MAJOR PROJECT

REMOVAL OF HEAVY METAL IONS USING POROUS MATERIALS

A Major Project Report submitted in partial fulfillment for the award of the degree of

MASTER OF Science (M.Sc.)

Chemistry

Submitted by

Amit Kumar

[2K21/MSCCHE/53]

Under the supervision of

Dr. Raminder Kaur

Department of Applied Chemistry

Delhi Technological University, Delhi-110042 (Formerly Delhi College of Engineering)Bawana Road, Delhi, 110042

CANDIDATE'S DECLARATION

I Amit Kumar, hereby certify that the work which is being submitted in this major project report entitled "Removal of Heavy metal ions using Porous Material" in the partial fulfilment for the award of the degree of Master of Science at Delhi Technological University is an authentic record of my own work carried out by me under the supervision of Dr. Raminder Kaur (Assistant Professor, Department of Applied Chemistry, DTU)

I, further declare that the project report has not been submitted to any other Institute/University for the award of any degree or diploma or any other purpose whatsoever. Also, it has not been directly copied from any source without giving its proper reference.

Amit Kumar

[2K21/MSCCHE/53]

Certificate

I hereby certify that the Project Dissertation titled " REMOVAL OF HEAVY METAL IONS USING POROUS MATERIALS " which is submitted by Amit kumar, 2K21/MSCCHE/53, Department of Applied Chemistry, Delhi Technological University in partial fulfilment of the requirement for the award of the degree of Master of Science, is a record of the project work carried out by the student under my supervision. To the best of my knowledge this work has not been submitted in part or full for any other Degree or Diploma to this University or elsewhere.

Place Prof. Raminder kaur

Date (supervisor)

ACKNOWLEDGEMENT

I would like to pay my heartiest thanks to my supervisor Dr Raminder Kaur, Assistant Professor, Department of Applied Chemistry, Delhi Technological University for her continuous motivation, healthy scrutiny, indispensable supervision and valuable suggestions at each phase of the project.

I am also grateful to Prof. (Dr.) Anil Kumar, Head of the Department, Department of Applied Chemistry, Delhi Technological University, for providing me the constant support to the best heights for this project work.

I would also like to thank the faculty members Dr. Ram Singh, Dr D. Kumar, Dr. Richa Srivastava, Dr. D. Santhya, Dr. Poonam Singh, for their support and encouragement throughout this project.

I would like to continue by thanking Miss Pooja Singh and Miss Gunjan Varshney for their massive help in making me understand the basic concepts and patiently responding to my constant doubts.

Amit Kumar

Abstract

The environment and living things are seriously threatened by heavy metal ions. The recovery and detection of heavy metal ions in water are extremely significant due to the consistent supply of heavy metal ions in water resources, which poses health risks to human and environment. The removal of heavy metal ions from wastewater is of primary importance for a clean environment and human health. Consequently, there has been an increase in interest in the creation of efficient adsorbents and sensors. A variety of reported methods have been devoted to the removal of heavy metal ions from various wastewater sources This project comprehensively and critically reviews and discusses these methods. The adsorption mechanism is defined by the physicochemical properties of adsorbent and heavy metals and operating conditions Generally, heavy metal ions can be adsorbed on to the adsorbent’s surface, This method has been reported to have low operating costs, high removal capacity, and easy implementation, and simple treatment by regenerating the adsorbed heavy metal ions. The porous organic-inorganic hybrid materials known as metal-organic frameworks (**MOFs**) comprise metal ions connected by the organic ligands. MOFs are eliminating these heavy metal ions with excellent results. I looked into the various MOFs and their ability to bind to these heavy metal ions in this report. This article reviewed recent development and current status of detection of heavy metal ions using porous materials. Additionally, a common mechanism for the adsorption of these heavy metal ions is explored. There have also been studies on peptide-based gels that are efficient at cleaning up organic dyes and oil spills.

Introduction

The amount of available water resources is fast declining as a result of the increased industrialization. Heavy metal (HM) ions are a significant source of water contamination. Heavy metal ions such as As^{3+}, Pb^{2+}, Cd^{2+}, As^{6+}, Hg^{2+}, Cr^{6+}, and uranium act as a great threat to the environment and human health, and many highly toxic organic dyes are also carcinogenic. Unprocessed dye discharge from industry pollutes water leads to serious problems for aquatic and mankind[1]. These highly poisonous and non-biodegradable heavy metal ions can pose a major threat to living things. There are several ways to remove HM ions from water, including ion exchange, chemical precipitation, flocculation, membrane filtration, and adsorption. Among all adsorption is most frequently used because it is inexpensive, doesn't require high temperatures, and is highly effective. Metal as an adsorbent is crucial for efficient adsorption. For this, a variety of typical adsorbents are employed, including activated carbon, zeolites, and carbon nanotubes[2]. However, the selectivity and adsorption capacity of these adsorbents are limited or less. Metal-organic frameworks (MOFs), also known as coordination networks or porous coordination polymers (PCPs), have received more attention over the past few years. MOFs are distinct from the adsorbents mentioned above. In addition to offering advantages of both homogeneous and heterogeneous catalysts, MOFs are created to take advantage of both organic and inorganic components. Large surface areas, persistent porosity, chemical stability, open metal sites, multifunctionality, and adaptable architectures are among their properties. MOFs are crystalline substances made of metal clusters and organic ligands. Using various functional groups and ligands, these MOFs can be modified to have unique structures and properties. MOFs have been employed in many different domains, such as the delivery of drugs, catalysis, and the elimination of dangerous pollutants. Numerous articles about MOFs have recently been published, demonstrating its significance for a variety of applications.

MOFs have become a popular novel adsorbent for the elimination of heavy metal ions from water in recent years. MOFs can be divided into two groups based on the types of organic ligands and core metal ions (metal clusters).The several MOF systems that are used to adsorb HMs are grouped either by the researchers who created them or by the kind of framework. For example, Materials of Institute Lavoisier (MIL) was first synthesized at the Institute Lavoisier. University of Oslo (UiO) synthesized zirconium (Zr)metal-based MOF. With the help of transition or lanthanide series as metal ions (or clusters) and trimesic acid or terephthalic acid as a linker, zeolitic imidazolate framework (ZIF) consists of inorganic metal ions linked by organic imidazole ligands Cu-BTC, copper-based[3]. Several type MOFs-templated materials including virgin MOFs, modified MOFs and magnetic MOFs composites have been prepared and are used for removing divalent heavy metal ions. For divalent heavy metal ions, MOFs materials have demonstrated superior adsorption capability over many other adsorbents. Virgin MOFs are synthesized by combining central metal ions or clusters with organic ligands without functional groups. To increase their activity, these MOFs have been researched with various modification techniques. Chemically altering MOF materials requires the employment of post-synthesis techniques, such as coating or hybridising virgin MOFs with various functional groups, such as asazine, amino, quinine, or thiol functional groups. For the removal of heavy metal, magnetic particles like iron (II, III) oxide contain magnetic nanoparticles with adsorbent; interest in these combinations of MOFs and magnetic nanoparticles has grown recently. In this case, separating the adsorbate from solution relies heavily on an adsorbent's magnetic characteristic[4].

Objective

Physical and chemical adsorption make up the majority of the heavy metal ion adsorption done using metal-organic frameworks. Adsorption that occurs physically is sometimes referred to as adsorptive adsorption, whereas adsorption that occurs chemically is referred to as reactive adsorption. Chemical adsorption involves chemical connections between the adsorbates and the adsorbent form, whereas physical adsorption largely involves the adsorbate interaction with these metal-organic frameworks through weak forces. Coordination interactions, chemical bonds, and acid-base interactions are all a part of chemical adsorption[5].

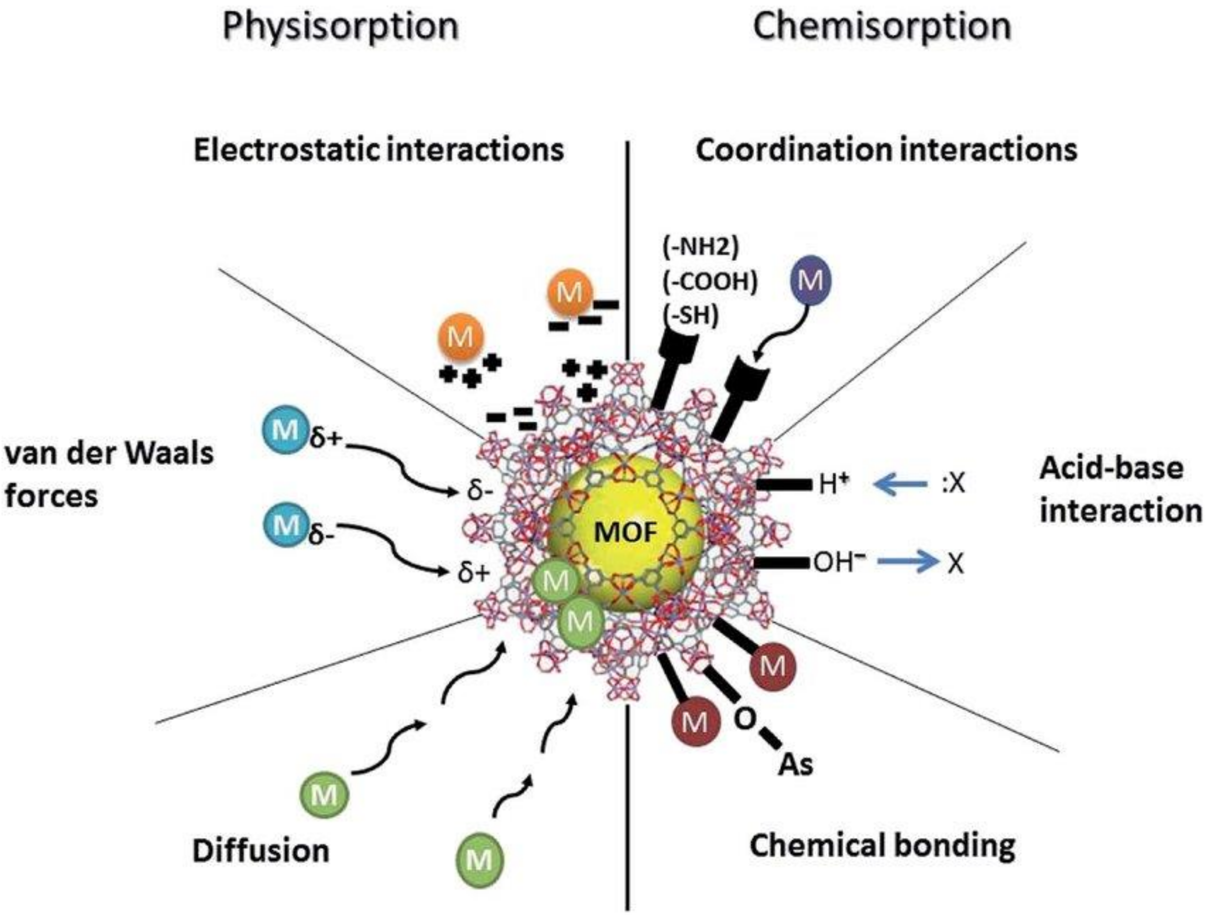

Figure1: Schematic Representation Adsorption Process

Chemical Adsorption:

Coordination interaction

Metal-organic framework which is modified with the help of different functional groups such as $-NH_2$, -COOH, -SH have coordination interaction with the heavy metal ions. Luo and his co-worker prepared MIL-101(Cr), an amino-functional metal- organic framework in which ethylenediamine grafted on coordinatively unsaturated Cr metal centres. When the solution was acidic the NH_2 group get protonated and form MOF- $(NH_2)33+$ and this will react with the heavy metal ions[6].

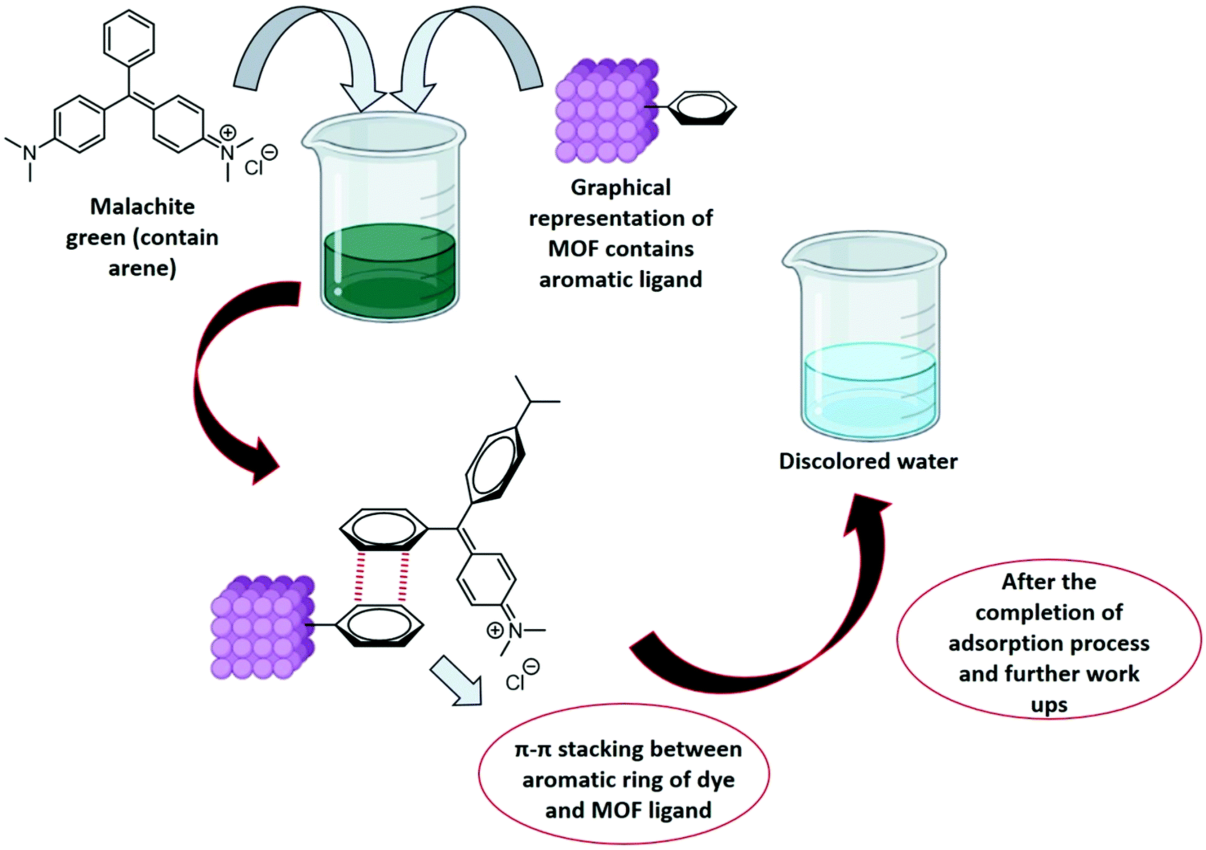

Figure 2: coordination interaction

Chemical Bonding

In many MOFs, a chemical bond is formed with the target heavy metal ion. Wu and his co-worker synthesised hierarchical ZIF-8 for the removal of As (III). The mechanism proceeds through Zn-OH which was generated from the breaking of Zn-N bonds and the As (III) is adsorbed using OH substitution resulting in the formation of Zn-O- as bond.

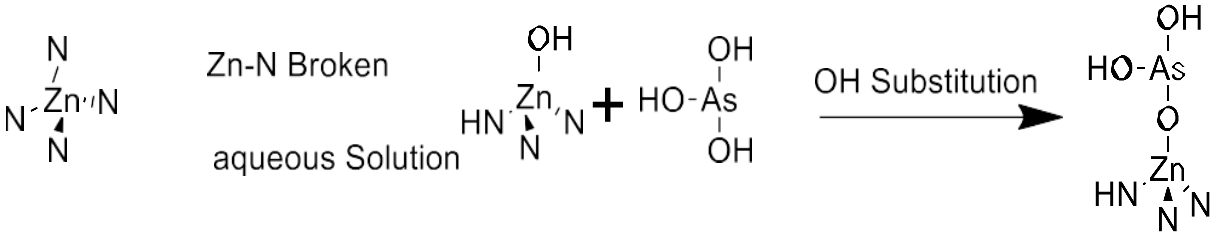

Figure 3 : chemical bond Zn-OH

Acid-base interaction

HSAB theory is the basis of acid-base interaction, which states that hard acid interacts better with the hard base and soft acid with soft base. Zhang and his co-worker synthesisedHS-mSi@MOF-5 a thiol-based metal-organic framework. Pb (II)) soft acids bind with thiol functional group which is soft base in HS-mSi@MOF-5[7].

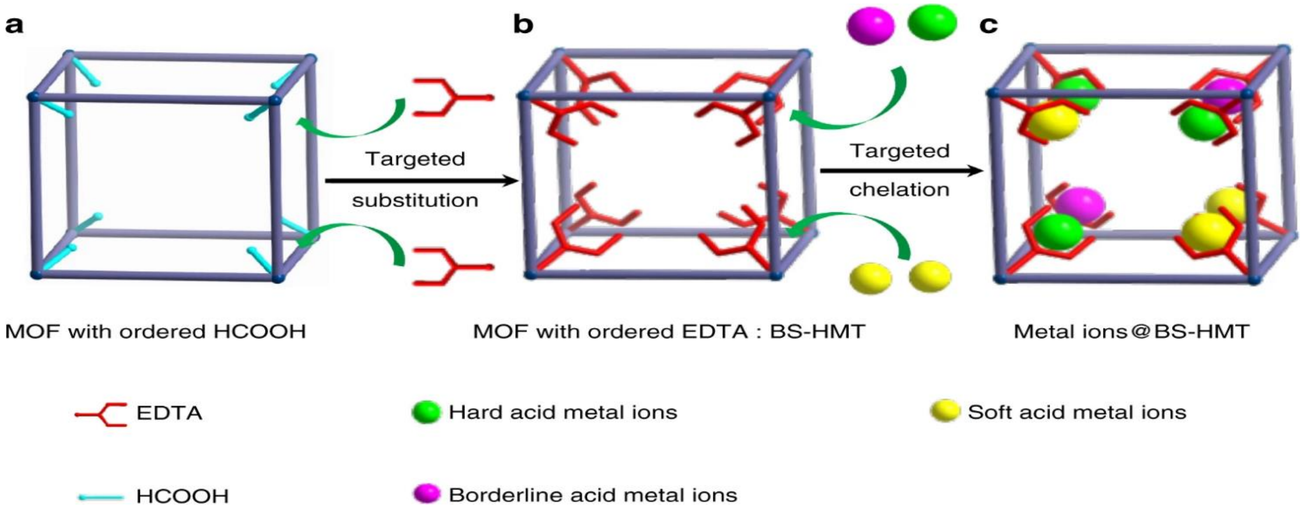

Figure 4: Representation hard base and soft acid with soft

Physical Adsorption:

Electrostatic interaction

MOF having the charged surface will interact with opposite charge adsorbate due to the electrostatic interaction. The surface charge can be varied using the pH of the solution. Adsorption of heavy metal ions also depends on the MOF surface zero potential (pzc). When pH<PZC, That solution is acidic. Large numbers of H+ ions will combine with positively charged metal ions to complete the process of adsorption. There won't be any metal-MOF interaction in this case since the MOF will be positively charged. The metal ion and MOF will be attracted to each other when the pH>PZC because MOF[8] will be negatively charged.

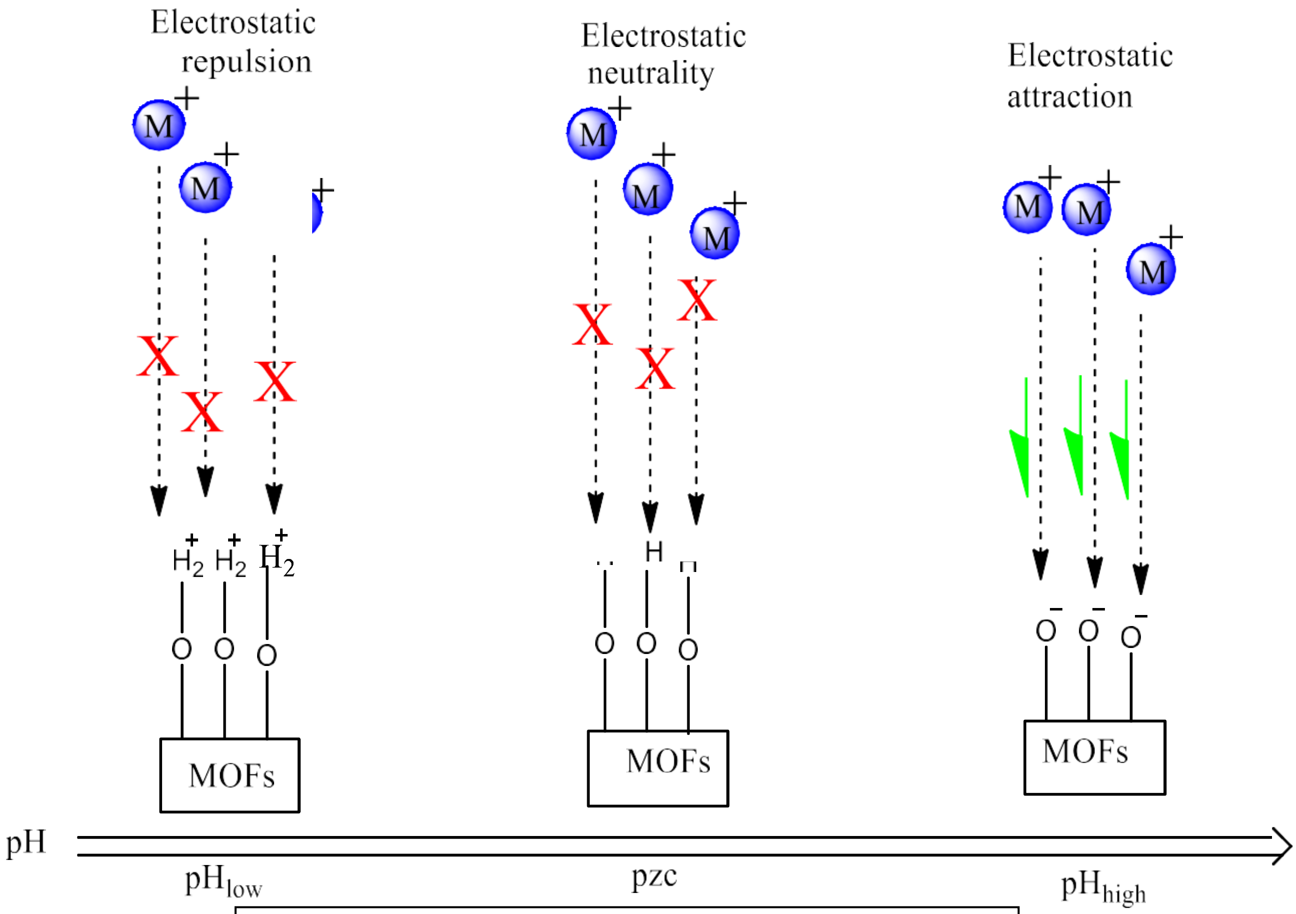

Figure 5: electrostatic interaction

Diffusion:

Diffusion also plays a significant part in the mechanism by which heavy metal ions are adsorbed on metal-organic frameworks.

Diffusion kinetics is given by the equation.

$$q_t = k_i t^{1/2} + C$$

Zhang and his co-worker studied the adsorption of Pb (II), Cd(II) and found out that diffusion also exists in the mechanism and confirmed by plotting the graph which gives the straight line[9].

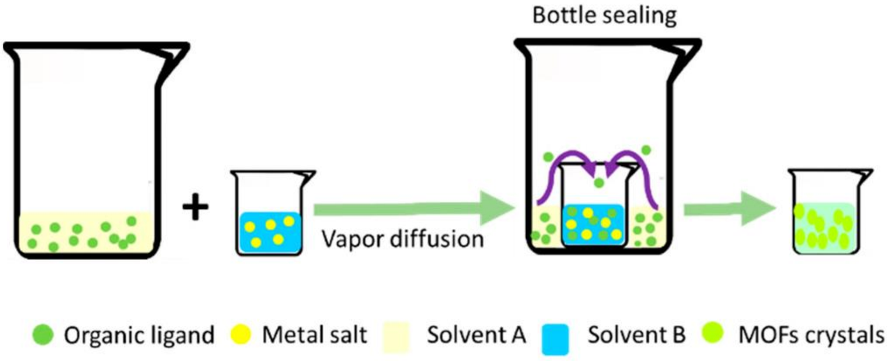

Figure 6: Diffusion kinetics

Vander Waal Forces:

Vander Waal forces are used as a general adsorption process when surface area and porosity are discussed. The surface area and porosity of MOFs can be adjusted. The weak Vander Waal forces can adsorb substances that do not exhibit the particular sort of interaction[10].

Removal of Chromium:

Chromium is released mainly through the dye industries, tannery, metal plating in the form of CrO_4^{-2}, $Cr_2O_7^{-2}$ or Cr^{3+}. A variety of MOFs with various adsorption capacities and equilibration times are synthesised in order to remove them from water. Saleem and his co-worker synthesised the MOF by modifying the UiO-66-NH_2 through introducing isothiocyanate and thiourea and got the adsorption capacity for Cr^{3+} using the UiO-66-NHC(S)NH Measured 117mg/g, which is higher than the earlier reported adsorbents. The addition of a functional group to the pore structure that contains Sulphur-containing groups is what is responsible for the increase in adsorption capacity. Adsorption of the soft metal cation, which raises the adsorption capacity, is a crucial function of this substance[11]. Tahmasebi and his co-worker synthesised the Zn based MOFs namely TMU-5,TMU-6,TMU-4 and found out the adsorption capacity for Cr^{3+} 123,118,127 mg/g. In these MOFs, adsorption capacity depends on the free site available on MOFs to interact with metal ion and also on the basicity of the nitrogen. MOFs having nitrogen functional groups like TMU-4 and TMU-5 have more adsorption capacity than TMU-6 because of N-atom are present in the resonance with benzene ring which will reduce the basicity of the N atom[12]. Li and his co-worker synthesised cobalt-based zeolite imidazole framework (ZIF-67) and found out the maximum adsorption capacity for Cr (VI)15.8mg/g.ZIF-67 is made up of tetrahedrally coordinated Co^{3+} ion with N- atom of the imidazole ring which is acting as the linker and due to this type of structure, the bulk Co^{3+} does not interact with any hydroxide or water in the reaction. However, the uncoordinated cobalt ion present at the surface will interact with hydroxide ion. The mechanism for ZIF-67 is dependent on the pH; as the pH decreases the CrO_4^{-2} will be present as $HCrO_4^-$ and this will be exchanged with the hydroxide ion and in the subsequent step the e- will be donated by the framework which partially reduces the more toxic Cr(VI) to Cr (III)[13].

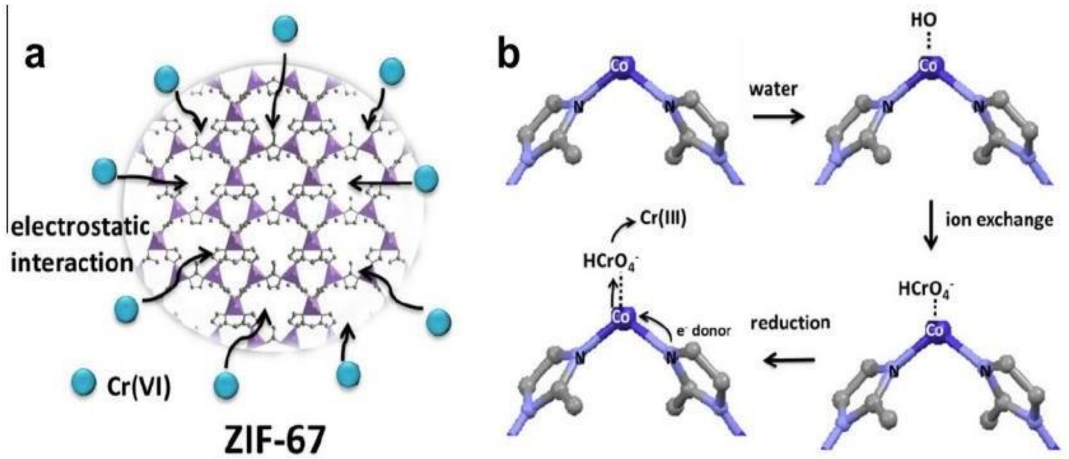

Figure 7 :Adsorption mechanism of Cr (VI) removal by the ZIF-67 microcrystals: (a) electrostatic interaction and (b) ion exchange.

Fei and his Co-worker synthesised Zn0.5Co0.5-SLUG-35 metal-organic cluster with π-π stack into the 2D Positively charged layers with metal ion tuneable and have adsorption capacity of 68.5 mg/g for the chromate ion. Zhang and his co-workers synthesised ZJU-101 Zr based MOF having the adsorption capacity of 245mg/g for dichromate which is highest for the removal of dichromate ion. ZJU-101 has high selectivity for the dichromate ion.This was confirmed by adding different other disturbing ions in the solution[14]. Aboutorabi and his co- worker's synthesis TMU-30 Metal-organic framework based on theisonicotinate N-oxide which has an adsorption capacity of 145 mg/g for Cr (VI).They successfully concluded that during the adsorption mechanism N of N-oxide have a positive charge which will be doingthe electrostatic interaction with the negatively charged oxygen atom of dichromate[15]. Rapti and his co-workers described metal-organic resins MOR-1 AND MOR-1-HA which are made by adding the organic functional group to the MOFs and these have the better capacity to adsorb the Cr(VI), MOR-1 and MOR-1-HA is an anion exchange composite material. MOR-1- HA is used as a stationary phase in column exchange. Protonated MOR shows the better adsorption capacity than the non-protonated MOR because in the latter one firstly protonation of NH_2 and after that insertion of Cl^- and exchange with Cr (VI) takes place[16].

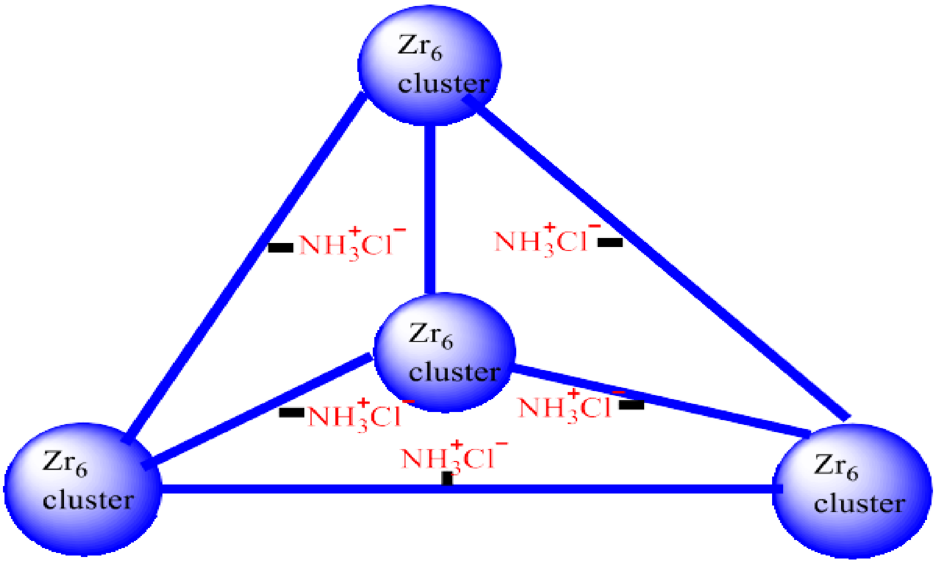

Figure 8: Representation Structure of MOR-I

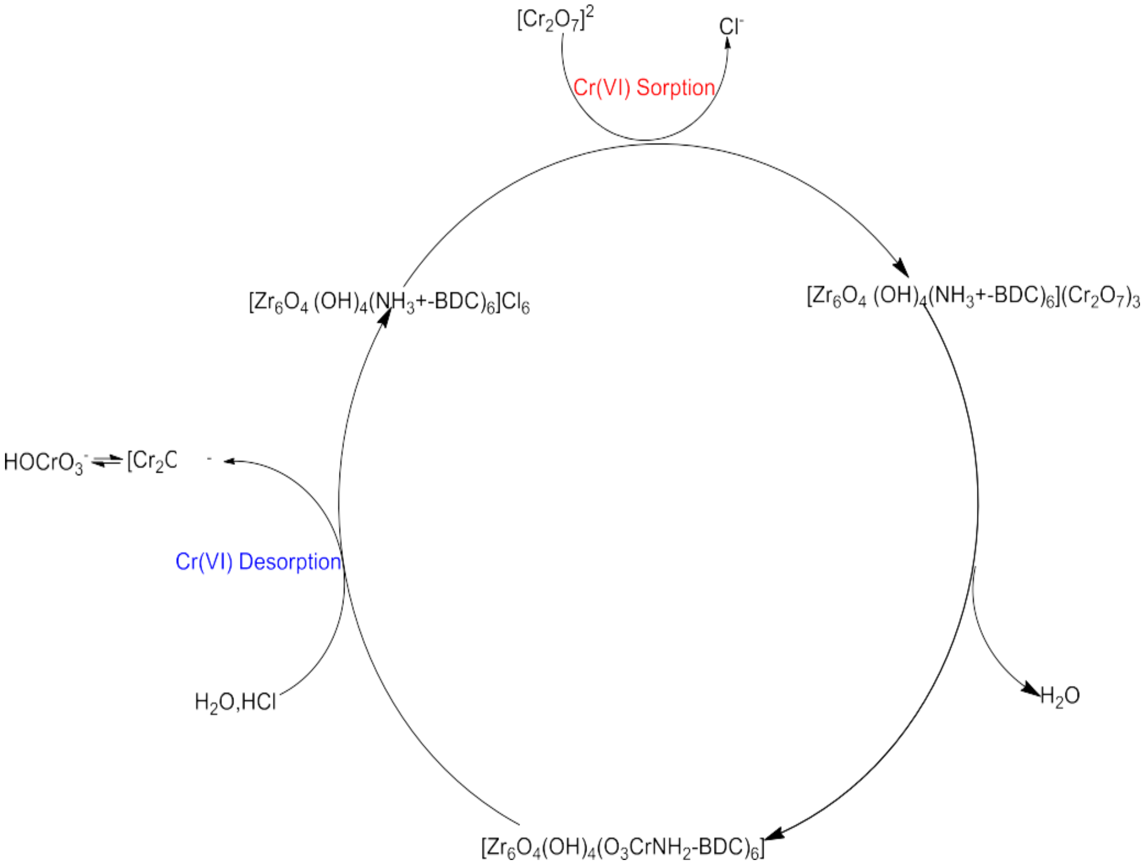

Figure 9: Mechanism of Cr(IV) Sorption and Desorption (protonated)

Removal of Lead:

Zhang and his co-workers synthesised metal-organic framework HS-mSi@MOF-5 which is based on thiol functional group and having the adsorption capacity of 312 mg/g for the lead ion. Mechanism for the removal of lead ion may involve the acid-base interaction accordance with the hard-soft acid-base interaction; thiol being a soft base will interact with the soft lead ion[17]. Luo and his co-Workers modified the metal-organic framework MIL-100 by introducing the coordination bonding between the Cr^{3+} and NH_2 group from the ethylenediamine and this result in the adsorption capacity of Pb^{2+} ion better than the previously synthesised MIL-100 metal-organic framework[18]. Ricco and his co-worker made the combination of metal-organic framework and magnetic nanoparticle and prepared MIL-53 based on Aluminum and iron nanoparticle and have the adsorption capacity of 492.4mg/g for Pb^{2+}. Liu and his co-workers designed UiO-66-NH2-CS aerogel monolith(UNCAM) having the adsorption capacity 104 mg/g for Pb^{2+} ion this is prepared by the self-crosslinking reaction between the CS(Chitosan) and NH_2 group. Adsorption of Pb^{2+} ion will proceed through the coordination interaction between the NH_2 and Pb^{2+}[19]. Liang and his co-workers prepared a titanium metal based organic framework MIL-125 and CS, and used it to remove the Pb^{2+} ion from the water[20].

Removal of Arsenic:

Arsenic ($As^{3+,}$ As^{5+}) is also a toxic heavy metal ion. Many Metal organic framework is designed in a way to remove them from the water. Li and his co-workers examined the ZIF-8 for the removal of arsenate from the water and it gives the adsorption capacity of 76.5 mgg^{-1}. ZIF-8 structure consists of the Zn^{2+} ions coordinated with 2-methylimidazole. Its high efficiency is mainly due to the mechanism of adsorption, which involves the presence of hydrogen on its surface because of the dissociative adsorption of water. So, this would help in better binding of As^{5+}. Moreover, they also studied the effect of the other common ions present in the solution on their removal efficiency and observed that the efficiency is mostly effected in case of P043-due to its similar nature with the AsO_4^{-3}[21].Yang and his co-workers synthesised $CoFe_2O_4$@MIL-100(Fe) hybrid magnetic nanoparticles (MNPs) which have adsorption capacity of 114.8mg/g for As (V) and 143.6 mg/g for As (III). Their adsorption mechanism involves the exchange of the OH group present on the surface of $CoFe_2O_4$@MIL-100(Fe) with the deprotonated arsenate and natural H_3AsO_4 involves the formation of multilayer due to the hydrogen bonding[22].

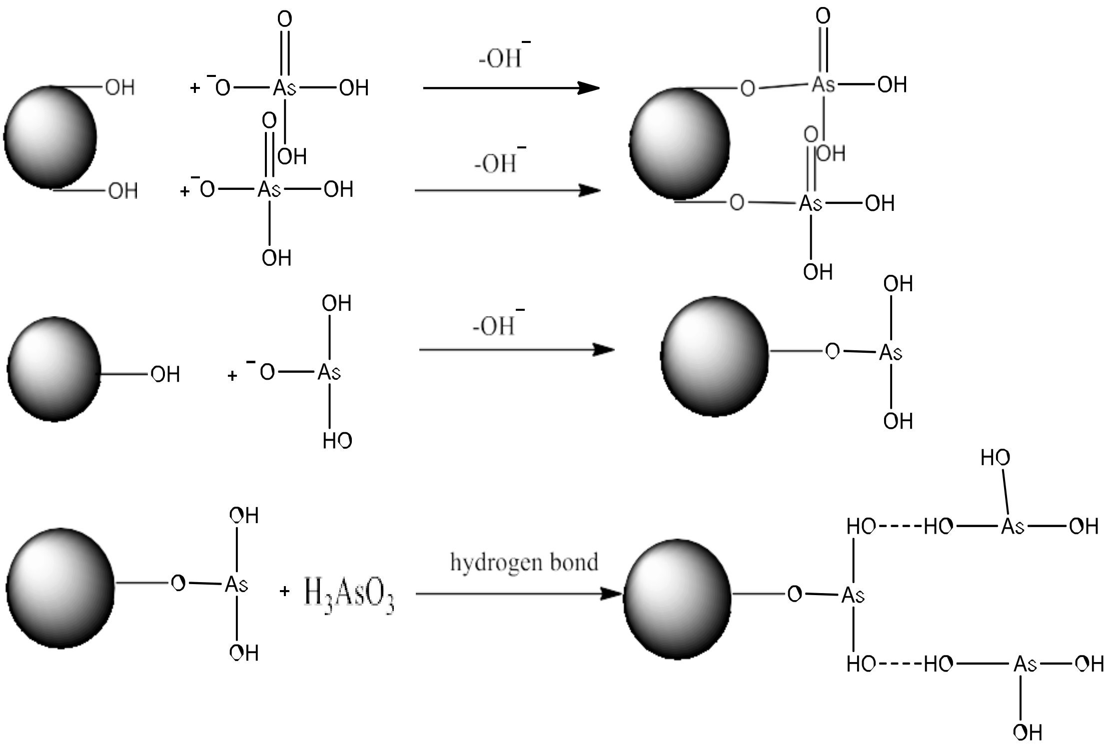

Figure 9:Mechanism of As adsorption

Broad Spectrum for heavy metal ion trap:

The metal organic prepared till date are specific for the specific metal ions. Peng and his co - workers designed the metal organic framework using the ethylenediaminetetraacetic acid which covers a broad spectrum of metal ions. This material also finds its uses in the catalysis. The metal-organic framework having the single functional and monodentate, so this makes them specific for the metal ion. When the functional groups are hard/soft they can selectively interact with their respective hard/soft metal ions so to increase the range of the metal ion. Peng and his co-workers introduced the ethylenediaminetetraacetic (EDTA) a good chelating ligand having the six coordination sites; two amine and 4 carboxyl groups so it can bind the various metal ions. This strategy can also be helpful in loading the metal ions to serve as catalyst. This can be confirmed by the performance of prepared Pd^{2+}@BS-HMT towards the Suzuki coupling reaction. MOF-808 having EDTA functional group is developed by Peng and his co-workers and they also confirmed that the EDTA is attached to MOF not adsorbed on the MOF. They also prepared two MOFs one with the oxalic acid (OX) as ligand which only remove the heavy metal ion and the other MOF with the 19hioglycolic acid MOF-808 TGA having the SH functionalized ligand which can remove the soft metal ions.MOF-808 EDTA can show selectivity for all three types of metal ions hard, soft and borderline[23].

Removal of heavy metal ions using biomolecules:

Biomolecules are also used to remove the heavy metal ions from the environment. The discharges from the industries get settled into the soil and cannot be degraded. Polypeptides starch cellulose can be used for removal of these heavy metal ions. The term bioavailability

refers as the ability of an element to be consumed by the living organism. Heavy metals having the higher mobility will also have the higher bioavailability and are more toxic to the living organism as they are consumed by them. Use of biomolecule in removing these is due to the naturally available and low prices removal from these also involve the adsorption mechanism[24].

Polysaccharides:

These are polymer of monosaccharide sugars these can be used to adsorb the heavy metal ions, have the better chelation ability due to the availability of -OH group in the glucose unit. Cellulose can be used with the help of chemical modification. Karnitz and his co-workers chemically modified the cellulose using EDTAD (ethylenediaminetetraaceticdianhydride) and this will be able to remove Cd^{2+},Cu^{2+},Pb^{2+}[25]. Chitosan can be obtained by doing the partial deacetylation of chitin. Chitosan have $-NH_2$ and -OH group which are responsible for the interaction with metal ions this can also be modified using the different functional group. Fan and his co-workers apply the thiourea chitosan on the surface of magnetite and having Ag^+ as imprinted ion Ag- TCM. This show good result in absorbing the Ag^+ ions, starch cyclodextrin can also be used to remove these heavy metal ions[26].

Amino acids:

Amino acids have both carboxylic and amine group, so they can do better chelation with the metal ions. Cysteine, is an important amino group having the thiol group on the side chain it can interact more with the metal ion due to the presence of the sulphur atom. Sljukic and his co-workers modified the glassy carbon spherical powder with the cysteine methyl ester and this can be used for the removal of the toxic Cd^{2+}. Histidine contains the imidazole ring in the side chain and this can act as base and acid and have the strong coordination tendency towards the metal ion. Birlik and his-workers synthesised MHA/Cr^{3+}used to remove the Cr^{3+}ions[27]. Interaction of biomolecule with heavy metal ions involve a special type of adsorption called biosorption in which the solid phase is of biomolecule and the liquid phase contain the species which is to be adsorbed and the theory which is majorly used to describe the metal ion uptake is the HSAB principle[28].

Removal of organic dye and heavy metal $Pb^{2+}$and Cd^{2+} using peptide based gel

Peptide amphiphile consists of two-part; a hydrophobic tail having the alkyl chain and a hydrophilic end with peptide sequence which is responsible for the formation of hydrogels and also this molecule can be assembled into organic medium to form organogels. Due to this property they are also called as ambidextrous gelator. Within the past few decades, researchers have gained their focus towards the supramolecular gels due to its controllable, distinct structural design and features. In this particular gel, a large number of nanofibers interlink with each other due to the presence of non-covalent interactions among them hence, making a network like structure which could easily store a large number of solvent particles leading to the formation of the gel. The hydrogels have the adsorption property due to the presence of interstitial voids in them whereas in the xerogels(dried gels) this property is exhibited due to the presence of п- surfaces; which are responsible for the absorption of toxic metal ions and dyes leading to management of wastewater. In these peptide amphiphiles the peptide sequence containing aromatic amino group are responsible for the π-π interaction as the amine favours the hydrogen bonding while the hydrophobic group is responsible for weak Vander Waal attraction. Xerogel which is abstracted from peptide gelator, is an efficient source towards the elimination of harmful chemical substances like organic dyes. Also, the hydrogels serve this purpose by eliminating the heavy and toxic transition metal ions like cadmium and lead both present in their +2-oxidation state from the wastewater efficiently. So, the peptide gelators could be used as the remedy to our environment due to their applications like above mentioned[29].

Synthesis of ZIF-67/EG intercalated structure for the determination of heavy metal ions

Ma and his co-workers designed the structure using intercalating the ZIF-67 nanoparticles into the layers of expanded graphite and this was used for the detection of heavy metal ions using the electrochemical technique[30]. Metal organic framework have poor conductivity, this type of modified structure have sufficient active sites and is electrochemically active, therefore can be used for the detection of heavy metal ions. There are coordinative interactions present in between the Co^{2+}, the hydroxyl and the epoxy group present in extended graphite[31]. In electrochemical technique three electrode system was used. The glassy carbon electrode (coated with ZIF-67) was used as working electrode, the platinum sheet as counter electrode and the saturated Ag/AgCl act as the reference electrode. Mechanism involves the adsorption of the heavy metal ions through bonding interaction on the surface of these framework and the ions are then released to the surface of glassy carbon electrode where reduction takes place, which then can be confirmed by stripping peak and the ion concentration can be reflected by the peak intensity[32].

Summary and Future Perspectives

Summarily, the recent studies on the adsorption capacity of various MOFs for some metal ions are discussed, along with their common mechanism involving in the adsorption are also discussed, studies also include the change in the adsorption capacity by changing the organic functional group (NH_2, SH, OH). Removal of chromium includes,UiO-66-NHC(S)NHMe, TMU-5, TMU-6, TMU-4 having adsorption capacity 117mg/g,123,118,127mg/g respectively. ZJU-101 Zr based MOF having the adsorption capacity of 245mg/g for dichromate which is highest for the removal of dichromate ion. Removal of lead includes HS-mSi@MOF-5 having the adsorption capacity of 312 mg/g,MIL-53 based on Aluminium and iron nanoparticle and have the adsorption capacity of 492.4mg/g, Metal organic framework using the ethylenediaminetetraacetic acid covers a broad spectrum of metal ions, ethylenediaminetetraacetic (EDTA) a good chelating ligand having the six coordination sites; two amine and 4 carboxyl groups so it can bind the various metal ions. Biomolecules are also used to remove the heavy metal ions from the environment Peptide based gel Xerogelis an efficient source towards the elimination of harmful chemical substances like organic dyes.

Future perspectives:

1) A few MOFs may be employed to adsorb the heavy metal ions, and their capacity to do so has to be researched.

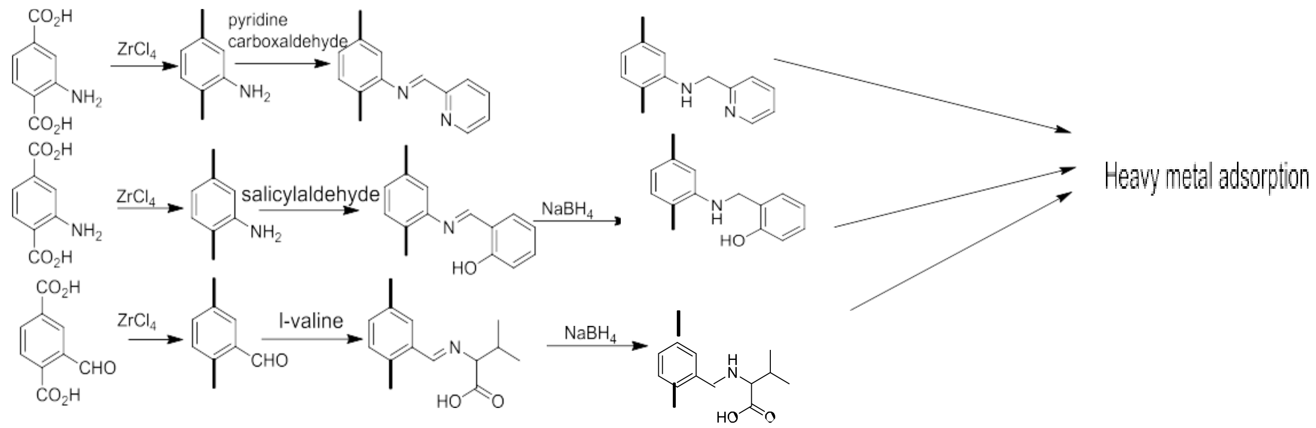

Figure 10: MOFs

2) Because it is also important, attention must be paid to the desorption process that will be carried out after the MOFs have absorbed the metals. MOFs cannot be dumped anyplace because doing so will only increase pollution.

3) The metal organic framework we're utilising might be delicate to moisture and less stable in watery medium. Therefore, a better water-stable metal organic framework might be created via modification.

4) The heavy metal ions in the aqueous solution are removed. As a result, future research may use non-aqueous samples to expand the scope of the removal of these metal ions from soil and sediments.

5) pH can affect the working mechanism of the metal organic framework as they have the limited range of pH in which they can effectively interact with the heavy ions. So, the studies may also include to widen the range of pH in which these Metal organic-framework can function.

6) Reusability also needs to be focused more, as most of the metal organic framework after their use in few cycles decreases their adsorption capacity.

References

1. Huang, Y.; Zeng, X.; Guo, L.; Lan, J.; Zhang, L.; Cao, D. Heavy metal ion removal of wastewater by zeolite-imidazolate frameworks. *Sep. Purif. Technol.* **2018**, *194*, 462–469.

2. Fu, F; Wang, Q,Removal of heavy metal ions from wastewaters:*J. Environ.Manage*. **2011**, *92*, 407-418.
3. Kuppler, R.J; Timmons, D.J; Fang, Q.R., Li, J.R.;Makal, T.A., Young, M.D., Yuan, D., Zhao, D.; Zhuang, W.; Zhou, H.C., Potential applications of metal-organicframeworks. *Coord. Chem. Rev*.**2009,**253, 3042-3066.
4. Ricco, R.;Konstas, K.; Styles, M.J.; Richardson, J.J.; Babarao, R.; Suzuki, K.;Scopece, P., Falcaro, P.,Leaduptake by aluminium based magnetic framework composites (MFCs) in water. *J. Mater. Chem*. **2015**,*3*, 19822-19831. : (Ricco, et al., 2015)
5. Khan, N.A.; Hasan, Z.,Jhung, S.H.,Adsorptive removal of hazardous materials using metal-organic frameworks (MOFs). *J. Hazard. Mater*. **2013,***244-245*, 444-456. (Khan & Hasan, 2009)
6. Abbasi, A.;Moradpour, T., Van Hecke, K. A new 3D cobalt (II) metalorganic framework nanostructure for heavy metal adsorption. *Inorg. Chim. Acta*.**2015,***430*, 261-267. (Abbasi & Moradpour, 2015)
7. Moradi, M.,Mercuric chloride adsorption on sulfur-containing BC 2 N nanotube: (Aboutorabi, 2016)toward HSAB concept. *Struct. Chem*. **2014,***25*, 1091-1097. (Moradi, 2014)
8. Hasan, Z.,Jhung, S.H. Removal of hazardous organics from water using metalorganic frameworks (MOFs): plausible mechanisms for selective adsorptions. *J. Hazard. Mater*. **2015**,*283*, 329-339. (Hasan, 2015)

Zhang, L.; Zeng, Y., Cheng, Z., Removal of heavy metal ions using chitosan and modified chitosan *J. Mol. Liq*. **2016,***214*, 175-191. (Zhang & Zeng, 2016)

Ahmed, I., Jhung, S.H., Adsorptive desulfurization and denitrogenation using metal-organic frameworks. *J. Hazard. Mater*, **2016**,*301*, 259-276. (Ahmed, 2016)

9. Saleem, H.; Rafique, U., Davies, R.P., Investigations on post-synthetically modified UiO-66-NH2 for the adsorptive removal of heavy metal ions from aqueous solution. *Micropor. Mesopor. Mat*.**2016**,*221*, 238-244. Saleem & Rafique, 2016

10. Tahmasebi, E.; Masoomi, M.Y.; Yamini, Y., Morsali, A., Application of mechanosynthesized azine-decorated zinc(II) metal-organic frameworks for highly efficient removal and extraction of some heavy-metal ions from aqueous samples: a

comparative study. *Inorg. Chem*. **2015**,*54*, 425-433. Tahmasebi, Masoomi, & Yamini,

2015

13. Li, X.; Gao, X.; Ai, L., Jiang, J., Mechanistic insight into the interaction and adsorption of Cr(VI) with zeolitic imidazolate framework-67 microcrystals from aqueous solution. *Chem. Eng.* J. **2015**,*274*, 238-246. Li, Gao, & Ai, 2015)

14. Fei, H.; Han, C.S.; Robins, J.C.; Oliver, S.R.J., A cationic metaleorganic solid solution based on Co(II) and Zn(II) for chromate trapping. *Chem. Mater* ,**2013,***25*, 647-652.

15. Aboutorabi, L., Morsali, A., Tahmasebi, E., Buyukgungor, O., Metal-organic framework based on isonicotinate N-Oxide for fast and highly efficient aqueous phase Cr(VI) adsorption. *Inorg. Chem*. **2016**, *55,* 5507-5513.

16. Rapti, S.; Pournara, A.; Sarma, D.; Papadas, I.T.; Armatas, G.S.; Tsipis, A.C.; Lazarides, T.; Kanatzidis, M.G.; Manos, M.J. Selective capture of hexavalent (Luo &

Ding, 2015)chromium from an anion-exchange column of metal organic resin-alginic acid composite. *Chem. Sci*. **2016**, *7,* 2427–2436.

17. Zhang, J.;Xiong, Z.; Li, C., Wu, C., Exploring a thiol-functionalized MOF for elimination of lead and cadmium from aqueous solution. *J. Mol. Liq.,* **2016,***221*, 43-50.

18. Luo, X.; Ding, L., Luo, J., Adsorptive removal of Pb (II) ions from aqueous samples with amino-functionalization of metalorganic frameworks MIL101(Cr). *J. Chem. Eng. Data* , (Zhang, Xiong, & Li, 2016)**2015,***60*, 1732-1743.

19. Liu, Q.; Li, S.; Yu, H.; Zeng, F.; Li, X.; Su, Z. Covalently crosslinked zirconium-based metal-organic framework aerogel monolith with ultralow-density and highly efficient Pb(II) removal. *J. Colloid Interface* Sci. **2020**, *561*, 211–219. (Liu, et al., 2020)

.

20 Liang, X.X.; Wang, N.; Qu, Y.L.; Yang, L.Y.; Wang, Y.G.; Ouyang, X.K. Facile preparation of metal-organic framework (MIL-125)chitosan beads for adsorption of Pb(II) from aqueous solutions. *Molecules.***2018**, *23*, 1524.

21 Li, J.; Wu, Y.N.; Li, Z.; Zhang, B.; Zhu, M.; Hu, X.; Zhang, Y.; Li, F. Zeolitic imidazolate framework-8 with high efficiency in trace arsenate adsorption and removal from water. *J. Phys. Chem*.**2014**, *118*, 27382–27387. (Li, et al., 2014)

22 Yang, J.C.; Yin, X.B. CoFe2O4@MIL-100(Fe) hybrid magnetic nanoparticles exhibit fast and selective adsorption of arsenic with high adsorption capacity. *Sci. Rep*. **2017**, *7,* 40955.

23 Peng, Y.; Huang, H.; Zhang, Y.; Kang, C.; Chen, S.; Song, L.; Liu, D., Zhong, A versatile MOF-based trap for heavy metal ion capture and dispersion. *Nature Communications* **2018,***9*, 187. (Peng, et al., 2018)

24 Bolan, N.;Kunhikrishnan, A.;Thangarajan, R.;Kumpiene, J.; Park, J.; Makino, T.; Kirkham,Scheckel M. B., Remediation of heavy metal(loid)s contaminated soils - to mobilize or to immobilize*? J. Hazard. Mater*., **2014.***266*, 141–166. (Bolan, et al., 2014)

25 Junior, K.; Gurgel, A.; Freitas, P.V.R., R.,Gil, L. F.Adsorption of Cu(II), Cd(II), and

Pb(II) from aqueous single metal solutions by mercerized cellulose and mercerized sugarcane bagasse chemically modified with EDTA dianhydride (EDTAD).*Carbohydr. Polym*., **2009**,*77*, 643–650.

(Junior, Gurgel, & Freitas, 2009), **2009**,*77*, 643–650.

26 Fan, L.; Luo, C.;Lv, Z.; Lu, F.,Qiu, H. Removal of Ag^+ from water environment using a novel magnetic thiourea-chitosan imprinted Ag^+. *J. Hazard. Mater*., **2011**,*194*, 193– 201. (Fan, Luo, Lv, & Lu, 2011)

27 Sljukic, B.; Crossley, G.G.W.A.; Jones, J. H.; Jiang, L.; Jones, T. G.J.,Compton, R. G. The thermodynamics of sequestration of toxic copper(II) metal ion pollutants from aqueous media by l-cysteine methyl ester modified glassy carbon spheres. *J. Mater. Chem*. **2006,***16*, 970–976. (Sljukic, Crossley, Jones, Jiang, & Jones, 2006)

28 Birlik, E.;Ersoz, A.; ıkkalp, E.;Denizli, A.,Say, R. Cr(III)-imprinted polymeric beads: Sorption and preconcentration studies. *J. Hazard. Mater*.,**2007,***140*, 110–116. (Birlik, Ersoz, ıkkalp, & Denizli, 2007)

29 Mondal, B.; Bairagi, D.; Nandi, N.; Hansda, B.; Das, K.S.; Gayle, C.J.C.; Castelletto, V.; Hamley, I.W., Banerjee, A. Peptide-Based Gel in Environmental Remediation Removal of Toxic Organic Dyes and Hazardous Pb^{2+} and Cd^{2+} Ions from Wastewater and Oil Spill Recovery. *Langmuir***2020**, *36*, 12942−12953. (29 Mondal, et al., 2020)

30 Ma, L.; Zhang, X.; Ikram, M.; Ullah, M.; Wu, H., Shi, K.Controllable synthesis of an intercalated ZIF-67/EG structure for the detection of ultratrace Cd^{2+}, Cu^{2+}, Hg^{2+} and Pb^{2+} ions. *Chemical Engineering Journal.*, **2020**,*395*, 125216 (Ma, Zhang, Ikram, Ullah, & Wu, 2020)

31 Rajasekaran, S., Devi, K.R.S., Pinheiro, D., Mohan, M.K., Iyyappa Rajan, P. (2022). Metal Organic Frameworks to Remove Arsenic Adsorption from Wastewater. In: Lichtfouse, E., Muthu, S.S., Khadir, A. (eds) Inorganic-Organic Composites for Water and Wastewater Treatment. Environmental Footprints and Eco-design of Products and Processes. Springer, Singapore. 2022

32 Hongjuan Liu, Tianyu Fu, and Yuanbing Mao Metal–Organic Framework-Based Materials for Adsorption and Detection of Uranium(VI) from Aqueous Solution *ACS Omega* 2022 *7* (17), 14430-14456 (Hongjuan Liu, 2022)