, T = 323 K, t = 120 min, AD = 0.05 g in 100 mL, C = 10 - 300 mg/L	295.3	–	Avrami fractional-order model	Langmuir Model	Electrostatic attraction, complexation, chemical precipitation and reductive action	(Qu et al., 2021)
nZVI	Sludge-based biochar	BET SSA = 43.97 m ² /g, V _t = 3.39 mm ³ /g	Sb(III)	pH = 4.8, T = 298 K, AD = 0.2 g/L, t = 24 h, C = 10 - 30 mg/L	160.40	96.92	PSO	Langmuir Model	advanced and oxidation	(Wei et al., 2020)
nZVI	LDH	–	V(V)	pH = 3.0, AD = 0.5 g/L, C = 50 mg/L, T = 298 K, t = 6 h	93.7	–	PSO	Freundlich Model	Complexation, reduction to V(III) and transformation to vanadium oxide	(Kong et al., 2020)
nZVI	Biochar	–	V(V)	pH = 5.7, C = 25 mg/L, T = 298 K, AD = 0.5 g/L, t = 180 min	48.5	99	PSO		Electrostatic attraction, redox and precipitation processes	(C. Fan et al., 2020)

nZVI	Carbon foam	BET SSA = 33,2 m ² /g	Pb(II)	pH = 6, T = 298 K, C = 10 - 200 mg/L, AD = 10 mg in 40 mL, t = 480 min	335.4	–	PSO	Langmuir Model	Adsorption, reduction and sedimentation	(S. Li et al., 2021)
nZVI	Graphene-like biochar	BET SSA = 60.08 m ² /g	As(III)	pH = 4, T = 298 K, AD = 0.2 g/L, C = 40 mg/L, t = 120 min	363		PSO	Langmuir Model	Inner sphere complex formation and partial oxidation	(K. Liu et al., 2020)
nZVI	Graphene-like biochar	BET SSA = 60.08 m ² /g	Cd(II)	pH = 7, te,p = 298 K, AD = 0.4 g/L, C = 20 mg/L, t = 120 min	92.8	–	PSO	Langmuir Model	Surface complexation	(K. Liu et al., 2020)
mZVI	Activated carbon	BET SSA = 16.9 m ² /g	Cr(VI)	pH = 3, C = 10 mg/L, AD = 1 g/L T = 298 K, t = 120 minutes	14.35	94.10	PSO	Langmuir Model	Adsorption, reduction and precipitation	(W. Wang et al., 2020)

nZVI	Calcium carbonate	BET SSA = 31.40 m ² /g	Pb(II)	pH = 6, t = AD = 0.25 g/L, T = 298 K, C = 10 - 1000 mg/L, t = 120 min	3828	98	PSO	Langmuir Model	Adsorption, metal reduction, exchange reaction and carbonate precipitation	(X. Zhang et al., 2019)
nZVI	Activated carbon	BET SSA = 704.71 m ² /g, Vt = 0.34 cm ³ /g, Pore size = 1.95 nm	Pb(II)	pH = 6, T = 298 K, AD = 2 g/L, C = 10 - 300 mg/L, t = 480 min,	59.35	95	PSO	Langmuir Model	Precipitation and reduction	(X. Liu, Lai, et al., 2019)
Sulfidated nZVI	Activated biochar	BET SSA = 414 m ² /g, Vt = 0.32 cm ³ /g	Cr(VI)	pH = 4, AD = 0.5 g/L, C = 10 - 100 mg/L, T = 298 K, t = 180 min	–	90	PSO	Langmuir Model	Physical adsorption and chemical reduction	(Zhuang et al., 2021)

nZVI	Oak wood biochar	BET SSA = 10.97 m ² /g, Vt = 0.015 cm ³ /g, Pore size = 2.18 nm	Cr(VI)	pH = 2, C = 50 mg/L, t = 12 h, T = 298 K, AD = 0.04 g in 40 mL, 1.0 L of CaCO ₃ saturated water (simulatd groundwater)	–	99.90	PSO	–	Sorption, reduction and co-precipitation	(Y. Zhang et al., 2020)
nZVI	Biomass derived carbon	–	Pb(II)	pH = 5, t = 4 h, T = 298 K, AD = 0.3 g/L, C = 30 mg/L	98.37	98.70	PSO	Langmuir Model	Electrostatic attraction, complexation and reduction	(L. Yang et al., 2023)
nZVI	Biomass derived carbon	–	Zn(II)	pH = 5, T = 298 K t = 4 h, AD = 0.3 g/L, C = 8 mg/L	26.38	99.40	PSO	Langmuir Model	Electrostatic attraction, complexation and reduction	(L. Yang et al., 2023)

2.3.7 Graphene-based adsorbents

Graphene is an allotrope of carbon having a two-dimensional structure and is considered an excellent material in the field of research relating to carbon materials. By definition, graphene is a single-atom-thick sheet consisting of carbon atoms that are arranged in a lattice nanostructure of hexagonal nature (X. Liu, Ma, et al., 2019). While the existence of crystals that are of two-dimensional structure was considered not possible under ambient conditions, partly because of their thermodynamic instability, the landscape change after the synthesis of graphene in 2004 by Nobel laureates Andre Geim and Kostantin Novoselov (Novoselov et al., 2004). Synthesized graphene has several excellent structural and mechanical properties that makes it unique and valuable for several applications. It has a BET specific surface area of 2630 m²/g, a thermal conductivity of 3000 W/m.K, an electron mobility of 200,000 cm²/V.s, a young modulus value reaching up to 1100 GPa, fracture strength of 125 GPa, a 97% optical transparency and a resistivity value of 10⁻⁶ (Chowdhury & Balasubramanian, 2014). These properties make graphene suitable for application in several fields and disciplines including biosensors, light emitting diodes of organic origin, coating protection, dye batteries, biomedical devices, aerospace, integrated circuits, electromagnetic shielding and importantly water and wastewater treatment (Rout et al., 2023). Further, graphene is considered as the parent of all graphitic forms and several products of the carbon family can be made by simply altering the dimensions of graphene sheet. When rolled, it forms 1D-carbon nanotube, and can also be stacked or wrapped to form 3D graphite or 0D fullerene, respectively (Figure 2.9i) (Saleh, 2015; Y. Zhou et al., 2015). Other important members of the graphene family nanomaterials include graphene oxide (GO; graphene with multiple oxygen containing surface functional groups), reduced graphene oxide (rGO; GO that has been reduced to contain less functionalities), few-layer graphene, graphene dots and graphene ribbons etc. (Yusuf

et al., 2015). The schematic representation of some selected graphene family nanomaterials is presented in Figure 2.9ii.

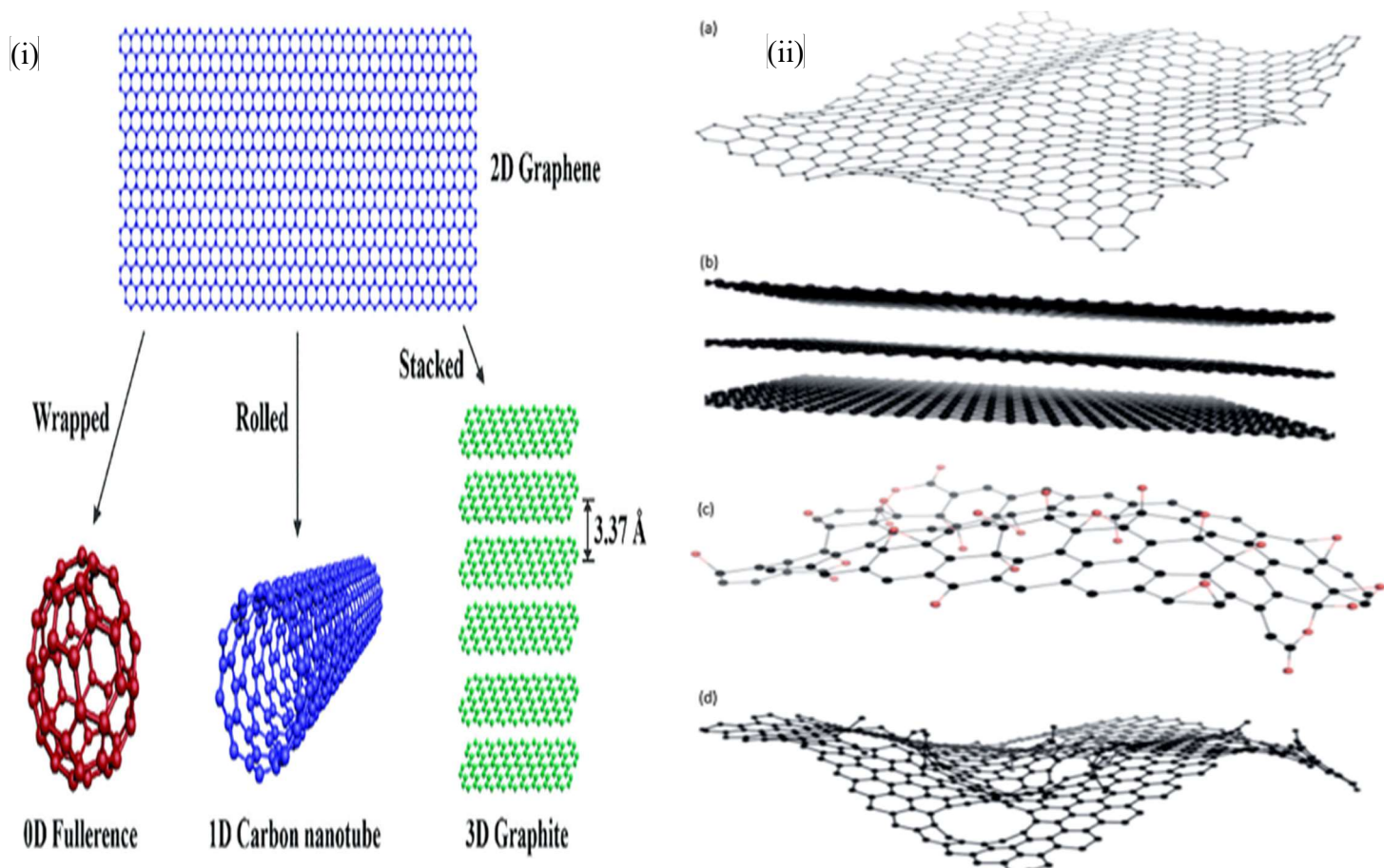


Figure 2.9 a) Pristine graphene and products obtained from altering its dimensions (Rout et al., 2023) b) chemical structure of members of graphene family nanomaterials (a) graphene (b) few-layer graphene (c) GO (O₂ in red) (d) rGO (Bianco, 2013).

Synthesis of pristine graphene

Several methods that are of chemical or mechanical nature are utilized for the synthesis of graphene. However, they can be broadly classified into bottom-up and top-down approaches. In the bottom-up approach, carbonaceous gas is utilized to generate graphene whereas the top-down

approach involves generating graphene from powdered raw graphite by subjecting the raw material to certain processes (Lim et al., 2018). Each method is unique and offers specific advantages and this section briefly discusses some of the methods that have been widely used to synthesize pristine graphene.

Top-down approach

Mechanical exfoliation is the first documented method for the synthesis of graphene and it involves single layer extraction of graphene flakes on a suitable substrate. The mechanical exfoliation process involves subjecting layered materials to transverse or longitudinal stress (Yi & Shen, 2015). The mechanical exfoliation process of graphene has the advantage of being low-cost and an established method, however, it produces low graphene yield. Another approach for production of graphene is through chemically reducing graphite oxide. Graphite oxide can be produced by oxidizing graphite and GO nanoplates can be obtained through the sonication of graphite oxide. The obtained GO nanoplates can then be thermally or chemically reduced to obtain graphene films (Lim et al., 2018). The graphene obtained from the reduction of GO is of high quality and the technique is facile while at the same time economical, however, the product has significant number of defects. Chemical exfoliation is another interesting graphene synthesis approach and can be conducted in two steps. Initially, the van der Waals forces between the inter-layer is reduced followed by rapid heating process or sonication which separates graphene into single to few layers thick (Obayomi et al., 2023). Other forms of exfoliation include electrochemical exfoliation and liquid phase exfoliation.

Bottom-up approach

Epitaxial growth involves the growth of graphene on suitable surfaces. Silicon carbide (SiC) has a lattice structure which is similar to that of graphene and when subjected to suitable conditions including high temperature (800 to 1150 °C) and pressure (109 to 1010 mbar) in vacuum conditions, it will sublime. This results in the formation of graphitic layers by the carbon remaining on the substrate (Kumari, 2021). The process of epitaxial growth happens in two steps, starting with nucleation and ending with layer-by-layer growth (Yazdi et al., 2016). The epitaxial growth is facile, economically feasible and the graphene produced from the process is of high quality, however, the process is energy intensive because it requires high reaction temperature. Another bottom-up approach is the chemical vapour deposition (CVD) which involves depositing gaseous reactants onto a substrate (Fogarassy et al., 2014; Lim et al., 2018). In a heated reaction chamber, substrate comes into contact with gases resulting in the formation of material film on the exterior of the substrate. The CVD can be utilized for mass production, however, it is an expensive process. Pyrolysis technique can also be applied to synthesize graphene through the solvothermal method. Sodium ethoxide can be pyrolyzed and sonicated to form graphene sheet. Figure 2.10 summarizes the procedures utilized for the synthesis of pristine graphene.

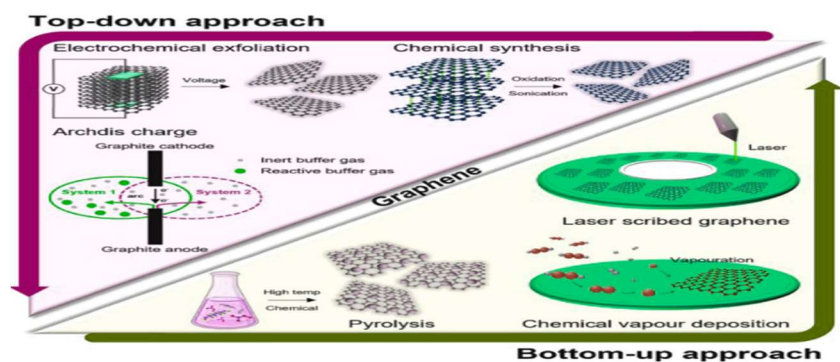


Figure 2.10. Top-down and bottom-up approaches for the synthesis of pristine graphene (Reddy et al., 2022).

Despite the excellent characteristics of pristine graphene and its high BET specific surface area, its application as a single material for the adsorptive removal of heavy metals and other contaminants from water has been limited due to its hydrophobicity. The hydrophobic nature of graphene results in its aggregation when placed in water, hence, significantly reducing its specific surface area, limiting active sorption sites and lowers potential for efficient mass transfer (Singha & Das, 2012). Secondly, pristine graphene has no surface functional group and limited to no porosity which significantly limits its contaminant adsorptive performance (Yusuf et al., 2015). Further, graphene and its derivative (GO and rGO) have shown to be toxic to some animals depending on the intake dose (Schinwald et al., 2012; K. Wang et al., 2011). This is another concern that should be addressed when using graphene-based material for water treatment applications. As such, graphene and its derivatives are functionalized and modified with several materials to enhance its contaminant adsorptive performance and maximize its appeal for water treatment applications. The resulting composites are not just materials with the aggregate properties of the base materials, rather, new materials with superior qualities and functionalities are desired and formed (S. Kumar et al., 2014). Many alternatives for graphene composites do exist including graphene-based nanocomposites and graphene-based polymer. The application of graphene-based composite has been tested for the removal of several heavy metal species, Table 2.8 presents recent studies that involve the use of graphene-based materials for the removal of heavy metal from the aqueous environment.

Table 2.8 Adsorptive removal of heavy metals from aqueous system using graphene-based adsorbents.

Graphene and derivatives	Modification	Textural properties	Heavy metal	Experimental conditions	Adsorption capacity (Q _{max} in mg/g)	Removal efficiency (%)	Kinetics	Isotherm	Proposed mechanism	Reference
GO	MgAl-LDH nanosheet assembly	BET SSA = 82.31 m ² /g, V _t = 0.099 cm ³ /g, Pore size = 14.33 nm	Cu(II), Cd(II) and Pb(II)	pH =6, AD = 0.05 g in 20 mL , T = 298 K, t = 240 min, C = 5 - 300 mg/L (Cu(II)), 5 - 500 mg/L (Cd(II)) and 20 -1000 mg/L (Pb(II))	89.26, 76.57 and 226.98	–	PSO	Freundlich Model for Cu(II) and Cd(II), Langmuir Model for Pb(II)	Surface complexation, precipitation and isomorphic substitution	(J. Li et al., 2022)
magnetic GO	MgAl-LDH nanosheet assembly	BET SSA = 114.2 m ² /g, V _t = 0.42 cm ³ /g, Pore size = 18.44 nm	Cu(II), Cd(II) and Pb(II)	pH =6, AD = 0.05 g in 20 mL , T = 298 K t = 240 min, C = 5 - 300 mg/L (Cu(II)), 5 - 500 mg/L (Cd(II)) and 20 -1000 mg/L (Pb(II))	80.72, 70.26 and 213.96	–	PSO	Freundlich Model for Cu(II) and Cd(II), Langmuir Model for Pb(II)	Surface complexation, precipitation and isomorphic substitution	(J. Li et al., 2022)
rGO	Mn ₃ O ₄ anchoring (modification)	–	Pb(II) and Cr(III)	pH = 4, C = 10 - 140 mg/L, t = 60 min ,T = 298 K, AD = 0.5 g/L (Pb(II)) and 120 (Cr(III))	130.28 and 138.51	–	PSO	Langmuir Model	pi electron donor-acceptor interaction, ion-exchange, electrostatic attraction and surface complexation	(Lingamdinne et al., 2022)

GO	Magnetic lignin-based composites	–	Pb(II) and Ni(II)	pH = 5, AD = 20 mg in 50 mL, C = 200 mg/L, t = 12 h, T = 298 K	147.88 and 110.25	–	PSO and PFO	Langmuir Model	Chelation and electrostatic attraction	(Du et al., 2022)
rGO	Nitrogen-enriched lignosulfonate exfoliated GO	–	Cr(VI)	pH = 2, T = 298 K, AD = 0.4 g/L, C = 10 -250 mg/L, t = 2100 min	416.97	–	PSO	Freundlich Model for Cu(II) and Cd(II), Langmuir Model for Pb(II)	Electrostatic attraction, adsorption coupled reduction, Surface chelation	(J. Geng et al., 2022)
GO	Hyperbranched polyamide-amine and cellulose functionalization	–	Pb(II), Cd(II) and Cu(II)	pH = 6, T = 298 K, t = 24 h, AD = 10 mg in 100 mL, C = 100 mg/L	680.3, 418.4 and 280.1	–	PSO	Langmuir Model	Chelation and complexation	
GO	–	–	Cu(II) and Pb(II)	pH = 5 (Cu(II)) and 6 (Pb(II)), T = 298 K, C = 100 mg/L, t = 120 min	55.47 and 85.17	–	PSO	Langmuir Model	Electrostatic attraction and active sites adsorption	(W. Yang & Cao, 2022)
GO	Carboxylation of GO	–	Cu(II) and Pb(II)	pH = 5 (Cu(II)) and 6 (Pb(II)), T = 298 K, C = 100 mg/L, AD = 1 g/L, t = 120 min	62.02 and 96.21	–	PSO	Langmuir Model	Electrostatic attraction and active sites adsorption	(W. Yang & Cao, 2022)

Magnetite graphene nanocomposite	Graphene embedded into activated carbon	–	Pb(II)	pH = 5, C = 50 - 400 mg/L, t = 150 min, T = 298 K, AD = 0.10 g in 100 mL	153.2	–	PSO	Langmuir Model	Chemisorption	(J. Yan & Li, 2022)
GO	Poly- cyanoguanidine modification	–	Hg(II)	pH = 5, AD = 1 g/L, T = 298 K, C = 200 mg/L, t = 8 h.	174.7	99.63	PSO	Freundlich Model	Chelation	(H. Lin et al., 2022)
GO	–	– BET SSA = 37.61 m ² /g, Vt = 0.066 cm ³ /g Pore size = 6.98 nm	Pb(II)	pH = 4, AD = 0.25 g/L, T = 293 K, C = 100 - 1250 mg/L, t = 20 min	55.80	98.87	PSO	Langmuir Model	–	(Azam et al., 2022)
rGO aerogel	Montmorillonite modification	–	Cd(II)	pH = 6.5, t = 1440 min, T = 298 K	262.79	–	PSO	Langmuir Model	–	(S. Zhou et al., 2022)
GO	Thiol and amido modified alginate modification	–	Pb(II) and Cu(II)	pH = 5.5 (Pb(II)) and 4 (Cu(II)), t = 40 min (Pb(II)) and 50 min (Cu(II)), T = 298 K, C = 200 mg/L	369.6 and 124.1	–	PSO	Langmuir Model	–	(H. Zhang et al., 2022)

GO	Partial reduction of GO	–	Hg(II)	pH = 7, C = 150 mg/L, T = 298 K, AD = 2.5 mg in 50 mL, t = 0.5 h.	110.21	75	PFO and PSO	Langmuir Model	Electrostatic attraction	(Tene et al., 2022)
Graphene	ZnO decoration coupled with glycol	BET SSA = 70.5 m ² /g, Vt = 0.15 cm ³ /g	Cr(VI)	pH = 3, t = 75 min, = AD = 0.8 g/L, T = 303 K, C = 300 mg/L	232.58	–	PSO	Langmuir Model	–	(Rout & Jena, 2022)
Magnetic GO	Piperazine modification	–	Pb(II)	pH = 6, AD = 7 mg in 10 mL, C = 15 mg/L, t = 27.5 min, T = 298 K	558.2	–	PSO	Langmuir and Freundlich Model	Chelation	(Alboghbeish et al., 2022)
rGO	Carboxymethyl cellulose incorporated LDH modification	BET SSA = 156.24 m ² /g, Vt = 0.28 cm ³ /g, Pore size = 2.10 nm	As(V)	pH = 7, T = 293 K, t = 24 h	258.39	98	PSO	Langmuir Model	Electrostatic attraction	(Priya et al., 2022)
rGO	–	–	Ni(II)	pH = 6, C = 2 mg/L, AD = 0.2 g/L, T = 298 K, t = 30 min	69	93	PSO	Langmuir Model	–	(A. E. D. Mahmoud et al., 2022)
Spherical graphene	Surface modification of graphene by LDH	BET SSA = 30.5 m ² /g, Vt = 0.138 cm ³ /g	As(III)	pH = 8, C = 50 mg/L, T = 298K, AD = 0.5 - 1 in x, t = 30 min	149.3	–	PSO and PFO	Langmuir Model	–	(Kamali et al., 2023)

Graphene quantum dots	Carbon foam, alginate, zinc oxide beads modification	BET SSA = 38.9 m ² /g, Vt = 0.25 cm ³ /g Pore size = 7.8 nm	Pb(II)	pH = 6, AD = 10 mg in 10 mL, C = 100 mg/L, t = 30 min, T = 298 K	133.8 mg/g	90.70%	PSO	Langmuir model	(M. E. Mahmoud et al., 2022)
Magnetic GO	Lanthanum sulfide nanoparticle decoration	–	Pb(II)	pH = 5, t = 40 min, C = 5 - 200 mg/L, T = 298K,	123.46 mg/g	95%	PSO	Langmuir model Electrostatic attraction and coordination	(Rezania et al., 2022)

2.3.8 Carbon nanotube-based adsorbents

Like graphene, carbon nanotube (CNT) is also an allotrope of carbon. The structure of CNT consists of carbon atoms organized in a hexagonal network through a honeycomb-like arrangement (F. H. Hussein et al., 2018). Unlike graphene, CNTs are rolled up graphene layers with diameter ranging from slightly less than 1 nanometer to about 150 nanometers (Eatemadi et al., 2014; Jensen et al., 2015). The CNTs have a hollow cylindrical structure which is 1-dimensional in nature and the length of the CNT tubule generally ranges between 200 nm to 500 nm (R. Q. Long & Yang, 2001). Depending on the number of shell structures (one or more) that form the CNTs structure, it can be broadly classified as either single-wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs). However, few-wall carbon nanotubes (FWCNTs) are also identified as an intermediate class between the single and multiwall carbon nanotubes (Onyancha et al., 2021). Further, SWCNTs and MWCNTs have distinctive material properties. SWCNTs have a diameter of 0.4 – 3.0 nm and a specific surface area of 150 – 790 m²/g whereas the diameter and specific surface area of MWCNTs range between 1.4 – 100 nm and 50 – 850 m²/g, respectively. Further the tensile strength of SWCNTs is 22 GPa while MWCNTs possess a tensile strength that can reach up to 63 GPa depending on the number of graphene layers that made up the MWCNTs shell (Onyancha et al., 2021). These properties, along with many other impressive properties, make the CNTs valuable materials for applications in many disciplines. Since their first presentation by Iijima in 1991 (Iijima, 1991), they have been used in the field of electronics, material science, optics and environmental applications including water and wastewater treatment. The performance of CNTs as adsorbents for aqueous contaminants is enhanced by its pore structure, curvature and high specific surface area as compared to other traditional adsorbents (Z. Yin et al., 2020). Another important CNTs classification is based on the 2-D form of their sheets. Based on the chiral vector and respective chiral indices (n, m), three distinct categories exist including armchair, zigzag and

chiral nanotubes. In the zigzag alignment, the value of n is 0 while the armchair alignment has $n = m$ (Balasubramanian & Burghard, 2005). The chiral structure indicates ‘handedness’ and denotes that the tube can be twisted in any direction (Fiyadh et al., 2019). Figure 2.11 shows the structure of the MWCNTs, SWCNTs and the different 2-D forms of CNTs sheet.

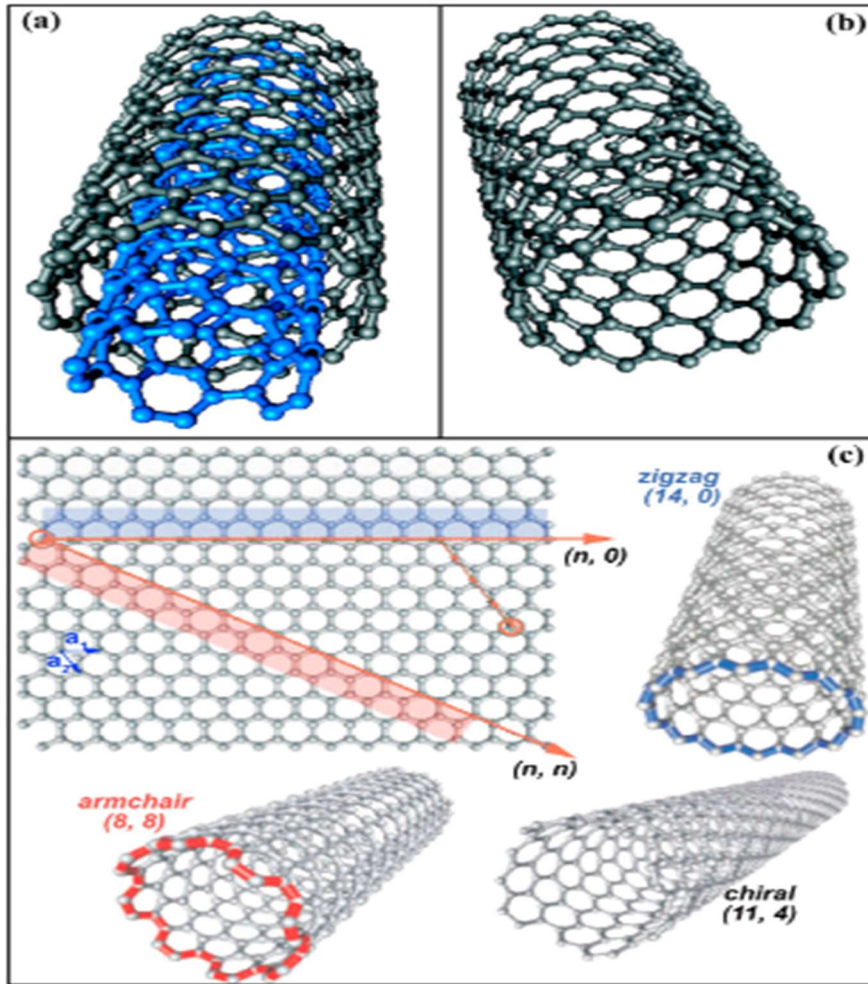


Figure 2.11. a) structure of MWCNT b) structure of SWCNT c) chiral vector alignment of CNTs (Hoang, Nizetić, et al., 2022)

Synthesis of CNTs

The CNTs have demonstrated exciting properties, however, their application in various disciplines is limited by challenges such as high cost of production, structural inhomogeneity, unfavourable

synthesis reaction conditions (high pressure and temperature) and imprecise structure formation post synthesis. Due to the aforementioned reasons, existing synthesis methods are continuously modified and new ones are created so as to enhance the properties of the synthesized CNTs structure. A brief discussion on some of the widely used CNTs synthesis method is provided below.

The chemical vapour deposition (CVD) has emerged as a promising method for the production of CNTs because it is of comparatively low cost, and utilizes relatively low growth temperature and pressure, in addition to high CNTs purity and yield (Shah & Tali, 2016). The synthesis procedure involves passing hydrocarbon vapour through a tube-like reactor made up of metal catalyst. The reaction temperature ranges between 600-1200 °C and the high temperature ensures that the hydrocarbons are decomposed. The growth of the CNT happens on the metal catalyst and the final product is collected after the system cools down to room temperature (Onyancha et al., 2021). Another common CNT synthesis procedure is the arc discharge method and it employs a reaction temperature that is above 1700 °C together with a pressure in the range of 50 – 700 mbar in an inert atmosphere (Onyancha et al., 2021). High-purity graphite electrodes with an electric arc in between them are needed and the passage of high-intensity electric current through the electrodes results in carbon evaporation leading to CNT synthesis. In the laser ablation method, a high-power laser beam is utilized to vaporize graphite that is placed in a quartz tube. The quartz tube is located inside a furnace that has its reaction temperature set to about 1200 °C in a helium or argon atmosphere, the furnace is connected to a cold collector which allows for the condensation of the reaction product (Onyancha et al., 2021). The pyrolysis approach is also utilized for CNTs production. It involves the pretreatment of carbon source with phosphoric acid followed by pyrolysis at about 500 °C which results in the formation of activated carbon (AC). AC is then

subjected to alkali activation followed by another pyrolysis step and the resulting product is mixed with transition metal catalyst and carbon source under high temperature conditions (900 -1200 °C) in an inert atmosphere to form CNTs (Hoang, Nižetić, et al., 2022; Omoriyekomwan et al., 2017). Liquid electrolysis method involves the use of ionic salts to achieve the decomposition of CO₂ electrolytically under very high-pressure conditions while the plasma torch method is relatively new and employs the use of silicon-based substrates to achieve high CNTs yield. Figure 2.12 gives a schematic representation of some of the discussed synthesis method when using biomass as a precursor for CNTs.



Figure 2.12. CNT production from biomass based on different synthesis procedures (Hoang, Nižetić, et al., 2022).

Purification step is often necessary after the synthesis of CNTs because of the presence of impurities in the form of small fullerenes, amorphous carbon, graphene sheets, metal catalysts and

substrate material (Bergmann & Machado, 2015). Physical methods such as settling, magnetic separation and other physical procedures that rely on the difference in particle size can be utilized (Terrones et al., 2010). The physical methods are mild and do not cause extreme damage to the CNT structure, however, they are generally less effective (Salernitano et al., 2007). A common chemical purification method involves oxidizing the impurities that have an oxidation rate that is higher than that of the CNTs. While oxidation method is very effective in cleaning up impurities especially when oxidants are carefully chosen and applied, it always introduces defects to the CNT structure, hence, causing changes in the morphology of the synthesized CNTs (Mahalingam et al., 2012).

The appeal for the use of CNTs for the removal of aqueous heavy metals is its high specific surface area and the abundance of efficient active sites in the CNT structure. However, because of the presence of carbonic nanostructures, interactive forces arise leading to the aggregation and poor dispersibility of CNTs in water. To enhance the performance of CNTs, functionalization or modification is carried out during or post synthesis of the CNTs to obtain materials of significantly better aqueous heavy metal adsorptive performance. Various functionalization agents do exist including oxidants in the form of strong acids (e.g. Sulfuric acid or nitric acid) (Esumi et al., 1996), strong oxidants (e.g. potassium permanganate) (Salam, 2013). Ionic liquids have been proposed as greener and more efficient alternatives to other form of oxidants, however, their usage is also limited by their high cost and potential waste disposal issues (Phadtare & Shankarling, 2010; Polo-Luque et al., 2013). Hence, deep eutectic solvents are also proposed to replace ionic liquids for effective functionalization of CNTs (Abbott et al., 2003). Other forms of CNT modification include biologicalization, esterification, polymer grafting, arylation and alkylation, thiolation and salination (Fiyadh et al., 2019; Haddon, 2002; Hirsch & Vostrowsky, 2007; P. C. Ma et al., 2010).

Figure 2.13 demonstrate the adsorptive removal mechanism of modified MWCNT for Cu(II) (heavy metal) along with pefloxacin (organic contaminant). Further, Table 2.9 Adsorptive removal of heavy metals from aqueous system using CNT-based adsorbents. gives a summary of recent studies that employed CNTs and modified CNTs for the adsorptive removal of heavy metals from contaminated water.

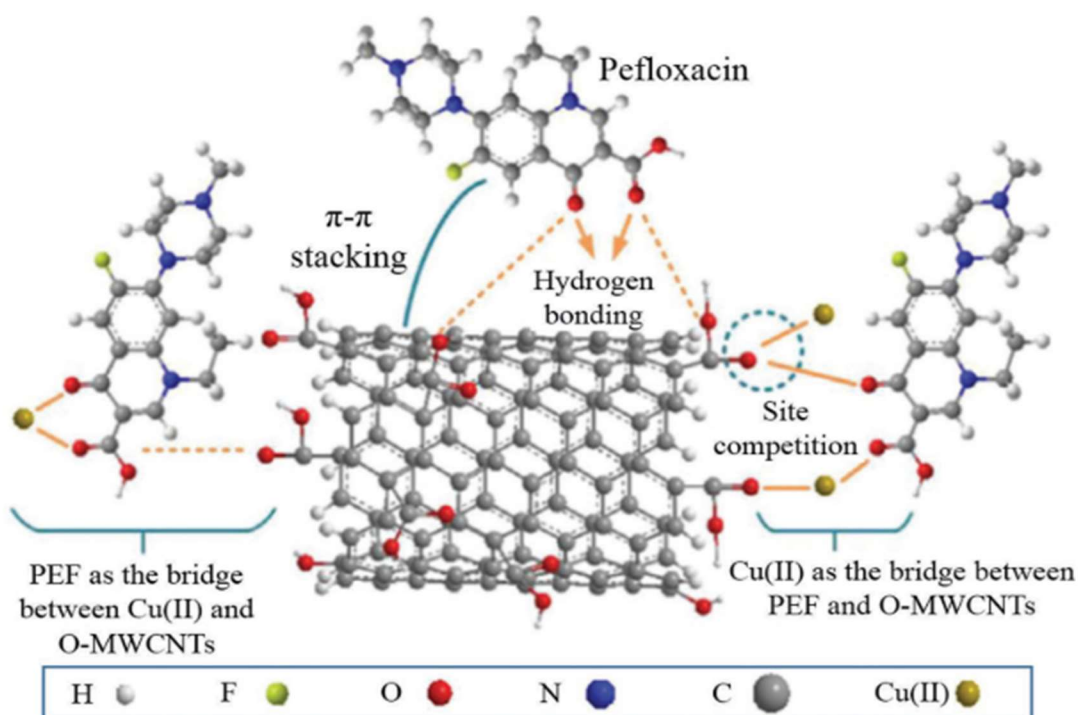


Figure 2.13. Mechanism for Simultaneous removal of Cu(II) and pefloxacin by oxydic MWCNTs (Z. Yin et al., 2020).

Table 2.9 Adsorptive removal of heavy metals from aqueous system using CNT-based adsorbents.

CNT	Modification	Textural properties	Heavy metal	Experimental conditions	Adsorption capacity (Q _{max} in mg/g)	Removal efficiency (%)	Kinetics	Isotherm	proposed mechanism	Reference
Polyethylene/lignin CNT	Ni/Al ₂ O ₃ composite	BET SSA = 52.13 m ² /g, V _t = 0.16 cm ³ /g	Pb(II)	pH = 6, AD = 0.05 mg in 50 mL, T = 298 K, t = 8 h, C = 20 - 400 mg/L	146.08	–	PSO	Langmuir Model	Complexation, electrostatic attraction, pi electron cation interaction	(Z. Wang, Qin, et al., 2021)
Polyethylene CNT	Ni/Al ₂ O ₃ composite	BET SSA = 48.87 m ² /g, V _t = 0.15 cm ³ /g	Pb(II)	pH = 6, AD = 0.05 mg in 50 mL, T = 298 K, t = 8 h, C = 20 - 400 mg/L	30.47	–	PSO	Langmuir Model	Complexation, electrostatic attraction, pi electron cation interaction	(Z. Wang, Qin, et al., 2021)
MWCNT	COOH functionalization (acid oxidation)	BET SSA = 105.03 m ² /g, V _t = 0.389 cm ³ /g, Pore size = 0.748 nm	Pb(II)	pH = 7, AD = 0.05 g in 50 mL, C = 2 - 10 mg/L, T = 298 K, t = 60 min	7.266	78	PSO	Langmuir Model	electrostatic attraction, ion exchange and surface complexation	(Zondo et al., 2022)

MWCNT	Au/Fe ₃ O ₄ decoration	BET SSA = 96.705 m ² /g. Vt = 0.388 cm ³ /g, Pore size = 0.716 nm	Pb(II)	pH = 7, AD = 0.05 g in 50 mL, C = 2 - 10 mg/L, T = 298 K, t = 60 min	1.233	–	PSO	Freundlich Model	electrostatic attraction, ion exchange and surface complexation	(Zondo et al., 2022)
MWCNT	Oxidization	BET SSA = 85.81 m ² /g. Vt = 0.54 cm ³ /g, Pore size = 22.98 nm	Pb(II)	pH = 5.6 - 5.8, AD = 5 mg in 8 mL, C = 0 - 200 mg/L T = 298 K, t = 48 h	123.02	–	PSO	Langmuir Model	Pore filling, complexation, ion exchange, electrostatic attraction and cation-pi interaction	(J. Zhang et al., 2021)
MWCNT	Graphitization	BET SSA = 81.23 m ² /g. Vt = 24.06 cm ³ /g, Pore size = 0.52 nm	Pb(II)	pH = 5.6 - 5.8, AD = 5 mg in 8 mL, C = 0 - 200 mg/L T = 298 K, t = 48 h	113.55	–	PSO	Langmuir Model	Pore filling, complexation, ion exchange, electrostatic attraction and cation-pi interaction	(J. Zhang et al., 2021)
MWCNT	–	–	Cr(VI)	pH = 2, AD = 0.05 g in 50 mL, C = 100 - 200 mg/L, T = 298 K, t = 20 h	84.75	–	PSO	Langmuir Model	Ion-exchange, intra-particle diffusion and electrostatic attraction	(B. Verma et al., 2021)

MWCNT	Acid oxidization (HNO ₃)		Cr(VI)	pH = 2, AD = 0.05 g in 50 mL, C = 100 - 200 mg/L, T = 298 K, t = 20 h	78.13	–	PSO	Langmuir Model	Ion-exchange, intra-particle diffusion and electrostatic attraction	(B. Verma et al., 2021)
Spherical porous carbon nanotubes	Geopolymer enhancement	BET SSA = 73.06 m ² /g. Vt = 0.098 cm ³ /g, Pore size = 5.36 nm	Pb(II) and Ni(II)	pH = 5, AD = 0.2 - 40 g/L (Pb(II)), 1 - 60 g/L (Ni(II)), C = 100 mg/L, T = 298 K, t = 10 h	52.743 and 8.915	–	PSO	Langmuir Model	Physisorption, chemisorption and ion-exchange	(S. Yan et al., 2022)
MWCNT	Polyamine modification	–	Cd(II)	pH = 6, AD = 30 mg in 20 mL, C = 1 - 5 mg/L, T = 298K, t = 2h	1.07	–	PSO	Freundlich Model	complexation, functional group interaction, pi-metal interaction and electrostatic attraction	(Adelabu et al., 2020)

CNT	Glutaraldehyde-cross-linked KFC/CNT/PVA ternary blend	BET SSA = 148,33 m ² /g, Vt = 0.68 cm ³ /g and pore size = 5.17 nm	Cd(II) and Cu(II)	pH = 5, AD = 1 g/L, C = 50 to 1000 mg/L, T = 298 K, t = 1 h	129.37 and 114.94	–	PSO	Freundlich Model	–	(Syed Masood Ameenur et al., 2021)
Oxidized MWCNT	Polypropylene imine dendrimer functionalization	BET SSA = 343 m ² /g, Vt = 1.762 cm ³ /g	Hg(II), Pb(II) and Ni(II)	pH = 7, AD = 0.06 g/L, C = 50 - 200 mg/L, T = 298 K	2000, 1750 and 1650	–	PSO	Langmuir Model	–	(Hayati et al., 2020)
CNT	Magnetic iron modification	BET SSA = 242 m ² /g, Vt = 0.534 cm ³ /g, Pore size = 3.40 nm	Sb(III)	pH = 6.3, AD = 0.4 g/L, C = 3-50 mg/L T = 298 K, t = 12 h	172	–	PSO	Redlich-Peterson Model	electrostatic attraction, ion exchange, surface complexation and redox reaction	(Z. Cheng et al., 2022)
CNT	Aromatic poly(amidoamine)(PAMAM) grafting followed by Ag nanoparticle deposition	–	Pb(II) and As(III)	pH = 7.67 (Pb(II)) and 8.11 (As(III)), AD = 10 mg in 50 mL, C = 1 - 10 mg/L, T = 298 K, t = 24 h	18.7 and 14.8	99 and 76	PSO	Langmuir Model	–	(Neelgund et al., 2022)

CNT	Steel slag composite	BET SSA = 37.92 m ² /g, Vt = 0.073 cm ³ /g and Pore size = 14.63 nm	Pb(II) and Cu(II)	pH = 6.5, AD = 20 mg in 100 mL, C = 80 - 160 mg/L (Pb(II)) and 40 - 160 mg/L (Cu(II)) T = 298 K, t = 3 h,	515.46 and 172.41	–	PSO	Langmuir Model	–	(P. Yang et al., 2022)
CNT	nZVI and Mxene modification	–	As(III)	pH = 3, AD = 0.4 g/L, C = 200 mg/L, T = 298 K, t = 120 min	443.32	–	PSO	Langmuir Model	Surface complexation, solid phase precipitation and catalytic oxidation	(S. Li et al., 2022)
MWCNT	Magnetic nanoparticles modification	–	Pb(II), Cu(II) and Cd(II)	pH = 6, AD = 20 mg in 100 mL, C = 215.5, T = 298 K, t = 60 min,	87.41 and 57.18	–	–	–	–	(Z. Wang, Xu, et al., 2021)
Oxidized MWCNT	Magnetic magnesium ferrite nanoparticle doping	–	Cr(VI)	pH = 2, C = 100 - 200 mg/L, T = 313 K, t = 150 min	175.43	–	PSO	Langmuir Model	–	(B. Verma & Balomajumder, 2020)

CNT	Polyethyleneimine and polydopamine modification	–	Cu(II)	pH = 7, AD = 10 mg in 50 mL, C = 10 mg/L, T = 298 K, t = 60 min,	67.79	–	PSO	Langmuir Model	–	(L. Guo et al., 2020)
CNT	Imprinted CNTs-chitosan hybrid sponge (COOH-CNTs/CS-IIS) (polymerization-lyophilization)	BET SSA = 28.9 m ² /g, Vt = 0.11 cm ³ /g	Gd(III)	pH = 7, AD = 10 mg in 10 mL, C = 25-200 mg/L, T = 298 K, t = 12 h	71.95	–	PSO	Langmuir Model	Chelation and pore adsorption	(E. Liu et al., 2021)
CNT	Non-imprinted CNTs-chitosan hybrid sponge (COOH-CNTs/CS-IIS) (polymerization-lyophilization)	BET SSA = 33.9 m ² /g, Vt = 0.17 cm ³ /g	Gd(III)	pH = 7, AD = 10 mg in 10 mL, C = 25-200 mg/L, T = 298 K, t = 12 h	58.91	–	PSO	Langmuir Model	Chelation and pore adsorption	(E. Liu et al., 2021)

2.3.9 MOFs-based adsorbents

Metal-organic frameworks (MOFs) are crystalline structures of low density that are constructed from secondary building units (SBU) in the form of metal ions or clusters and organic linkers connected to form a 3-D lattice (Kobielska et al., 2018; Shayegan et al., 2019, 2020). Since the creation of these porous coordination polymers by Omar Yaghi and his group in 1995 (Yaghi et al., 1995), MOFs have been the subject of research in many disciplines including separation (N. A. Khan et al., 2013a; Van De Voorde et al., 2014), drug delivery (Horcajada et al., 2009, 2010), proton conduction (Ramaswamy et al., 2014), catalysis (J. Liu et al., 2014), sensing (Bhardwaj et al., 2015; Furukawa et al., 2010; Nagarkar et al., 2013) and water treatment applications including photocatalysis (C. C. Wang et al., 2014) and adsorption (Abbasi et al., 2015; Rani et al., 2020). MOFs are distinguished by their several unique properties which make them suitable and valuable for such a diverse range of applications. Many MOFs are endowed with ultra-high specific surface area and in 2012, Farha et al reported a MOF with the largest BET SSA of any porous material as of that date ($\sim 7000 \text{ m}^2/\text{g}$). Additionally, theoretical computations have demonstrated that the BET SSA can be substantially increased (beyond $\sim 14600 \text{ m}^2/\text{g}$) by expanding the linker units (Farha et al., 2012). Further, the strong covalent bonds between organic linkers and the SBU results in flexible framework that has tunable pore topology, thermal and mechanical stability and permanent porosity (Q. Gao et al., 2019; Gelfand & Shimizu, 2016; Mottillo et al., 2014).

The type of metal ion or cluster and the organic ligand in addition to their coordination geometry results in different types and classes of MOFs. MOF with 2-D structure was synthesized by Yaghi's group using cobalt and BDC as precursors (Yaghi et al., 1995). In 1999, MOF-5 with 3-D structure was synthesized using zinc and BDC and the synthesis of this MOF was regarded as a major milestone in the MOF research (H. Li et al., 1999). Sequel to these discoveries, many more

MOFs have been synthesized including Materials of Institut Lavoisier (MIL; lanthanide series or transition metal as SBU and trimesic acid or terephthalic acid as linker), University of Oslo (UiO; zirconium metal-based SBU), Cu-BTC also called HKUST-1 is consist of copper as its SBU and zeolitic imidazolate framework (ZIF; cobalt or zinc as metal ion and imidazole ligands as organic linkers). Considering the prominence of ZIFs as a class of MOFs, they will be discussed under a separate section of this article. Figure 2.14 show the trend in major discoveries related to MOFs and MOF-based material and the application of MOFs in specific applications while Figure 2.15 shows various types of synthesized MOFs nanostructures.

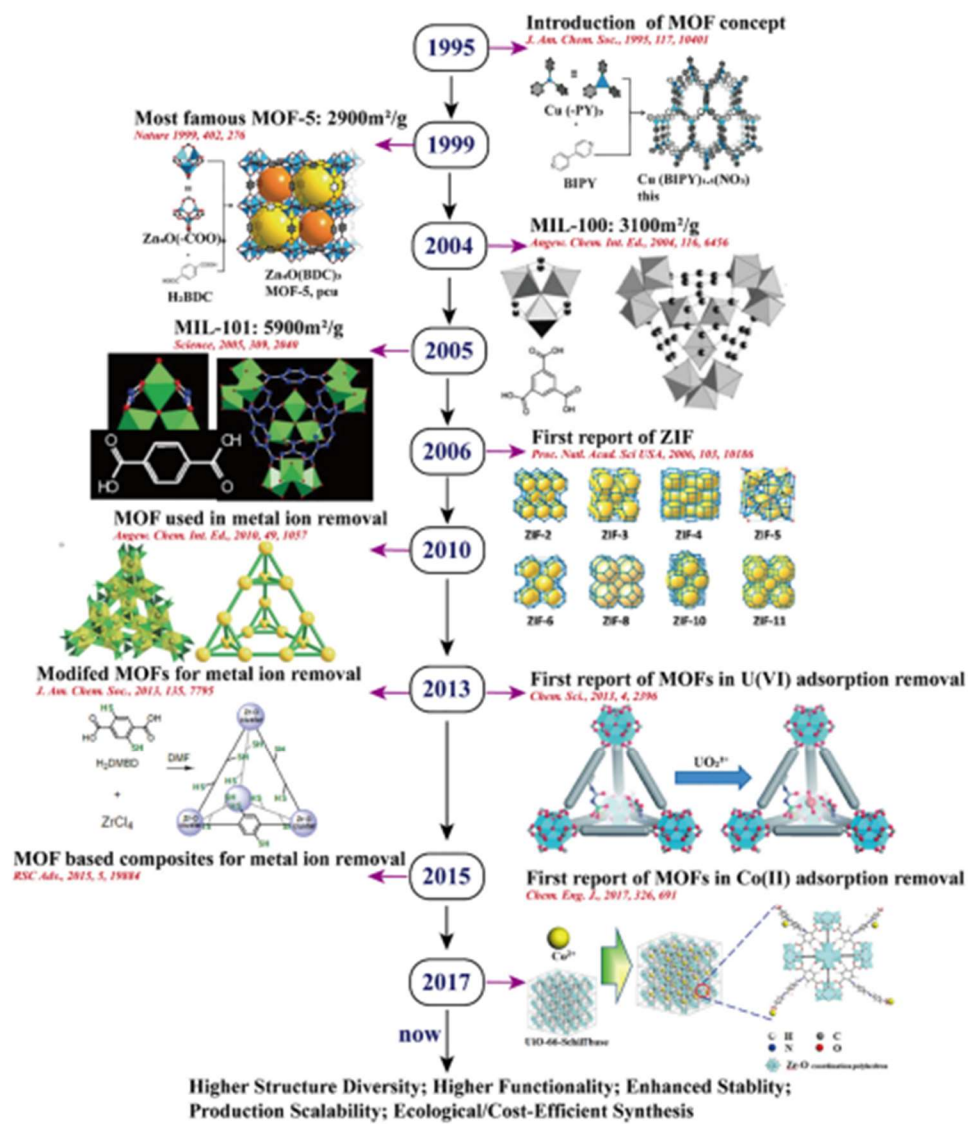


Figure 2.14. Timeline of MOFs' major milestone and application in aqueous heavy metal ion treatment (G. R. Xu et al., 2021)

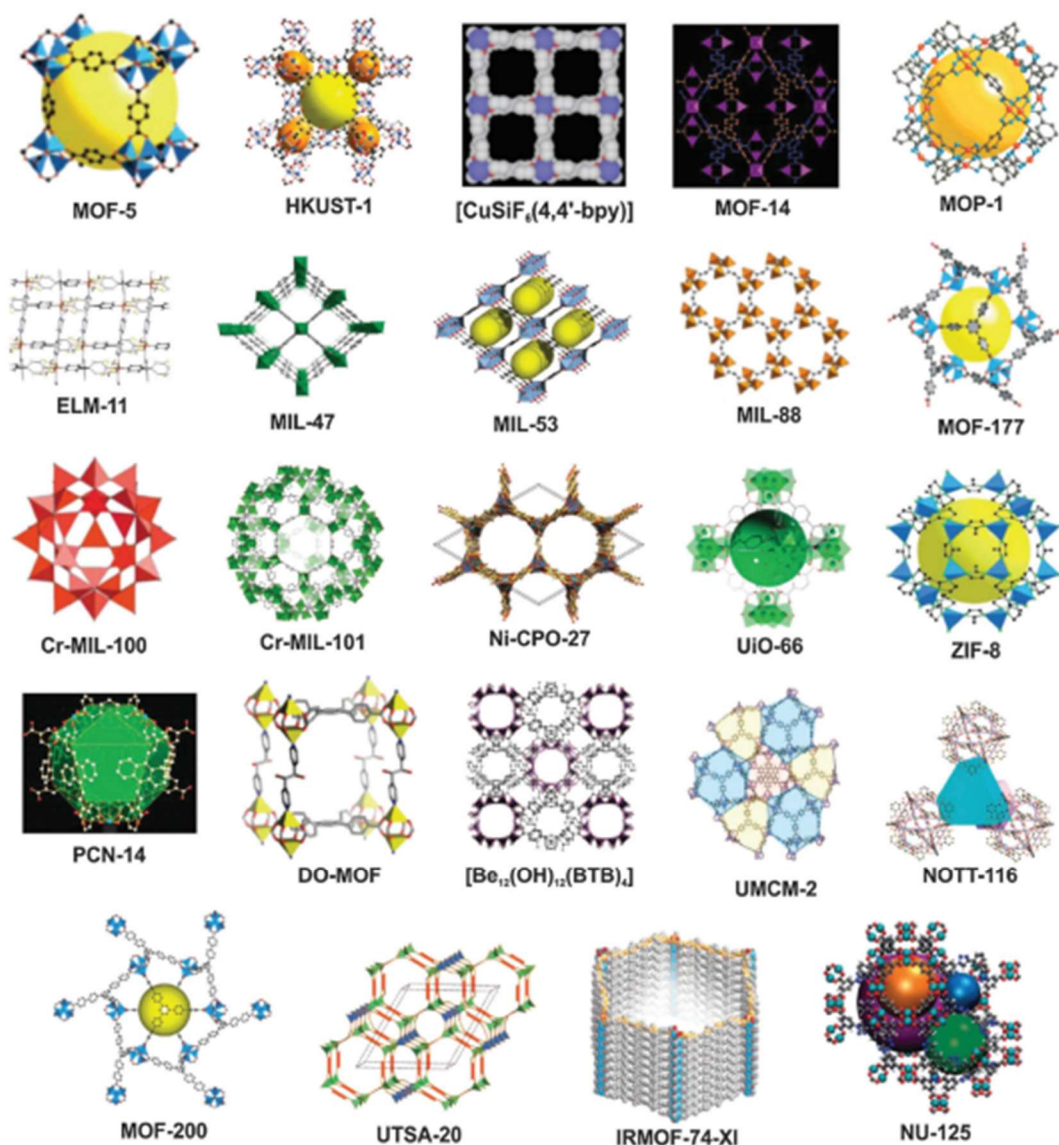


Figure 2.15. Structure of some selected of MOFs as presented by different authors (Silva et al., 2015).

Synthesis of MOFs

There exists a variety of methods for the synthesis of MOFs and many of them are characterized as simple and non-complex procedures. While the conventional synthesis methods have been effective in synthesizing MOFs, development of new methods offers the advantage of synthesizing materials that cannot be otherwise synthesized. Further, different synthesis routes lead to formation

of MOFs with varied morphologies, particle sizes as well as size distribution which can have significant influence on the properties of the synthesized materials (Stock & Biswas, 2012; Xiao et al., 2020). This section presents a brief discussion on some of the commonly used routes for the synthesis of MOFs.

In the conventional method, the synthesis reactions happen at an environment in which electrical heating is provided to the system through conventional means thereby excluding the need for parallelization of reactions. The reaction temperature is a significant parameter in this synthesis approach, and on the basis of temperature ranges, the conventional method can be classified as solvothermal and non-solvothermal method (Stock & Biswas, 2012). In the solvothermal synthesis, reactions take place under autogenous pressure at temperature above the solvents' boiling point in a closed vessel (Rabenau, 1985). The hydrothermal method, in which water is used as the solvent is a common form of the solvothermal synthesis method. The quantity of the solvent used and the amount of energy required in the conventional method has led to environmental concerns, hence, scientists have explored other means for the synthesis of MOFs. In the mechanochemical synthesis, the use of mechanical forces instead of electrically generated heat is employed. The application of mechanical forces on the precursors results in chemical transformation which is preceded by intramolecular bond breakage (Boldyrev & Tkáčová, 2000; Fernández-Bertran, 1999). The major advantages of the mechanochemical method includes the possibility of reaction occurring at room temperature and under solvent free conditions, additionally, the reaction time is short and particles of small size are generally obtained (Garay et al., 2007). The first report of electrochemical synthesis of MOFs occurred in 2005 by BASF researchers (Mueller et al., 2004). The motivation behind creating the electrochemical method was to eliminate the presence of impurities in the form of anions that are present in the metal salts used

as precursors. Hence, metal ions are introduced to the reaction medium (conducting salt and dissolved linker) through a continuous anodic dissolution. Further, electrochemical method can be run in a continuous process, hence, enhancing its suitability for synthesis of MOFs at an industrial scale (Stock & Biswas, 2012). Microwave-assisted synthesis depends on electromagnetic waves and their interaction with mobile electric charges in the form of polar solvent ions or molecules present in the solutions (Y. Sun & Zhou, 2015). Because of the nature in which microwave ovens are designed, the microwave-assisted synthesis allows for the monitoring of temperature and pressure whilst reaction is ongoing, hence, reaction conditions are more precisely monitored. The micro-wave assisted synthesis method offers the advantages of phase selectivity, morphology control, particle size reduction and high efficiency (Y. Sun & Zhou, 2015). The sonochemical synthesis method relies on the use of high-energy ultrasound in the reaction medium (Bang & Suslick, 2010; Mason & Peters, 2003). It was invented to serve as an environmentally friendly, fast, room temperature and energy efficient method for the synthesis of MOFs. Figure 2.16 shows the diagrammatical representation of the various MOF synthesis methods and the resulting MOF-based products because of applying the synthesis methods.

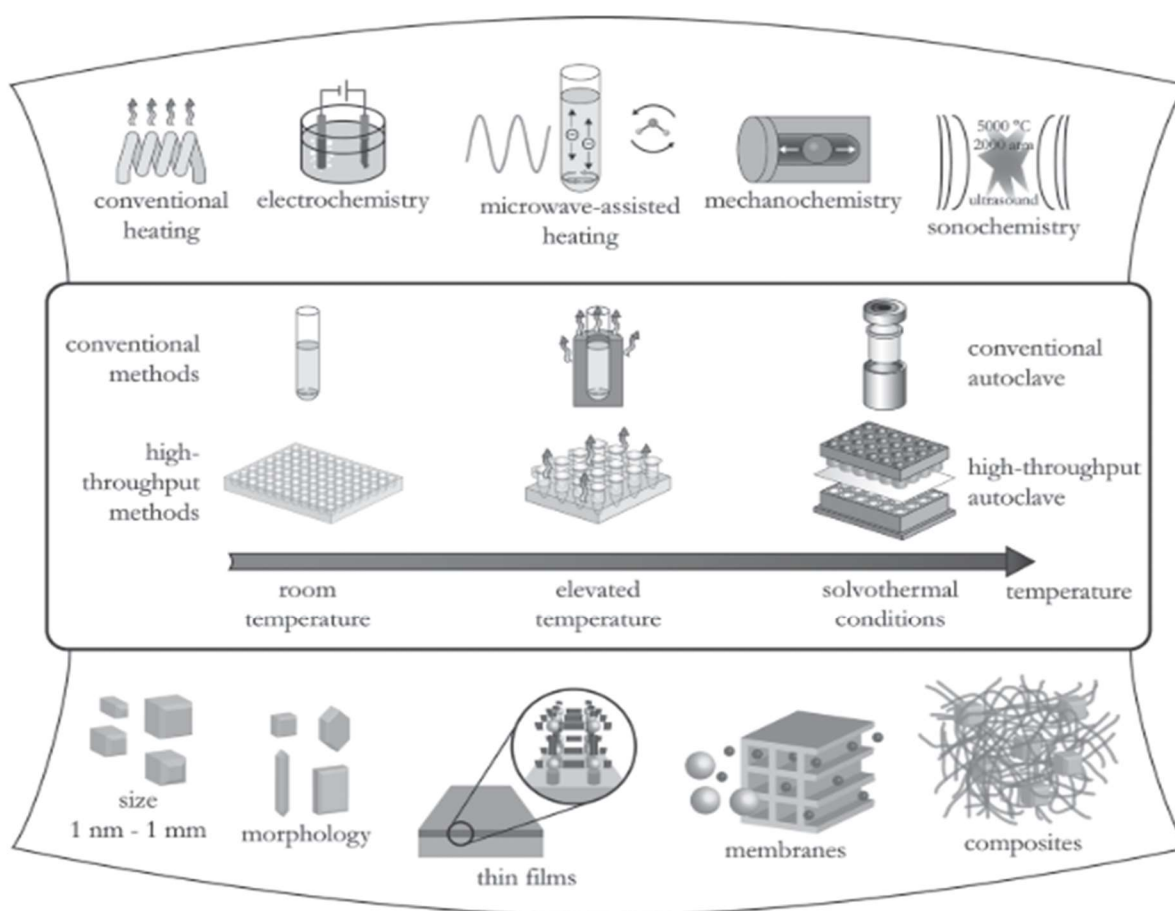


Figure 2.16. Different pathways to the synthesis of MOF-based materials (Stock & Biswas, 2012).

Many fascinating properties of MOFs have been highlighted, however, in terms of aqueous heavy metal adsorption, it is MOFs' large specific surface area and porosity that make it attractive for such application. Further, the organic linkers, metal nodes and functional groups fixed to MOFs surface could provide medium for the chelation of heavy metals in contaminated aqueous streams (G. R. Xu et al., 2021). Hence, MOFs have been applied in the removal of many heavy metals and are also considered as high-performance adsorbents towards such applications (Ghaedi et al., 2018; Gurung et al., 2012). Despite the promise shown by MOFs, there exist certain drawbacks that limit its real-life and large-scale application. Even though MOFs are thermally and mechanical stable, the majority have low chemical stability and the structure will collapse when subject to acidic or

basic medium (Naghdi et al., 2023). Water could also break the coordination between the ligand and the SBU leading to the disintegration of MOF structure (F. Tan et al., 2015; K. Tan et al., 2014). The destruction of MOFs in water environment happens through two known mechanisms. First, ligand could be substituted by water while the second mechanism happens through the process of hydrolysis. The collapse of MOF structure as a result of its introduction to water medium is shown in Equation I and II.



To apply MOFs for industrial scale adsorptive removal of aqueous heavy metals, its water stability needs to be significantly improved. The use of hydrophobic functional groups in the synthesis and modification of MOFs has been touted as a solution. For example, Wu et al. (T. Wu et al., 2010) synthesized a MOF with various water-repellent functional groups incorporated within its framework and the synthesized material was able to stay in boiling water for a period of a week. Ma et al (D. Ma et al., 2011) also improved the water stability of Zn-MOFs by the addition of water repellent functional groups. Another approach by Jiao and his team (Jiao et al., 2015) to improve the water stability of Mg-MOF was to replace the Mg in the metal center with either Ni or Co. The summary of the common mechanism and approaches for the improvement of water stability of MOFs is depicted in Figure 2.17. However, caution needs to be taken as such modifications will likely alter the adsorptive behaviour and other material characteristics of the synthesized MOF.

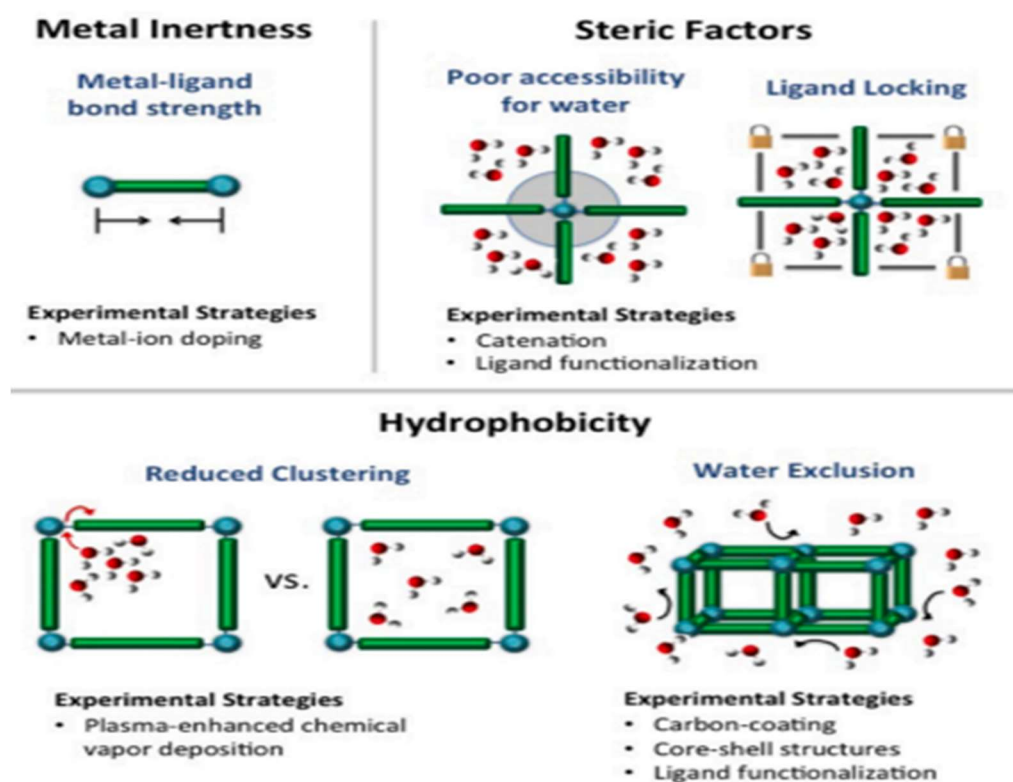
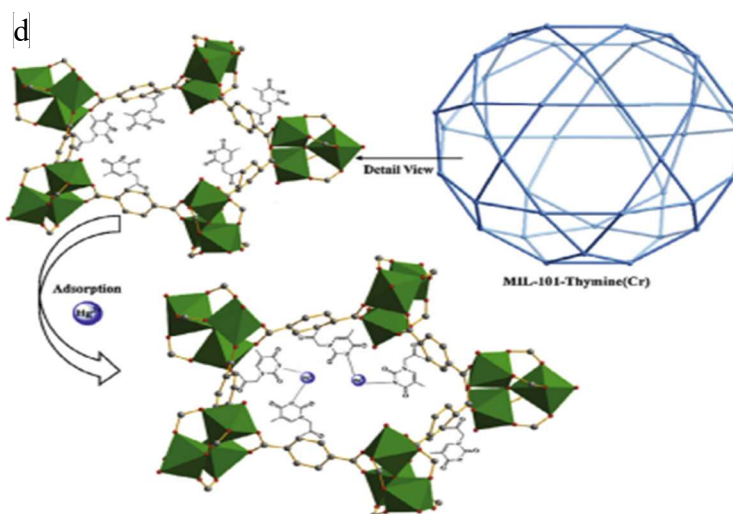
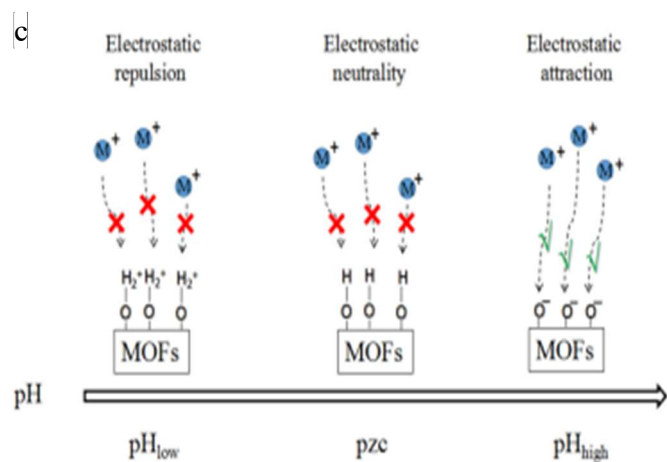
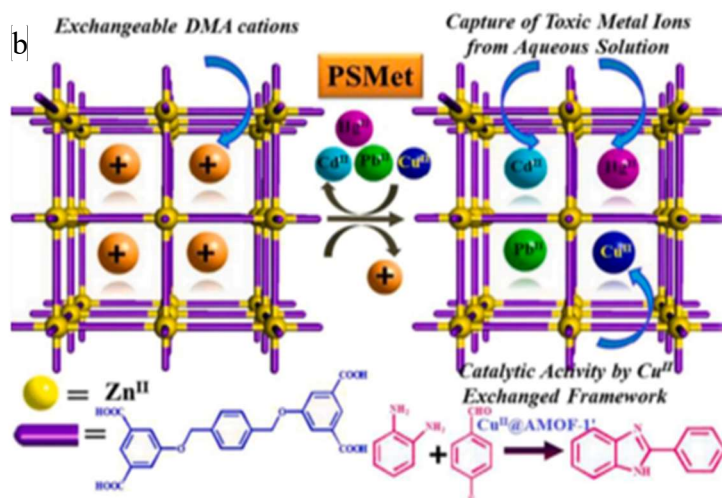
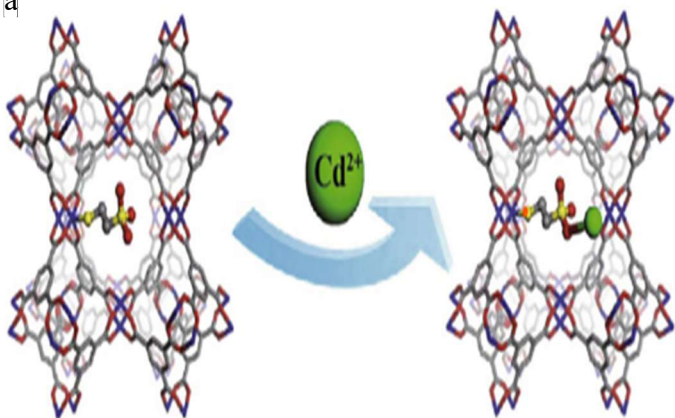


Figure 2.17. Approaches and Mechanism for MOFs water-stability improvement (Z. Li, Wang, et al., 2021).

Other issues that scientists and researchers are trying to resolve when applying MOFs for the aqueous removal of contaminants includes its tendency to agglomerate leading to formation of larger particles and difficulty in its separation from water after adsorption treatment (G. R. Xu et al., 2021). Two distinct approaches for the modification of MOFs to enhance its performance are widely adopted. First, a pre-synthetic approach that involves the use of modified ligands as precursors for the synthesis can be used. However, its major drawback is the tendency of ligands to decompose at high temperature leading to the loss of the functional material (Shamim et al., 2022). The post-synthetic approach is usually favoured because it allows for flexible addition of chemical reagents to the already fabricated MOF (Moghaddam et al., 2018; Rada et al., 2015; Shamim et al., 2022). Various functional groups can be added to the MOFs to enhance their heavy metal selectivity and adsorptive performance. Figure 2.18 shows the mechanism through which

a



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Table 2.10 Adsorptive removal of heavy metals from aqueous system using MOFs-based adsorbents.

MOF	Modification	Textural properties	Heavy metal	Experimental conditions	Adsorption capacity (Q _{max} in mg/g)	Removal efficiency (%)	Kinetics	Isotherm	Proposed mechanism	Reference
UiO-66	Formic acid and amino modification	BET SSA = 919 m ² /g, V _t = 0.49 cm ³ /g, Pore size = 2.14 nm	Cr(VI)	pH = 2, AD = 0.25 g/L, C = 100 mg/L, t = 18 h, T = 298 K	338.98	–	PSO	Langmuir Model	–	(P. Chen et al., 2023)
UiO-66	SO ₃ H functionalization	BET SSA = 1262 m ² /g, V _t = 0.380 cm ³ /g	Cd(II) and Pb(II)	pH = 6, AD = 0.02 g in 40 mL, C = 1000 mg/L, t = 2 h, T = 298 K	194.92 and 176.69	97 and 88	PSO	–	Chemisorption and coordination interaction	(S. Gul et al., 2022)
TMU-5	–	BET SSA = 436.52 m ² /g, V _t = 0.21 cm ³ /g, Pore size = 3.84 nm	Cd(II)	pH = 7, AD = 0.015 g/L, C = 20 mg/L, t = 24 h, T = 300 K	1929.42	–	–	Langmuir Model	Electrostatic attraction and precipitation	(Ul Mehdi & Aravamudan, 2022)

TMU-5	Silica coating	BET SSA = 52.2 m ² /g, V _t = 0.28 cm ³ /g, Pore size = 17.15 nm	Cd(II)	pH = 6, AD = 0.015 g/L, C = 20 mg/L, t = 24 h, T = 300 K	634	–	–	Langmuir Model	Electrostatic attraction and precipitation	(Ul Mehdi & Aravamudan, 2022)
UiO-66-NH ₂	Chitosan grafting	BET SSA = 363.94 m ² /g, V _t = 0.17 cm ³ /g, Pore size = 1.84 nm	Cu(II) and Pb(II)	pH = 6.5, AD = 0.25 g in, C = 400 and 600 mg/L, t = 160 min, T = 298 K	364.96 and 555.56	–	PSO	Langmuir Model	Physical adsorption and complexation	(Hu et al., 2022)
UiO-66-COOH	NiCo LDH modification	BET SSA = 69 m ² /g, V _t = 0.35 cm ³ /g	Hg(II) and Ni(II)	pH = 3 and 8.0, AD = 2 mg in 20 mL, C = 0.5 - 50 mg/L, t = 120 min, T = 295 K	509.8 and 441.0	–	Avrami and PFO	Langmuir Model	Complexation	(Soltani et al., 2021)

magnetic MIL-88A(Fe)	2-aminopropyltrimethoxysilane (APTMS) modification (anchoring)	BET SSA = 62.21 m ² /g, Vt = 9.45 cm ³ /g	Cd(II), Pb(II) and Cr(VI)	pH = 6 (Cd(II)), 6 (Pb(II)) and 2 (Cr(VI)), AD = 20 mg in 10 mL, C = 0.04 - 0.4 mol/L, t = 60 min, T = 298 K	693.0, 536.22 and 1092.22	—	PSO	Langmuir Model	Coordinate bonding (cationic species) and ion-pair attraction forces (anionic species)	(M. E. Mahmoud et al., 2020)
UiO-66	Ethylenediamine functionalization	—	Pb(II), Cd(II) and Cu(II)	pH = 6, AD = 8 mg in 10 mL, C = 20 - 300 mg/L, t = 360 min, T = 298 K	243.90, 217.39 and 208.33	—	PSO	Langmuir Model	Electron exchange, electron sharing, electrostatic and covalent interaction	(Ahmadijokani et al., 2021)
MOF-801	—	BET SSA = 492 m ² /g, Vt = 0.21 cm ³ /g, Pore size = 1.22 nm	Cu(II)	AD = 10 mg in 10 mL, C = 10 - 50 mg/L, t = 180 min, T = 298 K	16.58	97.80	PSO	Freundlich Model	Complexation and ion-exchange	(T. L. Tan et al., 2022)

MIL-121	Alginate beads modification	BET SSA = 36 m ² /g,	Cu(II) and Cd(II)	pH = 4.5, AD = 20 mg in 20 mL, C = 100 - 500 mg/L, t = 6 h, T = 298 K	204.5 and 88.7	–	PSO	–	–	(H. Ma et al., 2022)
Ti-MOF	Thiodiacetic acid modification	BET SSA = 168.3 m ² /g, Vt = 0.165 cm ³ /g, Pore size = 3.912 nm	Hg(II) and Pb(II)	pH = 5, AD = 10 mg in 10 mL, C = 150 - 400 mg/L, t = 24 h, T = 298 K	943 and 431	–	PSO	Langmuir Model	Chelation and electrostatic attraction	(B. Zeng et al., 2023)
AMO-MOF	–	BET SSA = 255.251 m ² /g, Vt = 0.117 cm ³ /g, Pore size = 8.069 nm	Pb(II)	pH = 4, AD = 10 mg in 10 mL, C = 500 mg/L, t = 20 h, T = 298 K	472.73	–	PSO	Langmuir Model	Chelation and electrostatic attraction	(H. Wang et al., 2023)
UiO-66-NDC	GO composite	–	Pb(II)	pH = 6, AD = 0.5 g/L, C = 50 - 250 mg/L, t = 150 min, T =	254.45	–	PSO	Temkin Model	–	(S. Singh, U, et al., 2023)

MOF-808	Zirconium-iron bimetallic modification	—	Sb(V) and Sb(III)	pH = 7, AD = 1 g/L, C = 100 - 1000 mg/L, t = 12, T = 298 K	526.3 and 343.6	—	PSO	Langmuir Model	Chelation and ligand exchange	(B. Sun et al., 2022)
MOF-808	—	—	Sb(V) and Sb(III)	pH = 7, AD = 1 g/L, C = 100 - 1000 mg/L, t = 12, T = 298 K	303.1 and 204	—	PSO	Langmuir Model	Chelation and ligand exchange	(B. Sun et al., 2022)
Fe-BTC MOF	Magnetite nanoparticle incorporation	BET SSA = 417 m ² /g, Vt = 0.86 cm ³ /g, Pore size = 3.71 nm	Cu(II), As(III), Pb(II) and Hg(II)	pH = 5 (Cu(II)), 6 (As(III)), 5 (Pb(II)) and 5.5 (Hg(II)) AD = 10 mg in 50 mL, C = 10 - 120 (As(III) and Hg(II)), 5 - 40 (Pb(II)) and 2 - 16 mg/L (Cu(II)), t = 3 h, T = 298 K	55, 57, 147 and 155	—	PSO	Langmuir Model (Cu(II), As(III) and Pb(II)) and Temkin Model (Hg(II))	—	(Castañeda-Ramírez et al., 2022)adsorbent

Fe-BTC MOF	–	BET SSA = 815 m ² /g, Vt = 0.92 cm ³ /g, Pore size = 3.26 nm	Cu(II), As(III), Pb(II) and Hg(II)	pH = 5 (Cu(II)), 6 (As(III)), 5 (Pb(II)) and 5.5 (Hg(II)) AD = 10 mg in 50 mL, C = 10 - 120 (As(III) and Hg(II)), 5 - 40 (Pb(II)) and 2 - 16 mg/L (Cu(II)), t = 3 h, T = 298 K	46, 37, 137 and 143	–	PSO	Langmuir Model (Cu(II), As(III) and Pb(II)) and Temkin Model(Hg(II))	–	(Castañeda- Ramírez et al., 2022)
PUC-5	–	BET SSA = 40.81 m ² /g, Vt = 0.06 cm ³ /g,	Fe(II), Pb(II) and V(V)	pH = 2 - 12, AD = 15 mg in 15 mL, C = 25 to 300 mg/L, t = 45 min , T = 298 K	208.7, 192.6 and 203.6	–	PSO	Langmuir Model	–	(Arya et al., 2023)

UiO-66-NH ₂	Glycidyl methacrylate (GMA)	BET SSA = 1144 m ² /g, V _t = 0.37 cm ³ /g and Pore size = 2.84 nm	Pb(II) and Cd(II)	pH = 6, AD = 8 mg in 10 mL, C = 20 - 1000 mg/L, t = 200 min, T = 298 K	238.80 and 208.45	–	PSO	Temkin Model	–	(Zaman et al., 2023)
UiO-66-NH ₂	Chitosan and epichlorohydrin crosslinking	BET SSA = 32.03 m ² /g, V _t = 0.06 cm ³ /g	Hg(II)	pH = 6, AD = 20 mg in 50 mL, C = 500 - 4000 mg/L, t = 2 h, T = 303 K	896.8	–	PSO	Langmuir Model	–	(X. Yan & Ge, 2023)
MOF-808	Thioglycolic grafting		Hg(II)	pH = 5, AD = 0.1 g/L, C = 120 mg/L, t = 180 min, T = 298 K	977.5	–	PSO	Langmuir Model	Chelation and pore size diffusion	(C. Ji et al., 2022)

MOF-808	Magnetite nanoparticle incorporation		Hg(II)	pH = 6, AD = 30 mg in 30 mL, C = 50 mg/L, t = 12 h, T = 298 K	45.1	90.20	Elovich Model	Freundlich Model	Chelation	(Paz et al., 2022)
MIL-53(Fe)	Copper bimetallic modification		Cr(VI)	pH = 3, AD = 0.5 g/L, C = 25 -800 mg/L, t = 180 min, T = 298 K	724.6	99.05	PSO	Langmuir Model	Monolayer chemical adsorption, electrostatic interaction, redox reaction, co-precipitation and coordination effect	(Yuan et al., 2023)
UiO-66	4,6-diamino-2-mercaptopyrimidine (DMP) functionalization	BET SSA = 513 m ² /g, Vt = 0.32 cm ³ /g.	Hg(II)	pH = 7, AD = 2 mg in 4 mL, C = 400 mg/L, t = 3 h, T = 298 K	822.00	–	PSO	Langmuir Model	Electrostatic and covalent interactions	(Chai et al., 2022)

				pH =5.5 , AD = 20 mg in 20 mL, C = 200 -1000 (Pb(II)), 50 - 400 (Cd(II)) and 25 - 300 (Cu(II))	558.67, 271.34 and 210.89	—	PSO	Langmuir	Coordination and hydrogen bond interaction	(Y. Yan et al., 2022)
UiO-66	Ethylenediamine tetramethylene-phosphonic acid immobilization	BET SSA = 130.88 m ² /g, V _t = 0.18 cm ³ /g, Pore size = 5.97 nm	Pb(II), Cd(II) and Cu(II)	, T = 298 K						

2.3.10 ZIFs-based adsorbents

Zeolitic Imidazolate Frameworks (ZIFs) is the name given to the category of metal-organic frameworks (MOFs) made of transition metals like zinc and cobalt (tetrahedrally coordinated metals) and imidazole or imidazole derivative as a bridging organic linker, with bond achieved through self-assembly (Ighalo et al., 2022). Specific surface area of ZIFs range between 1000 to 10000 m²/g, a value significantly higher than that of the traditional adsorbents (Furukawa et al., 2013a). ZIFs have a topological structure that resembles that of aluminosilicate zeolite in that the 145° at which imidazolate bridge the transition metals (M-im-M) is comparable to the Si-O-Si angle found in zeolite, hence the name zeolitic imidazolate framework (Ighalo et al., 2022; Y. Liu et al., 2021). The zeolite skeleton structure of ZIFs not only make them gain the structural benefit of other MOFs, but also provides them with better thermal and chemical stability (N. Hassan et al., 2020; Park et al., 2006). The presence of soft divalent metal ion as a soft Lewis acid and imidazolate linkers as soft Lewis base in the framework of ZIFs results in strong coordination bonds, hence leading to a more rigid framework (Demessence et al., 2009; Miranda-Quintana, 2017; Park et al., 2006). This is because of the Pearson's hard/soft acid/base (HSAB) theory which postulates that strong interaction between soft acid and soft base or hard acid and hard base generally leads to stronger coordination bond (Demessence et al., 2009). This makes the ZIFs able to withstand harsh environments that some other MOFs are incapable of performing in. ZIF was first synthesized in 2006 by Chen and his team and it was initially named as MAF-4 (X.-C. Huang et al., 2006). A later study by Yaghi research team renamed it as ZIF-8 (N. Hassan et al., 2020; Park et al., 2006). From then on, several ZIFs structures have been synthesized and used for many applications including adsorption and storage of gases, catalysis, drug transport, sensing and water treatment (Bonneau et al., 2020; J. Fu et al., 2016; L. Fu et al., 2021; S. Li et al., 2016; K. Zhang

et al., 2021; R. Zhang et al., 2019; S. Zhang et al., 2021). Different structures of ZIFs can easily be synthesized because it is not the type of ligands used that determines the structure of ZIFs but rather the interaction mode between the ligands (Y. Liu et al., 2021). In 2008 alone, more than 20 different ZIF crystals were synthesized by the Yaghi's group (Y. Liu et al., 2021). More recently, the tailorable structure and pore size of ZIFs are being taken advantage of to synthesize ZIF based composites that can be used for variety of purposes with water treatment applications inclusive. Figure 2.19 gives the trend in synthesis and application of ZIFs in water treatment applications whereas Figure 2.20 shows the structure of different type of ZIFs that have been synthesized.

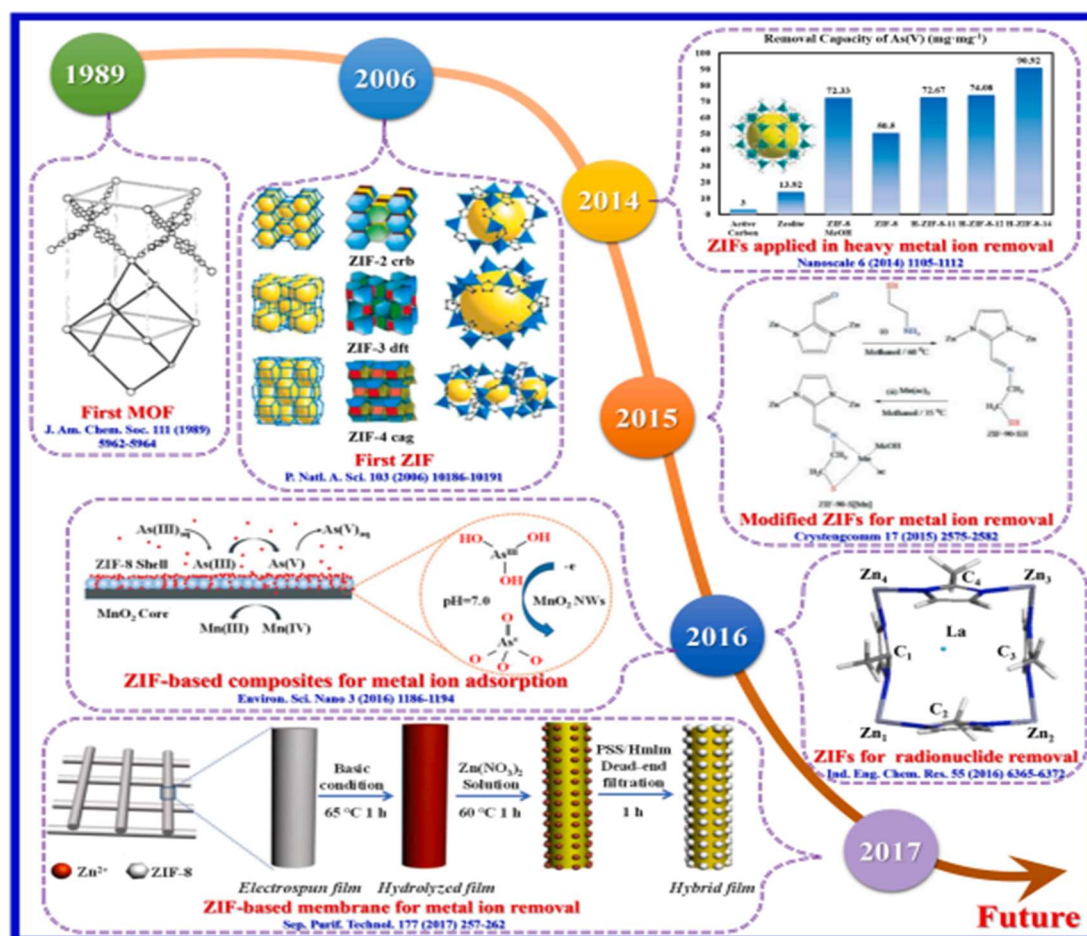


Figure 2.19. Trend in the development and application of ZIFs for water treatment applications (Y. Liu et al., 2021).

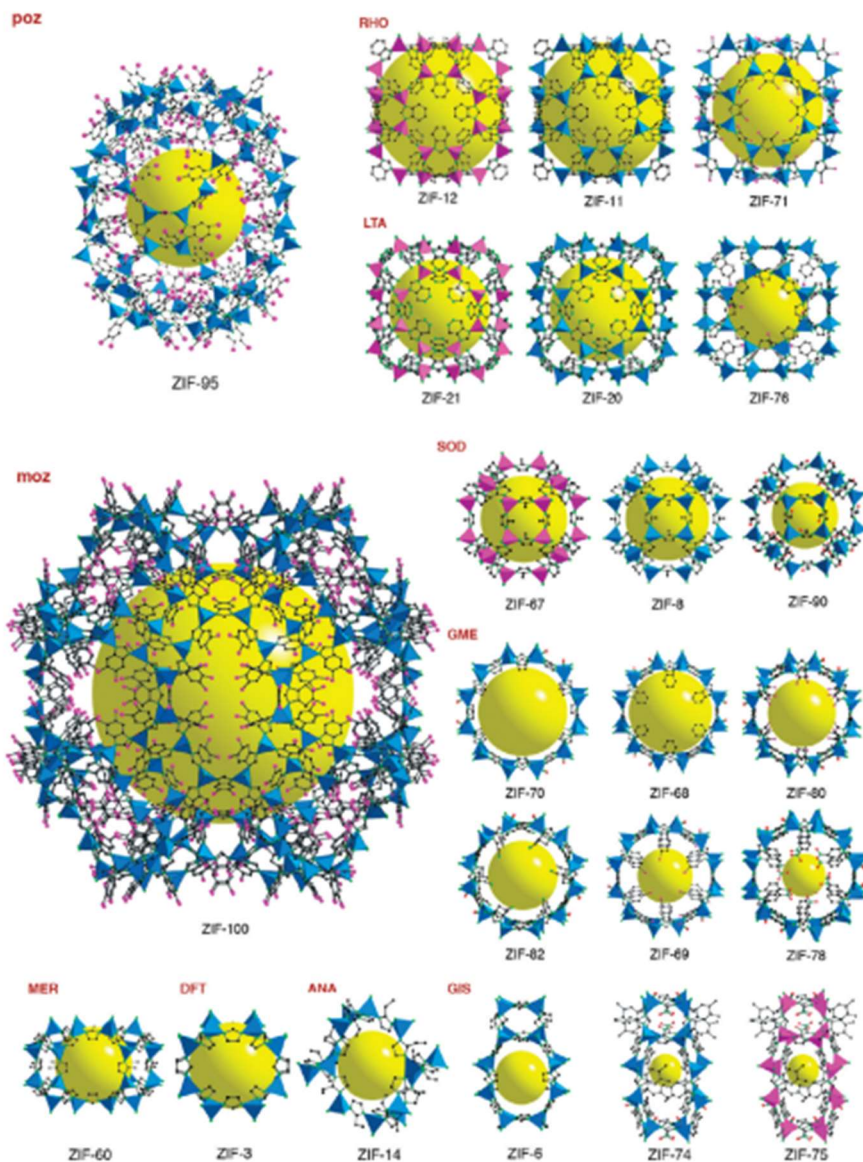


Figure 2.20. Different types of ZIF structure (Zinc ZIFs in blue and Cobalt ZIFs in pink). (Phan et al., 2010)

Synthesis of ZIFs

Several methods exist for the synthesis of ZIF crystals many of which are analogous to those used in the synthesis of other MOFs. The method used can cause ZIFs to have slightly change characteristics such as reduction in defective structures, increase in stability and change in purity levels. Citing reference with ZIF-8, when solvothermal/hydrothermal method is used, the ZIF

crystals are more stable and have purer structure. The structure is easier to adjust but less defective making it unsuitable for application in the field of defect engineering (Mo et al., 2022). Such merits and demerits should be considered when selecting a synthesis route for ZIF material. This section will present a general overview of the methods that have been used for the synthesis of ZIFs.

The solvothermal approach is the most common method for the synthesis of ZIFs and it generally involves dissolving the precursors (organic ligands and metal salts) in organic solvents like N,N-dimethylformamide (DMF), N,N-diethylformamide (DEF). The mixture is placed in an autoclave reactor for a certain duration and at specific temperature to achieve crystal growth (Y. Chen & Tang, 2019; Ding et al., 2018). When this method is used, the morphology of ZIF can be controlled by changing the concentration ratio of the used precursors, growth time and temperature at which the reaction occurs. Because of the high cost of the organic solvents that are generally used, the hydrothermal method which uses water and methanol as the solvents is gaining popularity. It was first reported by Pan et al (Pan et al., 2011) and it took few minutes to synthesize ZIF-8 when they used the hydrothermal method. Triethylamine was used to assist in nucleation of ZIF-8 and to avoid the formation of metal hydroxides. The precursors used for sonochemical method and solvothermal synthesis are the same, however, the major difference is the method at which growth of crystal is achieved. The sonication method uses acoustic activation to generate local pressure and temperature that are extremely high which results in formation of MOF structure (Son et al., 2008). It offers advantages such as the creation of homogeneous nucleation and the crystallization time is shorter than the conventional solvothermal method (Son et al., 2008). The mechanochemical method is simple and environmentally friendly because it does not require high volume of solvents and also offer advantages such as it can be used to produce huge quantities of ZIF on large scale bases (Fernández-Bertrán et al., 2006). The mechanochemical method involves

grinding the precursors in a mortar or ball-mill with little to no application of any solvent to form ZIF structure (Tanaka et al., 2013). Several other methods including microfluidic synthesis (Choi et al., 2015; Yamamoto et al., 2013) electrochemical synthesis (Martinez Joaristi et al., 2012; P. Wang et al., 2016), dry-gel conversion synthesis (Ahmed et al., 2012; Lee et al., 2015), and microwave synthesis (Y. J. Zhu & Chen, 2014) have been previously reported for the synthesis of ZIFs. Briefly, the microfluid method involves the use of micromixers for mixing and reaction reactants. It involves the continuous injection of the solvents in the micro-channels to produce the ZIF structure and offers the advantages of ease at which reaction parameters such as temperature, pressure, liquid flow rate and residence time are controlled (Y. Liu et al., 2021). Electrochemical synthesis is a modern technology and involves the use of electrochemical cells. The organic solvent is introduced as part of the electrolyte solution while the metals ions are released by the cathode and formation of ZIFs happens at the anode. Specific reaction conditions such as applied current, are needed for the process to complete (Martinez Joaristi et al., 2012). Dry-gel synthesis involves reaction of ground ZIF precursors in autoclave with little addition of methanol and it offers the advantage of environmental friendliness (P. Ji et al., 2020). While several other methods have been applied, the above discussion gives a synopsis of the more established methods. It is important to understand the application in which the synthesized ZIF will be used for prior to the selection of synthesis method, it has been noted that the method used influences important properties of the synthesized ZIF.

The ZIFs framework which consists of metal node, organic linker and available surface functional groups endows them with a plethora of heavy metal removal mechanisms including surface complexation, ion-exchange, pore diffusion and many others makes them an interesting choice of adsorbents (H. Dai et al., 2021; G. R. Xu et al., 2021). Remarkable performances were noted when

Huang et al. (Y. Huang et al., 2018a) used ZIF-8 and ZIF-67 for the adsorptive removal of Pb(II) from contaminated water, with maximum adsorption capacity reaching up 1119.80 and 1348.42 mg/g, respectively. Similarly, Ahmad et al. (K. Ahmad et al., 2021) explored the effect of metal atom in ZIFs by comparing the performance of Co-ZIF (ZIF-67) and Zn-ZIF (ZIF-8) in the removal of Hg(II) and Pb(II) from contaminated water. The adsorption capacity for Hg(II) reached up to 1436.11 and 1271.27 for ZIF-67 and ZIF-8, respectively. As for Pb(II), the adsorption capacity could be as high as 1978.63 and 1780.91 for ZIF-67 and ZIF-8, respectively. However, despite all the promise shown by single ZIF materials, they tend to suffer from two major drawbacks when applied in the field of adsorption. Firstly, they are poorly dispersed in aqueous solution and tend to agglomerate thereby significantly reducing their high specific surface area. Secondly, there is a demand for functional materials and as such single ZIF material would benefit greatly from the addition of beneficial materials to its structure, that could also help improve its regeneration and reuse which seem to be a concern (Mo et al., 2022). As such, other materials are combined with ZIFs to enhance the application range of ZIFs and overcome some inherent shortcomings of synthesized ZIF. Many functional materials can be obtained by combining ZIFs with other structures and the shape of some ZIF composites are presented in Figure 2.21.

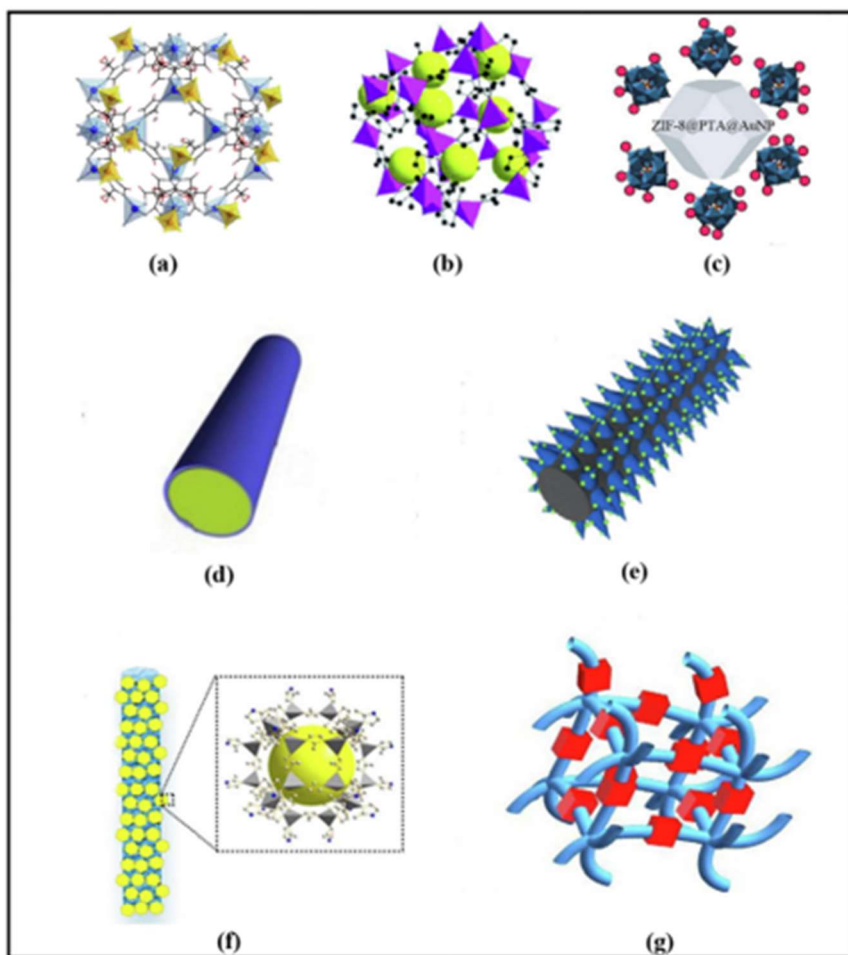


Figure 2.21. Diagrammatic representation of different types and shapes of ZIF-based composites (H. Dai et al., 2021).

Several approaches to the creation of functional ZIF composites do exist and few of them would be highlighted here. The In-situ method is one of the simplest methods, however, it requires high input in terms of material properties. The idea involves making use of certain functional groups or specific surface characteristics of materials to initiate interaction or biochemical reaction which will result in binding without need for treatment (Sharsheeva et al., 2019). Surface modification method involves the use of coupling agents, surfactant or crystal seed to treat the surface of ZIF particles with the aim of improving the binding force and adsorption that occurs between ZIF particles and the combined nanoparticles. Its merits include simplicity of operation and wide range

of applicability (L. Li et al., 2020; Q. Yang et al., 2016; Y. Yang et al., 2019). The template synthesis method can be divided into hard template method and soft template methods. It involves pre-stabilizing the nanoparticles which are then coated on ZIF-8 through introducing them into solution that contains molecular structure blocks of ZIF-8 (H. Dai et al., 2021). This method is suitable for application for ZIFs in comparison with other materials like zeolite because of the high porosity and adjustable pores that are present within the structure of the ZIF (Cai et al., 2020; C. Dai et al., 2014). A lot of research is put on ZIF based composite and there are several other novel methods that have been used for the synthesis of such materials including stepwise growth (LPE), microreactor synthesis and sonochemical method (X. Zeng et al., 2016). It is important to note that some of these methods can be used together to obtain ZIF based composite with synergistic effects. Many ZIF-based composites have been applied for the adsorptive removal of heavy metals from contaminated water and Figure 2.22 gives the schematic representation of the adsorption process. Further, Table 2.11 presents a list of recent studies that have applied ZIF-based materials for the removal of heavy metals from contaminated water.

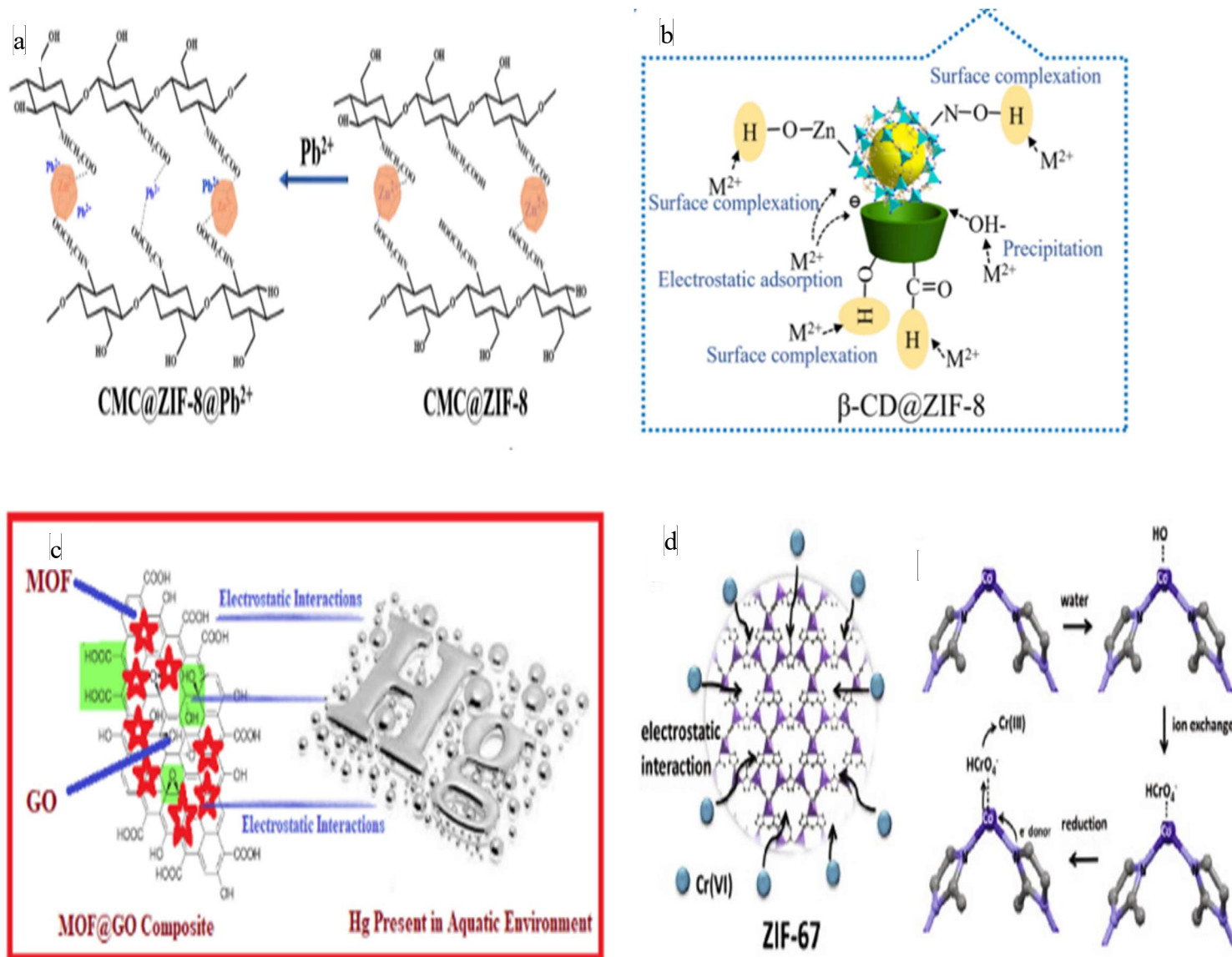


Figure 2.22. a) Adsorption mechanism of CMC@ZIF-8 toward lead (X. Zhu et al., 2022) b) adsorptive removal of divalent metals using beta-CD@ZIF-8 (C. Chen et al., 2022) c) removal of mercury from aquatic environment by ZIF-67@GO (Fallatah et al., 2022) d) ZIF-67 Cr(VI) removal through electrostatic attraction and ion-exchange (X. Li et al., 2015a).

Table 2.11 Adsorptive removal of heavy metals from aqueous system using ZIFs-based adsorbents.

ZIF	Modification	Textural Properties	Heavy metal	Experimental conditions	Adsorption capacity (Q _{max} in mg/g)	Removal efficiency (%)	Kinetics	Isotherm	Proposed mechanism	Reference
ZIF-60	–	–	Pb(II)	pH = 4, AD = 0.025 g/L, C = 10 - 400 mg/L, t = 24 h, T = 298 K	1905	–	Avrami Model	Langmuir Model	–	(Ismail et al., 2023a)
ZIF-67	GO composite	–	Hg(II)	pH = 7, AD = 10 mg in 50 mL, C = 10 - 20 mg/L, t = 90 min, T = 298 K	131.07	–	PSO	Freundlich Model	Surface and electrostatic interaction	(Fallatah et al., 2022)
ZIF-8	Fe ₃ O ₄ composite	BET SSA = 996.12 m ² /g, V _t = 0.60 cm ³ /g,	Cu(II)	pH = 6, AD = 50 mg in 50 mL, C = 20 mg/L, t = 60 min, T = 298 K	292.13	–	PSO and PFO	Langmuir Model	–	(Z. Xu et al., 2022)

ZIF-8	Fe ₃ O ₄ core-shell composite	BET SSA = 724.7 m ² /g, Vt = 0.58 cm ³ /g, Pore size = 3.23 nm	Pb(II) and Cu(II)	pH = 5, AD = 0.33 g/L, C = 20 - 260 (Pb(II)) and 20 - 300 (Cu(II)) mg/L, t = 24 h, T = 298 K	719.42 and 301.33	–	PSO	Langmuir Model	Ion-exchange and coordination	(Jiang et al., 2021)
ZIF-8	Fe ₃ O ₄ composite	BET SSA = 160 m ² /g, Vt = 0.33 cm ³ /g,	Cd(II) and Pb(II)	pH = 6, AD = 2.5 mg in 10 mL, C = 10 - 100 mg/L, t = 8 h, T = 298 K	370 and 666.7	–	PSO	Langmuir Model	Coordination interaction	(Abdel-Magied et al., 2022)
ZIF-8	Microflora composite	–	Cd(II)	pH = 7, C = 20 - 300 mg/L, t = 72 h, T = 303 K	276.84	99.91		Freundlich Model	covalent binding and electrostatic attraction	(S. Hou et al., 2022)
ZIF-8	Terephthalic acid (BDC) addition during synthesis	–	Cu(II)	pH = 6.8, AD = 5 mg in 10 mL, C = 100 - 800 mg/L, t = 60 min, T = 298 K	200	–	PSO	Langmuir Model	–	(Latrach et al., 2022)

ZIF-8	Multilayer GO composite	BET SSA = 249.7 m ² /g, pore size = 3 nm	Cu(II)	pH = 6, t = 70 min, T = 308 K	458.2	–	PSO	Langmuir Model	–	(Lv et al., 2022)
ZIF-8	nZVI composite	BET SSA = 208.6 m ² /g, pore size = 10.65 nm	Cr(VI)	pH = 5, AD = 10 mg in 20 mL, C = 50 mg/L, t = 120 min, T = 303 K	–	91.27	PFO	–	Surface adsorption, electrostatic attraction and reduction	(L. Zhou et al., 2022)
ZIF-8	Hydroxyapatite (HApB) modification	BET SSA = 267.22 m ² /g, Vt = 0.17 cm ³ /g, Pore size = 2.485 nm	Ni(II)	pH = 7, AD = 1 g/L, C = 10 - 100 mg/L, t = 40 min, T = 298 K	63.49	99.12	PFO	Freundlich Model	–	(Foroutan, Jamaledin Peighambardoust, et al., 2022)
ZIF-8	Agarose composite	–	Pb(II)	pH = 5 - 7, AD = 10 mg in 25 mL, C = 100 mg/L, t = 120 min, T = 303 K	1088.68	94.18	PSO	–	–	(Q. Fu, Zhou, et al., 2022)

ZIF-8	Cellulose composite	–	Cu(II)	pH = 5, AD = 0.05 g in 50 mL, C = 30 - 700 mg/L, t = 120 min, T = 303 K	270.2	–	PSO	Langmuir Model	Electrostatic attraction and coordination	(T. Cheng et al., 2022)
ZIF-8	GO composite	–	Cu(II)	pH = 6, AD = 0.1 g/L, C = 40 mg/L, t = 120 min, T = 318 K	482.29	–	PFO	Langmuir Model	Ion-exchange and surface complexation	(D. Li & Xu, 2021)
ZIF-67	Chitosan modification	–	Pb(II)	pH = 7, AD = 10 mg in 50 mL, C = 10 -120 mg/L, t = 240 min, T = 303 K	505.01	–	PSO	Langmuir Model	Chelation and ion exchange	(Q. Fu, Lou, et al., 2022)
ZIF-8	Carboxymethyl chitosan beads (BCMC) modification	–	Pb(II)	AD = 20 mg in 10 mL, C = 10 - 800 mg/L, t = 360 min, T = 298 K	566.09	–	PSO	Langmuir Model	Diffusion and sharing/transfer of electrons	(X. Zhu et al., 2022)

ZIF-8	Beta-cyclodextrin and PVDF composite	BET SSA = 1066 m ² /g, Vt = 1.733 cm ³ /g, Pore size = 2.367 nm	Pb(II) and Cu(II)	pH = 5.5, AD = 0.0035 g in 15 mL, C = 50 - 200 mL, t = 2 h, T = 298 K	708.12 and 651.38	–	PSO	Langmuir Model	Electrostatic attraction, surface complexation, and precipitation	(C. Chen et al., 2022)
ZIF-8	Quaternary ammonium modification and chitosan composite	BET SSA = 276 m ² /g,	As(V)	pH = 6, AD = 50 mg in 100 mL, C = 20 - 100 mg/L, t = 6 h, T = 298 K	54.2	–	PSO	Langmuir Model	electrostatic attraction and surface complexation	(S. Zhang et al., 2023)
ZIF-8	Chitosan composite	BET SSA = 285 m ² /g,	As(V)	pH = 6, AD = 50 mg in 100 mL, C = 20 - 100 mg/L, t = 6 h, T = 298 K	38.3	–	PSO	Langmuir Model	Electrostatic attraction and surface complexation	(S. Zhang et al., 2023)
ZIF-8	ZnO composite	BET SSA = 169.09 m ² /g, Vt = 0.18 cm ³ /g, Pore size = 4.27 nm	Pb(II)	pH = 5.0, AD = 10 mg in 10 mL, C = 100 - 1100 mg/L, t = 240 min, T = 303 K	665.27	–	PSO	Langmuir Model	Electrostatic attraction and chelation	(J. Liu et al., 2022)

ZIF-67	Fe ₃ O ₄ and biochar modification	BET SSA = 1212.4 m ² /g, Vt = 1.23 cm ³ /g, Pore size = 4.23 nm	Cd(II)	pH = 7, AD = 1 g/L, C = 10 - 80 mg/L, t = 60 min, T = 298 K	50.78	99.14	PFO	Langmuir and Temkin Model	Surface complexation, cation exchange, electrostatic attraction and precipitation	(Foroutan, Peighambaroust, et al., 2022)
ZIF-8	Chitosan beads composite	BET SSA = 712.7 m ² /g, Vt = 0.28 cm ³ /g, Pore size = 1.13 nm	Cu(II) and Pb(II)	pH = 5, AD = 1.2 g/L, C = 50 - 800 mg/L, t = 5 (Cu(II)) and 2 (Pb(II)) h, T = 298 K	165.7 and 131.4	—	PSO	Langmuir Model	Ion-exchange and coordination reaction	(C. Wang et al., 2022)
ZIF-8	Alginate composite hydrogel	—	Cu(II)	pH = 5, AD = 10 mg in 10 mL, C = 50 - 600 mg/L, t = 24 h, T = 298 K	166.94	—	PSO	Langmuir Model	Electrostatic interaction, ion exchange and complexation	(X. Zhang et al., 2021)
ZIF-67	Sodium alginate composite	BET SSA = 345.34 m ² /g, Vt = 1.95 cm ³ /g, Pore size = 22.56 nm	Cu(II)	pH = 5, AD = 10 mg in 10 mL, C = 600 mg/L, t = 24 h, T = 298 K	153.63	—	PSO	Langmuir Model	Physical adsorption, Coordination interaction and electrostatic attraction	(Z. Li, Guo, et al., 2021)

ZIF-8	Polyacrylonitrile (PAN)/Polyethylenimine (PEI) modification	–	Cr(VI)	pH = 3, AD = 10 mg in 50 mL, C = 20 - 400 mg/L, t = 960 min, T = 298 K	403.5	–	PSO	Langmuir Model	Electrostatic attraction and reduction	(Mohammed et al., 2023)
ZIF-8	GO-COOH functionalization	–	Cu(II) and Pb(II)	pH = 5 (Cu(II)) and 6 (Pb(II)), AD = 1 g/L, C = 50 - 500 mg/L, t = 1 h, T = 298 K	464.26 and 410.05	–	PSO and PFO	Langmuir Model	Coordination and pore channels	(W. Yang & Cao, 2023)

2.4 Effects of adsorption parameters

Considering that adsorption is a surface phenomenon that involves the transfer of mass from liquid or gaseous phase to the surface of a solid, the interaction between the adsorbate and the adsorbent will significantly depend on the environmental conditions/process parameters at which the process happens. Many process parameters including the pH, temperature, contact time, speed of agitation, adsorbent dose and initial adsorbate concentration are of significant importance to the design of the adsorption system. Further, researchers have strong affinity towards varying these process conditions to ascertain the optimum parameters that will be used to explore further microscopic level studies including the adsorption kinetics, interaction mechanisms, isothermal and thermodynamic analysis. This section will briefly discuss how variation in the process parameters affect the performance and efficiency of adsorbents in the removal of heavy metals from contaminated aqueous systems.

The pH is often termed as the most significant process parameter because it does not only affect the chemistry of water, but also the speciation of pollutants in water and the charge on adsorbent surface which is important for electrostatic attraction as an adsorption mechanism (Basu et al., 2017; Semerjian, 2018). The zeta potential or point of zero charge (PZC) analysis is significant as it informs researchers of the pH at which the charge on the surface of an adsorbent changes from positive to negative and vice-versa. When the pH of the system is low, protons will be donated to negatively charged adsorbents, hence, competing with heavy metal ions and reducing the uptake capacity and removal efficiency of the adsorbent toward the specific cationic pollutant (Afroze & Sen, 2018). Furthermore, the protonated adsorbent surface is likely to exhibit charge repulsion which further deteriorates adsorbents' removal efficiency. However, when dealing with adsorption of heavy metals, it is important to keep the pH of the solution within acidic or neutral regions

because of the tendency of heavy metals to precipitate out of the solution at high pH which negates adsorption as the major removal mechanism. The temperature at which the reaction proceeds also has a significant impact on the adsorption capacity of specific adsorbents. When the adsorption process is of physical nature, an increase in reaction temperature within a specific range is beneficial to the process because of the acceleration in the diffusion rate of pollutants through the external boundary layer and into the pores of the adsorbent (Sadat et al., 2019). But when adsorption proceeds in a chemical nature, then it is important to note whether the process is endothermic or exothermic. In a heat-absorbing process (endothermic), an increase in temperature has a positive impact on the adsorption capacity and/or removal efficiency of the adsorbent. However, to improve the efficiency of an adsorbent in an exothermic process, the temperature needs to be reduced (H. Dai et al., 2021). An increase in adsorbent dose generally results in an increase in removal efficiency due to increased adsorption site and available surface area for the uptake of aqueous heavy metals. Nevertheless, there seem to an optimal adsorbent dose above which removal efficiency may be negatively impacted due to agglomeration of particles, this leads to less adsorption site (Panda et al., 2019a). However, adsorption capacity of adsorbent may decrease with an increase in adsorbent dose (Mo et al., 2022). The initial concentration of heavy metal plays a major role in determining the adsorption capacity of an adsorbent towards the heavy metal of interest. This is because an increase in contaminant concentration results in higher adsorption capacity due to improvement in the force that is driving the mass transfer in the solution (Y. Zhang et al., 2016). The increase in mass transfer driving force ensures that resistance between the surface of the adsorbent and the adsorbate molecules is overcome. Increase in agitation speed increases contact between adsorbent and adsorbate resulting in faster kinetics. However, a moderate speed is desired because at high agitation speed, the vortex phenomenon maybe

experienced resulting in an inhomogeneous mixture between the absorbent and the adsorbate solution (Bilal et al., 2022; Tang et al., 2017). The contact time has less significance if the adsorption kinetics is very fast. Nevertheless, the time at which equilibrium is attained is significant to the design of adsorption systems, especially those of intermittent nature. Even though most researchers choose to conduct adsorption studies with a single pollutant, it is uncommon to find such conditions in systems dealing with real wastewater. Hence, some researchers are now finding it worth exploring the effect of ionic strength and other competing ions. Generally speaking, coexisting ions will compete with the target pollutant for active adsorption sites resulting in worsening of adsorption capacity of the adsorbent towards the target pollutant (H. Wang et al., 2015; Xiong et al., 2019). However, if the adsorbent has a high selectivity toward the specific contaminant, then the effect of coexisting ions would not be much of a concern (Z. Cheng et al., 2022). Figure 2.23 diagrammatically depicts the effect of variation of some of the process parameters base on several experimental studies conducted.

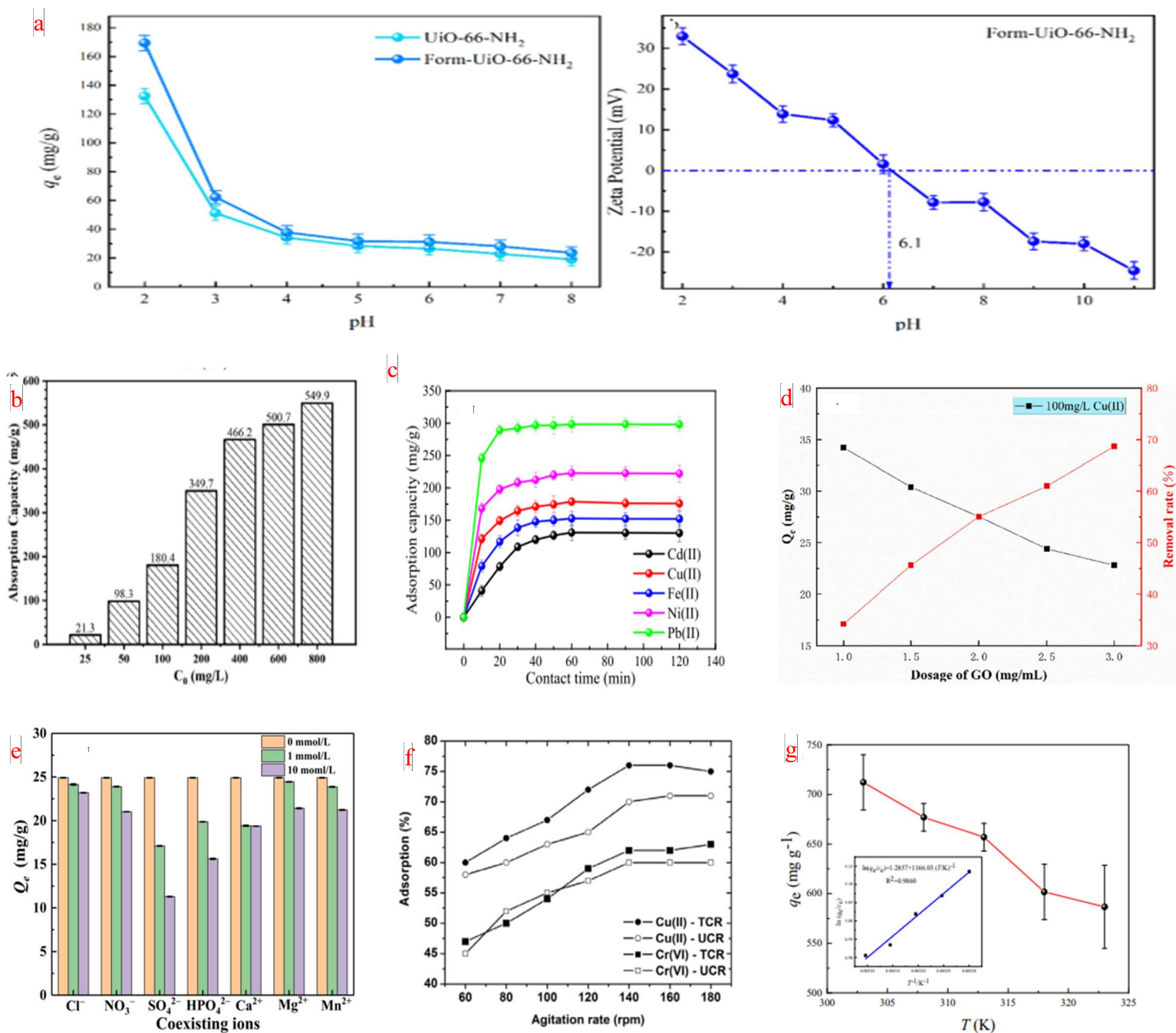


Figure 2.23. a) Effect of pH on the adsorption capacity of UiO-66-NH₂ and Form-UiO-66-NH₂ and the isoelectric point of Form-UiO-66-NH₂ (P. Chen et al., 2023). b) Effect of Cr(VI) initial concentration on adsorption capacity of Cu@MIL-53(Fe) (Yuan et al., 2023). c) Effect of contact time on the adsorption capacity of treated CNT toward several heavy metals (Abdulkareem et al., 2023). d) Effect of adsorbent dosage on removal efficiency and adsorption capacity of GO towards Cu(II) (W. Yang & Cao, 2022). e) Effect of ionic strength of coexisting anions on the uptake of activated carbon (Iron/chitosan modified) toward Cr(VI) (Y. Liu et al., 2023). f) Adsorption of Cr(VI) and Cu(II) onto untreated and treated coffee residue and the effect of mixing speed (Kyzas, 2012). g) Exothermic adsorption as depicted by the effect of temperature on the adsorption capacity of UNCS towards Hg(II) (chitosan modified MOF) (X. Yan & Ge, 2023).

2.5 Adsorption kinetics, isotherms, thermodynamic, and mechanism

The adsorption process is an important advanced treatment unit for abatement of contaminants from water and wastewater. On the microscopic level, the adsorption process appears to be a complicated process that begins with external diffusion, a process that involves movement of adsorbate across the liquid film and to the surface of the adsorbent. This process is followed by diffusion of adsorbate into the pores of the adsorbent, a process known as internal diffusion. The final step involves interaction between the adsorbate and the active sites of the adsorbent (J. Wang & Guo, 2020b). These processes are depicted in Figure 2.24.

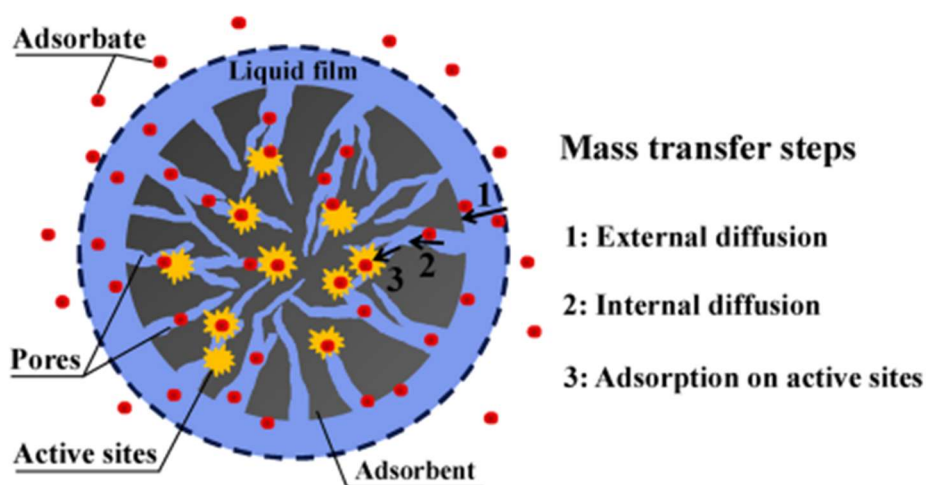


Figure 2.24. Mass transfer steps in adsorption process (J. Wang & Guo, 2020b).

For design of adsorption system that is adequate, an understanding of the adsorption process is required. The use of models to elucidate information regarding the interaction between the adsorbate and the adsorbent is commonly adopted (Oladoja, 2016). Widely used approaches include modelling the adsorption kinetics, isotherm and thermodynamics data to obtain information about reaction pathways, sorption rates, equilibration time and mechanism of adsorption reaction etc. Further, various characterization techniques including X-ray photoelectron spectroscopy (XPS), scanning electron microscope-energy dispersive X-ray (SEM-EDX), Fourier

transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) etc, analysis can be performed on adsorbent before and after adsorption process obtain detailed information regarding the proposed interaction mechanism between the adsorbate and adsorbent. Hence, this section briefly discusses the adsorption kinetics, isotherms, thermodynamics, and mechanisms related to adsorptive removal of heavy metals from aqueous contaminated streams.

2.5.1 Adsorption kinetics

Adsorption kinetics equations play a vital role in elucidating reaction pathways and provide room for hypothesizing adsorption mechanism for a certain pollutant given a specific reaction condition. Information as regards to how the adsorption rate is affected by the amount of aqueous sorbent or the adsorption capacity of the material under study is obtained after conducting kinetic studies. These details are valuable in the design of adsorption-based treatment systems, as they often define the detention time, which in turn has a direct relationship with volume of the tank required for effective treatment and flow rate of the system (Oladoja, 2016). Consequently, several adsorption kinetics models to which experimental data is fitted to are available and some of the most commonly used include pseudo-first-order (PFO), pseudo-second-order (PSO), Weber-Morris intra-particle diffusion (W-M IDP), Avrami and Elovich models. Most of the literature available on adsorption kinetic studies adopted the coefficient of determination (R^2) as the quality parameter to determine which of respective models provides the most fitting for the obtained kinetics experimental data. Depending on how the data is well fitted to the various kinetic models, several deductions about the adsorption process can be made. Data fitting well to the PFO model is indicative of a physisorption process that is controlled by internal/external diffusion and further highlights that there are few active sites in the adsorbent for which the adsorbate ion/molecule can interact with (X. Guo & Wang, 2019a; J. Wang & Guo, 2020b). An overwhelming majority of the

articles reviewed throughout this work were well fitted to the PSO model suggesting that the adsorption process is of chemical nature (chemisorption) and the adsorbents' available active sites influence the adsorption rate as well as the adsorption capacity (C. Fan et al., 2018; H. Wang et al., 2007). Fitting adsorption kinetics data to the intra-particle diffusion model would give information as regards to whether surface diffusion, internal pore diffusion or both processes are the rate limiting step of the entire adsorption process (Igwe et al., 2008). The Elovich model is based on the assumptions that adsorption time and activation energy are directly proportional and that the adsorbent has a heterogeneous surface. The Elovich model widely adopted the chemical adsorption of gas onto solids, however, it has also been used to model the adsorption of organic pollutants and metal ions on adsorbents (Elovich & Larionov, 1962). Table 2.12 gives the mathematical notations of the commonly used adsorption kinetics models as well as their linearized form where available. However, caution needs to be taken when applying these equations to model the adsorption process because some of them are purely empirical and the reasoning behind the deductions made from them has been faulted recently (H. N. Tran et al., 2017). Secondly, more often than not, the data fits well to more than one of the kinetics models, hence, making it difficult to make conclusive deduction about the mechanism governing the adsorption process. Further, the adsorption kinetics data obtained by many studies is fitted to the linearized form of the model due to the simple nature of linear regression analysis, however, in some instances, the parameters obtained after the analysis of the linear and non-linear forms of the models are widely disparate, hence, putting the linear analysis into question (Han et al., 2007; Ho, 2006; K. L. Tan & Hameed, 2017).

Table 2.12 Adsorption kinetic models and mathematical notations

Kinetic Model	Non-linear (integrated form)	Linear form	Plot	Model terms
PFO	$q_t = q_e(1 - e^{-k_1 t})$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$\ln(q_e - q_t) \text{ vs } t$	k_1 = rate constant (min^{-1})
PSO	$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	$\frac{t}{q_t} \text{ vs } t$	k_2 = rate constant ($g \cdot (mg \cdot \text{min})^{-1}$)
W-M IDP		$q_t = k_{id} \sqrt{t} + B$	$q_t \text{ vs } \sqrt{t}$	k_{id} = IDP rate constant ($mg \cdot (g \cdot \text{min}^{0.5})^{-1}$)
Elovich	$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t)$	$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t$	$q_t \text{ vs } \ln t$	α = initial adsorption rate ($mg \cdot (g \cdot \text{min})^{-1}$) β = desorption constant ($g \cdot mg^{-1}$)
Bangham		$\log \left(\log \frac{C_o}{C_o - q_t \cdot m} \right) = \log \left(\frac{k_o m}{2.303 V} \right) + \delta \log \cdot t$	$\log \left(\log \frac{C_o}{C_o - q_t \cdot m} \right) \text{ vs } \log \cdot t$	k_o and δ are model constant
Avrami	$q_t = q_e - \frac{q_e}{(k_n q_e^{n-1} t(n-1) + 1)^{\frac{1}{n-1}}}$: $n \neq 1$	$\ln \left(\ln \frac{q_e}{q_e - q_t} \right) = n \cdot \ln k + n \cdot \ln t$	$\ln \left(\ln \frac{q_e}{q_e - q_t} \right) \text{ vs } \ln t$	k = model constant (min^{-1}) n = model constant (dimensionless)

$q_t(\text{mg} \cdot \text{g}^{-1})$ = adsorption capacity at time t , $q_e(\text{mg} \cdot \text{g}^{-1})$ = adsorption capacity at equilibrium, $t(\text{min})$ = time, $C_o(\text{mg} \cdot \text{L}^{-1})$ = initial concentration.

2.5.2 Adsorption isotherms

The study of isotherm data is the most adopted approach used for exploring the mechanism of adsorption which is important to the design of adsorption systems and adsorbents. The adsorption isotherm reveals information about the performance of adsorbents in a system in a system that has reached equilibrium at a constant temperature. It also gives information about the maximum

adsorption capacity ($q_{\max}$), a significant parameter in determining the suitability of an adsorbent for a certain sorbate (Al-Ghouti & Da'ana, 2020; J. Wang & Guo, 2020a). As such, a variety of adsorption isotherms models to which the experimental data is fitted to are available and some of the commonly used include linear (Henry's law), Freundlich, Redlich-Peterson (R-P), Sips, Temkin, Dubinin-Radushkevich (D-R), Toth and BET isotherm models. Similar to the approach adopted in kinetics modelling, the R^2 is the most widely used tool for model evaluation. Depending on how well the data fits to the respective isotherm models, several inferences can be made about the mechanism of adsorption or some properties of the adsorbent/adsorbate. For example, the Henry's isotherm model gives information about the partitioning of adsorbate between the solid and liquid phases through physical adsorption mechanisms such as the van der Waals interactions, electrostatic interaction and hydrophobic interactions (X. Guo & Wang, 2019c, 2019b; J. Wang & Guo, 2020a). Experimental data fitting well to the Langmuir Isotherm model is suggestive of macroscopic homogeneous adsorption process whereas a good fit to the Freundlich model indicates a multilayer adsorption process on a heterogeneous surface (J. Wang & Guo, 2020a; F. C. Wu et al., 2010). The R-P isotherm is a three-parameter model that is a hybrid of Freundlich and Langmuir isotherm model created to overcome their inherent shortcomings. Both models assume that the interaction between adsorbate and adsorbent is strictly a heterogeneous or homogeneous adsorption process. However, when the R-P constant is very large, then it is assumed to be a Freundlich isotherm model whereas if it approaches 1 then it can be safely approximated as Langmuir Isotherm model (F. C. Wu et al., 2010). Similarly, the Sips model is another hybrid model that combines Freundlich and Langmuir model (Sips, 2004). The Toth model isotherm model is based on the assumption that adsorption energies of the majority of adsorption sites is less than the mean energy and it was developed to extend the application of the Langmuir model

to heterogenous systems (Ho et al., 2002). D-R isotherm model is linked to the distribution of Gaussian energy onto heterogeneous surface and it is commonly adopted to describe the adsorption of gases and vapors on microporous adsorbents (Al-Ghouti & Da'ana, 2020; Çelebi et al., 2007). Temkin isotherm model is only valid for intermediate range of concentration and assumes that heat of all molecules which is a function of temperature to be declining linearly as surface coverage increases (Aharoni & Ungarish, 1977; Vadi et al., 2013). The BET isotherm model is theoretical adsorption isotherm that has been used to compute the specific areas and pore size of adsorbents while the Aranovich isotherm model is a modified version of the BET isotherm model. Table 2.13 gives the mathematical notations of the commonly used adsorption isotherm models with both linearized and non-linear forms presented where available. Similar concerns experienced while using the kinetic models are also experienced when the adsorption isotherm models are used to model experimental data.

Table 2.13 Adsorption isotherm models and mathematical notations

Isotherm Model	Non-linear (integrated form)	Linear form	Plot	Model terms
Henry's law		$q_e = K_{HE} C_e$	q_e vs C_e	K_{HE} =Henry's Constant (Dimensionless)
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	$\log q_e$ vs $\log C_e$	K_F (L.g ⁻¹) and n (dimensionless) are model constants
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L C_e}$	$\frac{C_e}{q_e}$ vs C_e	K_L = Langmuir Constant (L.mg ⁻¹) q_m = Maximum adsorption capacity (mg.g ⁻¹)
R-P	$q_e = \frac{K_R C_e}{1 + a_R C_e^g}$	$\ln \left(K_R \frac{C_e}{q_e} - 1 \right) = g \ln(C_e) + \ln(a_g)$	$\ln \frac{C_e}{q_e}$ vs $\ln C_e$	K_R (L.g ⁻¹) and a_g (L ^g .mg ^{-g}) and g are model constants
Sips	$q_e = \frac{q_m K_s C_e^{\frac{1}{n}}}{1 + K_s C_e^{\frac{1}{n}}}$	$\ln \left(\frac{q_e}{q_m - q_e} \right) = \frac{1}{n} \ln(C_e) + \ln(K_s)$	$\ln \left(\frac{q_e}{q_m - q_e} \right)$ vs $\ln(C_e)$	K_s (L..g ⁻¹) and n (dimensionless) are model constant.

Toth	$q_e = \frac{K_T C_e}{(a_T + C_e)^{\frac{1}{t}}}$	$\ln\left(\frac{q_e}{K_T}\right) = \ln(C_e) - \frac{1}{t} \ln(a_T + C_e)$	$\ln\left(\frac{q_e}{K_T}\right) \text{ vs } \ln(C_e)$	K_T (mg.g ⁻¹), a_T (mg ^t .L ⁻¹) is the Toth constant. t is a constant
D-R	$q_e = q_s e^{-K\varepsilon^2}$	$\ln q_e = q_s - K\varepsilon^2$; $\varepsilon = RT \ln \frac{C_s}{C_e}$	$\ln q_e \text{ vs } \varepsilon^2$	K (mol ² .kJ ⁻²) is model constant, q_s (mg.g ⁻¹) is the maximum amount adsorbed, ε (kJ.mol ⁻¹) is the Polanyi potential
Temkin	$q_e = \frac{RT}{b_T} \ln A_T C_e$	$q_e = \frac{RT}{b_T} \ln A_T + \left(\frac{RT}{b_T}\right) \ln C_e$	$q_e \text{ vs } \ln C_e$	A_T (L.g-1) and b_T (J.mol ⁻¹) are model constants
BET	$q_e = \frac{q_m C_{BET} C_e}{(C_s - C_e) \left[1 + (C_{BET} - 1) \left(\frac{C_e}{C_s}\right)\right] \left[1 + (C_{BET} - 1) \left(\frac{C_e}{C_s}\right)\right]}$	$\frac{C_e}{q_e(C_s - C_e)} = \frac{1}{q_m C_{BET}} + \frac{(C_{BET} - 1) C_e}{q_m C_{BET} C_s}$	$\frac{C_e}{q_e(C_s - C_e)} \text{ vs } \frac{C_e}{C_s}$	C_{BET} = constant (dimensionless), q_m = maximum adsorption capacity (mg.L ⁻¹), C_s (mg.L ⁻¹) = solubility of the adsorbate

q_e (mg.g⁻¹) = adsorption capacity at equilibrium, C_e (mg.L⁻¹) = concentration at equilibrium, R = Universal gas constant (8.314 J mol⁻¹K⁻¹), q_m = Maximum adsorption capacity (mg.g⁻¹).

Considering that the generated isotherm models are only valid at a given temperature, it is important to understand how variation in the reaction temperature affects the interaction between the adsorbate and the adsorbent, and also the maximum adsorption capacity. Hence, conducting a thermodynamics investigation to reveal the value of thermodynamic parameters including the enthalpy change (ΔH), entropy change (ΔS) and standard free energy change (ΔG) becomes important. The value of the standard free energy change (ΔG) denotes the spontaneity of the adsorption process, a negative value indicates that the reaction is favourable and spontaneous under the given reaction conditions whereas a positive value denotes the opposite (Al-Ghouti & Da'ana, 2020; Saha & Chowdhury, 2011; Ullah et al., 2020). The value of entropy change (ΔS) gives information about the affinity of the adsorbent towards the adsorbate, a positive value indicates significant randomness in the solid-solution layer of the adsorption system and a process that is entropy driven (Abdel-Magied et al., 2019; Lyu et al., 2017a). If the value of ΔH is computed to be positive, then it means that the adsorption process is endothermic and an increment in temperature is beneficial to the process whereas a negative ΔH is indicative of an exothermic process and the uptake of the contaminant by the adsorbent would benefit from lowering the temperature of the system (Al-Ghouti & Da'ana, 2020; Saha & Chowdhury, 2011; Ullah et al.,

2020). Further, the magnitude of ΔH could be used to elicit information about the nature of adsorption process. A value less than 20 kJ mol^{-1} indicates that physisorption process is dominant while chemisorption dominates the process if the value of ΔH is between $80 - 400 \text{ kJ mol}^{-1}$. A value between $20 - 80 \text{ kJ mol}^{-1}$ indicates a combination of both chemisorption and physisorption processes (Andersson et al., 2011). The following equations are used to compute the values of the thermodynamics parameters:

$$\Delta G = -RT \ln K_o \quad \text{III}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{IV}$$

$$\ln K_o = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \text{V}$$

Where the universal gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$) is denoted by R, T is the system temperature in K, ΔG (kJ mol^{-1}), ΔS ($\text{kJ mol}^{-1}\text{K}^{-1}$) and ΔH (kJ mol^{-1}). The value of K_o , which is an equilibrium constant is obtained as the intercept of the plot of $\ln \frac{q_e}{C_e}$ vs q_e . ΔH and ΔS are computed from the slope and intercept of $\ln K_o$ vs $\frac{1}{T}$ as depicted in Equation 5. It is worth noting that many researchers adopt the wrong approach in computing K_o by assuming wrong constants such as using the distribution coefficient K_d (L.g^{-1}), however, the correct approach to computing K_o is through conducting isothermal studies (Lima et al., 2019, 2020).

2.5.3 Adsorption mechanism

There exist a variety of adsorptive mechanisms through which heavy metals can be removed from aqueous systems after the introduction of adsorbents into the system. Some of the mechanisms include electrostatic interaction, pore filling and diffusion, formation of complexes through coordination interaction and chelation, chemical bonding, acid-base interaction and van der Waals

interactions etc. These processes can be broadly classified as physisorption and chemisorption processes. The physical adsorption process is commonly referred to as adsorptive adsorption whereas chemical adsorption process is termed as reactive adsorption (N. A. Khan et al., 2013b). The major distinction between the two processes is the strength of the interaction between the adsorbate and the adsorbent (Sims et al., 2019). In physisorption, adsorbates are bond onto adsorbents through weak interaction forces while adsorption in chemisorption process is achieved through the formation of covalent bond between the adsorbents and adsorbates which involves transfer or sharing of electrons. Hence, chemisorption interactions are two orders of magnitude stronger than physisorption interactions (Al-Ghouti & Da'ana, 2020). For this reason, physical adsorption processes tend to be reversible in nature whereas chemical adsorption processes are irreversible (Kaushal, 2017). This has major implications for the selection of efficient and cost-effective adsorbent since there is need to regenerate adsorbents after treatment, and operators of treatment plants prefer bonds that could be easily broken, this eases the adsorbent regeneration process. Hence, adsorption in which physisorption processes dominates is preferred for large scale industrial applications. This section briefly discusses adsorptive and reactive adsorption mechanisms and also highlights some of the other removal pathways that adsorbents may exhibit in addition to the adsorption process in water treatment systems.

The electrostatic interaction is a significant type of physisorption process that depends on the surface charge of the adsorbent and the charge of the interacting adsorbate. Negatively charge adsorbent will attract positively charge heavy metal ion leading to interactions such as London and Dipole-dipole forces (Hasan & Jhung, 2015). Adsorptive removal due electrostatic interaction is largely dependent on the isoelectric point of the adsorbent and the speciation of heavy metal ion in solution both of which are a function of the solution pH. Other weak interactions could result

from van der Waals forces (intermolecular forces), hydrogen bonding and hydrophobic interactions (Bilal et al., 2022). The diffusion of heavy metals into pores of adsorbents is another physical adsorption means through which aqueous heavy metal could be removed from contaminated media. Contaminants may fill the pores of the adsorbent and get trapped without any chemical interaction, hence, physically abated. As for chemical adsorption, reaction between heavy metal ions and functional ligands on the surface of adsorbent through coordination interaction is a major removal mechanism (X. Feng et al., 2022). This results in the formation of complexes with metal occupying the central position and bounded by ligand to form a mononuclear complex. In the case of more than one metal occupying the central position, then polynuclear complexes are formed. Chelation is an advanced type of complexation where polydentate ligands are involved and structures that are very stable are formed due to the multiple bonding that is involved (Bilal et al., 2022). Other forms of chemical bonding that results in strong interaction between the adsorbate and adsorbent may also exists. The hard/soft acid/base (HSAB) theory has been used as the basis for explanation of heavy metal ion removal through the acid-base interaction. As postulated by the HSAB theory, hard acids react in a strong manner with hard base while soft acid reacts have strong reaction toward soft base (Moradi, 2014). The HSAB theory was used to explain the removal of lead and cadmium both of which are soft acids by thiol group which is a soft base in HS-mS@MOF-5 (J. Zhang et al., 2016). The Lewis acid-base theory which depends on electron pair acceptor and donor relation also plays a role in explaining the reactive adsorption processes for removal of aqueous heavy metals. However, it is worth noting that more than one mechanism is involved in the removal of pollutants from aqueous streams. An understanding of the major mechanisms that are involved for the removal of specific pollutants is important, especially in the real wastewater streams where it is required to remove multiple

pollutants at a time. Various micro-spectroscopy analyses techniques including X-ray photoelectron spectroscopy (XPS), X-ray absorption fine structure (XAFS), nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR) etc. are used to investigate the mechanism of interaction between the adsorbate and adsorbent. Further, due to the nature of the functional materials currently in used and under investigation for adsorptive removal of aqueous contaminants, other pathways for removal of contaminants like oxidation and reduction, precipitation and ion exchange etc, happen simultaneously with adsorption and also contribute to the removal of contaminants in addition to the adsorptive removal (J. Xu et al., 2018).

Table 2.14 presents a list of adsorbents that have been recently experimentally tested for the removal of heavy metals from contaminated aqueous media along with the reported best fit adsorption kinetics and isotherm models, thermodynamic nature of adsorption and the proposed adsorption and other associated mechanisms.

Table 2.14 Summary of findings from heavy metals adsorption studies for different types of adsorbents.

Adsorbent	Adsorbate	Experimental Conditions	Fitting Kinetic model	Fitting isotherm Model	Thermodynamic nature	Proposed Mechanism	Reference
Fe ₃ O ₄ @ZIF-8	Pb(II) and Cu(II)	pH = 5, AD = 0.33 g/L, C = 20 - 260 (Pb(II)) and 20 - 300 (Cu(II)) mg/L, t = 24 h, T = 298 K	PSO	Langmuir Model	Exothermic	Ion-exchange and coordination	(Jiang et al., 2021)
ZiF-8 and microflora composite (ZMC)	Cd(II)	pH = 7, C = 20 - 300 mg/L, t = 72 h, T = 303 K	–	Freundlich Model	Exothermic	Covalent binding and electrostatic attraction	(S. Hou et al., 2022)

Fe ₃ O ₄ @ZIF-8	Cd(II) and Pb(II)	pH = 6, AD = 2.5 mg in 10 mL, C = 10 - 100 mg/L, t = 8 h, T = 298 K	PSO	Langmuir Model	Endothermic	Coordination interaction	(Abdel-Magied et al., 2022)
ZIF-8@GO	Cu(II)	pH = 6, AD = 0.1 g/L, C = 40 mg/L, t = 120 min, T = 318 K	PFO	Langmuir Model	Endothermic	Ion-exchange and surface complexation	(D. Li & Xu, 2021)
ZIF67@Chitosan	Pb(II)	pH = 7, AD = 10 mg in 50 mL, C = 10 - 120 mg/L, t = 240 min, T = 303 K	PSO	Langmuir Model	Endothermic	Chelation and ion exchange	(Q. Fu, Lou, et al., 2022)
BCMC@ZIF-8(Carboxymethyl chitosan beads (BCMC))	Pb(II)	AD = 20 mg in 10 mL, C = 10 - 800 mg/L, t = 360 min, T = 298 K	PSO	Langmuir Model	Endothermic	Diffusion and sharing/transfer of electrons	(X. Zhu et al., 2022)
beta-CD@ZIF-8	Pb(II) and Cu(II)	pH = 5.5, AD = 0.0035 g in 15 mL, C = 50 - 200 mg/L, t = 2 h, T = 298 K	PSO	Langmuir Model	Endothermic	Electrostatic attraction, surface complexation, and precipitation	(C. Chen et al., 2022)
ZIF-8/CS-N	As(V)	pH = 6, AD = 50 mg in 100 mL, C = 20 - 100 mg/L, t = 6 h, T = 298 K	PSO	Langmuir Model	Endothermic	Electrostatic attraction and surface complexation	(S. Zhang et al., 2023)
ZIF8/Chitosan	As(V)	pH = 6, AD = 50 mg in 100 mL, C = 20 - 100 mg/L, t = 6 h, T = 298 K	PSO	Langmuir Model	Endothermic	Electrostatic attraction and surface complexation	(S. Zhang et al., 2023)
ZnO@ZIF-8	Pb(II)	pH = 5.0, AD = 10 mg in 10 mL, C = 100 - 1100 mg/L, t = 240 min, T = 303 K	PSO	Langmuir Model	Exothermic	Electrostatic attraction and chelation	(J. Liu et al., 2022)
Banana biochar/Fe ₃ O ₄ /ZIF-67	Cd(II)	pH = 7, AD = 1 g/L, C = 10 - 80 mg/L, t = 60 min, T = 298 K	PFO	Langmuir and Temkin Model	Exothermic	Surface complexation, cation exchange, electrostatic	(Foroutan, Peighambaroust, et al., 2022)

						attraction and precipitation	
ALG@ZIF-67	Cu(II)	pH = 5, AD = 10mg in 10 mL, C = 600 mg/L, t = 24 h, T = 298 K	PSO	Langmuir Model	Endothermic	Physical adsorption, Coordination interaction and electrostatic attraction	(Z. Li, Guo, et al., 2021)
PAN/PEI@ZIF-8	Cr(VI)	pH = 3, AD = 10 mg in 50 mL, C = 20 - 400 mg/L, t = 960 min, T = 298 K	PSO	Langmuir Model	Endothermic	Electrostatic attraction and reduction	(Mohammed et al., 2023)
ZIF8@GO-COOH	Cu(II) and Pb(II)	pH = 5(Cu(II)) and 6 Pb(2+), AD = 1 g/L, C = 50 - 500 mg/L, t = 1, T = 298 K	PSO and PFO	Langmuir Model	Endothermic	Coordination and pore channels	(W. Yang & Cao, 2023)
UiO-66-SO ₃ H	Cd(II) and Pb(II)	pH = 6, AD = 0.02 g in 40 mL, C = 1000 mg/L, t = 2 h, T = 298 K	PSO		Exothermic	Chemisorption and coordination interaction	(S. Gul et al., 2022)
Chitosan (CS) grafted UiO-66-NH ₂ (CGUNCN)	Cu(II) and Pb(II)	pH = 6.5, AD = 0.25 g in, C = 400 and 600 mg/L, t = 160 min, T = 298 K	PSO	Langmuir Model	Endothermic	Physical adsorption and complexation	(Hu et al., 2022)
LDH/UiO-66-(Zr)-(COOH) ₂	Hg(II) and Ni(II)	pH = 3 and 8.0, AD = 2 mg in 20 mL, C = 0.5 - 50 mg/L, t = 120 min, T = 295 K	Avrami and PFO	Langmuir Model	—	Complexation	(Soltani et al., 2021)
nFe ₃ O ₄ @MIL-88A(Fe)/APTMS	Cd(II), Pb(II) and Cr(VI)	pH = 6 (Cd(II)), 6 (Pb(II)) and 2 (Cr(VI)), AD = 20 mg in 10 mL, C = 0.04 - 0.4 mol/L, t = 60 min, T = 298 K	PSO	Langmuir Model	Endothermic	Coordinate bonding (cationic species) and ion-pair attraction forces (anionic species)	(M. E. Mahmoud et al., 2020)

UiO-66 EDA	Pb(II), Cd(II) and Cu(II)	pH =6 , AD = 8 mg in 10 mL, C = 20 - 300 mg/L , t = 360 min, T = 298 K	PSO	Langmuir Model	Endothermic	Electron exchange, electron sharing, electrostatic and covalent interaction	(Ahmadijokani et al., 2021)
Ti-MOF-SH	Hg(II) and Pb(II)	pH = 5, AD = 10 mg in 10 mL, C = 150 - 400 mg/L, t = 24 h, T = 298 K	PSO	Langmuir Model	Endothermic	Chelation and electrostatic attraction	(B. Zeng et al., 2023)
AMO-MOF	Pb(II)	pH = 4, AD = 10 mg in 10 mL, C = 500 mg/L, t = 20 h, T = 298 K	PSO	Langmuir Model	Exothermic	Chelation and electrostatic attraction	(H. Wang et al., 2023)
UiO-66-NDC/GO	Pb(II)	pH = 6, AD = 0.5 g/L, C = 50 - 250 mg/L, t = 150 min, T = 298K	PSO	Temkin Model	Exothermic		(S. Singh, U, et al., 2023)
thioglycollic grafting	Hg(II)	pH = 5, AD = 0.1 g/L, C = 120 mg/L, t = 180 min, T = 298 K	PSO	Langmuir Model	Endothermic	Chelation and pore size diffusion	(C. Ji et al., 2022)
UiO-66-DMP (4,6-diamino-2-mercaptopyrimidine)	Hg(II)	pH = 7, AD = 2 mg in 4 mL, C = 400 mg/L, t = 3 h, T = 298 K	PSO	Langmuir Model	Exothermic	Electrostatic and covalent interactions	(Chai et al., 2022)
UiO-66-EDTMPA (ethylenediamine tetramethylene phosphonic acid	Pb(II), Cd(II) and Cu(II)	pH =5.5 , AD = 20 mg in 20 mL, C = 200 - 1000 (Pb(II)), 50 - 400 (Cd(II)) and 25 - 300 (Cu(II)) mg/L, t = 2 h , T = 298 K	PSO	Langmuir	Endothermic	Coordination and hydrogen bond interaction	(Y. Yan et al., 2022)
Carbon materials/Ni/Al ₂ O ₃	Pb(II)	pH = 6, AD = 0.05 mg in 50 mL, T = 298 K, t = 8 h, C = 20 - 400 mg/L	PSO	Langmuir Model	Endothermic	Complexation, electrostatic attraction, pi electron cation interaction	(Z. Wang, Qin, et al., 2021)
O-CNTs	Pb(II)	pH = 5.6 - 5.8, AD = 5 mg in 8 mL, C = 0 - 200	PSO	Langmuir Model	Exothermic	Pore filling, complexation, ion exchange,	(J. Zhang et al., 2021)

		mg/L T = 298 K, t = 48 h,				Electrostatic attraction and cation-pi interaction	
G-CNTs	Pb(II)	pH = 5.6 - 5.8, AD = 5 mg in 8 mL, C = 0 - 200 mg/L T = 298 K, t = 48 h,	PSO	Langmuir Model	Exothermic	Pore filling, complexation, ion exchange, electrostatic attraction and cation-pi interaction	(J. Zhang et al., 2021)
MWCNTs	Cr(VI)	pH = 2, AD = 0.05 g in 50 mL, C = 100 - 200 mg/L, T = 298 K, t = 20 h,	PSO	Langmuir Model	Endothermic	Ion-exchange, intra-particle diffusion and electrostatic attraction	(B. Verma et al., 2021)
Oxidized MWCNTs	Cr(VI)	pH = 2, AD = 0.05 g in 50 mL, C = 100 - 200 mg/L, T = 298 K, t = 20 h,	PSO	Langmuir Model	Endothermic	Ion-exchange, intra-particle diffusion and electrostatic attraction	(B. Verma et al., 2021)
CNTs/GP (geopolymer)	Pb(II) and Ni(II)	pH = 5, AD = 0.2 - 40 g/L (Pb(II)), 1 - 60 g/L (Ni(II)), C = 100 mg/L, T = 298 K, t = 10 h,	PSO	Langmuir Model	Endothermic	Physisorption, chemisorption and ion-exchange	(S. Yan et al., 2022)
Polyamine-CNT	Cd(II)	pH = 6, AD = 30 mg in 20 mL, C = 1 - 5 mg/L, T = 298K, t = 2h ,	PSO	Freundlich Model	Endothermic	complexation, functional group interaction, pi-metal interaction and electrostatic attraction	(Adelabu et al., 2020)
Steel slag-CNTs composite (SS@CNTs)	Pb(II) and Cu(II)	pH = 6.5, AD = 20 mg in 100 mL, C = 80 - 160 mg/L (Pb(II)) and 40 - 160 mg/L (Cu(II)) T = 298 K, t = 3 h,	PSO	Langmuir Model	Endothermic		(P. Yang et al., 2022)
nZVI/Mxene@CNTs	As(III)	pH = 3, AD = 0.4 g/L, C = 200 mg/L, T = 298 K, t = 120 min,	PSO	Langmuir Model	Endothermic	Surface complexation, solid phase precipitation and	(S. Li et al., 2022)

						catalytic oxidation	
CNT@PDA@PEI composite	Cu(II)	pH = 7, AD = 10 mg in 50 mL, C = 10 mg/L, T = 298 K, t = 60 min,	PSO	Langmuir Model	Endothermic		(L. Guo et al., 2020)
rGO-Mn ₃ O ₄	Pb(II) and Cr(III)	pH = 4, C = 10 - 140 mg/L, t = 60 (Pb(II)) and 120 (Cr(III)) min, T = 298 K, AD = 0.5 g/L	PSO	Langmuir Model	Endothermic	pi electron donor-acceptor interaction, ion-exchange, electrostatic attraction and surface complexation	(Lingamdinne et al., 2022)
Nitrogen-enriched lignosulfonate exfoliated GO (N-LEGO)	Cr(VI)	pH = 2, T = 298 K, AD = 0.4 g/L, C = 10 - 250 mg/L, t = 2100 min	PSO	Freundlich Model for Cu(II) and Cd(II), Langmuir Model for Pb(II)	Endothermic	Electrostatic attraction, adsorption coupled reduction, Surface chelation, cationic adsorption and low C = adsorption	(J. Geng et al., 2022)
GO-COOH	Cu(II) and Pb(II)	pH = 5 (Cu(II)) and 6 (Pb(II)), T = 298 K, C = 100 mg/L, AD = 1 g/L, t = 120 min	PSO	Langmuir Model	Endothermic	Electrostatic attraction and active sites adsorption	(W. Yang & Cao, 2022)
Poly-cyanoguanidine/GO composite (DCDA-GO)	Hg(II)	pH = 5, AD = 1 g/L, T = 298 K, C = 200 mg/L, t = 8 h.	PSO	Freundlich Model	Endothermic	Chelation	(H. Lin et al., 2022)
GO	Pb(II)	pH = 4, AD = 0.25 g/L, T = 293 K, C = 100 - 1250 mg/L, t = 20 min	PSO	Langmuir Model	Exothermic		(Azam et al., 2022)
Montmorillonite-rGO	Cd(II)	pH = 6.5, t = 1440 min, T = 298 K	PSO	Langmuir Model	Exothermic		(S. Zhou et al., 2022)

Partially reduced GO	Hg(II)	pH = 7, C = 150 mg/L, T = 298 K, AD = 2.5 mg in 50 mL, t = 0.5 h.	PFO and PSO	Langmuir Model	Exothermic	Electrostatic attraction	(Tene et al., 2022)
ZnO/rGO-PEG	Cr(VI)	pH = 3, t = 75 min, = AD = 0.8 g/L, T = 303 K, C = 300 mg/L	PSO	Langmuir Model	Endothermic		(Rout & Jena, 2022)
ZnO/C-Foam/GQDs/Alginate	Pb(II)	pH = 6, AD = 10 mg in 10 mL, C = 100 mg/L, t = 30 min, T = 298 K	PSO	Langmuir model	Endothermic		(M. E. Mahmoud et al., 2022)
Magnetic-GO lanthanum sulfide nanoparticle decorated (MGO@LaS)	Pb(II)	pH = 5, t = 40 min, C = 5 - 200 mg/L, T = 298K,	PSO	Langmuir model	Endothermic	Electrostatic attraction and coordination	(Rezania et al., 2022)
nZVI@HPAC(hydrophilic activated carbon)	Pb(II)	pH = 5.0, T = 323 K, t = 120 min, AD = 0.05 g in 100 mL, C = 10 - 300 mg/L	Avrami fractional-order model	Langmuir Model	Endothermic	Electrostatic attraction, complexation, chemical precipitation and reductive action	(Qu et al., 2021)
GB/nZVI (Graphene-like biochar)	As(III)	pH = 4, T = 298 K, AD = 0.2 g/L, C = 40 mg/L, t = 120 min	PSO	Langmuir Model	–	Inner sphere complexes formation and partial oxidation	(K. Liu et al., 2020)
nZVI@LDH	V(V)	pH = 3.0, AD = 0.5 g/L, C = 50 mg/L, T = 298 K, t = 6 h	PSO	Freundlich Model	–	Complexation, reduction to V(III) and transformation to vanadium oxide	(Kong et al., 2020)
mZVI/AC (Activated carbon)	Cr(VI)	pH = 3, C = 10 mg/L, AD = 1 g/L T = 298 K, t = 120 min	PSO	Langmuir Model		Adsorption, reduction and precipitation	(W. Wang et al., 2020)
E-LDH (etidronic acid intercalation)	Zn(II) and Fe(III)	pH = 5, C = 50 - 500 mg/L, t = 60, T = 298 K	PSO	Langmuir Model	Endothermic	Chelation	(S. Zhu et al., 2022)

polyethylene glycol modified LDH	Cu(II), Pb(II) and Cd(II)	AD = 0.03 in 20 mL, t = 240 min, pH = 5.01 C = Cu(II) and Cd(II) = 10-800 mg/L, Pb(II) = 20 - 1000 mg/L T = 298 K	PSO	Langmuir Model	—	Precipitation and complexation	(W. Song et al., 2023)
LDH/MoS ₄	Pb(II) and Cd(II)	pH = 5, C = 50 - 1000 mg/L, AD = 1 g/L, T = 298 K, t = 1440 min	PSO	Langmuir Model	—	chelation and isomorphic substitution, complexation	(F. He et al., 2022)
MgCuCaAl-LDH	Pb(II)	pH = 5.5, T = 298 K, t = 5 h, AD = 0.1 g on 100 mL, C = 300 mg/L	PSO	Sips Model	Endothermic	Physisorption	(Mahmoudi et al., 2022)
MgAl-LDH/Cys (L-cysteine)	Pb(II) and Cd(II)	pH = 6, C = 10 - 1000 mg/L, AD = 1 g/L, t = 720 min, T = 298 K	PSO	Freundlich Model	—	isomorphous replacement, precipitation, chelation	(D. Wang et al., 2022)
MgAl-LDH	Cr(VI)	pH = 2, C = 50 - 200 mg/L AD = 0.5 - 6 g/L, t = 90 min, T = 323 K	PFO	Langmuir Model	Endothermic	Intercalation, ion-exchange, other sphere complexation, precipitation and substitution	(B. Zeng et al., 2022)
Rarasaponin aliginate bentonite composite	Cr(VI)	pH = 3, C = 1000 mg/L, AD = 0.5 g in 100 mL, T = 50, t = 8 h	PFO	Freundlich Model	—		(Santoso et al., 2023)
Bentonite clay modified HTDMA (hexadecyl trimethyl ammonium bromide)	Pb(II)	pH = 5.0, t = 120 min, T = 303 K, AD = 0.2 g in 100 mL, C = 50 - 200 mg/L	PSO	Sips Model	Exothermic	Inner sphere complexation	(Dinh et al., 2022)
sepiolite@polyethyleneimine/sodium alginate modification	Pb(II)	pH = 5.5, T = 298 K, AD = 1.0 g/L, C = 200 mg/L T = 24 h	PSO	Langmuir Model	Endothermic		(X. Wu et al., 2022)

TiO ₂ supported on acid-activated kaolinite clay TiO ₂ (TiO ₂ -aac)	Mn(II), Fe(III), Pb(II) and Cu(II)	Mining wastewater, pH = 5.2, t = 120 min, C = 4.291, 20.013, 0.975 and 0.3113 mg/L, T = 343 K	PSO	Langmuir Model	Endothermic	Electrostatic interaction	(Ajala et al., 2022)
X-PI3, X-OLJ1 and X-TPb bacteria	Pb(II)	pH = 5.0, C = 100 mg/L, AD = 0.2 g/L, t = 60 min	PSO	Langmuir Isotherm	–	Ion exchange, microprecipitation and surface complexation	(N. Wang et al., 2019)
Bacillus Subtilis lipopeptides	Pb(II)	pH = 4 T = 298 K, AD = 35 mg in 50 mL, C = 100 mg/L, t = 30 min	PFO	Langmuir Model	–	Complexation and chelation	(P. Zhao et al., 2020)
Extracellular polymeric substances (EPS) extracted from the Klebsiella sp. NT8 and Bacillus sp. NT10 (EPS-K and EPS-B)	Hg(II)	pH = 6.0, C = 100 mg/L, AD = 5 mL 50 mg/L EPS in x mL, t = 3.5 h, T = 298 K	PSO	Langmuir Model	–	Complexation and chelation	(Xia et al., 2020)
Scoria@UF1 (microbial material)	Pb(II) and Cd(II)	AD = 0.2 g in 50 mL, C = 1 mmol/L, T = 298 K, t = 24 h, pH 6-9	PFO	Langmuir Model	Endothermic	surface complexation, microprecipitation and biological fixation	(H. Song et al., 2021)
Fe ₃ O ₄ @TCA@CS	Pb(II)	pH = 5.5, T = 298K, AD = 0.015 g in 25 mL, t = 180 min, C = 20 mg/L	PFO	Freundlich Model	Exothermic	Electrostatic attraction, coordination interaction	(Algamdi et al., 2023)
Chitosan-pectin gel beads	Cu(II), Cd(II), Hg(II) and Pb(II)	pH = 7, C = 100 mg/L, AD = 50 mg in 50 mL, T = 298 K.	PSO	Langmuir Model	–	Complexation	(Z. Shao et al., 2021)
CsSB/MnFe ₂ O ₄ @BC (Chitosan Schiff base and MnFe ₂ O ₄)	Cr(VI)	pH = 2.0, t = 360 min, AD = 10 mg in 100 mL, C = 40 mg/L, T = 308 K	PSO	Freundlich Model	–	Ion exchange, surface complexation, electrostatic attraction and pore adsorption	(L. Yan et al., 2023)

Thermally treated sugarcane bagasse	Hg(II)	pH = 6, AD = 0.01 g in 50 mL, C = 1 mg/L, t = 2 h, T = 298 K	PSO	Langmuir, Freundlich, Temkin and D-R Model	–	Complexation, electrostatic attraction	(Giraldo et al., 2020)
Bermuda grass derived activated carbon	Cr(VI)	pH = 2.0, AD = 0.5 g/L, C = 50 -400 mg/L, T = 298 K	PSO	Langmuir model	–	Adsorption, reduction, precipitation	(Tu et al., 2020)
water hyacinth derived activated carbon functionalized with 2-aminothiazole (AT-MAC)	Hg(II)	pH = 5.5, t = 60 min, C = 50 mg/L, 0.1 g in 10 ml, T = 298 K	PSO	Langmuir model	–	Complexation, chemisorption	(Waly et al., 2021)
KOH activated Enteromorpha prolifera derived biochar	Cd(II)	pH = 7, C = 5 - 100 mg/L, AD = 0.02 -0.16 g in 25mL. T = 298 K	PSO	Langmuir model	–	Electrostatic attraction	(C. Wang et al., 2021)
					–	Physical sorption, ion exchange, electrostatic attraction, coordination through complexation	(Shahokhi-Shahaki et al., 2021)
Tire derived activated carbon	Pb(II)	pH = 7, AD = 0.2g in 50 mL, t = 24 h, C = 500 mg/L	PSO	Langmuir model	–	Electrostatic attraction, surface complexation, co-precipitation	(Z. Zhang et al., 2021)
Rape straw powder	Cd(II)	pH = 6.0, AD = 0.25 g/L, t = 12 h, temp, 298 K	PSO	Freundlich model	–		

2.6 Conclusions and future outlooks

The increase in concentration levels of heavy metals in aqueous environment calls for urgent need for innovative and cost-efficient ways for their treatment. Even though some of the contamination originates from natural sources including leaching of metals from rocks into surface and groundwater, a good proportion of it stems from anthropogenic sources related to urbanization, industrial, mining, agricultural and domestic activities. Hence, it is important for regulators and

policy makers to enforce policies that prevent major emitters of aqueous heavy metals from discharging their highly contaminated effluent directly into the receiving environment. This should be done to ensure that contamination levels are kept in check and prevented from reaching levels that would otherwise be catastrophic. One approach that could be adopted is the treatment of contaminated effluent prior to its discharge. However, for this approach to work effectively and efficiently, the chosen treatment method needs to be simple in terms of operation and of relative low-cost. Further, due to the recalcitrant nature of aqueous heavy metals, treatment methods like photocatalysis, reduction and oxidation are not very efficient in degrading them into benign products.

Adsorption due to its specific merits, is seen as a treatment approach that can be used to combat the increase in various heavy metals contamination levels in aqueous streams. When dealing with adsorption as a contaminant abatement technique, the most important factors to consider include the type and class of the adsorbent material and the target adsorbate. Due to the various combination of adsorbent and adsorbate that are available, there have been a lot of studies that discussed the adsorptive removal of specific heavy metal/metals using a certain adsorbent. Therefore, this review articles focused on tracking the progress on the adsorptive removal of heavy metals from the aqueous environment using adsorbents that are derived from activated carbon, natural materials, biosorbents, clay minerals, LDHs, ZVIs, graphene, CNTs, MOFs and ZIFs. Further the suitability and challenges associated with using the different classes of the adsorbents were discussed. Most of the articles that were documented were published in the current decade and the adsorption capacity along with the removal efficiency were used as the performance measure for determining the suitability of adsorbents for the removal of the target pollutant. Further, the review highlighted the effect of adsorption process parameters on the performance of

adsorbents and also presented a section on the importance of interaction mechanism between the adsorbent and adsorbate which can be postulated through modelling techniques (adsorption kinetics, isotherms and thermodynamic investigation) or other sophisticated characterization techniques (SEM, XAFS, XPS, NMR FTIR analysis etc.).

Even though there has been a lot of progress on studies involving the adsorptive removal of heavy metals using novel adsorbents, most of the studies employed the use of synthetic water with only a single heavy metal spiked into it to evaluate the adsorptive performance of the material under study. While the progress is welcomed, this is far from the reality as real wastewater consists of complex mixture of both organic and inorganic contaminants, hence, it will be essential to test the performance of developed adsorbents under such complex conditions before its efficient against the targeted pollutant can be confirmed. Further, most of the studies employ a batch adsorption set up to investigate the performance of adsorbents for decontamination of heavy metals infested water, however, most commercial and treatment processes are set up in continuous nature for obvious reasons, therefore, it is imperative for adsorption studies to be conducted in such a nature if researchers are serious about scaling up the treatment process that they are studying at the laboratories.

Most of the adsorbents that are reported in this review article are functionalized/hybrid materials, however, most researchers did not systematically study the effect of combining functional materials with the parent materials. Rather, the focus was on studying the effect of varying the adsorption parameters on the performance of the synthesized adsorbent. The suitability and effectiveness of the fabricated material toward the removal of specific heavy metal/metals can be significantly improved if the synthesis procedure of the composite material is optimized.

The issue of functionalizing adsorbents is also related to the cost of fabricating composite materials. While natural adsorbents like clay minerals, natural waste materials, siliceous materials and biosorbents are cheap and abundant, their performance and selectivity are relatively poor when compared with more sophisticated materials that are CNTs, graphene and MOFs based. As such, large quantities of these low-cost adsorbents are needed for efficient aqueous heavy metal treatment. However, as adsorption is a phase transfer phenomenon, once these sorbents are spent, they will need to be disposed of which will lead to another environmental hazard in the form of solid waste contamination. As for the more sophisticated material that are CNTs, graphene, MOFs and ZIFs based, their stability in water is a subject of major concern. For example, ZIFs materials are known to leach the metal atom in the secondary building unit (SBU) and the imidazole linker when in contact with water while CNTs and graphene were also reported to be toxic to both flora and fauna. However, these issues are rarely reported or studied in the literature that has been reviewed in this article. For these novel adsorbents to be adopted in real wastewater treatment facilities, details about the setbacks that may be encountered when using them needs to be reported so that effective approach to counter the challenges can be developed and adopted.

The recovery and reusability of adsorbents from treated water are factors of significant importance from health, environmental and economic perspectives. Adsorbents that are not recovered get into the environment translating not only into the loss of valuable functional materials but also might present a threat to the environment because of contaminants that are bound to it. In an ideal situation, adsorbents that are recovered should be regenerated and reused even after numerous cycles of treatment. However, it must be noted that the performance of adsorbents generally declines after the first few cycles and that the regeneration process is quite tedious and involves the use of expensive and somewhat harmful substances like concentrated acids and bases.

Nevertheless, once adsorbents become spent and can no longer be regenerated, then disposal becomes a necessity. Commonly adopted disposal approaches include landfilling and incineration. While the former cause soil and groundwater pollution due to the leaching of contaminants, the latter causes air pollution due to the release of ash and harmful gases generated as a result of the process. As such, innovative ways of reusing spent adsorbents need to be studied and discussed to avoid secondary contamination. Some of the alternatives include the use of adsorbents as fillers for construction materials, drilling fluid formulation, binders in asphalt and in fire retardants. All in all, very few studies discuss the fate of spent adsorbents, even though it is an area of research that is worth exploring.

Further, many studies adopt a non-sophisticated experimental approach such as the point of zero charge test, adsorption kinetics, isotherm and thermodynamic investigations to obtain information as regards to the heavy metal adsorption mechanism of the synthesized adsorbent. However, the molecular complexity of the adsorption process makes the findings on the interaction mechanism only speculative. Sophisticated equipment such as the extended X-ray absorption fine structure (EXAFS), X-ray absorption near edge structure (XANES), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and X-ray photoelectron spectroscopy (XPS) can be used in real time to study the adsorbate-adsorbent interaction for detailed and conclusive investigation about the interaction mechanism. However, it must be noted that this approach is also very challenging to adopt due to the complex nature of real wastewater and the cost associated with the use of such intricate techniques. As such, theoretical and computation techniques such density functional theory, molecular docking and machine learning techniques can be used to complement the sophisticated experimental approach. The major challenge as regards the use of the theoretical and computational approach is the lack of technical know-how, researchers and scientist would

greatly benefit if they invested time and resources into learning the principles and usage of such techniques in the field of adsorptive removal of heavy metals from the aqueous environment.

To sum up, the volume of literature published in the current decade on the adsorptive removal of heavy metals from aqueous contaminated media is a clear indication that adsorption has a role to play in decontamination of water and effluent infested with such pollutants. However, despite the promising performance shown by many adsorbents in terms of uptake of single contaminants in a batch operation system, the large-scale application of these novel materials in complex environmental systems is still a long shot. Nevertheless, breakthrough innovations often emerge slowly, and if the shortcomings and the challenges, many of which have been mentioned as regards to the application of adsorbents for the removal of heavy metals from water are to be addressed, then adsorption can emerge as the most suitable large scale and commercial treatment method for abatement of heavy metal contamination from the environment.

CHAPTER 3

Research Objectives

The specific objectives of the research work are listed below:

1. To synthesize ZIF based material that can be used for the effective removal of heavy metals from aqueous systems.
2. To optimize the performance of the synthesized ZIF based material for the removal of selective heavy metal species from aqueous streams.
3. To study the removal behaviour of the synthesized ZIF based material toward selective heavy metal species under a varying set of process conditions.

CHAPTER 4

Aqueous Pb(II) removal using ZIF-60: Adsorption studies, response surface methodology and machine learning predictions

4.1 Introduction

Demand for water is increasing across the globe because of industrial and agricultural growths, and the steady increase in human population. Additionally, the rate at which water bodies are contaminated endangers human health (Shannon et al., 2008). Thus, World Health Organization (WHO) projects that by 2025, about 50% of the global population will suffer from freshwater shortage (Bilal et al., 2022). Thus, it is essential to treat water as a valuable resource. Heavy metals as a class of inorganic contaminants are considered as both toxic and recalcitrant pollutants present in polluted waters (M. Verma et al., 2022). Because of their widespread use in industrial processes, they are injected into the aquatic streams as part of industrial effluent. Many of the heavy metals are hazardous substances that are mutagenic, carcinogenic and teratogenic that can migrate with water flow, as such presenting multiple routes for human exposure. Further, they can be taken up by plants and animals resulting in bioaccumulation and biomagnification (Ibrahim et al., 2022; Rehman et al., 2018; Sankhla et al., 2016). In particular, ingestion of lead above the permissible limit (10 and 15 ng/L according to WHO and USEPA, respectively) can result in hepatitis, anemia, encephalopathy and nephritic syndrome (S. Singh, N, et al., 2023). Thus, it is important to find innovative ways for the effective removal of lead from aqueous systems.

Many technologies including electrolysis (L. Q. Huang et al., 2014), ion-exchange (Maliou et al., 1992), chemical precipitation (Matlock et al., 2002), coagulation (Aljaberi, 2018; Matlock et al.,

2002), phytoremediation (D. Singh et al., 2012), and adsorption (Goel et al., 2005) have been applied and improved for the treatment of water contaminated with lead (Mo et al., 2022). While every method has its own advantages, most of them suffer from certain drawbacks that limit their applicability on industrial scale operations. However, adsorption has emerged as a suitable treatment method due to its simplicity, efficiency, low cost and ability to remove multiple pollutants from waste streams (Ismail et al., 2023b). Traditional adsorbents such as activated carbon, chitosan, biomass, molecular sieves and polymers have been widely used to remove water pollutants. However, their adsorption capacity is often not high, in addition to their poor selectivity towards many contaminants (Chairunnisa et al., 2021), making the development of more effective adsorbents a necessity.

Zeolitic imidazolate frameworks (ZIFs), a subclass of the metal organic frameworks (MOFs), have recently emerged as attractive materials for various applications such as drug delivery, catalysis and energy storage (K. Ahmad et al., 2022; Furukawa et al., 2013b). ZIFs are crystalline materials with large porosity and specific surface area which may reach up to 10,000 m²/g, making them interesting candidates for adsorption of contaminants from water (Furukawa et al., 2013b; Y. Liu et al., 2021). They also usually possess better thermal and chemical stabilities relative to MOFs. ZIFs permanent porosity allows for easy introduction of functional groups which can help increase active site for efficient adsorption, hence, creating functional materials (Y. Liu et al., 2021). Further, the structure of ZIFs which is made up of a metal node, organic linker and available surface functional groups leads to its several documented heavy metal removal mechanisms including ion-exchange, pore diffusion, coordination and many others makes them appealing adsorbents (H. Dai et al., 2021; G. R. Xu et al., 2021). However, so far, studies on the application of ZIFs for water decontamination mainly focus on ZIF-8 and ZIF-67. Ahmad et al. (K. Ahmad et

al., 2021) synthesized both ZIF-67 and ZIF-8, and applied them for the removal of lead from contaminated water with adsorption capacity reaching up to 1978.6 and 1780.9 mg/g, respectively. Huang et al. (Y. Huang et al., 2018b) also developed ZIF-67 and ZIF-8, and tested their performance for lead adsorption from aqueous solutions; they found that the lead adsorption capacity reached 1348.4 and 1119.8 mg/g, respectively. Although ZIF-8 and ZIF-67, and their composites, have been widely studied in the literature, the application of other ZIF materials (e.g., ZIF-60) for water decontamination is still greatly lacking.

Therefore, the key objective of this study is to investigate the removal of lead from contaminated water samples using ZIF-60. To the best of our knowledge, this is the first study on utilizing ZIF-60 for the adsorptive removal of any water pollutants. The effect of varying the process parameters on the removal of lead were studied using the response surface methodology (RSM) technique and regression models were developed using the same technique. Furthermore, classical adsorption studies including adsorption kinetics, isotherms and thermodynamics were also conducted. Finally, the obtained experimental data were used to develop machine learning algorithms that were used for the prediction of lead removal from aqueous solutions using ZIF-60 adsorbent. The field of machine learning and artificial intelligence is gaining prominence in many disciplines, however, it has been scarcely applied in aspects pertaining to the use of novel materials for water treatment applications. Hence, another key objective of this study is to use the obtained experimental data for testing the predictive performance of machine learning algorithms in terms of lead removal from contaminated water samples using ZIF-60 material.

4.2 Materials and methods

4.2.1 Chemicals and analytical instruments

The reagents employed in this study were of high purity including zinc nitrate hexahydrate (Sigma-Aldrich), imidazole (Sigma-Aldrich), 2-methylimidazole (Sigma-Aldrich), N,N-dimethylformamide (Honeywell), tri-ethyl amine (Sigma-Aldrich), sodium hydroxide (EMSURE®), lead nitrate (BDH), hydrochloric acid (Fisher Scientific). Ultra-pure water (CORNING Mega Pure™) was used for sample preparation and dilution. The glassware used were thoroughly washed, cleaned and dried before each use.

X-ray diffractometer (XRD Rigaku Miniflex-II) was used to investigate the crystal phases of the synthesized ZIF-60; current was set at 15 mA while the CuK α 1 radiation was kept at 40 kV. The 2 θ angle range for the analysis was set between 5 to 40° at a scanning rate of 7.00°/min. Thermal stability of ZIF-60 was tested using thermogravimetric analysis (TA Instruments) in N₂ atmosphere using a heating rate of 10 °C/min in the temperature range from 30 to 800 °C. FTIR spectra were collected using Smart iTR NICOLET iS10 FTIR spectroscopy for surface functional groups investigation.

The lead concentration in the aqueous solutions was determined using atomic absorption spectroscopy (PerkinElmer); the samples were passed through 0.2 μ m filter (Whatmann) before subjecting them to analysis. pH measurements were conducted using OAKTON® pH 700.

4.2.2 Synthesis of ZIF-60

Herein, the solvothermal method was employed for the synthesis of ZIF-60 as reported by Yaghi group (Banerjee et al., 2008) with some modifications. Briefly, 2.68 g zinc nitrate hexahydrate was added to 60 mL N,N-dimethylformamide (DMF) and stirred till it dissolved. A separate solution was prepared by adding 1.84 g imidazole and 0.74 g 2-methylimidazole and stirred till completely

dissolved. The two solutions were then mixed together and 1 mL tri-ethyl amine was injected to the mixture. The obtained solution was then stirred for 1 h, at room temperature, with the aid of a magnetic stirrer while the beaker was carefully covered with aluminium foil to avoid the absorption of water moisture. The mixture was then transferred to an autoclave reactor and incubated in an oven (Fisher Scientific) for 48 h at 85 °C. Afterwards, synthesized ZIF-60 was first washed with N,N-dimethylformamide using a centrifuge (Sigma Laborzentrifugen GmbH) followed by several washes with de-ionized water. The washed sample was then placed in the oven at 50 °C until it completely dried out. The dried ZIF-60 was stored in tightly closed vials until use.

4.2.3 Experimental design

The study made use of a multivariate approach instead of the traditional univariate approach to conduct the experiments. The effects of the process parameters and their interaction were explored using the RSM technique. The experiments were designed with three factors in a typical face-centered central composite design (M. Vohra et al., 2022). The independent variables of the study include ZIF-60 dose, lead initial concentration and the temperature at which the experiments were conducted while the dependent variable (response) was the percentage removal of lead. The factors of interest and their respective levels are presented in Table 4.1.

Table 4.1 Independent variables and their respective levels as employed in the RSM modeling.

Factors	Level		
	-1	0	1
A = adsorbent dose (g/L)	0.025	0.05	0.075
B = lead concentration (ppm)	50	100	150
C = temperature (°C)	25	35	45

Several regression models were generated for response prediction, and the model that provided the best fit of the experimental data was selected and reported based on several quality parameters including the coefficient of determination (R^2), adjusted and predicted R^2 . Along the same line,

the analysis of variance (ANOVA) was used to confirm the validity and performance of the generated models. Design Expert version 13 software was employed for the RSM modelling and ANOVA technique.

4.2.4 Batch adsorption experiments

Initially, a 1000-ppm stock solution of lead was prepared by dissolving the analytical grade lead in de-ionize water. Serial dilution was then used to prepare the desired lead concentrations. For each test, 100 mL of the desired lead concentration was placed in 125 mL Pyrex flask prior to the addition of the required adsorbent dose. The mixture was then placed inside an incubator shaker (Bioevopeak) and kept for 24 h at the required temperature. An agitation speed of 250 rpm was used throughout the experiments. The lead removal efficiency and the adsorption (uptake) capacity were then computed using Equations 1 and 2, respectively.

$$R = \frac{C_o - C_e}{C_o} \times 100 \quad 1$$

$$qe = \frac{C_o - C_e}{m} \times V \quad 2$$

Where R, q_e , C_o and C_e represent the removal efficiency (%), adsorption capacity (mg/g), lead initial concentration (ppm) and lead concentration (ppm) after 24 h of experiment. V represents sample volume in litres and m is the amount of adsorbent added in g.

For adsorption kinetics experiments, a ZIF-60 dose of 0.025 g/L was used while the lead initial concentration was fixed at 150 ppm. The temperature was kept at 25 °C and aliquots were collected at different time intervals between 10 and 1440 min, and subjected to analysis. Adsorption isotherm experiments were conducted for 24 h at 25 °C, a ZIF-60 dose of 0.025 g/L was added while the lead initial concentration was varied over a range of 10 – 400 ppm. As for

thermodynamics study, a ZIF-60 dose of 0.05 g/L was fixed as well as an initial lead concentration of 100 ppm using an equilibration time of 24 h. The temperature was varied within the range of 25 – 45 °C. All lead solutions were prepared at an initial pH of 4 to ensure that the removal is attributed to the addition of ZIF-60 and not lead hydroxide precipitation. Lead exists mainly as Pb(II) at pH less than 6.0; however, slightly above this pH, precipitates and other Pb compounds begin to appear (Jamshidifard et al., 2019; W. Yang & Cao, 2023).

4.2.5 Machine learning algorithms

The use of machine learning algorithms for the prediction of adsorbent performance in removing contaminants from aqueous streams is gaining prominence (Kooh et al., 2022; Lingamdinne et al., 2023; Nguyen et al., 2022). However, the application of machine learning and other artificial intelligence approaches to the field of wastewater treatment is limited by the availability of experimental data due to various cost and operational factors. As such, this study collated the batch adsorption experimental data that were obtained and used them to test the predictive performance of several machine learning algorithms. The statistical summary of the dataset used for this investigation is given in Table 4.2. Further, short descriptions of the working principles of the algorithms used in this study are also presented below.

Table 4.2 Descriptive statistics of the dataset used in machine learning study.

	Adsorbent dose (g/L)	Lead concentration (mg/L)	Temperature (°C)	Removal Efficiency (%)
Mean	0.0394	128.462	30.769	63.310
Standard Error	0.004	22.474	1.586	6.149
Median	0.025	100	25	68.980
Mode	0.025	50	25	#N/A
Standard Deviation	0.020	114.593	8.086	31.353
Sample Variance	0.0004	13131.540	65.385	983.030
Kurtosis	-0.727	4.284	-0.727	-1.201
Skewness	0.960	2.011	0.960	-0.428
Range	0.05	490	20	91.75
Minimum	0.025	10	25	7.74
Maximum	0.075	500	45	99.49
Sum	1.025	3340	800	1646.062
Count	26	26	26	26

Artificial neural network (ANN)

ANN is also termed as multi-layer perceptron and it is one of the most widely used artificial intelligence techniques. It derives its concept from the mathematical delineation of the nervous system (McCulloch & Pitts, 1943). The structure of ANN consists of three distinct layers with the first recognized as the input layer while the last is the output layer. In between them is the hidden layer which can be one or several. The layers consist of multiple neurons in the form of nodes which are connected to each other. Weights between the nodes can be altered to enhance the model performance with the help of an appropriate cost function. Activation functions such as sigmoid and rectified linear unit (ReLU) are used for nonlinear computations. Back propagation technique is often used to train the model (Sadek et al., 2023). The illustration of the feed forward-ANN is given in Figure 2.1a and the ANN output prediction is given by Equation 3.

$$y = f(W + B) \quad (3)$$

y represents the output, W is the weight, B stands for bias and f is the activation function.

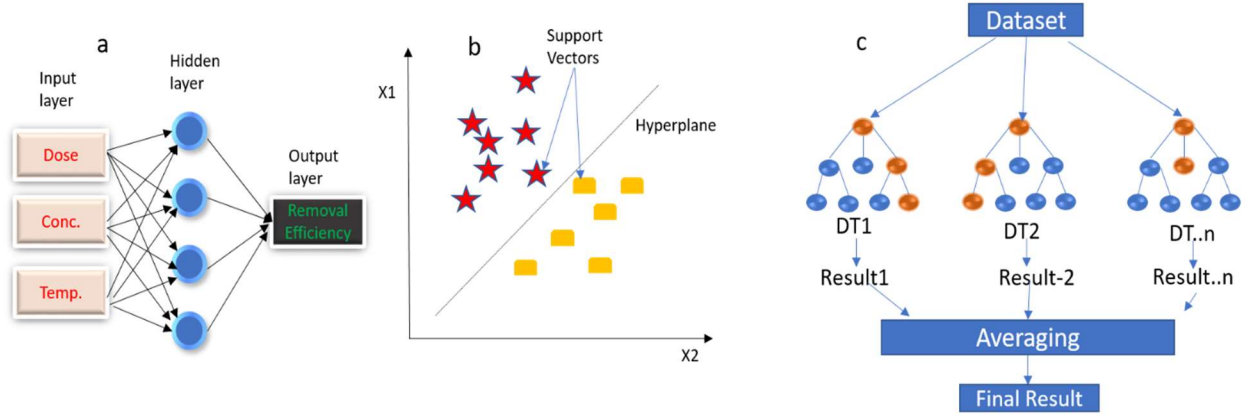


Figure 4.1. a) Structure of the ANN algorithm, b) SVM classification using linear hyperplane, c) Architecture of the RF algorithm.

Support Vector Machine (SVM)

While the SVM was originally devised to solve classification problems, it has been developed to solve regression problems even with relatively small sized dataset (M. Li et al., 2019). This is because the SVM works on the concept of mapping input vector into feature space that is of high dimension. This enables the SVM to distinguish between two classes in the feature space by drawing a hyperplane between the increased margin separating the classes involved (Alam et al., 2022). Different kernel functions are used to obtain the mapping. The working principle of the SVM is depicted in Figure 4.1b while Equation 4 is used to generate the output.

$$y = \sum_{i=1}^n \alpha_i K(x_i, x_j) + b \quad (4)$$

Where y is the predicted output value, α_i is the Lagrange multiplier, $K(x_i, x_j)$ is the kernel function, and b represents a threshold parameter.

Random Forest (RF)

The random forest is considered as an ensemble learning technique that uses several decision trees to solve regression or classification problems. The random forest was derived to solve the inherent problems including computational cost and overfitting that are associated with the decision tree (DT). Output prediction with the random forest begins with a random sampling with replacement. Several decision trees are generated and ran independently with their outputs finally aggregated to come up with a single output (Beigzadeh et al., 2020). The schematic representation of the random forest working principle is given in Figure 4.1c.

The Waikato Environment for Knowledge and Analysis (WEKA) version 3.8.6 was used to build the above prediction models. The N-fold cross validation was used for training and validation of the generated models. To evaluate model performance, correlation coefficient (R), R^2 and RMSE were used.

4.3 Results and Discussion

4.3.1 Material characterizations

To confirm the formation of ZIF-60, a comparison between the FTIR spectra of the organic linkers (imidazole and 2-methylimidazole) and the as-synthesized ZIF-60 was conducted. As shown in Figure 4.2a, the various broad and strong N-H bands between around 3300 and 2500 cm^{-1} present in the FTIR spectra of the precursors have disappeared from the spectra of the as-synthesized ZIF-60. Further, the sharp peak at around 3125 cm^{-1} and the weak band close to 1815 cm^{-1} ascribed to C-H vibration are also not present in the as-synthesized ZIF-60 FTIR spectra. This gives an indication that the imidazole and 2-methylimidazole are fully deprotonated upon the formation of ZIF-60 structure (X. Li et al., 2015b; F. Xu et al., 2013).

In addition to FTIR analysis, XRD characterization of the as-synthesized ZIF-60 was also conducted and the results are shown in Figure 4.2b. The intense peaks at several positions of the XRD profile of ZIF-60 displayed indicate the crystalline structure of the synthesized material. Peaks appeared at diffraction angles of 7.68° , 10.80° , 15.24° , 16.20° , 17.25° , 18.69° , 27.00° , 31.65° , and 36.03° are similar to those found in other ZIF structures (K. Y. A. Lin & Chang, 2015; T. van Tran et al., 2020). The most intense peak was noted at a diffraction angle of 15.24° , and it is in an agreement with previous literature in which ZIF-60 was synthesized (Banerjee et al., 2008; F. Xu et al., 2013).

To probe the thermal stability of the as-synthesized ZIF-60, the material was subjected to thermal treatment under an inert atmosphere (i.e., nitrogen) up to 800°C , and results are shown Figure 4.2c. As displayed in this figure, there is a negligible material loss (less than 2.5 wt.%) upon heating ZIF-60 up to 520°C . This signifies that the as-synthesized ZIF-60 is as thermally stable as other ZIF materials (Banerjee et al., 2008; Lyu et al., 2017a). Increasing the temperature beyond 520°C resulted in an accelerated decrease in the sample weight. This relatively fast weight loss is due to thermal decomposition of the ZIF structure (Y. Liu et al., 2010; Schejn et al., 2014). Despite the significant material loss from the ZIF-60 framework at high temperatures (i.e., $> 520^{\circ}\text{C}$), which is also the case for other ZIFs (Banerjee et al., 2008; I. U. Khan et al., 2018; Y. Liu et al., 2010; Lyu et al., 2017b; Qian et al., 2012; Schejn et al., 2014), this is not a concern for utilizing ZIF-60 for mild to moderate temperature processes. TGA analysis was conducted post lead adsorption (Figure 4.2d) and the lead adsorbed ZIF-60 showed somewhat less stability at higher temperature that could result from respective adsorption interaction.

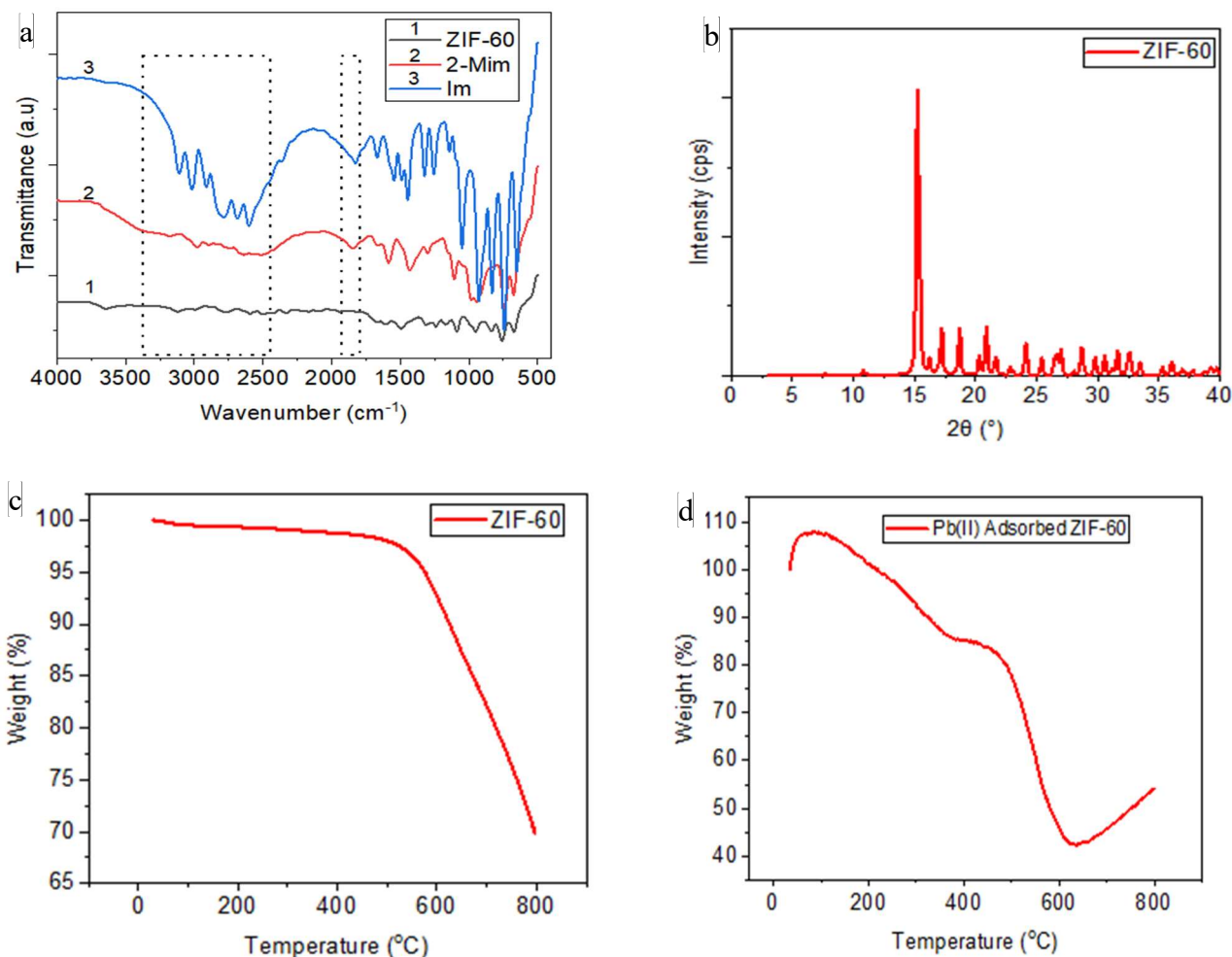


Figure 4.2. (a) FTIR spectra of ZIF-60 and organic precursors (b) XRD pattern of ZIF-60 (c) its TGA analysis plot and (d) TGA analysis plot of post lead adsorbed ZIF-60

4.3.2 Response Surface Methodology and Analysis of Variance

The adsorption experiments were conducted based on the runs generated by the RSM model and the full design matrix together with the experimental lead removal (%) presented in

Table 4.3. It is noted that at least 99.0% lead removal is achieved when an adsorbent dose of 0.075 g/L is used and lead initial concentration is kept at 50 ppm, independent of the adsorption temperature. Overall, the experiments indicate that ZIF-60 can be used to efficiently remove lead

from contaminated water streams based on the excellent performance of ZIF-60 at varied initial concentrations of lead as shown in

Table 4.3.

Table 4.3 RSM design matrix for lead removal experiments.

Std	Run	A:Dose g/L	B:Concentration Ppm	C:Temperature °C	Removal Efficiency %
1	1	0.025	50	25	71.5
12	2	0.05	150	35	49.6
3	3	0.025	150	25	28.3
8	4	0.075	150	45	74.1
13	5	0.05	100	25	77.4
10	6	0.075	100	35	96.9
14	7	0.05	100	45	94.8
2	8	0.075	50	25	99.5
7	9	0.025	150	45	29.7
9	10	0.025	100	35	55.4
4	11	0.075	150	25	62.3
6	12	0.075	50	45	99.0
11	13	0.05	50	35	98.4
5	14	0.025	50	45	66.5
15	15	0.05	100	35	84.2

The results were used to generate regression models, and the quadratic model was selected because it provided a strong correlation between the experimental and the predicted lead removal. The R^2 , adjusted R^2 and predicted R^2 values were found to be 97.65, 93.41 and 78.22%, respectively. The visualization of the good fitting between the actual and the predicted lead removals is given in Figure 4.3. The difference between the adjusted and predicted R^2 was found to be less than 20%, which further signifies the adequacy of the quadratic model (Hussaini & Vohra, 2022; Labaran & Vohra, 2017). The generated quadratic model is given by Equation 5.

$$\text{Removal Efficiency} = 84.70 + 18.05 A - 19.09 B + 2.50 C + 2.24 AB + 1.87 AC + 2.33 BC - 8.70 A^2 - 10.83 B^2 + 1.23 C^2 \quad (5)$$

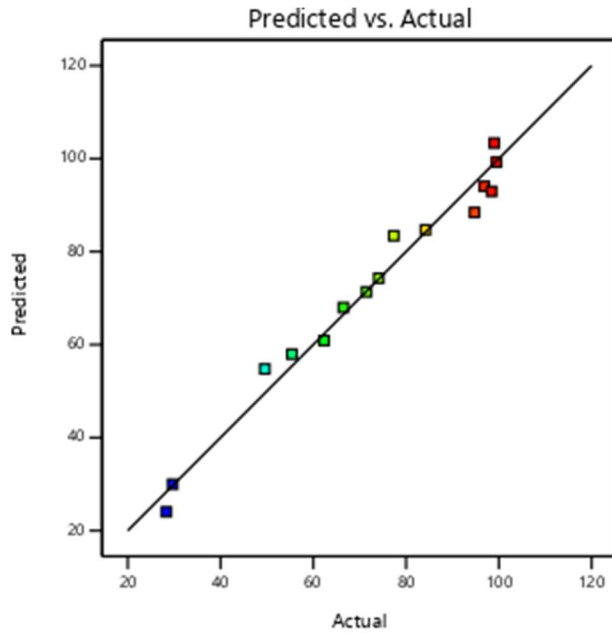


Figure 4.3. Plot of predicted lead removal efficiency vs actual lead removal efficiency.

The RSM based results were further subjected to analysis of variance to understand the factors that most significantly affect the response, and also to reveal the effect of varying the process parameters on the removal of lead from the aqueous system under study. The ANOVA analysis results are shown in Table 4.4. The significance of the model and its terms were studied using a confidence interval of 95%. The p-value of the model is less than 5%, indicating its significance (Montgomery DC, 2017; M. S. Vohra & Labaran, 2020). Additionally, the ZIF-60 dose, lead concentration and the quadratic effect of the initial lead concentration were found to be the factors that most significantly influence the output of the generated model.

Table 4.4 Analysis of variance result for the lead removal model.

Source	Adj SS	DF	Adj MS	F-value	p-value
Model	7911.21	9	879.02	23.05	0.0015
A-Dose	3256.58	1	3256.58	85.40	0.0002
B-Concentration	3644.66	1	3644.66	95.58	0.0002
C-Temperature	62.75	1	62.75	1.65	0.2558
AB	40.05	1	40.05	1.05	0.3524
AC	27.98	1	27.98	0.7337	0.4308
BC	43.24	1	43.24	1.13	0.3356
A ²	194.58	1	194.58	5.10	0.0734
B ²	301.82	1	301.82	7.92	0.0374
C ²	3.87	1	3.87	0.1014	0.7630
Residual	190.66	5	38.13		
Cor Total	8101.86	14			

To further validate the generated model, it was tested to ensure that it did not violate the assumptions of the error term. Figure 4.4a proved that the residuals are normally distributed, while Figure 4.4b shows that there was no dependence between the order of run and the residuals that were generated; this is signified by the random pattern exhibited by the points in the plot.

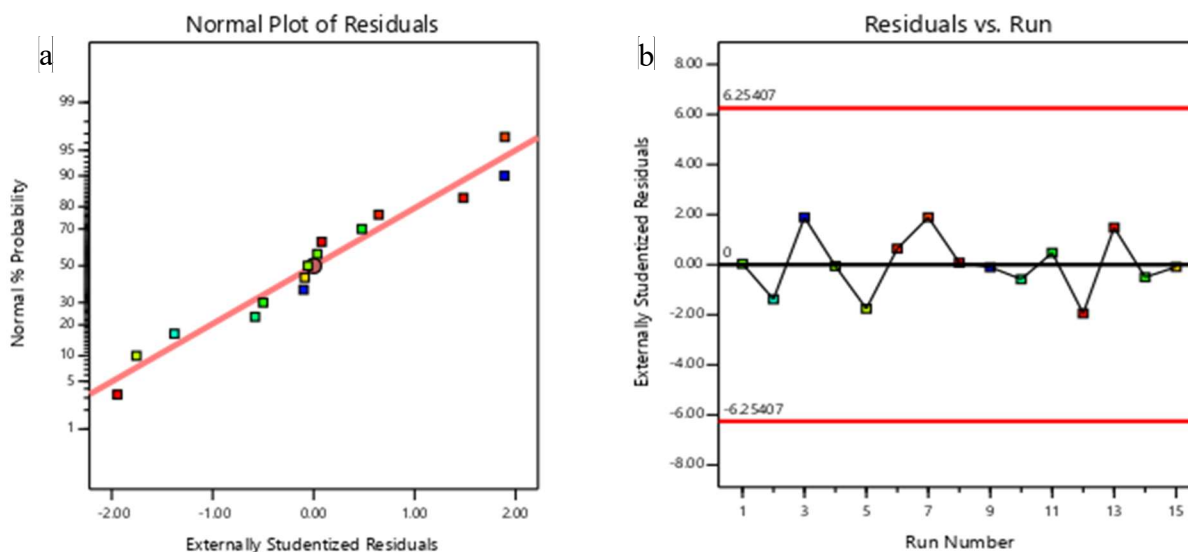


Figure 4.4. Model adequacy check plots a) Normal probability plot b) plot of residuals vs order of run.

The effect of the respective process parameters on lead removal were also investigated based on the ANOVA results. The factorial plots in Figure 4.5 show how varying the independent variables causes a reduction or increment in the lead removal. Figure 4.5a shows that an increase in ZIF-60 dose leads to an improvement in the removal efficiency; this can be attributed to the increase in number of available adsorption sites for the uptake of lead from the aqueous stream (X. Li et al., 2015b; Panda et al., 2019b). In contrast, Figure 4.5b indicates that an increase in the initial lead concentration is detrimental to its removal. This decrease in lead removal with increasing its initial concentration is due to the minute adsorbent dose used in the experiments. At low adsorbent dosages such as the ones used in this study, the adsorption sites get saturated, and the remaining lead cannot be taken up by the saturated ZIF-60 (X. Li et al., 2015b; Panda et al., 2019b). However, if the adsorption capacity is considered, then an increase in initial concentration is beneficial to the uptake of lead because the mass transfer driving force for lead to accumulate at the adsorbent surface increases in this case (Balarak et al., 2021).

Based on the RSM design space, the effect of the temperature was found not to be significant as shown in Figure 4.5c. However, the trend in the plot indicates that an increase in the temperature favours the adsorption of lead by the ZIF-60, hence, suggesting that the process is endothermic in nature. Further exploration on the effect of the temperature is reported in the adsorption thermodynamics investigation section presented and discussed later. The outcome of the RSM study guided us in selecting the values of the adsorption parameters that were used in the subsequent adsorption studies. It was kept in mind that the temperature was not significant, whereas high adsorbent dose and low lead concentration would likely favour the uptake of Pb(II) by ZIF-60.

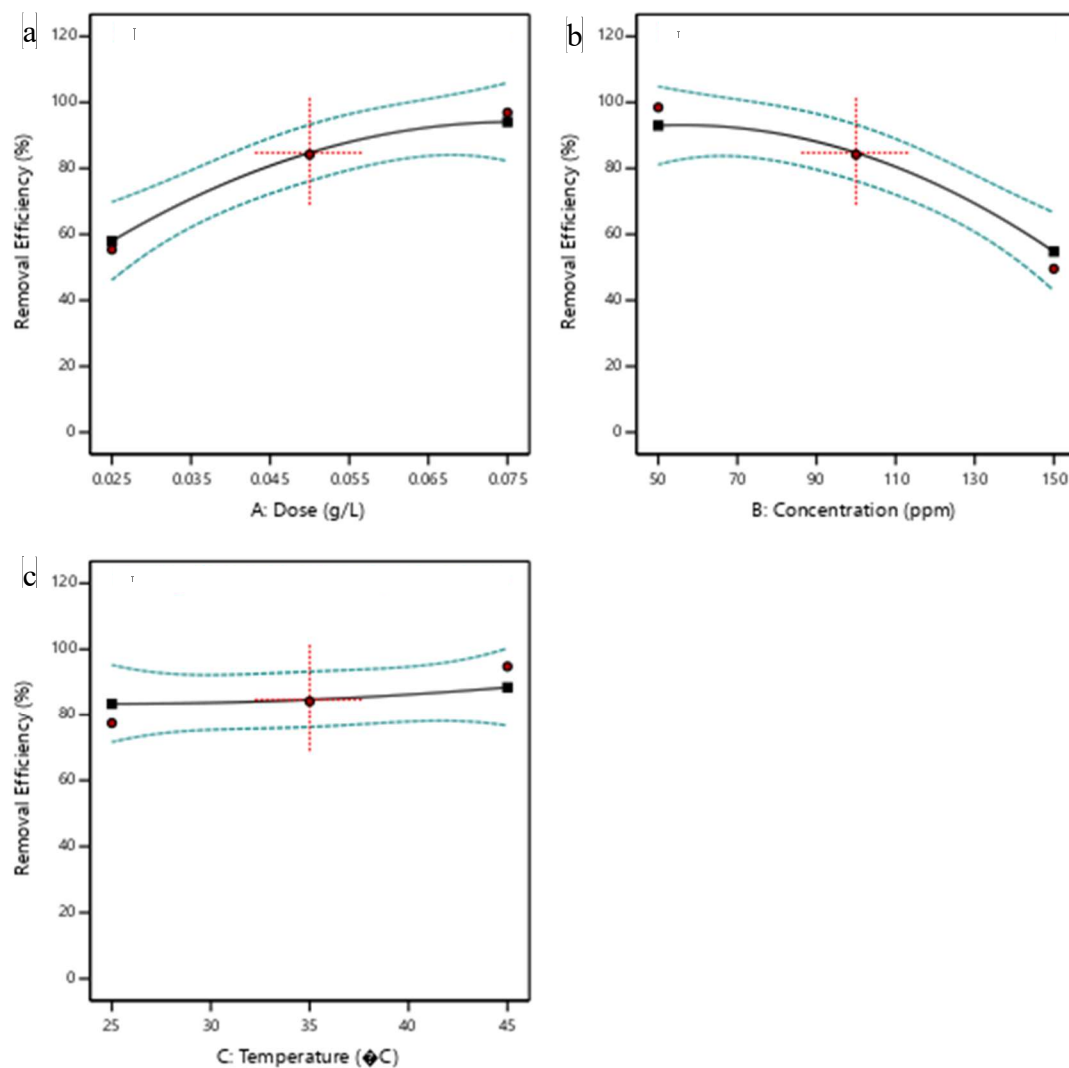


Figure 4.5. Effect of a) Adsorbent dose b) Initial lead concentration c) Temperature on lead removal efficiency

One major advantage of using the multivariate approach over the one factor at a time approach is the ability to study the effect of the interaction between the independent variables on the response of interest (lead removal in this study). The contour plots showing the effect of the interaction are given in Figure 4.6 a – c. From Figure 4.6a, it is noted that a near complete removal is noted when the adsorbent dose of 0.075 g/L is used and the initial lead concentration is kept at 50 mg/L. The contour plots in Figure 4.6 a – c also support the finding that the initial lead concentration and ZIF-

60 dose are the most important factors affecting the lead removal efficiency based on the RSM design that was adopted in the study.

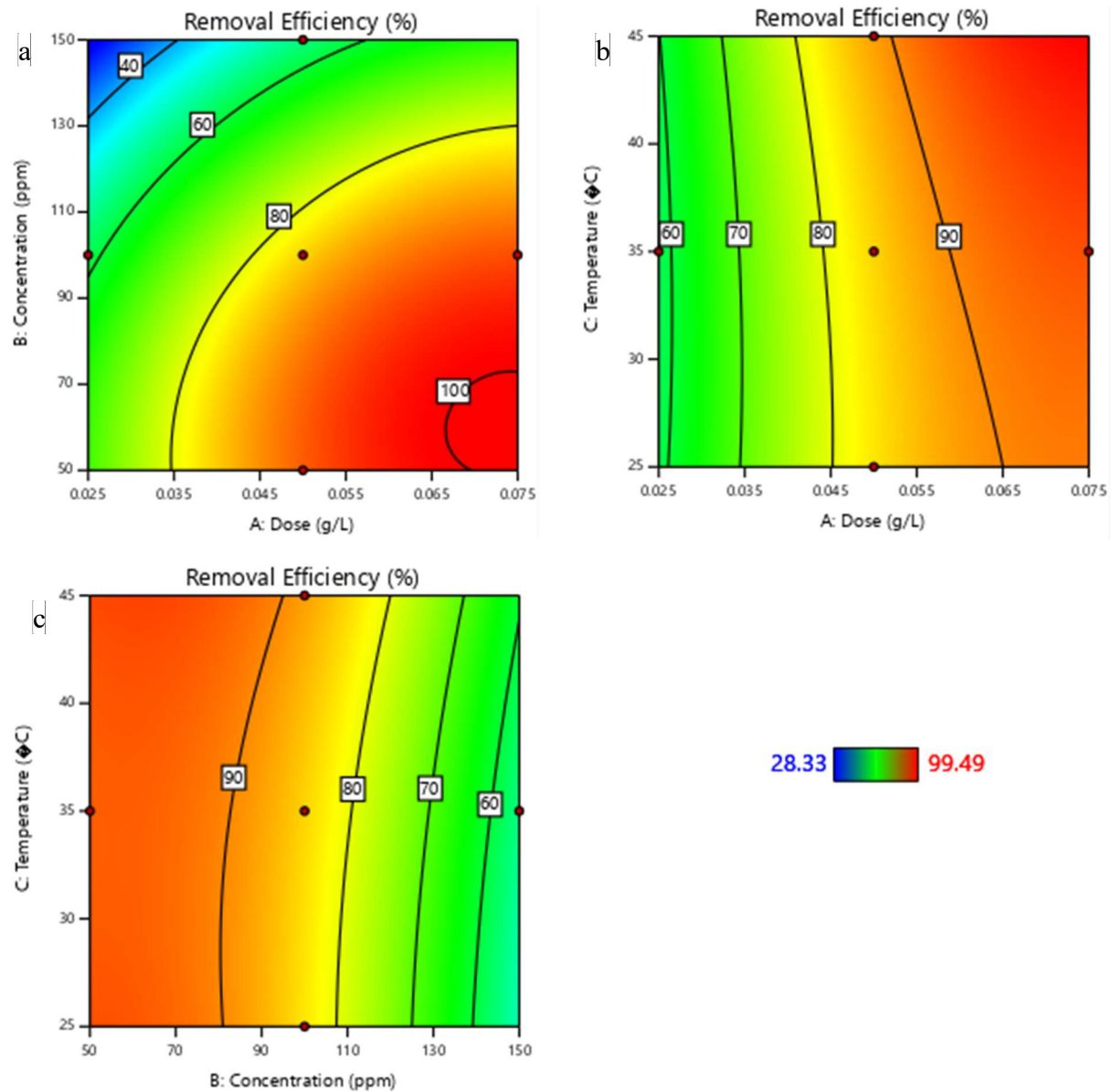


Figure 4.6. Contour plots for the interaction between a) Adsorbent dose and Initial lead concentration b) Adsorbent dose and temperature c) Initial concentration and temperature.

4.3.3 Adsorption kinetics

Adsorption kinetics equations play a vital role in elucidating adsorption pathways and in providing a room for hypothesizing adsorption mechanism for a certain pollutant under certain adsorption conditions. Information as regards to how the adsorption rate is affected by the amount of sorbent presented in the contaminated water sample or the adsorption capacity of the material under study are obtained after conducting kinetic studies (Oladoja, 2016). As such, the adsorption kinetics data for the uptake of lead using the ZIF-60 material was obtained and fitted to kinetic models including the pseudo first order, pseudo first order and the intraparticle diffusion model. The plot of the experimental data fitted to the respective models is presented in Figure 4.7.

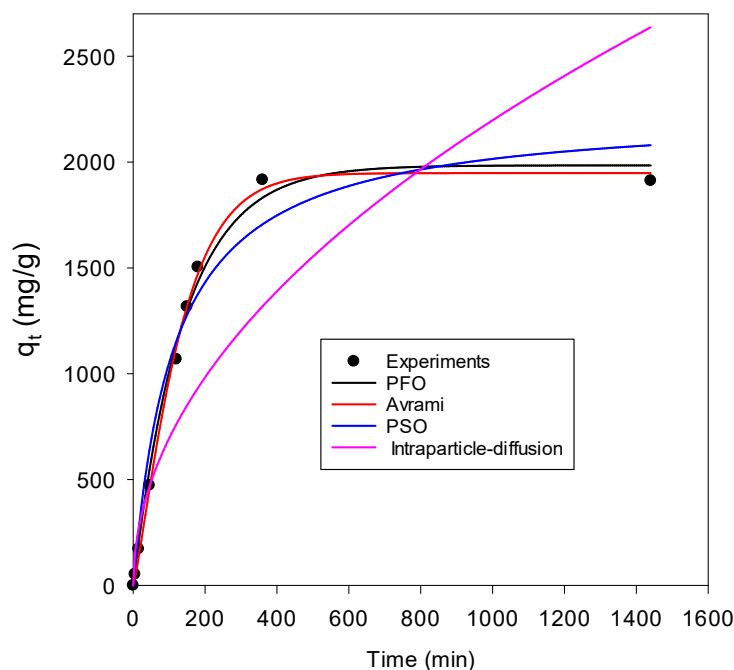


Figure 4.7. Fitting of kinetics models to experimental data for lead adsorption onto ZIF-60 ($C_o = 150$ ppm, initial pH = 4, ZIF-60 dose = 0.025 g/L, temperature = 298 K)

As evident in Figure 4.7, the pseudo first order (PFO) kinetic model, Avrami model and to a lesser extent, the pseudo second order (PSO) kinetic model all reasonably fit well the experimental data,

indicating that the uptake of lead by ZIF-60 is a complex process and both physisorption and chemisorption processes are involved in controlling the adsorption rate (Jian et al., 2015; Y. Liu et al., 2021). However, caution needs to be taken when using some of these kinetic models to elucidate the reaction mechanism as they are empirical in nature (J. Wang & Guo, 2020a). The constants generated for the utilized kinetic models are given in Table 4.5. The experimental data showed relatively poor fitting to the intraparticle diffusion model suggesting that the intraparticle diffusion is not the rate limiting step of lead adsorption onto ZIF-60 (W. Yang & Cao, 2023). Further, the R^2 for the fitted experimental data with reference to the kinetic models was obtained and the values are also reported in Table 4.5.

Table 4.5 Constants for lead adsorption kinetic models.

Pseudo First Order Model			Pseudo Second Order Model			Intraparticle Diffusion Model		Avrami Model			
$q_t = q_e(1 - e^{-k_1 t})$			$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$			$q_t = k_{id} t^{0.5}$		$q_t = q_e \left(1 - e^{-\frac{(k_a t)^n}{n}} \right)$			
K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 ($\text{g/mg} \cdot \text{min}$)	q_e (mg/g)	R^2	K_{id} ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$)	R^2	q_e (mg/g)	k_a (min^{-1})	n	R^2
0.0071	1984.5	0.9940	3.9358×10^{-6}	2243.2	0.9723	69.48	0.6828	1947.9	0.0086	1.2064	0.9980

4.3.4 Adsorption isotherms

The study of isotherm data is the most adopted approach used for exploring the mechanism of adsorption which is important to the design of adsorption systems and adsorbents. It also gives information about the maximum adsorption capacity ($q_{\max}$), a significant parameter in determining the suitability of an adsorbent for a certain sorbate (J. Wang & Guo, 2020a). Consequently, an adsorption isotherm study was conducted on the ZIF-60 material to understand its uptake behaviour towards lead at the given experimental conditions. The isotherm data obtained were fitted to the Freundlich, Langmuir and Redlich-Peterson (R-P) isotherms as shown in Figure 4.8. The experimental data fitted well to the Langmuir model as evident by the obtained R^2 value of

0.9817 which is significantly greater than the value obtained when the data was fitted to the Freundlich model. This suggests that the adsorption of lead to ZIF-60 is a macroscopic homogeneous adsorption and not a multi-layer adsorption on heterogamous surface (J. Wang & Guo, 2020a; F. C. Wu et al., 2010). The R-P isotherm is a three-parameter model that was developed to overcome the shortcomings of both the Freundlich and Langmuir models (Ayawei et al., 2017). The obtained experimental data are fitted well to the Redlich-Peterson model as shown in Figure 4.7; this is not surprising because as the value of the constant g approaches 1, the Redlich-Peterson isotherm can be approximated as the Langmuir isotherm (F. C. Wu et al., 2010). The ZIF-60 material showed an impressive lead uptake capacity with $q_{\max}$ predicted using the Langmuir isotherm equal to 1905.0 mg/g; this value is very close to the experimental adsorption capacity obtained at the highest lead initial concentration of 400 ppm utilized in this study, which is 1938.0 mg/g. The lead uptake capacity by ZIF-60 obtained in this study is significantly higher than what was obtained by many other adsorbents (to be presented later), which signifies that the ZIF-60 material can be utilized for the removal of lead from aqueous systems. The parameters of the respective isotherm models are given in

Table 4.6.

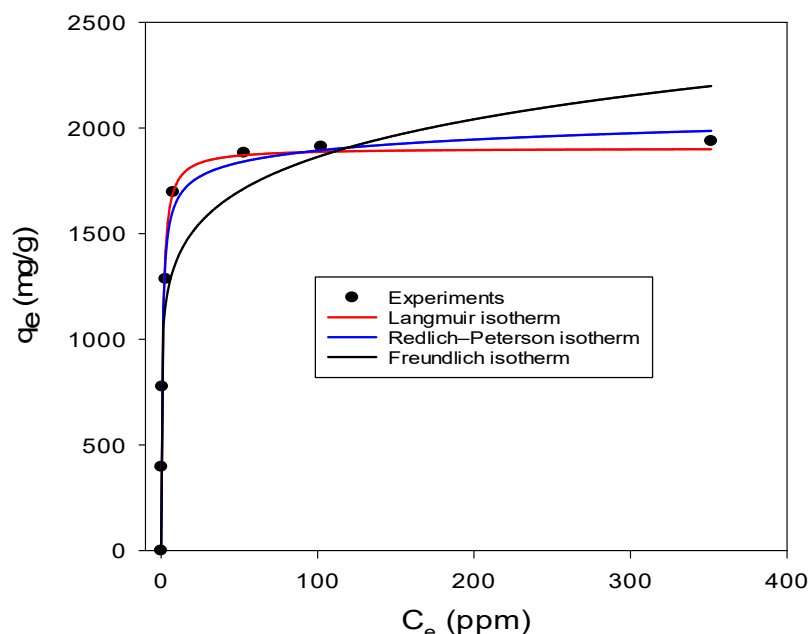


Figure 4.8. Adsorption isotherm models for lead uptake by ZIF-60 ($C_o = 10 - 400$ ppm, initial pH = 4, ZIF-60 dose = 0.025 g/L, temperature = 298 K)

Table 4.6. Model parameters for the adsorption isotherms under study

Langmuir adsorption isotherm $q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e}$			Freundlich adsorption isotherm $q_e = K_F C_e^{1/n}$			Redlich–Peterson adsorption isotherm $q_e = \frac{K_R C_e}{1 + a_R C_e^g}$			
$q_{\max}$ (mg/g)	K_L (L/mg)	R^2	N	K_F (L/mg)	R^2	K_R (L/g)	a_R (L/mg)	G	R^2
1905.0	1.0577	0.9817	7.6	1016.3	0.9002	2794.9	1.72	0.9656	0.9866

4.3.5 Thermodynamic studies

The adsorption temperature influences the equilibrium adsorption capacity as well as the rate at which solute diffuses through external boundary layer and into the internal pores of the adsorbent (Ighalo et al., 2022). Knowledge about the thermodynamic parameters of an adsorption process helps in determining a suitable temperature for conducting the adsorption process and also gives an insight about the mechanism through which the process occurs. As such, a thermodynamic analysis of the adsorption of lead onto ZIF-60 was conducted and the parameters of interest including the enthalpy change (ΔH), entropy change (ΔS) and standard free energy change (ΔG)

are reported in Table 4.7. The parameters were computed using the van't Hoff model (S. Singh, N, et al., 2023; W. Yang & Cao, 2023) and the linear plot is shown in Figure 4.9.

Table 4.7 Thermodynamics parameters for lead uptake by ZIF-60

Pollutant	T (K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (KJ/(mol•k))
Pb(II)	298	10.47	65.34	0.25
	308	-11.95		
	318	-15.58		

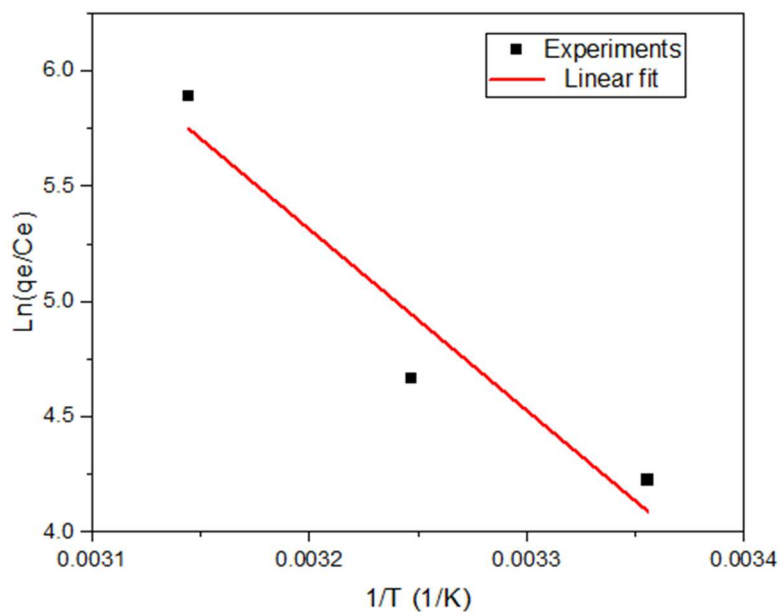


Figure 4.9. Van't Hoff linear plot for effect of temperature on lead adsorption onto ZIF-60 ($C_o = 100$ ppm, ZIF-60 dose = 0.05 g/L, initial pH = 4)

The negative values of ΔG indicate that the adsorption process is feasible and spontaneous under the given experimental conditions. Furthermore, an increase in temperature resulted in a more negative ΔG suggesting that increasing the temperature results in more spontaneity. The analysis also revealed a positive ΔH indicating that the adsorption of lead onto ZIF-60 is a heat-absorbing process and increase in temperature favours the adsorption capacity (i.e., an endothermic

adsorption process) (Lyu et al., 2017a). This finding supports the hypothesis that was made earlier while analyzing the RSM results that the adsorption process is endothermic in nature. The positive ΔS indicates significant randomness in the solid-solution layer of the adsorption system and that the adsorption of lead onto ZIF-60 is an entropy-driven process (Abdel-Magied et al., 2019; Lyu et al., 2017a).

4.3.6 Performance of machine learning algorithms in predicting ZIF-60 lead removal efficiency

Prior to model development, a hyperparameter tuning exercise was conducted. This was done to ensure that the optimum conditions to maximize the performance of each of the tested algorithms are ascertained. The ANN, SVM and RF have their own respective hyperparameters, and the hyperparameters along with the values that they were set at are reported in Table 4.8.

Table 4.8 Hyperparameter values for the individual algorithms.

ANN		SVM		RF	
Parameter	Value	Parameter	Value	Parameter	Value
N-Fold cross validation	4	N-Fold cross validation	4	N-Fold cross validation	3
Learning rate	0.1	Kernel	Pearson VII universal kernel	Number of trees	60
Momentum	0.5	Regression optimizer	SMOreg improved	Max features	$\text{Int}(\log_2(\#\text{predictors}) + 1)$
Hidden layers	1	Cost	3	Max depth	None
Training time	600	Epsilon	10^{-12}		
		Epsilon parameter	0.001		
		Tolerance	0.01		

All the optimized models provided a reasonably high correlation between the actual and predicted values. The Pearson correlation coefficient (R) was found to be 0.9632, 0.9494 and 0.8907 for RF, ANN and SVM, respectively. Similarly, the root mean squared error (RMSE) was found to be

9.13, 9.79 and 14.04, respectively. The model generated by the random forest (RF) algorithm had the largest R and the smallest RMSE, hence, the most accurate in predicting the lead removal efficiency by the synthesized ZIF-60. The visualization of the performance of the individual models is presented in Figure 4.10. The findings show that machine learning algorithms can be used to obtain valuable information as regards to the performance of adsorbents in the removal of contaminants from aqueous systems. The performance of the models can be enhanced provided that more dataset is used in training the models which are used for predicting the adsorbents performance in removing water pollutants.

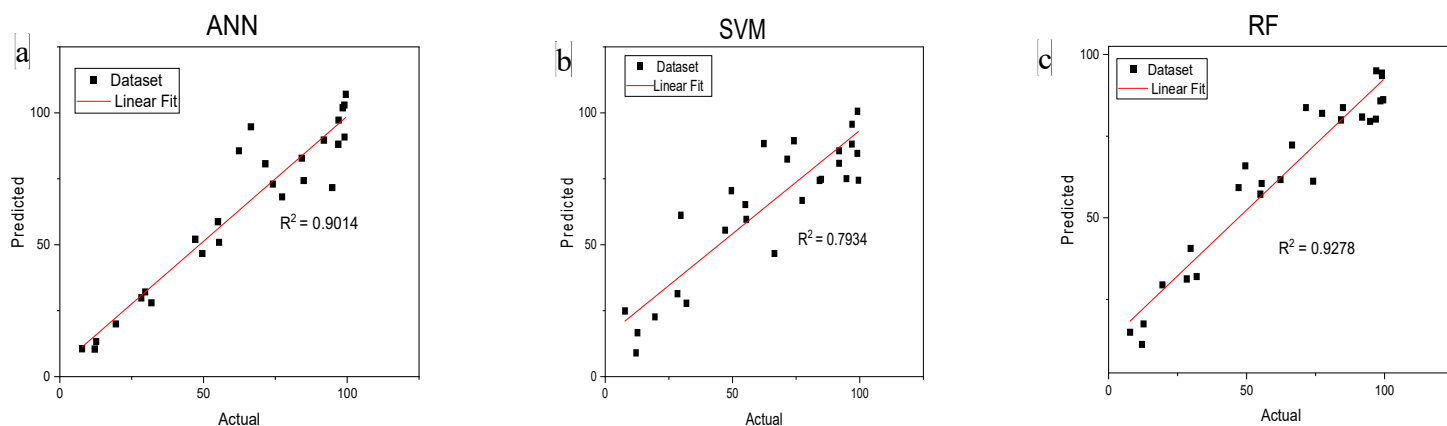


Figure 4.10. Plots of actual vs predicted lead removal efficiencies using a) ANN b) SVM c) RF models.

4.3.7 Comparison of adsorption parameters with other studies

This study revealed the excellent removal efficiency and adsorption capacity lead by ZIF-60. The results achieved are remarkable and better than those obtained using many MOF materials. Table 4.9 gives a comparison between the performance of ZIF-60 and other MOF materials taking note of the process parameters, kinetic models, adsorption isotherm and thermodynamic parameters.

Table 4.9 Lead adsorption capacity comparison between ZIF-60 and other MOFs.

Material	C ₀ (ppm)	pH	Time (h)	Temp (°C)	Dosage (g/L)	q _{max} (mg/g)	Kinetics model	Isotherm model	Thermodynamic parameters (ΔG , ΔH (KJ/mol) ΔS (KJ/(mol•k))	Reference
ZIF-60	10 – 400	4	24	25	0.025	1905.0	PFO and Avrami	Langmuir and Redlich-Peterson	$\Delta G = -10.47$, $\Delta H = 65.33$, $\Delta S = 0.25$	This study (Rivera et al., 2016) (Y. Huang et al., 2018b) (Y. Huang et al., 2018b) (Jamshidifard et al., 2019) (Minh Thanh et al., 2018) (Minh Thanh et al., 2018) (Y. Song et al., 2019) (L. Zhou et al., 2020) (J. Wang et al., 2019) (Akbarzadeh et al., 2020) (J. Chen et al., 2019) (K. Ahmad et al., 2021) (K. Ahmad et al., 2021) (W. Yang & Cao, 2023)
MOF-5	20 -100	5	6	45	0.25	658.5	PSO	Langmuir and BET	—	
ZIF-8	200	5.1	2	25	0.1 -2.0	1119.8	PSO	—	—	
ZIF-67	200	5.1	2	25	0.1 -2.0	1348.4	PSO	—	—	
PAN/chitosan/Uio-66-NH ₂ MOF	20 - 1000	6	1	25	0.2	441.2	PSO	Redlich-Peterson	$\Delta G = -8.01$, $\Delta H = -46.78$, $\Delta S = 0.15$	
Fe-MIL-101	9.12-90.12	6	3.5	30	0.5	86.2	PSO	Langmuir and Freundlich	$\Delta G = -2.55$, $\Delta H = 45.35$, $\Delta S = 0.16$	
MIL-101	9.12-90.12	6	3.5	30	0.5	58.0	PSO	Langmuir	$\Delta G = -1.38$, $\Delta H = 18.55$, $\Delta S = 0.07$	
ZIF-8@CA	5 – 1000	5	2	25		1321.2	PSO	Langmuir	—	
nFE@ZIF-8	50	5	1	45	0.025	227.3	PSO	Langmuir	$\Delta G = -7.40$, $\Delta H = 11.64$, $\Delta S = 0.06$	
ZIF@GO		5	1.7	25	0.15	356.0	PSO	Langmuir	$\Delta G = -10.82$, $\Delta H = 4.11$, $\Delta S = 0.05$	
ZIF@NiTiO ₃ carbon sphere@ZIF-8	100	5	2	25	0.67	155.0	PSO	Langmuir	—	(J. Chen et al., 2019) (K. Ahmad et al., 2021) (K. Ahmad et al., 2021) (W. Yang & Cao, 2023)
	100-600	5.5	5	25	1	310.5	PSO	Langmuir	—	
ZIF-8	20	6.5	2	25	1	1782.3	PSO	Langmuir	—	
ZIF-67	20	6.5	2	25	1	1972.1	PSO	Langmuir	—	
ZIF-8@GO-COOH	20 – 500	6	1	25	1	410.1	PFO and PSO	Langmuir	$\Delta G = -22.96$, $\Delta H = 33.23$, $\Delta S = 0.18$	

4.4 Conclusions

ZIF-60 was synthesized in this study, and its application in the field of water treatment was pioneered. The crystal phase, surface functional groups and thermal stability of the synthesized ZIF-60 were investigated using XRD, FTIR and TGA characterization techniques, respectively. Using a multivariate approach (RSM), the effect of process parameters including adsorbent dose, initial concentration and temperature on the performance of ZIF-60 toward removal of lead from aqueous solutions was studied. The experimental results revealed up to 99% lead removal when a ZIF-60 dose of 0.075 g/L and 50 ppm lead concentration were used. Further, the results of the RSM technique were used to generate regression models, and the quadratic model proved to be the most accurate with the highest R^2 . Analysis of variance was used to ensure that the quadratic model reported was valid. The results from the RSM techniques provided information as regards to the selection of the process parameters that were then used for adsorption kinetics, isotherm and thermodynamics studies. The result of the adsorption kinetics exercise revealed that experimental data fitted well to both pseudo first and second order kinetic equation which suggests that uptake of lead onto ZIF-60 is a complex process involving both physisorption and chemisorption. The adsorption isotherm data fitted well to the Langmuir and Redlich-Peterson isotherms indicating that the process is a macroscopic homogeneous adsorption and not a multi-layer adsorption on heterogamous surface. The maximum monolayer adsorption capacity of ZIF-60 was computed using the Langmuir isotherm and was found to be 1905.0 mg/g, a value greater what was obtained when many adsorbents were used. The thermodynamics investigation showed that the adsorption process is endothermic and spontaneous in nature indicating that increase in temperature is of positive influence on the process. Finally, the experimental date obtained was used to test the predictive prowess of several machine learning algorithms including the ANN, SVM and RF.

Based on the R and RMSE, the model generated by the random forest algorithm showed the highest efficiency in the prediction of lead removal by ZIF-60 in aqueous system.

CHAPTER 5

Adsorption of other aqueous contaminants onto ZIF-60: Preliminary results and screening exercise

5.1 Introduction

Prior to the selection of lead (Pb(II)) as our model heavy metal contaminant for extensive batch adsorption studies, a screening exercise was conducted to test the performance of ZIF-60 towards the uptake of several classes of contaminants including other heavy metals, dyes and other organic pollutants. The other heavy metals include cadmium (Cd(II)) and chromium (Cr(VI)). These heavy metals with lead inclusive were selected based on their proven deleterious effects even when ingested at low concentration and also based on the analytical capabilities of the instrument (AAS) that was used for the study. As regards to dyes, 6 distinct dyes including methylene blue, methyl orange, rhodamine blue, acid red, Congo red and crystal violet were subjected to batch adsorption study using the as-synthesized ZIF-60. The other organic pollutants that were screened include phenol and two other antibiotics namely aspirin and salicylic acid. This section briefly gives a summary of the results obtained from the screening exercise and further gives justification as to why lead was selected as the model contaminant for the extensive study that was conducted as part of these thesis work. The same methodology that was used in the published paper was also used in the screening exercise, however, without the response surface methodology and machine learning technique components. The schematic illustration of the procedure is shown in Figure 5.1.

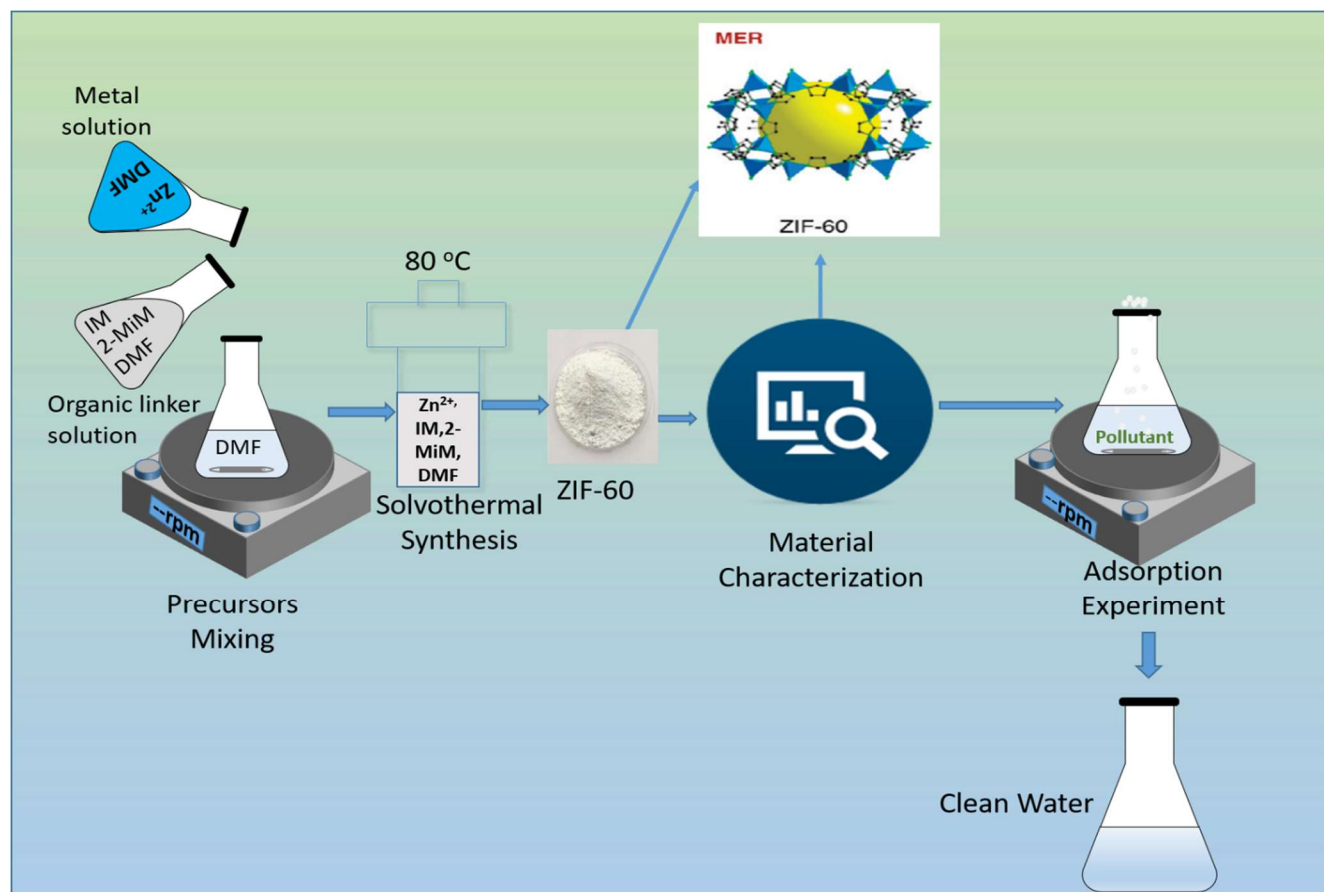


Figure 5.1. Procedure for preliminary adsorption exercise.

5.2 Adsorption of heavy metals using ZIF-60

The toxic effects of exposure to aqueous heavy metals and the permissible limits set by various organizations for concentrations of heavy metals in water have been discussed in chapter 2 of this work. The results of the screening exercise reported according to the adsorption capacity and removal efficiency of ZIF-60 towards the respective heavy metals are shown in Figure 5.2a and b, respectively.

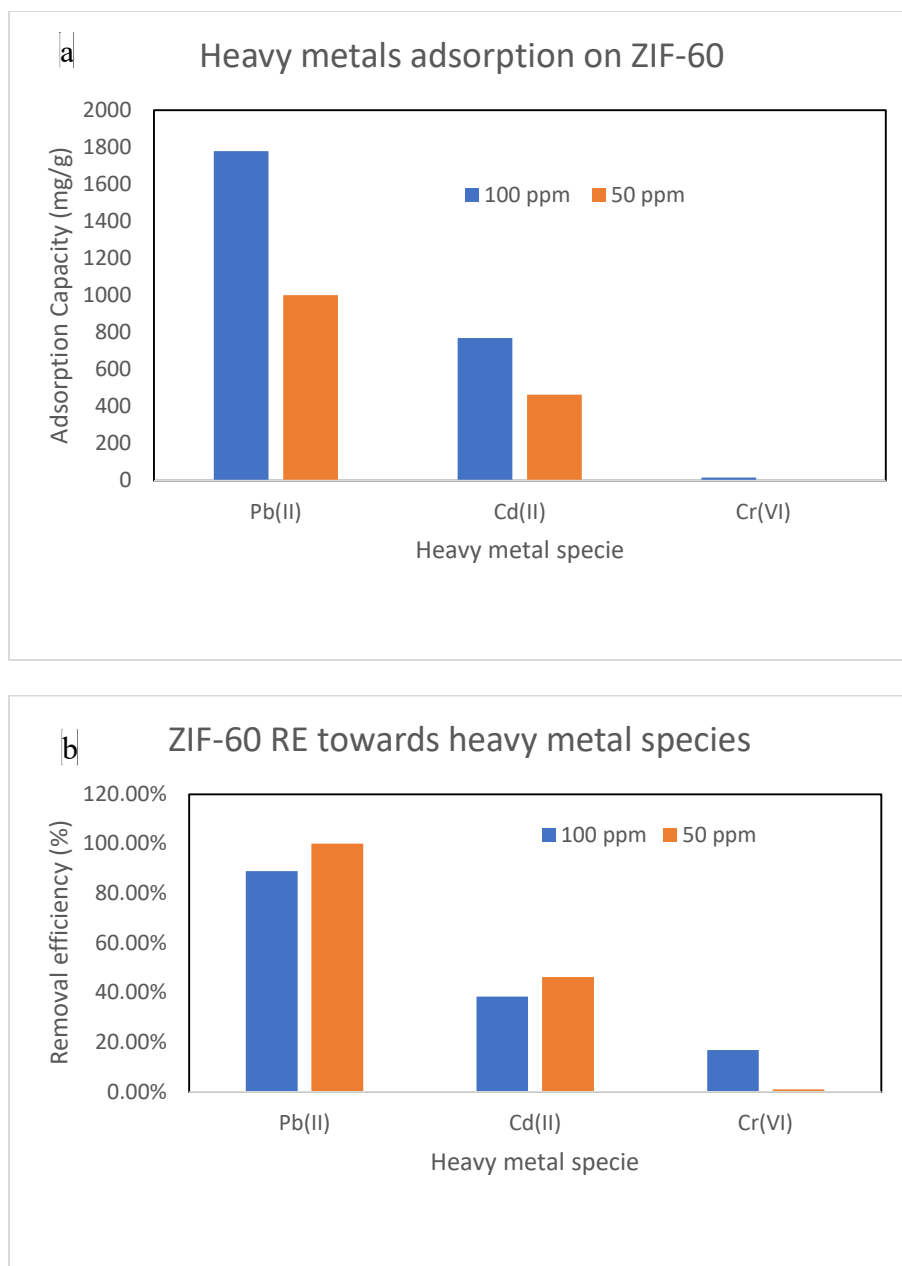


Figure 5.2. Performance of ZIF-60 towards abatement of aqueous heavy metals reported based on a) adsorption capacity b) removal efficiency. (Experimental conditions: ZIF-60 dose; 0.05 g/L, pH; unadjusted, temperature; room, stirring speed; 250, time; 24 h)

As shown in Figure 5.2a, when an initial concentration of 50 ppm was used for each of the pollutants, a remarkable ZIF-60 adsorption capacity was noted for lead. Almost of the lead was taken up by the ZIF-60 and an adsorption capacity of about 1000 mg/g was recorded. As the lead

initial concentration was increased to 100 ppm, the adsorption capacity improved further to about 1800 mg/g, this increment in adsorption capacity can be attributed to two reasons. First, as the initial concentration is increased, the force driving the mass transfer also increases leading to the contaminant to easily overcome the resistance between the surface of the adsorbent and the adsorbate (Balarak et al., 2021). Secondly, considering that almost all the lead when taken up when 50 ppm initial concentration was used, there is still more room for the 0.05 g/L ZIF-60 dose to take up more lead mass. The performance of ZIF-60 towards the uptake cadmium was noted to be promising, especially when the initial cadmium concentration was kept at 100 ppm. However, it was not close to the performance noted when lead was the contaminant of interest was lead. Interestingly, when the contaminant existed in an anionic form (chromate), ZIF-60 showed very poor affinity towards the uptake of Cr(VI). Reasons as to why such an occurrence happened were not explored further.

As regards the ZIF-60 removal efficiency of the various contaminants (Figure 5.2b), a similar trend was noted as explained from the adsorption capacity perspective. However, the major difference is that as the initial concentration is increased, the removal efficiency decreases. This is because at high initial concentration, the active sites of the adsorbent become saturated and the excess contaminant mass cannot be taken up by the adsorbent leading to a drop in the overall performance on the basis of the removal efficiency (Ismail et al., 2023b)

5.3 Adsorption of dyes onto ZIF-60

Due to their specific physical and chemical properties, dyes have been utilized for various applications that involve colouring of products such as textile, rubber, leather, plastics, papers etc. It has been reported that over 10000 distinct dyes and pigments are employed in industrial application and around seven hundred thousand tons of dyes are globally synthesized yearly

(Ogugbue et al., 2011; Y. Zhou et al., 2019). Further, it is estimate that 10 -15% of the volume of dye produced is discarded as wastewater (Hunger, 2004). Dyes can be categorized into various classes and Figure 5.3 depicts classification of dyes based on ionic charge. Further, Table 5.1 gives examples of some dyes on the basis of their classification.

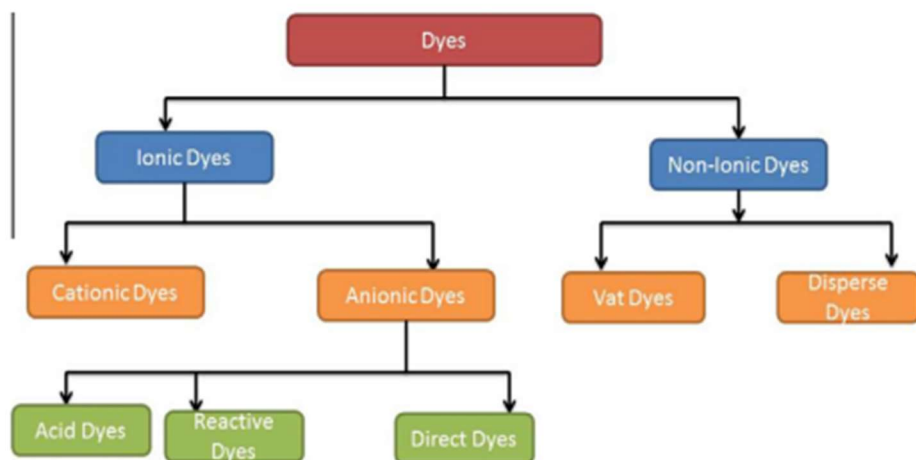


Figure 5.3. Dyes categorization according to ionic charge (Hunger, 2004).

Table 5.1 Examples of dyes, their basic properties and applications (Hunger, 2004; K. B. Tan et al., 2015).

Dye class	Types	Properties	Use	Health concern
Vat	Vat orange 28, vat blue 4, vat green 11, vat yellow 20, vat orange 15	Use soluble leuco salts after reduction in an alkaline bath (NaOH)	Cellulosic fibres	Dermatitis, rhinitis, allergic conjunctivitis, occupational asthma
	Reactive red 120, reactive blue 19, reactive black 5, reactive blue 4, reactive green 19, reactive red 195, reactive red 198	Similar to direct dyes but brighter dyeing properties. Forms covalent bond with fibers	Nylon, ink-jet printing, wool, cotton	
Direct	Direct blue 86, direct red 23, direct orange 39 and Congo red	Soluble in water and anionic, chelates with metals	Leather, paper, cotton, regenerated cellulose	Bladder cancer
	Disperse yellow 1, disperse red 1, disperse orange 3 and disperse red	Insoluble in water, non-ionic; hydrophobic aqueous dispersion	Cellulose, nylon, cellulose acetate, polyester, acrylic fibers	
Cationic	Basic green 5, rhodamine 6G, janus green, methylene blue, basic violet 10	Soluble in water, cations released in solution. Biological activity is shown by some dyes	Modified polyesters, paper, polyacrylonitrile, medicinal use as antiseptics, modified nylon.	Carcinogenic
	Acid green 27, sunset yellow, acid red 183, acid orange 12, acid red 10, acid red 18, acid red 73, acid orange 8	Anionic and soluble in water	Ink-jet printing, wool, silk, nylon, paper	
Acidic				Carcinogenic

From the non-exhaustive list of dyes, six including methylene blue, methyl orange, rhodamine blue, acid red, Congo red and crystal violet were selected and the adsorptive performance of ZIF-60 was tested toward there abatement was tested and reported based on adsorption capacity as reported in Figure 5.4.

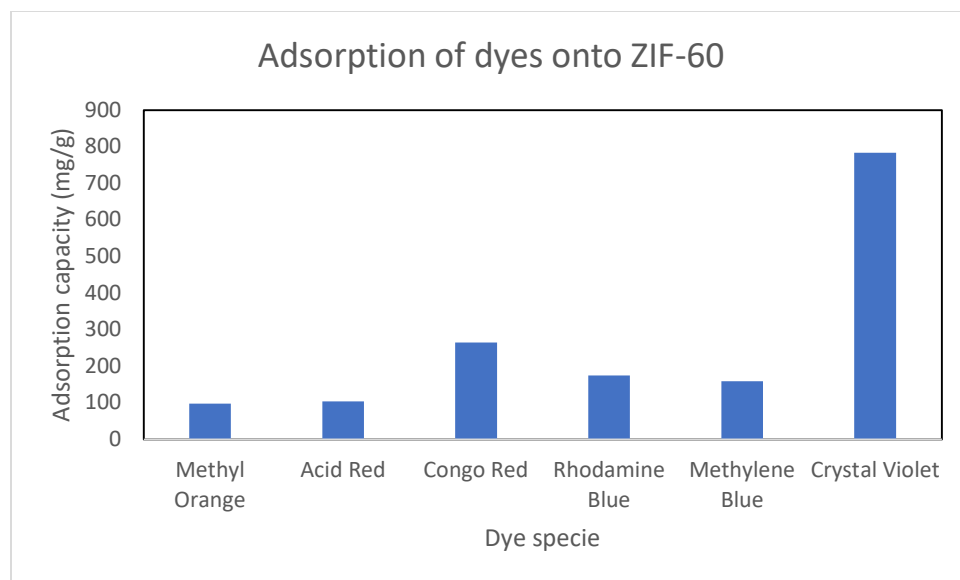


Figure 5.4. Adsorptive performance of ZIF-60 toward uptake of dyes. (Experimental conditions: ZIF-60 dose; 0.05 g/L, pH; unadjusted, temperature; room, stirring speed; 250, time; 24 h)

As shown in Figure 5.4, ZIF-60 showed favourable performance in terms of uptake of crystal violet with adsorption capacity of about 800 mg/g. However, despite the favourable performance, ZIF-60 displayed much greater affinity for Pb(II), hence, reinforcing the decision to conduct an extensive study on the uptake of Pb(II) by ZIF-60.

5.4 Adsorption of other organic pollutants using ZIF-60

Other organic pollutants including phenol and two other antibiotics including salicylic acid and aspirin were also screened for removal using the synthesized ZIF-60. Phenols have the capacity to cause toxic effects on several biological processes and many of them are recognized as carcinogens. Further, they can cause odour and unpleasant taste in drinking water (Dąbrowski et al., 2005). Sources of phenolic compounds in the environment includes coal gasification sites, oil refineries, petrochemical units etc. Further, phenolic derivatives are used as intermediates in the production of colours, plastics and insecticides (Dąbrowski et al., 2005). Salicylic acid and aspirin are antibiotics that have several beneficial effects, however, they are considered as emerging

contaminants because of their potential to cause toxic effects when found in the aqueous environment at high concentrations. Figure 5.5, gives a summary of the performance of ZIF-60 against the three contaminants listed in this section.

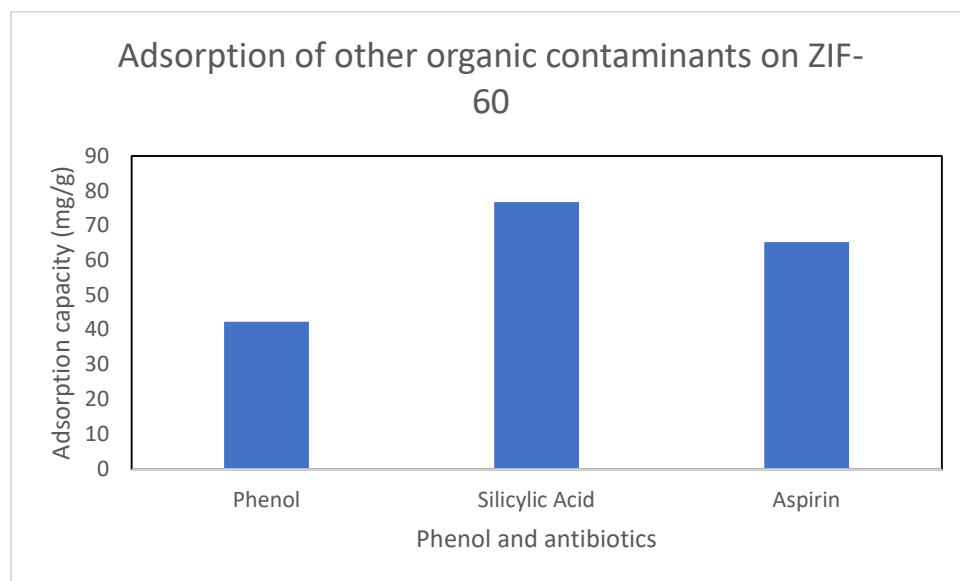


Figure 5.5. Adsorptive performance of ZIF-60 toward uptake of some organic pollutants.

(Experimental conditions: ZIF-60 dose; 0.05 g/L, pH; unadjusted, temperature; room, stirring speed; 250, time; 24 h)

Based on the results shown in Figure 5.5, relatively poor ZIF-60 performance was noted with an adsorption capacity of around 80 mg/g for salicylic acid, which was the highest.

5.5 Conclusion

This section gave a summary of the preliminary results and screening exercise that were conducted prior selecting Pb(II) as our model heavy metal contaminant. The results revealed that ZIF-60 had the highest affinity for lead among all the contaminants that were tested with an adsorption capacity of around 1800 mg/g based on the experimental condition used in the screening study.

The results informed our decision to select lead and extensive studies were conducted which have published and also attached as the chapter 4 of this work.

CHAPTER 6

Conclusions and recommendations

6.1 Conclusions

Through the experimental part of this work, ZIF-60 was synthesized and tested for the removal of several aqueous contaminants with a focus on the removal of heavy metals from aqueous system. From the results of the screening exercise, ZIF-60 displayed the highest affinity for Pb(II) and the findings led to an extensive study in which the performance of ZIF-60 towards removal of Pb(II) from aqueous systems was investigated. Response surface methodology (RSM) was adopted as the technique to study the effect of process parameters and RSM regression-based models for performance optimization were also generated. The quadratic model was found to be the optimum model on the basis of its highest coefficient of determination and satisfying the conditions of other model adequacy checks. Additionally, the experimental data was also used to test the performance of machine learning models in predicting the removal of Pb(II) from contaminated water and the model generated by the random forest algorithm was found to be the most efficient on the basis of its highest R^2 and lowest RMSE. Other classical adsorption experiments including adsorption kinetics, isotherms and thermodynamic investigation were also conducted. This results have been published and the paper is titled “Aqueous Pb(II) removal using ZIF-60: adsorption studies, response surface methodology and machine learning predictions”. The results are interesting, and that has led to filing a patent titled “ZIF-60 for aqueous Pb(II) treatment from contaminated waters” a process that is still ongoing. In addition to the experimental work, an extensive literature review was conducted, and it covers the progress and effectiveness of commonly used adsorbents

in the uptake of heavy metals from contaminated aqueous systems. The adsorbents covered include the composites of activated carbon, natural sorbents, biosorbents, clay minerals, LDHs, ZVI, graphene, CNTs, MOFs and ZIFs.

6.2 Recommendations

This work pioneered the application of ZIF-60 in water treatment application, while excellent performance was noted when Pb(II) was used as model contaminant, there is still room for further investigation and a few recommendations are given below:

- Excellent performance of ZIF-60 towards Pb(II) removal was noted in a single system, exploring the removal of lead in a competitive setting will provide valuable information about the affinity of ZIF-60 towards Pb(II).
- Regeneration and reusability of adsorbents is important for their commercial application, hence, a study exploring such characteristics of ZIF-60 is desired.
- The study was conducted in a batch reactor, conducting a flow through experiment can provide more useful information as regards to use of ZIF-60 in commercial systems.
- The performance of ZIF-60 towards abatement of other contaminants including Cd(II), Cr(VI), methylene blue, methyl orange, rhodamine blue, Congo red, acid red, crystal violet, phenol, salicylic acid and aspirin was noted during the preliminary exercise, however, the performance can be enhanced through preparation of suitable composites.

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EDUCATION

1. **King Fahd University of Petroleum & Minerals**
2021-2023
Msc Civil Engineering (Water Resources and Environmental Engineering Concentration)
CGPA: 3.964/4.00
2. **Bayero University, Kano**
2015-2020
BEng Civil Engineering
CGPA: 4.89/5.00

PUBLICATIONS

1. **Ismail, U. M.,** Onaizi, S. A., & Vohra, M. S. (2023b). Aqueous Pb(II) Removal Using ZIF-60: Adsorption Studies, Response Surface Methodology and Machine Learning Predictions. *Nanomaterials* 2023, Vol. 13, Page 1402, 13(8), 1402. <https://doi.org/10.3390/NANO13081402>
2. **Ismail, U. M.,** Onaizi, S. A., & Vohra, M. S. (2023). Novel MgCuAl-layered triple hydroxide for aqueous selenite and selenate treatment. *Emergent Materials*. <https://doi.org/10.1007/s42247-023-00462-7>
3. **Ismail, U. M.,** Elnakar, H., & Khan, M. F. (2023). Sources, Fate, and Detection of Dust-Associated Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS): A Review. *Toxics*, 11(4), 335. <https://doi.org/10.3390/toxics11040335>

ACADEMIC & PROFESSIONAL EXPERIENCE

1. **King Fahd University of Petroleum & Minerals/ Graduate assistant**
2021-Present
Teaching assistant: CE 547 physical and chemical processes, CE 404 climate engineering, CE 330 environmental engineering principles, CE 375 environmental chemistry laboratory and CE 202 statics
Departmental course development committee member
2. **Kano State Polytechnic/Lecturer**
Dec, 2020-Sept, 2021
Soil science and irrigation engineering (CEC 208), theory of structure (CEC 205), basic principles of surveying (SUG 101), and introduction to structural design (CEC 206)
3. **Sasha W.D.C Enterprise/site and design engineer**
Jan, 2020-Sept, 2021
Project management, supervision and structural design
4. **Student Industrial Work Experience Scheme (SIWES)/intern**
Dantata & Sawoe Construction Company
Jun, 2018-Dec, 2018
Kururtno Stroitelstvo Int'l Project Ltd
Nov, 2017-Feb, 2018

AWARDS AND PRIZES

1. KFUPM University scholarship
2021
2. Vice-Chancellor prize for the overall best graduating student, BUK, 2018/2019 session
2020
3. Ahmad Adamu Mu'azu prize for best graduating student in faculty of engineering, BUK
2020
4. Engr. Rabi Musa Kwankwaso prize for the best graduating student in civil engineering, BUK
2020
5. Michael Taiwo Annual standardized exam fee scholarship
2020
6. NICESA award for the best graduating student in Civil Engineering, Bayero University, Kano
2019
7. University Scholarship for the Best Year 3 &4 Civil Engineering student
2018 - 2019
8. Petroleum technology development fund (PTDF) scholarship
2016

