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Removal of Heavy Metals Using Novel Adsorbent Materials

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REMOVAL OF HEAVY METALS USING NOVEL ADSORBENT MATERIALS

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DEDICATION

First and foremost, I want to dedicate this work to the God our Father and the Lord Jesus Christ. Without his grace, blessings, gifts, and encouragement, this dissertation would never have begun. A relationship with Jesus Christ and his forgiveness makes it possible for me to get up in the morning and do the research that is found in this document.

I also want to thank my family and friends for their support. I want to thank my parents, Phebe and Samuel Joseph, and my sister, Renee Joseph (who is the first doctor in our family) for pushing me to greater heights. I also want to thank my children, Jael, Hadassah, Selah, and Josiah Joseph, for their love and support as I worked on my research. Seeing them every day always give me the encouragement that I need and experiencing their love, even when things do not go my way, always puts a smile on face.

Most importantly, I want to dedicate this dissertation to my amazing wife, Jonita Joseph. She is the one who takes care of the children and the home while I am in the lab. She is the one who has been with me on this PhD journey from the Columbia, SC to Baltimore, MD to Corpus Christi, Texas, and back to Columbia, SC. You believed when I stopped believing. You encouraged me when I was discouraged. You cared for me when I was sick. You are the reason that I am able to write this dissertation. The Bible is accurate when it says, “He who find a wife finds a good thing and obtains favor from the LORD” (Proverbs 18:22). You are my good thing. Thank you for being there and continuing to support me. I love you more than anything. This is for you.

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ABSTRACT

Heavy metal contamination is a growing concern throughout the world, particularly as industrial and urban activities have increased. Inadequate water and wastewater treatment, coupled with increased industrial activity, have led to increased heavy metal contamination in rivers, lakes, and other water sources in developing countries. To address these concerns, a significant amount of research has been conducted on various novel adsorbents to evaluate their ability to remove heavy metals. Thus, in this study, MIL-100(Fe) and MIL-101(Cr) are fabricated and investigated to determine their ability to remove copper (Cu^{2+}), cadmium (Cd^{2+}), and lead (Pb^{2+}) from aqueous solution. The experimental data fit most closely to the Freundlich model, followed closely by the Linear isotherm model. However, the values for the Freundlich parameter *n* were close to 1, which suggests that the adsorption followed the Linear isotherm model. The K_{LIN} coefficient [(mg/g)/(mg/L)] for the Linear isotherm model was the largest for Cu^{2+}, followed by Cd^{2+} and Pb^{2+}. MIL-100(Fe) and MIL-101(Cr) exhibited fast adsorption kinetics, achieving equilibrium in approximately 0.5 hours. Electrostatic interactions were determined to be the dominant adsorption mechanism for the removal of Cu^{2+}, Cd^{2+}, and Pb^{2+} by MIL-100(Fe) and MIL-101(Cr), which is consistent with similar adsorption studies. This study shows that MIL-100(Fe) and MIL-101(Cr) are effective adsorbents for the removal of heavy metals from aqueous solution.

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CHAPTER 1

INTRODUCTION

Heavy metal pollution is a rising concern, particularly in the developing world, due to the increase in industrial and urban activities The release of contaminated wastewater from various industries, including coal-fired power plants (Demirak et al., 2006) and mining operations (D Archundia et al., 2017), along with waste recycling and solid waste disposal activities (Sunil Herat & Pariatamby Agamuthu, 2012), represents a major source of pollution. Meanwhile emissions from vehicles and other urban activities also contribute to the increase in water contamination (J Pandey & U Pandey, 2009). According to the United Nations, an estimated 80% of all industrial and municipal wastewater in the developing world is released to the environment without any prior treatment (UN-Water, 2018a). Moreover, additional contributions to water pollution include polluted urban stormwater runoff, agricultural runoff, and rainwater transport into potential drinking water sources (M. S. Kambole, 2003). Heavy metals are of particular concern due to their toxic and carcinogenic nature, along with their documented harmful effects to human health (Sutirtha Chakraborty, Arup R Dutta, Saubhik Sural, Debkishore Gupta, & Susruta Sen, 2013). Heavy metal pollution is also a concern because many of the drinking water treatment techniques used in the developing world, including chlorination, boiling, and solar disinfection, are ineffective at removing heavy metals (M De Kwaadsteniet, PH Dobrowsky, A Van Deventer, W Khan, & TE Cloete, 2013).

Adsorption can serve as a potential solution to the proliferation of heavy metal contamination. While other technologies, such as membrane filtration (Sewoon Kim et al., 2018), electrocoagulation (Al-Qodah & Al-Shannag, 2017), microbial remediation (Ayansina Segun Ayangbenro & Olubukola Oluranti Babalola, 2017; P.-S. Li & H.-C. Tao, 2015), and carbon nanotechnology (Peng, Li, Liu, & Song, 2017; AIA Sherlala, AAA Raman, MM Bello, & A Asghar, 2018; J. Xu et al., 2018), have been shown to remove heavy metals effectively, these water treatment approaches are not feasible for developing countries. Adsorption provides an opportunity to remove heavy metals without the need for additional energy input or chemical modifications. Locally available materials, such as agricultural waste, fruit and vegetable waste materials, and naturally occurring soil have been shown to remove heavy metals from water sources (G Annadurai, Juang, & Lee, 2003; Božić et al., 2013; Velyana G Georgieva, Mariana P Tavlieva, Svetlana D Genieva, & Lyubomir T Vlaev, 2015; R. Leyva-Ramos, L. Bernal-Jacome, & I. Acosta-Rodriguez, 2005). Moreover, metal-organic frameworks have also emerged as a promising novel material that can be used in water treatment applications. Its ability to remove contaminants of emerging concern (Dhaka et al., 2019) has sparked a significant amount of attention in the scientific community. This project seeks to establish the effectiveness of these materials in the removal of heavy metals, along with the impact of varying water quality conditions on adsorption. This project also seeks to enhance our understanding of the mechanisms that facilitate the removal of heavy metals using these materials.

CHAPTER 2

OBJECTIVES AND SCOPE

This research will advance the scientific understanding of the adsorption of heavy metals by various novel materials. This research will develop the scientific base for the removal of heavy metals using MOFs, which is not prominent in the literature. Moreover, the use of fruit peel to remove heavy metals will be more closely investigated for real-world applicability and removal mechanisms that may be applied to similar materials often found in the developing world. Overall, this research will provide a practical understanding of heavy metal removal that may be applied to contaminated water sources throughout the world. The objectives for this research are as follows:

The first objective is to review and summarize the current research on the use of low-cost materials to remove heavy metals from water sources. A wide variety of locally available materials, along with their heavy metal removal efficiencies, will be reviewed. Moreover, an evaluation of the removal mechanisms will also be closely evaluated.

The second objective is to review and summarize the current research on the use of metal-organic frameworks (MOFs) in various water treatment applications. For this review, the focus will be on the use of MOFs to remove contaminants of emerging concern (CECs). This review will summarize the effectiveness of MOFs in the removal of CECs and the mechanisms that are involved. The synthesis methods and procedures for MOFs will also be reviewed.

The third objective is to investigate the removal of selected heavy metals (cadmium, copper, and lead) using two different types of MOFs: 1) MIL-100(Fe) and 2) MIL-101(Cr). Adsorption isotherm experiments and kinetic experiments will be performed to evaluate the heavy metal removal efficiency of each MOF. Experiments will also be conducted to investigate the impact of water quality conditions (e.g., pH, organic matter, ionic strength) on the removal of heavy metals using MOFs. Detailed characterization of the MOFs will also be performed to understand their physicochemical properties.

CHAPTER 3

REMOVAL OF HEAVY METALS FROM WATER SOURCES IN THE DEVELOPING WORLD USING LOW-COST MATERIALS: A REVIEW[1]

Abstract

Heavy metal contamination is a growing concern in the developing world. Inadequate water and wastewater treatment, coupled with increased industrial activity, have led to increased heavy metal contamination in rivers, lakes, and other water sources in developing countries. However, common methods for removing heavy metals from water sources, including membrane filtration, activated carbon adsorption, and electrocoagulation, are not feasible for developing countries. As a result, a significant amount of research has been conducted on low-cost adsorbents to evaluate their ability to remove heavy metals. In this review article, we summarize the current state of research on the removal of heavy metals with an emphasis on low-cost adsorbents that are feasible in the context of the developing world. This review evaluates the use of adsorbents from four major categories: agricultural waste; naturally occurring soil and mineral deposits; aquatic and terrestrial biomass; and other locally-available waste materials. Along with a summary

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[1] Joseph, L. et al., 2019. Removal of heavy metals from water sources in the developing world using low-cost materials: A review. *Chemosphere* 229: 142-159. Reprinted here with permission of publisher.

of the use of these adsorbents in the removal of heavy metals, this article provides a summary of the influence of various water-quality parameters on heavy metals and these adsorbents. The proposed adsorption mechanisms for heavy metal removal are also discussed.

3.1 Introduction

Freshwater is a basic requirement for humans and wildlife. The availability of clean drinking water is critical for maintaining a healthy life. However, while global water demand increases annually, various forms of pollution have compromised potential water sources (UN-Water, 2018b). Moreover, researchers have found that the impacts of climate change, such as higher temperatures and changes to the water cycle, will also exacerbate these water issues and potentially result in increased flooding, more severe droughts, and enhanced toxicity of chemical contaminants in the environment (Milly, Wetherald, Dunne, & Delworth, 2002; Noyes et al., 2009; Xi et al., 2017). Polluted water sources can be harmful to humans due to potential exposure to pathogens or toxic chemicals via irrigation of plants with contaminated water, the consumption of toxins in aquatic organisms, or the use of contaminated surface water for recreational purposes (*e.g.*, swimming) (Schwarzenbach, Egli, Hofstetter, Gunten, & Wehrli, 2010). However, for the majority of individuals living in the developing world, human health is most commonly affected by the direct consumption of contaminated water.

In developing countries, the impact of increased pollution is particularly problematic because these populations do not have the resources to effectively treat contaminated water or access to clean drinking water systems that can supply water to their homes. The World Health Organization (WHO) estimates that 844 million people do not have a basic drinking water source and that 230 million people spend more than 30 min/d collecting water from an improved water source, which may include piped water, boreholes, protected wells and springs, rainwater, and packaged/delivered water (WHO, 2017). The inability for people in developing countries to have consistent access to an improved drinking water source increases the likelihood of water-related diseases. According to WHO estimates, approximately 1.6 million people die every year from preventable water-related diseases, such as diarrhea, and 90% of these deaths are children under 5 years of age (Pandit & Kumar, 2015). In the developing world, drinking water contamination due to microbial agents (*e.g.*, bacteria and viruses) represents the greatest threat to human health. However, the proliferation of heavy metals in drinking water sources is also a growing concern. Table 3.1 provides the characteristics of common heavy metals found in the developing world.

In recent years, industrial and urban activities have increased throughout the developing world, which has subsequently contributed to increased heavy metal pollution. The release of contaminated wastewater from various industries, including coal-fired power plants (Demirak, Yilmaz, Tuna, & Ozdemir, 2006) and mining (D. Archundia et al., 2017), along with waste recycling and solid waste disposal activities (S. Herat & P. Agamuthu, 2012; Olafisoye, Adefioye, & Osibote, 2013; Perkins, Brune Drisse, Nxele, & Sly, 2014; Q. Wu et al., 2015), represents a major source of pollution, while emissions from vehicles and other urban activities also contribute to it (J. Pandey & U. Pandey, 2009; Prasse, Zech, Itanna, & Glaser, 2012).

Table 3.1: Characteristics of common heavy metals

Heavy metal	Human health effects	Common sources	Maximum Contaminant Level	
			USEPA[a]	*WHO*[b]
Arsenic (As)	Skin damage Circulatory system issues	Naturally occurring Electronics production	0.010 mg L^{-1}	0.010 mg L^{-1}
Cadmium (Cd)	Kidney damage Carcinogenic	Naturally occurring Various chemical industries	0.005 mg L^{-1}	0.003 mg L^{-1}
Chromium (Cr)	Allergic dermatitis Diarrhea, nausea, and vomiting	Naturally occurring Steel manufacturing	0.1 mg L^{-1}	0.05 mg L^{-1}
Copper (Cu)	Gastrointestinal issues Liver or kidney damage	Naturally occurring Household plumbing systems	1.3 mg L^{-1}	2.0 mg L^{-1}
Lead (Pb)	Kidney damage Reduced neural development	Lead-based products Household plumbing systems	0.0 mg L^{-1}	0.01 mg L^{-1}
Mercury (Hg)	Kidney damage Nervous system damage	Fossil fuel combustion Electronics industries	0.002 mg L^{-1}	0.006 mg L^{-1}

[a] Values established by the United States Environmental Protection Agency (USEPA, 2019)

[b] Values established by the World Health Organization (WHO, 2017)

According to the United Nations, an estimated 80% of all industrial and municipal wastewater in the developing world is released to the environment without any prior treatment (UN-Water, 2018b). Moreover, additional contributions to water pollution include polluted urban stormwater runoff, agricultural runoff, and rainwater transport into potential drinking water sources (M. Kambole, 2003; Lye, 2009). Heavy metals are of particular concern due to their toxic and carcinogenic nature, along with their documented harmful effects to human health (S. Chakraborty, A. R. Dutta, S. Sural, D. Gupta, & S. Sen, 2013; Gleason et al., 2016; Jarup, 2003; Schwartzbord, Emmanuel, & Brown, 2013). Heavy metal pollution is also a concern because many of the drinking water treatment techniques used in the developing world, including chlorination, boiling, and solar disinfection, are ineffective at removing heavy metals (M. De Kwaadsteniet, P. Dobrowsky, A. Van Deventer, W. Khan, & T. Cloete, 2013).

When considering the impact of heavy metals in the developing world, numerous review papers have investigated the prevalence of heavy metals in drinking water sources in several developing countries (Chowdhury, Mazumder, Al-Attas, & Husain, 2016; Emmanuel, Pierre, & Perrodin, 2009; Rahman, Naidu, & Bhattacharya, 2009; Rossiter, Owusu, Awuah, Macdonald, & Schafer, 2010), along with the human health hazards associated with heavy metal contamination (Amadia, Igwezeb, & Orisakwea, 2017; Holecy & Mousavi, 2012; Jarup, 2003; Odongo, Moturi, & Mbuthia, 2016). Many researchers have conducted detailed studies on the heavy metal contamination of water sources in specific developing countries, including China (S. Cao et al., 2015; Z. Li, Ma, van der Kuijp, Yuan, & Huang, 2014; Qu et al., 2012; Y. Xu, Wu, Han, & Li, 2017; Zou et al., 2015), India (A. K. Awasthi, X. Zeng, & J. Li, 2016; A.K. Awasthi, X. Zeng, & J. Li, 2016; J. Pandey &

U. Pandey, 2009; Ramasamy, Jayasooryan, Chandran, & Mohan, 2017; Sridhar et al., 2017), Bangladesh (Gleason et al., 2016; S. Islam, Ahmed, Habibullah-Al-Mamun, & Hoque, 2015; Linderholm et al., 2011; Nahar, Zhang, Ueda, & Yoshihisa, 2014; A. Wang et al., 2016), Ethiopia (Prasse et al., 2012; Yohannes et al., 2013), Pakistan (Bhowmik et al., 2015; Nawab et al., 2016; Nawab et al., 2017; Rasheed, Slack, Kay, & Gong, 2017; Rehman, Zeb, Noor, & Nawaz, 2008), and various other developing countries (D. Archundia et al., 2017; Belabed, Meddour, Samraoui, & Chenchouni, 2017; Nweke & Sanders, 2009; Tarras-Wahlberg & Nguyen, 2008). Moreover, due to the well-documented impacts of heavy metals to human health, a significant amount of research has been conducted on methods of removing heavy metals from drinking water sources, as well as municipal wastewater, industrial wastewater, and other water sources. Many recent review articles highlight treatment methods and technologies that achieve high removal efficiencies for heavy metals and are currently being explored for use in many developed countries, such as membrane filtration (S. Kim, K. Chu, et al., 2018), electrocoagulation (Al-Qodah & Al-Shannag, 2017; Bazrafshan, Mohammadi, Ansari-Moghaddam, & Mahvi, 2015), microbial remediation (A. S. Ayangbenro & O. O. Babalola, 2017; P. S. Li & H. C. Tao, 2015), activated carbon adsorption (J. Li et al., 2018; Renu., Agarwal, & Singh, 2017), carbon nanotechnology (Peng et al., 2017; A. Sherlala, A. Raman, M. Bello, & A. Asghar, 2018; J. Xu et al., 2018), and various modified adsorbents (Y. Jiang et al., 2018; Sajida, M., Ihsanullah, N., & Osman, 2018; Zare, Motahari, & Sillanpaa, 2018). However, these technologies are not feasible or cost-effective in the context of the developing world. To treat water in the developing world, proposed technologies must be easy to obtain, constructed by local workers with limited education, and have low operating and maintenance costs.

Therefore, in this review paper, we focus on the use of low-cost, often locally available, materials that do not require additional energy input or modifications to remove heavy metals from water sources. While providing an exhaustive review of the studies conducted in the developing world regarding heavy metal removal is challenging, the objective of this review paper is to examine the major categories of materials that would be most readily available and utilized in the context of the developing world. The materials investigated in this review are divided into four broad categories: agricultural waste, which includes various types of residual waste from nuts (*e.g.*, peanut, cashew, pistachio, *etc*.), along with fruit and vegetable waste materials (*e.g.*, rice straw, corn, orange, banana peels, lemons, beets, grapefruit, *etc*.); naturally- occurring soil and mineral deposits; aquatic and terrestrial biomass (*e.g.*, seaweeds, water hyacinth, trees, *etc*.); and other waste materials that are commonly found in developing countries (*e.g.*, tea waste, local seashells, industrial by-products, *etc*.). We examined the removal of various heavy metals using these materials and surveyed the proposed removal mechanisms associated with these materials. To date, few review papers have surveyed the use of low-cost materials for the removal of heavy metals from water. The most recent review was published over approximately a decade ago (Babel & Kurniawan, 2003; Kurniawan, Chan, Lo, & Babel, 2006).

3.2 Effect of water quality characteristics on heavy metal removal

When investigating the removal of heavy metals, it is important to evaluate the behavior of the heavy metals, along with the characteristics of the adsorbent, under varying water quality conditions. Among the most important water quality parameters related to heavy metal removal are pH, temperature, the presence of natural organic matter (NOM), and ionic strength. While heavy metal contamination is most often associated with industrial wastewater, in the developing world, heavy metals have been detected in various water sources, including domestic wastewater effluent (Emmanuel et al., 2009; Khatib et al., 2012), groundwater (Armah, 2014; Emmanuel et al., 2009; Kumarasinghe et al., 2017; Sridhar et al., 2017; S. Wang & Mulligan, 2006), rivers (M. Islam, Ahmed, Raknuzzaman, Habibullah-Al-Mamun, & Islam, 2015; S. Islam et al., 2015; Mohiuddin, Ogawa, Zakir, Otomo, & Shikazono, 2011; Mwanamoki et al., 2015) and lakes (D. Archundia et al., 2017; Y. Xu et al., 2017; Yohannes et al., 2013). These water sources have varying water quality characteristics, which ultimately influence the ability of an adsorbent to effectively remove heavy metal contamination from them. The following sections describe the chemical characteristics of heavy metals and the effects of water quality on heavy metals and their removal.

3.2.1 Chemical Characteristics of Heavy Metals

Heavy metals typically enter the environment through various industrial activities, agricultural practices, and improper waste disposal (Chowdhury et al., 2016). Heavy metals are particularly problematic because of their persistence in the environment. Heavy metals are non-biodegradable and accumulate in humans and animals as they are exposed through the consumption of contaminated food and water. While humans, along with all living organisms, need varying amounts of heavy metals, such as iron, zinc, copper, and chromium, for proper growth and development, these metals can be toxic when consumed at elevated concentrations (Tchobanoglous, Burton, & Stensel, 2003). Table 3.2 provides the chemical properties of common heavy metals found in the environment.

3.2.2 Effect of pH

The pH of the water source has a significant impact on the presence of heavy metals and their characteristics. The speciation of heavy metals in aqueous solution is highly dependent on the pH. At neutral to low pH values, heavy metals generally exist in their cationic state and tend to be more soluble and mobile in water sources. As the pH rises, complexes begin to form with hydroxides and other anions that may be present in the water. Along with these effects of the heavy metals, pH can also affect the surface charge of the adsorbent, the concentration of ions on the functional groups of the adsorbent, and the ionization state of the adsorbent (Taşar, Kaya, & Özer, 2014).

Several studies have demonstrated the influence of pH on heavy metal speciation and removal. For example, the stability and mobility of copper have both been shown to increase with decreasing pH (Kumpiene, Lagerkvist, & Maurice, 2008). However, as the pH increases, the heavy metals form complexes with hydroxide ions, thus affecting the oxidation state of the heavy metal. In many cases, as the pH increases above neutral, the heavy metals form solids, which precipitate out of the water. The oxidation state for chromium, for example, has been shown to change from Cr(III), its more stable form, to Cr(VI), its more toxic form, as the pH increases (Pantsar-Kallio, Reinikainen, & Oksanen, 2001). Moreover, a wide variety of chromium species with various charges, such as H_2CrO_4, $HCrO_4^-$, Cr_2O_7, and CrO_4^{2-}, can be observed at different pH values (Sari & Tuzen, 2008). In the case of lead, lower pH values increase the concentration of free lead ions in the water source, while increased pH values lead to immobilization, primarily due to precipitation (Kumpiene et al., 2008).

Table 3.2: Chemical properties of heavy metals

Heavy metal	Molecular weight ($g\ mol^{-1}$)	Oxidation state(s)[a]	Van der Waals radius (10^{-12} m)	Electronegativity (Pauling Scale)	Log K_{OW}
Arsenic	74.9	-3, **+3**, **+5**	119	2.18	NA
Cadmium	112.4	+2	158	1.69	3.86 ± 0.36[b]
Chromium	52.0	0, +2, **+3**, **+6**	200	1.66	NA
Cobalt	58.9	-1, 0, **+2**, +3	200	1.88	NA
Copper	63.5	+1, **+2**	140	1.90	NA
Lead	207.2	**+2**, +4	202	2.33	4.02 ± 0.28[b]
Manganese	54.9	-1, 0, **+2**, +3, +4, +6, +7	205	1.55	3.98 ± 0.25[b]
Mercury	200.6	+1, **+2**	155	2.00	0.62[c]
Nickel	58.7	0, **+2**, +3	163	1.91	NA
Zinc	65.4	+2	139	1.65	NA

[a] **Bold** values represent the most common oxidation state(s) for the heavy metal.
[b] Values determined experimentally by (Sakultantimetha, Bangkedphol, Lauhachinda, Homchan, & Songsasen, 2009).
[c] Values provided by Michigan Department of Environmental Quality
NA = not available

Moreover, when evaluating the removal of heavy metals by adsorption, water sources with low pH values (< 4.0) have high concentrations of H^+ ions, which often interfere with the interactions between soluble metal ions and adsorbent surfaces by competing for adsorption sites, thus reducing overall heavy metal removal (Al-Anber & Matouq, 2008; H. Chen, Zhao, Dai, Wu, & Yan, 2010; X. Li, Zhang, Sheng, & Qing, 2018; Thirumavalavan, Lai, Lin, & Lee, 2010). However, when the pH increases, adsorption often increases as the surface of the adsorbent becomes more negatively charged and interacts more readily with the positively-charged heavy metals (Krishnani, Meng, Christodoulatos, & Boddu, 2008; R. Leyva-Ramos, L. A. Bernal-Jacome, & I. Acosta-Rodriguez, 2005; Tan, Yuan, Liu, & Xiao, 2010; Vimala & Das, 2009). This phenomenon has been observed using a wide variety of adsorbents. The removal of the majority of heavy metal ions by adsorption is minimal at low pH values (< 3) (Bozbas & Boz, 2016; Rao & Khan, 2009; Taşar et al., 2014; C. S. Zhu, Wang, & Chen, 2009). Meanwhile, as the pH increases, heavy metal removal increases as the concentration of H^+ ions is reduced and more adsorption sites become available (Qi & Aldrich, 2008; Taşar et al., 2014; C. S. Zhu et al., 2009). One notable exception is the removal of chromium, which exists in anionic species as the pH increases (*e.g.*, $HCrO_4^-$, CrO_4^{2-}). In this instance, adsorption has been shown to decrease as the pH of the solution increases. This is due to the electrostatic repulsion resulting from negative surface charges on the adsorbent, which inhibits the adsorption of anionic species (Ahmad et al., 2017; V.G. Georgieva, M.P. Tavlieva, S.D. Genieva, & L.T. Vlaev, 2015).

Overall, when considering the behavior and potential removal of heavy metals, pH is a significant parameter that affects the behavior and removal of heavy metals. From the published research that was reviewed, the general consensus is that low pH values (< 4) have been shown to hinder the adsorption of heavy metals, while pH values between 5 and 7 have been shown to be the most effective. In the context of the developing world, the pH of the water source to be treated should be maintained at neutral levels to maximize heavy metal adsorption.

3.2.3 Effect of temperature

Temperature is another important parameter that should be considered when evaluating the behavior of heavy metals and their subsequent removal. Many of the mechanisms that have been identified for the removal of heavy metals are enhanced at higher temperatures, including surface complexation reactions and various forms of ion exchange (H. Chen et al., 2010). For instance, in a previous study, the removal of Ni(II) using tea waste increased by approximately 22% when the temperature was increased from 25 to 60 °C, which was attributed to the increased mobility of the heavy metals, as well as the increased number of adsorption sites due to bond rupturing (Malkoc & Nuhoglu, 2005). In another study, increased removal of Cr(VI) using pistachio hull waste was achieved by increasing the temperature from 5 to 40 °C, which was attributed to the possible development of additional adsorption sites on the surface of the adsorbent (Moussavi & Barikbin, 2010). Another study found that the adsorption of Cu(II) onto hazelnut shells increased with increased temperature, which was attributed to the potential increased pore size of the shells and the increased kinetic energy of the Cu(II) ions, which facilitated more contact with the adsorbent (Demirbas, Dizge, Sulak, & Kobya, 2009). Along with increased adsorption, the adsorption process has also been shown to proceed more quickly at higher temperatures, due to the increased driving force of diffusion across the boundary layer and an increased diffusion rate within the adsorbent (Weng et al., 2014).

However, in many cases, increased temperatures have resulted in a decrease in the removal of heavy metals. For instance, in one study, the removal of total chromium by red algae was reduced from 90 to 78% with increasing temperature, possibly due to the tendency for ions to remain in the aqueous phase (Sari & Tuzen, 2008). Moreover, several researchers have reported a reduction in the removal of heavy metals such as Pb(II) and Ni(II) with increasing temperature, which was attributed to decreased surface activity (Senthil Kumar et al., 2011; SenthilKumar, Ramalingam, Sathyaselvabala, Dinesh Kirupha, & Sivanesan, 2011; Taşar et al., 2014). A study that investigated the adsorption of Cr(III) and Cu(II) onto peanut shells reported increased removal as the temperature rose to 50 °C, then a decrease when the temperature increased to 60°C. This outcome was possibly due to potential damage to the adsorption sites on the peanut shells (Witek-Krowiak, Szafran, & Modelski, 2011). In another study that evaluated the removal of Cd(II) using olive cake, the adsorption capacity of the olive cake decreased by 32% when the temperature was raised from 28 to 45 °C (Al-Anber & Matouq, 2008). Therefore, when assessing the effects of temperature on the removal of heavy metals, each adsorbent and the corresponding metal ion must be evaluated specifically to determine the overall impact of temperature changes on the adsorption process.

3.2.4 Effect of ionic strength

The ionic strength of the water source has also been shown to have an effect on heavy metals and the ability to remove them. The presence of chloride can lead to the formation of neutral or negatively-charged heavy metal-chloride complexes that are soluble and difficult to remove (Ferraz & Lourenco 2000). This phenomenon was observed by (Villaescusa et al., 2004), who reported a significant decrease in the removal efficiency of Cu(II) and Ni(II) as the ionic strength increased, due to the increased formation of heavy metal-chloride complexes that had a low affinity for adsorption. Researchers who studied the behavior of trace metals in an estuary also observed a strong correlation between increased salinity and increased concentration of dissolved metals, particularly copper, cadmium, and zinc (W. Wang, Chen, Guo, & Wang, 2017).

When interactions between heavy metals and other surfaces are strongly influenced by electrostatic forces, increased ionic strength in a solution can have a significant effect on the behavior and removal of heavy metals. Based on theories related to surface chemistry, an electric double layer decreases with increasing ionic strength influencing electrostatic interactions, which leads to reduced adsorption of heavy metals as the ionic strength increases (Onyancha, Mavura, Ngila, Ongoma, & Chacha, 2008). For example, Zhang (2011) investigated the effects of ionic strength on the removal of heavy metals, including Cu(II), Pb(II), and Zn(II), by dairy manure compost and reported that the overall removal of heavy metals decreased as the ionic strength increased (M. Zhang, 2011).

However, other studies have demonstrated that heavy metal removal increases with ionic strength. Yang et al., 2016 reported that the removal of As(III) and Ni(II) increased by approximately 25% as the ionic strength of the solution increased from 0.01 to 1.0 M Cl^-, due to the involvement of inner-sphere surface complexation. Moreover, a study on the adsorption of Co(II) and Cu(II) onto crab shell particles demonstrated increased removal of 2–5% when the ionic strength of the solution was increased by adding competing ions, such as Na^+ and K^+ (Vijayaraghavan, Palanivelu, & Velan, 2006).

3.2.5 Effect of NOM

NOM is commonly understood to consist of humic and fulvic acids that are derived from the decomposition of plant and animal matter (Merdy, Huclier, & Koopal, 2006). NOM is a complex array of organic acids and is highly reactive with heavy metals. Interactions can occur between NOM and heavy metals, which can alter the reactivity of the heavy metals in the environment and affect their mobility, bioavailability, and toxicity (Merdy et al., 2006). The specific impact of NOM on heavy metals can be difficult to ascertain, primarily due to the wide array of additional factors that contribute to the manner in which NOM affects heavy metals, including pH, the humification of the specific NOM, and the oxidation state of the heavy metal (Kumpiene et al., 2008). In many instances, the acidic nature of the NOM allows them to interact with heavy metals through various mechanisms, including ion exchange, chelation, and surface adsorption (Reuter & Perdue, 1977).

For example, arsenic has been found to form complexes with both humic and fulvic acids, which may contribute to increased arsenic immobilization (S. Wang & Mulligan, 2006). Metals, such as copper and zinc, also form complexes with NOM (W. Wang et al., 2017). (Du, Lian, & Zhu, 2011)) reported that the presence of organic matter slightly enhances the removal of Cd(II), Pb(II), and Zn(II) by mollusk shells. Moreover, research has shown that the presence of NOM can reduce chromium from its toxic, hexavalent form, Cr(VI), to its less harmful, more stable form, Cr(III) (Kumpiene et al., 2008). However, NOM can reduce arsenic from its less toxic form, As(V), to its more toxic and mobile form, As(III) (Kumpiene et al., 2008). These studies demonstrate that NOM can often unpredictably affect the removal of heavy metals and complicate the identification of the prevailing mechanisms associated with heavy metal removal.

3.3 Removal of heavy metals using low-cost materials

3.3.1 Agricultural waste

The use of agricultural waste to remove heavy metals has been widely investigated by researchers in both developed and developing countries. When considering the removal of heavy metals in the context of a developing country, agricultural waste often represents a source of abundant, effective adsorbents to implement into water treatment processes. For example, dairy manure compost is a unique material that has been shown to effectively remove heavy metals by achieving maximum adsorption capacities of 15.5, 27.2, and 95.3 mg g^{-1} for Zn(II), Cu(II), and Pb(II), respectively (M. Zhang, 2011).

Residual waste materials from rice are a prevalent form of agricultural waste that are produced in large volumes, particularly in the developing world. These types of waste include rice bran, rice straw, and rice husk. These waste materials have been shown to effectively remove heavy metals from aqueous solutions. For instance, rice straw and rice bran have been shown to remove Cu(II) with maximum adsorption capacities of 18.4 and 21.0 mg g^{-1}, respectively (Singha & Das, 2013). Several studies have demonstrated the ability of rice husk to remove heavy metals from water sources. A study of the removal efficiencies of nine different heavy metals using rice husk observed maximum adsorption capacities ranging from 5.5 to 58.1 mg g^{-1}, with the values increasing in the following order: Ni(II) < Zn(II) ≈ Cd(II) ≈ Mn(II) ≈ Co(II) < Cu(II) ≈ Hg(II) < Pb(II) (Krishnani et al., 2008). Another study on the removal of Cu(II) using rice husks reported a maximum adsorption capacity of 17.9 mg g^{-1} (Singha & Das, 2013). In a study on the use of rice husks for the adsorption of Cr(VI), significant removal (> 95%) only occurred in the case of low pH (< 3.0), primarily due to the speciation of the Cr(VI) ions (V.G. Georgieva et al., 2015). Bansal et al., 2009 evaluated the removal of Cr(VI) using rice husk and achieved a maximum adsorption capacity of 8.5 mg g^{-1}; they also found that treating rice husk with formaldehyde enhanced removal by approximately 23%. Another study used phosphate-treated rice husk to evaluate the removal of Cd(II) from wastewater and achieved a high maximum adsorption capacity (103 mg g^{-1} at 20 °C) (Ajmal, Rao, Anwar, Ahmad, & Ahmad, 2003).

Residuals from peanuts were also found to be an effective adsorbent for the removal of heavy metals. A maximum adsorption capacity of 39 mg g^{-1} was achieved for the removal of Pb(II) using peanut shells; significant removal was observed at various temperatures and pH conditions (Taşar et al., 2014). Peanut shells were also shown to remove Cr(VI) at low pH values, achieving a maximum adsorption capacity of 4.3 mg g^{-1} (Ahmad et al., 2017). Moreover, researchers achieved effective removal of Cr(III) and Cu(II) using peanut shells with maximum adsorption capacities of 27.9 and 25.4 mg g^{-1}, respectively (Witek-Krowiak et al., 2011). Researchers also observed significant heavy metal removal with peanut husks, achieving maximum adsorption capacities of 7.7, 10.2, and 29.1 mg g^{-1} for Cr(III), Cu(II), and Pb(II), respectively (Q. Li, Zhai, Zhang, Wang, & Zhou, 2007). Peanut hull, which is an abundant agricultural by-product, has also been shown to remove Cu(II) with a maximum adsorption capacity of 21.3 mg g^{-1} (C. S. Zhu et al., 2009).

Wastes from other nuts have also been shown to remove heavy metals from different water sources. Several studies have investigated the ability of cashew nut shells to remove heavy metals from aqueous solutions. When evaluating the removal of Cu(II), researchers achieved significant removal (> 85%) and a maximum adsorption capacity of 20 mg g^{-1} with cashew nut shells (SenthilKumar et al., 2011). Another study evaluated the removal of Ni(II) using cashew nut shells and achieved 60-75% and a maximum adsorption capacity of 18.9 mg g^{-1} (Senthil Kumar et al., 2011). The removal of these heavy metals using cashew nut shells has been attributed primarily to its high surface area, which allows for significant number of active sites for adsorption to occur (Senthil Kumar et al., 2011; SenthilKumar et al., 2011). Pistachio hull waste also demonstrated significant removal (> 98%) of Cr(VI) from various water sources, achieving a maximum adsorption capacity of 116.3 mg g^{-1} (Moussavi & Barikbin, 2010). The high adsorption capacity of Cr(VI) by pistachio hull waste was attributed to the electrostatic attraction, as well as binding to various functional groups on the surface of the adsorbent (Moussavi & Barikbin, 2010). Another study investigated the use of pecan shells to remove Cu(II), Pb(II), and Zn(II) by utilizing a variety of modification techniques to enhance removal, including acid, steam, and carbon dioxide activation (Bansode, Losso, Marshall, Rao, & Portier, 2003). In this study, Pb(II) was removed at the highest rate, followed by Cu(II) and Zn(II), for each type of modified pecan shell, with maximum adsorption observed for acid-activated pecan shells (Bansode et al., 2003). Almond shells also demonstrated approximately 20-40% removal of Cr(VI) when adjusting the pH and the adsorbent dose in the solution (Dakiky, Khamis, Manassra, & Mer'eb, 2002). Hazelnut shells also demonstrated effective removal of Cu(II), achieving a maximum adsorption capacity of 58.3 mg g^{-1} (Demirbas et al., 2009). Groundnut shells were also used as an adsorbent in the removal of heavy metals. Shukla and Pai (2005) achieved maximum adsorption capacities of 4.9, 8.05, and 11.0 mg g^{-1} for

Cu(II), Ni(II), and Zn(II), respectively, with groundnut shells (Shukla & Pai, 2005). These adsorption capacities were also enhanced by 40-70% with chemical modifications to the groundnut shells using reactive dye (Shukla & Pai, 2005).

Various fruit wastes have been shown to effectively remove heavy metals from aqueous solutions. For instance, lemon peel was shown to effectively remove Zn(II), Pb(II), Cd(II), Cu(II), and Ni(II), achieving maximum adsorption capacities of 27.9, 37.9, 54.6, 71.0, and 80.0 mg g^{-1}, respectively (Thirumavalavan et al., 2010). Orange peel also demonstrated effective heavy metal removal in a variety of studies. Ajmal et al., 2000 achieved significant removal of Ni(II) (97.5%) with orange peel, along with lower removal efficiencies of Cu(II), Pb(II), Zn(II), and Cr(VI). Thirumavalavan et al., 2010 investigated the adsorption of Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) with orange peel and demonstrated significant removal, achieving maximum adsorption capacities of 41.8, 63.3, 81.3, 27.1, and 24.1 mg g^{-1}, respectively. Another study demonstrated similar removal of Pb(II) using orange peel, achieving a maximum adsorption capacity of 27.9 mg g^{-1} (Abdelhafez & Li, 2016). Annadurai et al., 2002 also achieved much lower removal of five different heavy metals using orange peel with maximum adsorption capacities ranging from 1.9 to 7.8 mg g^{-1} in the following order of adsorption: Pb(II) > Ni(II) > Zn(II) > Cu(II) > Co(II). Significant removal of Cd(II), Cu(II), Pb(II), and Ni(II) was also achieved with chemically-modified orange peel with maximum adsorption capacities of 293, 289, 476, and 162 mg g^{-1}, respectively (N. Feng, Guo, & Liang, 2009; N. Feng, Guo, Liang, Zhu, & Liu, 2011). Banana peel also exhibited varying degrees of heavy metal removal in aqueous solution. Thirumavalavan et al., 2010 demonstrated significant removal of a variety of heavy metals, achieving maximum adsorption capacities of 21.9, 25.9, 34.1, 52.4, and 54.4

mg g^{-1} for Zn(II), Pb(II), Cd(II), Cu(II), and Ni(II), respectively. A study conducted by DeMessie et al., 2015 achieved a maximum adsorption capacity of 7.4 mg g^{-1} for Cu(II) using banana peel, which increased to 38.3 and 38.4 mg g^{-1} after the banana peel was pyrolyzed at 500 ℃ and 600 ℃, respectively. Another study observed relatively low removal for several heavy metals using banana peel, achieving maximum adsorption capacities ranging from 2.6 to 7.9 mg g^{-1} in the following order of adsorption: Pb(II) > Ni(II) > Zn(II) > Cu(II) > Co(II) (G. Annadurai et al., 2002). Grapefruit peel was also found to be an effective adsorbent for the removal of Cd(II) and Ni(II) from aqueous solution, achieving maximum adsorption capacities of 42.1 and 46.1 mg g^{-1}, respectively (Torab-Mostaedi, Asadollahzadeh, Hemmati, & Khosravi, 2013). The adsorption onto the grapefruit peel was attributed to the ion-exchange mechanism and, to a lesser extent, complexation with –OH functional groups (Torab-Mostaedi et al., 2013). Grape stalk wastes have also demonstrated the ability to remove heavy metals, achieving maximum adsorption capacities of 10.1 and 10.6 mg g^{-1} achieved for Cu(II) and Ni(II), respectively (Villaescusa et al., 2004).

Other types of vegetable waste have been shown to remove heavy metals from water source. Mushroom residues were shown to be effective in the removal of heavy metals. Based on an evaluation of four different types of mushroom residues, removal efficiencies for Cu(II), Zn(II), and Hg(II) ranged from 39.7% to 81.7% (X. Li et al., 2018). Another study investigated the removal of Cd(II) and Pb(II) using three different mushrooms and achieved maximum adsorption capacities of 35.0 and 33.8 mg g^{-1}, respectively (Vimala & Das, 2009). Corncob was also shown to remove heavy metals from aqueous solutions. When investigating its removal of Cd(II), researchers achieved a maximum adsorption capacity of 5.1 mg g^{-1}, along with an 4-10 fold increase in removal when the corncob was chemically modified using nitric and citric acid (R. Leyva-Ramos et al., 2005). Moreover, corncob successfully removed Pb(II), with a maximum adsorption capacity of 16.2 mg g^{-1} (Tan et al., 2010). The adsorption capacity for the removal of Pb(II) using corncob increased significantly (43.4 mg g^{-1}) when the corncob was treated with sodium hydroxide (Tan et al., 2010). A summary of selected studies evaluating the ability of agricultural wastes to remove heavy metals can be found in Table 3.3.

Several comprehensive review papers that discuss the removal of heavy metals, along with other inorganic and organic contaminants, using agricultural waste products as adsorbents have been published (Dai et al., 2018; Mo et al., 2018; Nguyen et al., 2013; Sulyman, Namiesnik, & Gierak, 2017).

3.3.2 Naturally occurring soil and mineral deposits

Numerous studies have investigated whether soil and other mineral deposits can remove heavy metals from aqueous solutions. Natural soil and mineral deposits are heterogeneous and thus have varying degrees of affinity for heavy metals and other harmful constituents. The variability in their affinity for heavy metals is often attributed to the solubility (K_{sp}) of the heavy metal, which may result in the precipitation of metal carbonates and hydroxides, along with other physical and chemical properties, such as charge density, electronegativity, and the hydrolysis constant (pK_H) of the heavy metal (Appel, Ma, Rhue, & Reve, 2008). When considering the economic and technological constraints of a developing country, the use of soils and other natural materials may be an ideal and effective way of removing heavy metals from aqueous solution.

Table 3.3: Removal of heavy metals by agricultural waste products

Adsorbent	Heavy metal	Surface area (m^2 g^{-1})	C_0 (mg L^{-1})	q_{max} (mg g^{-1})	Reference
A. Hypogea (peanut) shells	Chromium (VI)	1.8	0-40	4.3	(Ahmad et al., 2017)
Almond	Chromium (VI)	N.R.	20-1,000	10.2	(Dakiky et al., 2002)
Apple residues	Copper (II)	N.R.	30	10.8	(Lee & Yang, 1997)
Banana peel	Cadmium (II)	1.3	100-800	34.1	(Thirumavalavan et al., 2010)
	Cobalt (II)	N.R.	5-25	2.6	(G. Annadurai et al., 2002)
	Copper (II)	1.3	100-800	52.4	(Thirumavalavan et al., 2010)
	Copper (II)	N.R.	5-25	4.8	(G. Annadurai et al., 2002)
	Copper (II)	38.49	10-30	7.4	(DeMessie et al., 2015)
	Lead (II)	1.3	100-800	25.9	(Thirumavalavan et al., 2010)
	Lead (II)	N.R.	5-25	7.9	(G. Annadurai et al., 2002)
	Nickel (II)	1.3	100-800	54.4	(Thirumavalavan et al., 2010)
	Nickel (II)	N.R.	5-25	6.9	(G. Annadurai et al., 2002)
	Zinc (II)	1.3	100-800	21.9	(Thirumavalavan et al., 2010)
	Zinc (II)	N.R.	5-25	5.8	(G. Annadurai et al., 2002)
Cashew nut shells	Copper (II)	395	10-50	20.0	(SenthilKumar et al., 2011)
	Nickel (II)	395	10-50	18.9	(Senthil Kumar et al., 2011)
Coconut shells	Chromium (VI)	0.5	54.5	18.7	(Singha & Das, 2011)
	Copper (II)	N.R.	5-300	19.9	(Singha & Das, 2013)
Coconut-shell biochar	Cadmium (II)	212	100-2,000	3.5	(Paranavithana et al., 2016)
	Lead (II)	212	100-2,000	13.4	(Paranavithana et al., 2016)
Corncob	Cadmium (II)	< 5	5-120	5.1	(R. Leyva-Ramos et al., 2005)
	Lead (II)	N.R.	20.7-414	16.2	(Tan et al., 2010)
Dairy manure compost	Copper (II)	N.R.	31.8	27.2	(M. Zhang, 2011)
	Lead (II)	N.R.	103.6	95.3	(M. Zhang, 2011)
	Zinc (II)	N.R.	32.7	15.5	(M. Zhang, 2011)
Grapefruit peel	Cadmium (II)	N.R.	50	42.1	(Torab-Mostaedi et al., 2013)

	Nickel (II)	N.R.	50	46.1	(Torab-Mostaedi et al., 2013)
Grape stalks	Copper (II)	N.R.	15.3-153	10.1	(Villaescusa et al., 2004)
	Nickel (II)	N.R.	14.1-141	10.6	(Villaescusa et al., 2004)
Groundnut shells	Copper (II)	N.R	73-465	4.5	(Shukla & Pai, 2005)
	Nickel (II)	N.R.	107-554	3.8	(Shukla & Pai, 2005)
	Zinc (II)	N.R.	38-244	7.6	(Shukla & Pai, 2005)
Hazelnut shells	Copper (II)	441.2	25-200	58.3	(Demirbas et al., 2009)
Lemon peel	Cadmium (II)	1.3	100-800	54.6	(Thirumavalavan et al., 2010)
	Copper (II)	1.3	100-800	70.9	(Thirumavalavan et al., 2010)
	Lead (II)	1.3	100-800	37.9	(Thirumavalavan et al., 2010)
	Nickel (II)	1.3	100-800	80.0	(Thirumavalavan et al., 2010)
	Zinc (II)	1.3	100-800	27.9	(Thirumavalavan et al., 2010)
Orange peel	Cadmium (II)	N.R.	50-1200	293	(N. Feng et al., 2011)
	Cadmium (II)	2.0	100-800	41.8	(Thirumavalavan et al., 2010)
	Cobalt (II)	N.R.	5-25	1.8	(G. Annadurai et al., 2002)
	Copper (II)	N.R.	5-25	3.7	(G. Annadurai et al., 2002)
	Copper (II)	2.0	100-800	63.3	(Thirumavalavan et al., 2010)
	Lead (II)	N.R.	5-25	7.8	(G. Annadurai et al., 2002)
	Lead (II)	N.R.	50-1,200	476	(N. Feng et al., 2011)
	Lead (II)	0.21	57	27.9	(Abdelhafez & Li, 2016)
	Lead (II)	2.0	100-800	27.1	(Thirumavalavan et al., 2010)
	Nickel (II)	N.R.	5-25	6.0	(G. Annadurai et al., 2002)
	Nickel (II)	N.R.	50-1,200	162	(N. Feng et al., 2011)
	Nickel (II)	2.0	100-800	81.3	(Thirumavalavan et al., 2010)
	Zinc (II)	N.R.	5-25	5.3	(G. Annadurai et al., 2002)
	Zinc (II)	2.0	100-800	24.1	(Thirumavalavan et al., 2010)
Peanut shells	Chromium (III)	N.R.	10-1,000	27.9	(Witek-Krowiak et al., 2011)
	Copper (II)	N.R.	10-1,000	25.4	(Witek-Krowiak et al., 2011)
	Lead (II)	0.84	100-350	39.0	(Taşar et al., 2014)

Peanut hull	Copper (II)	N.R.	10-400	21.3	(C. S. Zhu et al., 2009)
Peanut husk	Chromium (III)	N.R.	0-50	7.7	(Q. Li et al., 2007)
	Copper (II)	N.R.	0-50	10.2	(Q. Li et al., 2007)
	Lead (II)	N.R.	0-50	29.1	(Q. Li et al., 2007)
Pistachio hull waste	Chromium (VI)	1.04	50-200	116	(Moussavi & Barikbin, 2010)
Rice bran	Chromium (VI)	0.1	54.5	12.3	(Singha & Das, 2011)
	Copper (II)	N.R.	5-300	21.0	(Singha & Das, 2013)
Rice husk	Cadmium (II)	N.R.	50-200	16.6	(Krishnani et al., 2008)
	Chromium (VI)	0.5	54.5	11.4	(Singha & Das, 2011)
	Chromium (VI)	N.R.	100	8.5	(Bansal et al., 2009)
	Cobalt (II)	N.R.	50-200	9.6	(Krishnani et al., 2008)
	Copper (II)	N.R.	5-300	17.9	(Singha & Das, 2013)
	Copper (II)	N.R.	50-200	10.9	(Krishnani et al., 2008)
	Lead (II)	N.R.	50-200	58.0	(Krishnani et al., 2008)
	Mercury (II)	N.R.	50-200	36.1	(Krishnani et al., 2008)
	Nickel (II)	N.R.	50-200	5.5	(Krishnani et al., 2008)
	Zinc (II)	N.R.	50-200	8.1	(Krishnani et al., 2008)
Rice straw	Chromium (VI)	1.2	54.5	12.2	(Singha & Das, 2011)
	Copper (II)	N.R.	5-300	18.4	(Singha & Das, 2013)
S. Lychnophera Hance	Cadmium (II)	N.R.	0.25-1.0	27.1	(Y. Liu, Chang, Guo, & Meng, 2006)
Sugar beet pulp	Copper (II)	N.R.	25-250	28.5	(Aksu & Isoglu, 2005)
Sugar cane bagasse	Cadmium (II)	0.49	10-30	0.96	(Moubarik & Grimi, 2015)
	Lead (II)	92.3	57	87.0	(Abdelhafez & Li, 2016)

For example, Appel et al., 2008 investigated three different soils from Puerto Rico with respect to their ability to remove Pb(II) and Cd(II). Each soil removed Pb(II) and Cd(II), achieving maximum adsorption capacities ranging from 4.1-6.7 and 1.6-3.5 mg g^{-1} for Pb(II) and Cd(II), respectively. Kul and Koyuncu (2010) also evaluated the removal of Pb(II) using native and activated bentonite. A maximum adsorption capacity of 19.2 mg g^{-1} was achieved in the case of native bentonite, while the activated bentonite was much less effective at removing Pb(II) (q_{max} = 1.7 mg g^{-1}) (Kul & Koyuncu, 2010). (Q. Tang et al., 2009) evaluated the removal of Pb(II) using natural kaolin and observed significant adsorption, achieving a maximum adsorption capacity of 165.1 mg g^{-1}. The high adsorption capacity of kaolin was attributed to interactions between Pb(II) and the carbonate in the natural kaolin, along with the consistently negative charge of the surface of the kaolin particles, which were independent of pH (Q. Tang et al., 2009). Qin et al., 2006 investigated the removal of Cd(II), Cu(II), and Pb(II) using two types of peat. For each type of peat, Pb(II) was the most favorably adsorbed heavy metal, followed by Cd(II) and Cu(II), with maximum adsorption capacities ranging from 88.7-118.7, 32.0-50.2, and 25.4-31.4 mg g^{-1} for Pb(II), Cd(II), and Cu(II), respectively. These levels of heavy metal removal by peat have been attributed to the presence of polar functional groups, such as carboxylic, hydroxylic, and phenolic groups, which can all contribute to heavy metal adsorption (Qin et al., 2006).

Tiede, Neumann, & Stuben (2007) investigated the use of mineral deposits containing manganese-oxyhydroxides as filter material to remove Cd(II), Ni(II), and Zn(II) from drinking water. Using these deposits, the researchers achieved maximum adsorption capacities of 10.4, 14.2, and 32.0 mg g^{-1} for Ni(II), Zn(II), and Cd(II), respectively.

(Elouear et al., 2008) evaluated the removal of Cd(II), Cu(II), Pb(II), and Zn(II) using phosphate rock obtained from Tunisian ores. In their study, the phosphate rock achieved maximum adsorption capacities ranging from 8.5-12.8 mg g^{-1}, with the following order of adsorption: Pb(II) > Cd(II) > Cu(II) > Zn(II). The authors also reported that phosphate rock that was activated with sodium hydroxide and nitric acid solution achieved a 25-50% higher adsorption capacity than untreated phosphate rock (Elouear et al., 2008).

Several comprehensive review papers on the removal of heavy metals using soil and other natural remediation techniques have been published. Derakhshan, Jung, & Kim (2018) reviewed the use of various types of soil amendments, including mud, phosphate rock, and other soil materials, to remove heavy metals from water sources. Kumpiene et al., 2008 also reviewed the use of amendments to remediate heavy metal contamination in soil. Many of these amendments include various soils and other minerals that serve to immobilize heavy metals and reduce their toxicity. Furthermore, Wang and Mulligan (2006) extensively documented and reviewed natural processes for removing arsenic, which include naturally-occurring iron and manganese oxides, clays, and natural organic matter (S. Wang & Mulligan, 2006). Jimenez-Castaneda and Medina (2017) reviewed the use of zeolites and clays to remove heavy metals from water sources with an emphasis on the impact of the application of surfactants to enhance overall performance (Jimenez-Castaneda & Medina, 2017). With continuously growing interest in the use of abundant, locally available soils, minerals, and other natural organic material to remove heavy metals, research in this area is anticipated to continue, particularly as developing countries seek less-expensive methods of addressing heavy metal contamination. Table

3.4 summarizes selected studies that highlight the ability of naturally occurring soil and mineral deposits to remove heavy metals.

3.3.3 Aquatic and terrestrial biomass

Various forms of trees, plants, and other terrestrial and aquatic materials that are plentiful in developing countries have also been considered for bioremediation. For example, *Moringa oleifera* (MO) has received significant attention due to its potential ability to remove heavy metals. MO is a tropical, drought-tolerant tree that has been evaluated for its water and wastewater treatment capabilities (Shan, Matar, Makky, & Ali, 2017). MO exhibits high removal (> 90%) of a wide variety of heavy metals, including Cd(II), Fe(II), Cr(III), Zn(II), and Cu(II) from water and wastewater (Kansal & Kumari, 2014; Shan et al., 2017). However, a recent study showed that MO is not effective at removing Pb(II) from wastewater (Shan et al., 2017). Along with the removal of heavy metals, researchers have reported that the use of MO does not have a significant effect on the characteristics of the source water (*e.g.*, pH, ionic strength) (Shan et al., 2017). Several removal mechanisms have been proposed for MO, including adsorption, charge neutralization, complexation, and interparticle bridging (Kansal & Kumari, 2014).

Tree fern is another plant-based material that is effective at removing heavy metals. An equilibrium isotherm study conducted by (Ho, Huang, & Huang, 2002) found that tree ferns native to Taiwan effectively removed Zn(II), Cu(II), and Pb(II), achieving maximum adsorption capacities of 7.6, 10.6, and 39.8 mg g^{-1}, respectively. These adsorption capacities were attributed to the cellulose-based structure of the tree fern, which is negatively charged and exhibits a strong affinity for metal cations (Ho et al., 2002).

Table 3.4: Removal of heavy metals by naturally occurring soil and mineral deposits

Adsorbent	Heavy metal	Surface area (m^2 g^{-1})	C_0 (mg L^{-1})	q_{max} (mg g^{-1})	Reference
Bentonite	Lead (II)	72.0	5-25	19.2	(Kul & Koyuncu, 2010)
Kaolin	Lead (II)	8.0	80-320	165	(Q. Tang et al., 2009)
Mn-oxyhydroxide mineral	Cadmium (II)	143	0-225	32.0	(Tiede et al., 2007)
	Nickel (II)	143	0-117	10.4	(Tiede et al., 2007)
	Zinc (II)	143	0-131	14.2	(Tiede et al., 2007)
Peat (Danish)	Cadmium (II)	13.3	225	50.2	(Qin et al., 2006)
	Copper (II)	13.3	127	34.1	(Qin et al., 2006)
	Lead (II)	13.3	414	119	(Qin et al., 2006)
Peat (Heilongjiang)	Cadmium (II)	9.7	225	32.0	(Qin et al., 2006)
	Copper (II)	9.7	127	25.4	(Qin et al., 2006)
	Lead (II)	9.7	414	88.7	(Qin et al., 2006)
Phosphate rock	Cadmium (II)	13.5	10-500	10.5	(Elouear et al., 2008)
	Copper (II)	13.5	10-500	10.0	(Elouear et al., 2008)
	Lead (II)	13.5	10-500	12.8	(Elouear et al., 2008)
	Zinc (II)	13.5	10-500	8.5	(Elouear et al., 2008)
Soil (Entisols)	Cadmium (II)	28.5	100-2,000	3.4	(Paranavithana et al., 2016)
	Lead (II)	28.5	100-2,000	9.3	(Paranavithana et al., 2016)
Soil (Mollisols)	Cadmium (II)	17.3	134.9	3.0	(Appel et al., 2008)
	Lead (II)	17.3	248.6	5.7	(Appel et al., 2008)
Soil (Oxisols)	Cadmium (II)	41.9	134.9	1.6	(Appel et al., 2008)
	Lead (II)	41.9	248.6	4.1	(Appel et al., 2008)
Soil (Ultisols)	Cadmium (II)	37.8	134.9	3.5	(Appel et al., 2008)
	Lead (II)	37.8	248.6	6.7	(Appel et al., 2008)
Zeolite (Clinoptilolite)	Arsenic (V)	1.6	5-300	0.36	(Krauklis et al., 2017)

In a study on the adsorption capacity of *Lagerstroemia speciosa*, a tree that is native to India, on Cr(VI), the use of the tree was investigated in its native form and a maximum adsorption capacity of 20.4 mg g^{-1} was achieved (Srivastava, Agrawal, & Mondal, 2015). The use of leaves from the *Cinnamomum camphora* tree exhibited the effective removal of Pb(II), achieving adsorption capacities ranging from 74.1 to 75.8 mg g^{-1} (H. Chen et al., 2010). Moreover, the leaves from the *Cassia Fistula* tree removed Cr(VI), with a maximum adsorption capacity of 4.5 mg g^{-1} (Ahmad et al., 2017).

Sawdust is another material that has been frequently investigated for its adsorptive qualities. Several studies have demonstrated effective removal of heavy metals using sawdust from a variety of trees. Maple sawdust has achieved high removal (> 80%) of Cr(VI) (L. J. Yu, Shukla, Dorris, Shukla, & Margrave, 2003), while beech sawdust effectively removed Cu(II), Ni(II), Cd(II), and Zn(II) (Bozic, Stankovic, Gorgievski, Bogdanovic, & Kovacevic, 2009). Moreover, sawdust from poplar and linden trees also exhibited varying degrees of removal of Zn(II), Ni(II), Cd(II), Cu(II), and Mn(II) (Bozic et al., 2009). Another study that investigated the removal of heavy metals using sawdust from poplar trees achieved adsorption capacities of 5.5, 6.6, and 21.1 mg g^{-1} for Cr(III), Cu(II), and Pb(II), respectively (Q. Li et al., 2007). Along with these results, sawdust from teakwood also achieved maximum adsorption capacities of 4.9, 8.05, and 11.0 mg g^{-1} for Cu(II), Ni(II), and Zn(II), respectively (Shukla & Pai, 2005). These adsorption capacities were enhanced by 40-70% with chemical modifications to the sawdust using reactive dye (Shukla & Pai, 2005). Sawdust from the Indian jujube tree achieved a maximum adsorption capacity of 3.7 mg g^{-1} for Cr(VI) (Ahmad et al., 2017). Meanwhile, sawdust taken from

Palestinian trees also demonstrated approximately 20-60% removal of Cr(VI) when the pH and adsorbent dose in the solution was adjusted (Dakiky et al., 2002).

Lignin is another commonly researched biomass material that has been used to remove heavy metals from water. Lignin is a natural polymer that is found in the cell walls of plants and makes them rigid and woody. Lignin is the primary binding agent for fibrous plant components and typically comprises 16–33% of plant biomass, and more than 50 million tons have been produced by paper industries throughout the world (Guo, Zhang, & Shan, 2008; Y. Wu, Zhang, Guo, & Huang, 2008). Studies have shown that lignin is an effective adsorbent for the removal of heavy metals. In an extensive study by (Guo et al., 2008), lignin obtained as a waste product from the paper industry achieved effective removal of several heavy metals, including Pb(II), Cu(II), Zn(II), and Ni(II). Other studies have reported the effective removal of chromium and cadmium using lignin (F. Liang, Song, Huang, Zhang, & Chen, 2013; Y. Wu et al., 2008). Researchers have stated that the removal of heavy metals using lignin is facilitated by the presence of carboxylic and phenolic functional groups, which interact strongly with heavy metals and potentially serve as ideal sites for heavy metal adsorption (Guo et al., 2008). Along with these specific studies, several review papers have been published on the adsorption of heavy metals using lignin and other lignocellulosic materials (Y. Ge & Li, 2018; Neris, Luzardo, Silva, & Velasco, 2019).

Aquatic biomass, such as seaweed and algae, has also been shown to effectively remove heavy metals from a variety of water sources. For example, two freshwater algae, *S. Condensata* and *R. Hieroglyphicum*, have been shown to effectively remove Cr(III) from industrial wastewater, achieving maximum adsorption capacities of 14.8 and 12.5 mg g^{-1}, respectively (Onyancha et al., 2008). In another study, an artificially-cultured marine algae, *U. pinnatifida*, demonstrated effective removal of Ni(II) and Cu(II), achieving maximum adsorption capacities of 29.9 and 78.9 mg g^{-1}, respectively. Moreover, Romera et al., 2008 conducted an extensive study of the removal of Cd(II), Ni(II), and Zn(II) using brown (*A. nodosum*), red (*C. crispus*), and green (*C. vermialara*) algae in a variety of combinations and systems. In each instance, effective removal of each heavy metal (> 90%) was achieved, even when they were examined in different combinations. The effective removal (> 90%) of chromium by a red algae species (*C. Virgatum*), with a maximum adsorption capacity (26.5 mg g^{-1}), was achieved at a pH of 1.5, which would not occur consistently among the types of water sources that are typically found to contain chromium (Sari & Tuzen, 2008). A study of the removal of Cd(II) using brown, red, and green seaweeds showed a wide range of adsorption capacities based on the type of seaweed used. The maximum adsorption capacities ranged from 17.9 to 82.9 mg g^{-1}, with brown seaweeds being the most effective, followed by green and red seaweeds (Hashim & Chu, 2004).

A study that investigated the use of *S. polyrhiza*, a freshwater macrophyte, to remove Cu(II), Mn(II), and Zn(II) demonstrated maximum adsorption capacities of 52.6, 35.7, and 28.5 mg g^{-1}, respectively (Meitei & Prasad, 2014). Moreover, various aquatic weeds, including water lilies and mangrove leaves, have been shown to remove chromium, with adsorption capacities ranging from 6.1-7.2 mg g^{-1} for Cr(III) and 1.7-5.1 mg g^{-1} for Cr(VI) (Elangovan, Philip, & Chandraraj, 2008). Neem leaves and hyacinth roots have also been shown to remove Cu(II), with maximum adsorption capacities of 17.5 and 21.8 mg g^{-1}, respectively (Singha & Das, 2013).

In many instances, modifications and various treatments have been investigated to enhance the removal of heavy metals by biomass. For example, when removing Cu(II) and Ni(II), the adsorption capacities of *U. pinnatifida* increased by 10 mg g^{-1} after being washed with a 0.2 M $CaCl_2$ solution for 24 h (Z. Chen, Ma, & Han, 2008). The removal efficiency of Cr(VI) by various aquatic weeds increased after being washed with a 4 N solution of H_2SO_4. However, the removal of Cr(III) by these aquatic weeds was reduced after being washed with 4 N solutions of H_2SO_4 and NaOH (Elangovan et al., 2008). A summary of selected studies evaluating the ability of aquatic and terrestrial biomass to remove heavy metals is provided in Table 3.5.

3.3.4 Other locally available waste material

A significant amount of research has been conducted to evaluate the effectiveness of locally available waste material to remove heavy metals from aqueous solutions. Due to variation in local environments, energy sources, agricultural practices, and cultures, different types of waste may be produced in excess of others. For example, approximately 857,000 tons of tea is produced annually in India (Wasewar, Atif, Prasad, & Mishra, 2009), which leads to an inordinate amount of tea waste. Moreover, countries that produce a significant amount of energy from coal, such as India and China, must deal with a large amount of waste products from the combustion process, such as coal ash.

Table 3.5: Removal of heavy metals by aquatic and terrestrial biomass.

Adsorbent	Heavy metal	Surface area ($m^2\ g^{-1}$)	C_0 ($mg\ L^{-1}$)	q_{max} ($mg\ g^{-1}$)	Reference
A. Bisporus (mushroom)	Cadmium (II)	NA	10-100	29.7	(Vimala & Das, 2009)
	Lead (II)	NA	10-100	33.8	(Vimala & Das, 2009)
A. Nodosum (brown algae)	Cadmium (II)	NA	10-150	69.7	(Romera et al., 2008)
	Nickel (II)	NA	10-150	35.2	(Romera et al., 2008)
	Zinc (II)	NA	10-150	41.2	(Romera et al., 2008)
A. Polytricha (mushroom)	Copper (II)	NA	10-100	6.6	(X. Li et al., 2018)
	Mercury (II)	NA	10-100	6.0	(X. Li et al., 2018)
	Zinc (II)	NA	10-100	6.1	(X. Li et al., 2018)
Beech sawdust	Copper (II)	NA	5-200	4.5	(Bozic et al., 2013)
	Nickel (II)	NA	5-200	4.0	(Bozic et al., 2013)
	Zinc (II)	NA	5-200	2.0	(Bozic et al., 2013)
C. Crispus (red algae)	Cadmium (II)	NA	10-150	65.2	(Romera et al., 2008)
	Nickel (II)	NA	10-150	35.2	(Romera et al., 2008)
	Zinc (II)	NA	10-150	42.5	(Romera et al., 2008)
C. Fistula leaves	Chromium (VI)	1.1	0-40	4.5	(Ahmad et al., 2017)
C. Indica (mushroom)	Cadmium (II)	NA	10-100	24.1	(Vimala & Das, 2009)
	Lead (II)	NA	10-100	23.4	(Vimala & Das, 2009)
C. Vermilara (green algae)	Cadmium (II)	NA	10-150	21.4	(Romera et al., 2008)
	Nickel (II)	NA	10-150	12.9	(Romera et al., 2008)
	Zinc (II)	NA	10-150	21.6	(Romera et al., 2008)
F. Velutipes (mushroom)	Copper (II)	NA	10-100	7.2	(X. Li et al., 2018)
	Mercury (II)	NA	10-100	7.9	(X. Li et al., 2018)
	Zinc (II)	NA	10-100	6.3	(X. Li et al., 2018)
Green taro	Chromium (III)	NA	10-150	6.1	(Elangovan et al., 2008)
	Chromium (VI)	NA	10-150	1.4	(Elangovan et al., 2008)

H. Splendens (moss)	Cadmium (II)	NA	10-400	32.5	(Sari, Mendil, Tuzen, & Soylak, 2008)
	Chromium (III)	NA	10-400	42.1	(Sari et al., 2008)
Hyacinth roots	Chromium (VI)	5.8	54.5	15.3	(Singha & Das, 2011)
	Copper (II)	NA	5-300	21.8	(Singha & Das, 2013)
Juniper bark	Cadmium (II)	NA	29.2	8.6	(Shin, Karthikeyan, & Tshabalala, 2007)
Juniper wood	Cadmium (II)	NA	29.2	3.2	(Abdolali et al., 2016)
L. speciosa bark	Chromium (VI)	0.4	5-30	24.4	(Srivastava et al., 2015)
Lignin	Cadmium (II)	21.7	23-281	25.4	(Guo et al., 2008)
	Chromium (III)	21.7	5-130	18.0	(Y. Wu et al., 2008)
	Copper (II)	21.7	13-159	22.9	(Guo et al., 2008)
	Lead (II)	21.7	41-518	89.5	(Guo et al., 2008)
	Nickel (II)	21.7	12-147	6.0	(Guo et al., 2008)
	Zinc (II)	21.7	13-164	11.3	(Guo et al., 2008)
Loess	Zinc (II)	24.1	10-700	216	(X. Tang, Li, & Chen, 2008)
Mangrove leaves	Chromium (III)	NA	10-150	6.5	(Elangovan et al., 2008)
	Chromium (VI)	NA	10-150	5.7	(Elangovan et al., 2008)
Meranti sawdust	Chromium (III)	< 0.6	1-200	37.9	(Rafatullah, Sulaiman, Hashim, & Ahmad, 2009)
	Copper (II)	< 0.6	1-200	32.1	(Rafatullah et al., 2009)
	Lead (II)	< 0.6	1-200	34.2	(Rafatullah et al., 2009)
	Nickel (II)	< 0.6	1-200	36.0	(Rafatullah et al., 2009)
Neem leaves	Chromium (VI)	0.6	54.5	16.0	(Singha & Das, 2011)
	Copper (II)	NA	5-300	17.5	(Singha & Das, 2013)
P. Eryngii (mushroom)	Copper (II)	NA	10-100	3.4	(X. Li et al., 2018)
	Mercury (II)	NA	10-100	2.8	(X. Li et al., 2018)
	Zinc (II)	NA	10-100	2.9	(X. Li et al., 2018)
P. Platypus (mushroom)	Cadmium (II)	NA	10-100	35.0	(Vimala & Das, 2009)

	Lead (II)	NA	10-100	27.1	(Vimala & Das, 2009)
P. Ostreatus (mushroom)	Copper (II)	NA	10-100	4.5	(X. Li et al., 2018)
	Mercury (II)	NA	10-100	3.4	(X. Li et al., 2018)
	Zinc (II)	NA	10-100	5.1	(X. Li et al., 2018)
Pine cone biochar	Arsenic	6.6	0.05-0.2	0.006	(Van Vinh, Zafar, Behera, & Park, 2015)
Pine needles	Chromium (VI)	NA	20-1,000	21.5	(Dakiky et al., 2002)
Poplar sawdust	Chromium (III)	NA	0-50	5.5	(Q. Li et al., 2007)
	Copper (II)	NA	0-50	6.6	(Q. Li et al., 2007)
	Lead (II)	NA	0-50	21.1	(Q. Li et al., 2007)
Reed mat	Chromium (III)	NA	10-150	7.2	(Elangovan et al., 2008)
	Chromium (VI)	NA	10-150	1.7	(Elangovan et al., 2008)
S. Lychnophera Hance	Cadmium (II)	NA	0.25-1.0	27.1	(Y. Liu et al., 2006)
	Lead (II)	NA	0.25-1.0	27.1	(Y. Liu et al., 2006)
Sawdust	Chromium (VI)	NA	20-1,000	15.8	(Dakiky et al., 2002)
Teakwood sawdust	Copper (II)	NA	73-465	4.9	(Shukla & Pai, 2005)
	Nickel (II)	NA	107-554	8.1	(Shukla & Pai, 2005)
	Zinc (II)	NA	38-244	11.0	(Shukla & Pai, 2005)
Tree fern	Copper (II)	1.59	30-150	10.6	(Ho et al., 2002)
	Lead (II)	6.4	30-150	39.8	(Ho et al., 2002)
	Zinc (II)	1.2	30-150	7.58	(Abdolali et al., 2016)
Water hyacinth	Chromium (III)	NA	10-150	6.6	(Elangovan et al., 2008)
	Chromium (VI)	NA	10-150	0.3	(Elangovan et al., 2008)
Water lily	Chromium (III)	NA	10-150	6.1	(Elangovan et al., 2008)
	Chromium (VI)	NA	10-150	5.1	(Elangovan et al., 2008)
Z. Mauritiana sawdust	Chromium (VI)	1.5	0-40	3.7	(Ahmad et al., 2017)

Several researchers have investigated the adsorptive capabilities of tea waste over the last two decades. Tea waste has been shown to effectively remove a wide variety of heavy metals. Malkoc and Nuhoglu (2005) achieved a maximum adsorption capacity of 18.4 mg g^{-1} for Ni(II) using tea waste (Malkoc & Nuhoglu, 2005). Wasewar et al., 2009 also reported significant removal of Zn(II) (> 98%) using tea waste. Other researchers have modified tea waste with the objective of increasing its heavy metal removal efficiency. Weng et al., 2014 investigated various modification methods, including acid and base washing, steam, and ultrasound, to enhance the removal of Cu(II) using black tea waste. With each method, the removal of Cu(II) increased compared to untreated adsorbent, achieving maximum adsorption with base-treated black tea waste (Weng et al., 2014). The increased removal obtained using these modification techniques has been attributed to the changes induced in the physical and chemical properties of the adsorbent, such as increased surface area and porosity, along with the higher number of functional groups (Weng et al., 2014). Yang et al., 2016 also reported that base-treated green tea waste improved the adsorption of heavy metals, specifically As(III) and Ni(II). They observed that the use of base treatment via immersion in a 0.05-M solution of $Ca(OH)_2$ increased the number of –OH and amine functional groups on the surface of the green tea waste, which contributed to the increased As(III) and Ni(II) removal (S. Yang et al., 2016). A comprehensive review of the extensive use of tea waste for the removal of heavy metals and other contaminants was carried out by (Hussain, Anjali, Hassan, & Dwivedi, 2018).

Coal ash, which is an abundant by-product of fossil fuel combustion, has also been shown to remove heavy metals from aqueous solution. Attari et al., 2017 showed that coal fly ash could remove up to 95% of Hg(II) from industrial wastewater. Another study that examined the removal of Cr(III), Pb(II), and Zn(II) using coal fly ash achieved maximum adsorption capacities of 22.7, 45.3, and 17.7 mg g^{-1}, which was attributed to electrostatic attraction between the heavy metals and the charged surface of the adsorbent (A. D. Papandreou, Stournaras, Panias, & Paspaliaris, 2011). Several review articles have been published on the effectiveness of coal ash as an adsorbent (J. Ge, Yoon, & Choi, 2018; Rashidi & Yusup, 2016; S. Wang & Wu, 2006).

Shells from various aquatic species have been shown to effectively remove heavy metals from aqueous solutions. Shells from the mollusk *Anadara inaequivalvis* (*A. inaequivalvis*), which are primarily found in the Adriatic, Aegean, and Black Seas, effectively removed Cu(II) and Pb(II), achieving maximum adsorption capacities of 330.2 and 621.1 mg g^{-1}, respectively (Bozbas & Boz, 2016). Razor clam shells demonstrated significant removal of Cd(II), Pb(II), and Zn(II), achieving maximum adsorption capacities of 501.3, 656.8, and 553.3 mg g^{-1}, respectively (Du et al., 2011). Moreover, oyster shells achieved effective removal of Cd(II), Pb(II), and Zn(II), achieving maximum adsorption capacities of 118.0, 1,591, and 564.4 mg g^{-1}, respectively (Du et al., 2011). Crab shell particles have also been shown to remove Co(II) and Cu(II), achieving maximum adsorption capacities of 322.6 and 243.9 mg g^{-1}, respectively (Vijayaraghavan et al., 2006). Various other locally-available waste materials have been evaluated for their ability to remove heavy metals from aqueous solutions. Boonamnuayvitaya et al., 2004 investigated the adsorptive capabilities of coffee residues for removing various heavy metals, including Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II). In this study, coffee residues were mixed with clay and achieved maximum adsorption capacities ranging from 11.0 to 39.5 mg g^{-1} for five heavy metals in the following order of adsorption: Cd(II) > Cu(II) > Pb(II) > Zn(II) >

Ni(II) (Boonamnuayvitaya et al., 2004). Meunier et al., 2003 evaluated the adsorptive capabilities of cocoa shells by determining the removal efficiency for a wide variety of heavy metals in a multi-solute solution, including Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Mn(II), Ni(II), Pb(II), and Zn(II). This study found maximum adsorption capacities that were relatively low ($\leq$ 1.1 mg g^{-1}) compared to other adsorbents with the following order of adsorption: Pb(II) > Cr(III) > Cd(II) ≈ Cu(II) ≈ Fe(III) > Zn(II) ≈ Co(II) > Mn(II) ≈ Ni(II) (Meunier et al., 2003). Neem oil cake, which is waste matter extracted from the fruit of the Neem (*A. Indica*) plant, has been shown to effectively remove Cu(II) and Cd(II). Researchers demonstrated maximum adsorption capacities of 9.4 and 11.8 mg g^{-1} for Cu(II) and Cd(II), respectively (Rao & Khan, 2009). Tobacco dust has also been shown to remove heavy metals from aqueous solutions. Qi and Aldrich (2008) investigated the use of tobacco dust to remove Pb(II), Cu(II), Cd(II), Zn(II), and Ni(II) and achieved maximum adsorption capacities of ranging from 24.5 to 39.6 mg g^{-1} with the following order of adsorption: Pb(II) > Cu(II) > Cd(II) > Ni(II) ≈ Zn(II) (Qi & Aldrich, 2008). The removal of heavy metals by tobacco dust was attributed to strong surface acidity exhibited by the tobacco dust and its negative surface charge across a wide pH range, which contributed to the removal of the heavy metals (Qi & Aldrich, 2008). A study investigating the removal of Cd(II) using olive cake, which is a waste product of olive oil production, demonstrated effective removal, achieving a maximum adsorption capacity of 65.4 mg g^{-1} (Al-Anber & Matouq, 2008). Dakiky et al., 2002 has also investigated a wide variety of locally-available materials in Palestine, including olive cake, cactus leaves, coal, and wool, for their ability to remove Cr(VI). In this study, the highest adsorption capacity was achieved with wool (41.2 mg g^{-1}), followed by olive cake (33.4 mg g^{-1}), cactus leaves (7.1 mg g^{-1}), and coal

(6.8 mg g^{-1}) (Dakiky et al., 2002). The effectiveness of the wool in the removal of Cr(VI) was attributed to its loose structure, which allowed for multi-layered adsorption to occur, while the other adsorbents were more compact, resulting in reduced adsorption (Dakiky et al., 2002). A summary of selected studies evaluating the ability of locally available wastes to remove heavy metals can be found in Table 3.6.

3.4 Proposed mechanisms for heavy metal removal

When examining the ability of these low-cost adsorbents to remove heavy metals in the context of the developing world, adsorption has received the most attention as a removal method. With interactions between heavy metals and various materials, adsorption typically occurs in two different ways: surface adsorption and interstitial adsorption. During surface adsorption, heavy metal ions migrate by diffusion from the aqueous solution to the surface of the adsorbent, which contains an opposite surface charge. Then, once the heavy metal ions have passed through the boundary layer, they attach to the surface of the adsorbent and are subsequently removed from the solution. This type of adsorption is often achieved by Van Der Waals forces, dipole interactions, or hydrogen binding (Sulyman et al., 2017). Fig. 3.1 illustrates this type of adsorption.

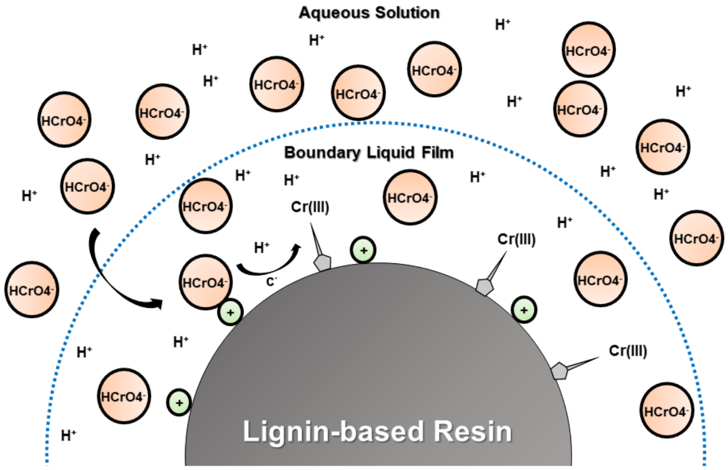

Figure 3.1: Cr(VI) adsorption via surface adsorption (F. Liang et al., 2013).

Table 3.6: Removal of heavy metals by various locally available waste materials

Adsorbent	Heavy metal	Surface area ($m^2\ g^{-1}$)	C_0 ($mg\ L^{-1}$)	q_{max} ($mg\ g^{-1}$)	Reference
A. inaequivalvis shells	Copper (II)	1.82	20-100	330	(Bozbas & Boz, 2016)
	Lead (II)	1.82	20-100	621	(Bozbas & Boz, 2016)
Black tea waste	Cadmium (II)	192	5-100	13.8	(Mohammed, 2012)
	Cobalt (II)	192	5-100	12.2	(Mohammed, 2012)
	Copper (II)	2.04	N.R.	43.2	(Weng et al., 2014)
	Zinc (II)	192	5-100	12.2	(Mohammed, 2012)
Cactus leaves	Chromium (VI)	NA	20-1,000	7.1	(Dakiky et al., 2002)
Coal	Chromium (VI)	NA.	20-1,000	6.8	(Dakiky et al., 2002)
Coal fly ash	Cadmium (II)	10.2	20-80	19.0	(A. Papandreou, Stournaras, & Panias, 2007)
	Chromium (III)	20	10-200	22.7	(A. D. Papandreou et al., 2011)
	Copper (II)	10.2	20-80	20.9	(A. Papandreou et al., 2007)
	Lead (II)	20	10-400	45.3	(A. D. Papandreou et al., 2011)
	Mercury (II)	NA	10	0.4	(Attari et al., 2017)
	Zinc (II)	20	10-200	17.7	(A. D. Papandreou et al., 2011)
Cocoa shells	Cadmium (II)	NA	28.1	0.18	(Meunier et al., 2003)
	Chromium (III)	NA	13.0	0.2	(Meunier et al., 2003)
	Cobalt (II)	NA	14.7	0.2	(Meunier et al., 2003)
	Copper (II)	NA	15.9	0.5	(Meunier et al., 2003)
	Iron (III)	NA	14.0	1.1	(Meunier et al., 2003)
	Manganese (II)	NA	13.7	0.1	(Meunier et al., 2003)
	Nickel (II)	NA	14.7	0.2	(Meunier et al., 2003)
	Lead (II)	NA	51.8	5.2	(Meunier et al., 2003)
	Zinc (II)	NA	16.3	0.001	(Meunier et al., 2003)
Coffee residues	Cadmium (II)	6.48	25-250	39.5	(Boonamnuayvitaya et al., 2004)
	Copper (II)	6.48	25-250	31.2	(Boonamnuayvitaya et al., 2004)

	Nickel (II)	6.48	25-250	11.0	(Boonamnuayvitaya et al., 2004)
	Lead (II)	6.48	25-250	19.5	(Boonamnuayvitaya et al., 2004)
	Zinc (II)	6.48	25-250	13.4	(Boonamnuayvitaya et al., 2004)
Crab shell particles	Cobalt (II)	NA	500-2,000	323	(Vijayaraghavan et al., 2006)
	Copper (II)	NA	500-2,000	244	(Vijayaraghavan et al., 2006)
Green tea waste	Arsenic (III)	0.75	7-23	0.4	(S. Yang et al., 2016)
	Nickel (II)	0.75	7-23	0.3	(S. Yang et al., 2016)
Neem oil cake	Cadmium (II)	NA	10-100	11.8	(Rao & Khan, 2009)
	Copper (II)	NA	10-100	9.4	(Rao & Khan, 2009)
Olive cake	Cadmium (II)	NA	100	65.4	(Al-Anber & Matouq, 2008)
	Chromium (VI)	NA	20-1,000	33.4	(Dakiky et al., 2002)
Olive stone	Cadmium (II)	0.38	10-30	0.93	(Moubarik & Grimi, 2015)
Oyster shells	Cadmium (II)	NA	0-300	118	(Du et al., 2011)
	Lead (II)	NA	0-500	1,591	(Du et al., 2011)
	Zinc (II)	NA	0-300	564	(Du et al., 2011)
Razor clam shells	Cadmium (II)	NA	0-300	501	(Du et al., 2011)
	Lead (II)	NA	0-500	657	(Du et al., 2011)
	Zinc (II)	NA	0-300	553	(Du et al., 2011)
Tea Waste	Nickel (II)	0.39	50-300	18.4	(Malkoc & Nuhoglu, 2005)
	Zinc (II)	1.3	25-200	8.9	(Wasewar et al., 2009)
Tobacco dust	Cadmium (II)	NA	0-50	29.6	(Qi & Aldrich, 2008)
	Copper (II)	NA	0-50	36.0	(Qi & Aldrich, 2008)
	Lead (II)	NA	0-50	39.6	(Qi & Aldrich, 2008)
	Nickel (II)	NA	0-50	25.1	(Qi & Aldrich, 2008)
	Zinc (II)	NA	0-50	24.5	(Qi & Aldrich, 2008)
Wool	Chromium (VI)	NA	20-1,000	41.2	(Dakiky et al., 2002)

During interstitial adsorption, heavy metal ions diffuse towards the adsorbent. However, the ions enter the pores of the adsorbent and adsorb to the surfaces on the interior of the material. This type of adsorption occurs most frequently with microporous adsorbents. Fig. 3.2 illustrates this type of adsorption.

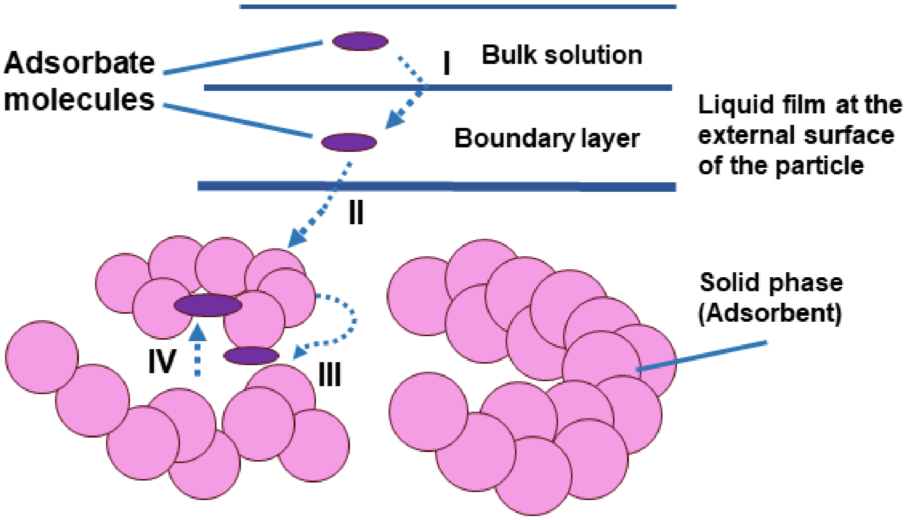

Figure 3.2: Heavy metal removal via interstitial adsorption (Sulyman et al., 2017).

Several adsorption mechanisms have been proposed for the removal of heavy metals. Several researchers have suggested that ion exchange between the adsorbent and metal ions is the dominant mechanism, based on the activation energies of the reactions (H. Chen et al., 2010) and the consistent adsorption capacities across various water quality conditions (Bozic et al., 2009). For example, researchers have found that compounds with phenol groups are able to replace protons with metal ions, which is quickly followed by a decrease in pH, according to the following chemical formula (Bozic et al., 2009):

$$Me^{2+} + 2(-ROH) = Me(-RO)_2 + 2H^{+}$$

Fig. 3.3 shows an illustration of this proposed mechanism.

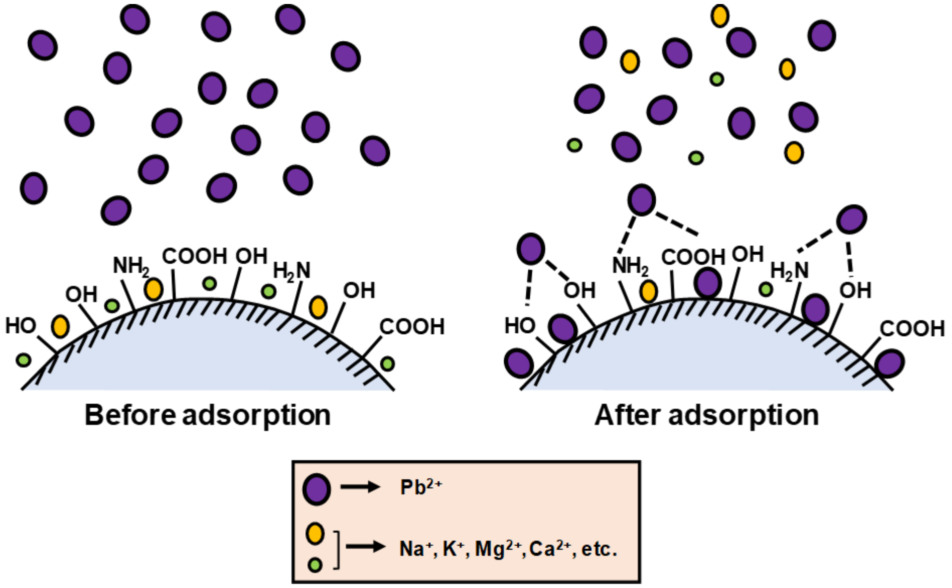

Figure 3.3: Ion exchange removal mechanism (H. Chen et al., 2010)

A review by Dai et al., 2018 described the ion exchange mechanism of heavy metal removal and suggested that the removal of heavy metals using these adsorbents is facilitated by carboxyl and hydroxyl groups, which are attached by a divalent heavy metal ion via two pairs of electrons and subsequently release two Na^+ and/or H^+ ions into the solution. This mechanism is illustrated in Fig. 3.4.

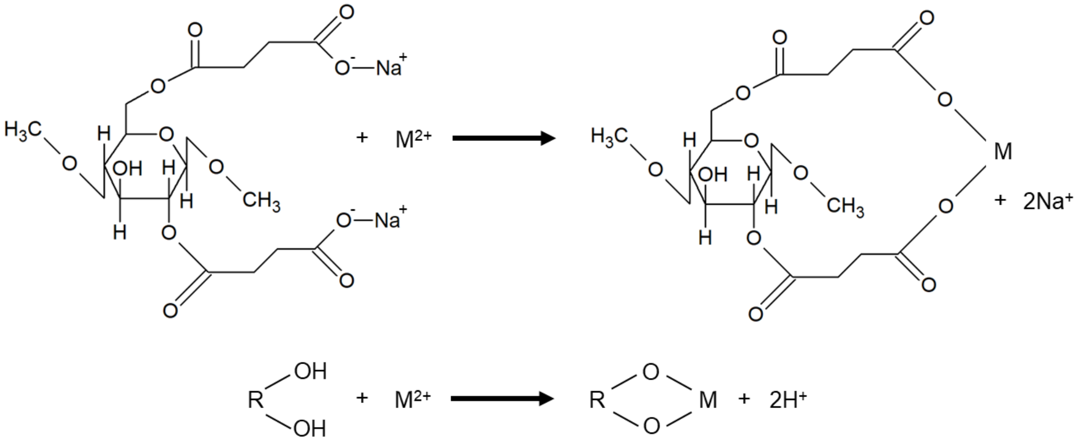

Figure 3.4: Ion exchange with release of Na^+ and H^+ ions (Dai et al., 2018).

The pH of the solution plays a significant role in the ion-exchange mechanism. Several researchers have reported decreased adsorption at lower pH values (Taşar et al., 2014;

Witek-Krowiak et al., 2011), which has been attributed to the increase in H^+ ions, which compete with aqueous heavy metal ions for adsorption sites (Bozic et al., 2009; Demirbas et al., 2009; Rafatullah et al., 2009; Vijayaraghavan et al., 2006).

Electrostatic forces have also been identified as a contributing factor to the adsorption of heavy metals. The presence of electrostatic forces is heavily dependent on the pH. Lower pH values contribute to the protonation of the various functional groups associated with the adsorption of heavy metals, which results in an overall positive charge on the adsorbent (Onyancha et al., 2008). As a result, electrostatic repulsion occurs, preventing the adsorption of positively charged heavy metal ions (Thirumavalavan et al., 2010). Conversely, electrostatic repulsion decreases with increasing pH, which is evident due to the increase in the adsorption of heavy metals (Rao & Khan, 2009). The influence of electrostatic forces during adsorption can be clearly seen when evaluating the removal efficiency of the adsorbent relative to the pH value that represents the point of zero charge (pH_{PZC}) of the adsorbent. The pH_{PZC} is the pH value at which the surface charge of the adsorbent is neutral (Singha & Das, 2013). The surface charge of the adsorbent is positive when the pH of the solution is less than the pH_{PZC}, while its surface charge is negative when the pH of the solution is greater that the pH_{PZC}. As a result, the removal of heavy metals, particularly those that exist in cationic form, is low when $pH < pH_{PZC}$ and increases when $pH > pH_{PZC}$, which suggests a significant presence of electrostatic forces in the adsorption process (R. Leyva-Ramos et al., 2005; Singha & Das, 2013). The influence of electrostatic forces can also be seen with variations in ionic strength.

Adsorption has also been attributed to interactions between heavy metals and various functional groups on the surface of biomass. The functional groups that are often identified as adsorption sites for heavy metals include carboxylate (–COO$^-$), amide (–NH$_2$), phosphate (PO$_4^{3-}$), thiols (–SH), and hydroxide (–OH) (Onyancha et al., 2008; Qi & Aldrich, 2008). The ability of these functional groups to serve as adsorption sites for heavy metals is significantly impacted by the pH of the solution. The dissociation constant (pK$_a$) of many functional groups, including carboxylic and phenol groups, range from 3.5-5.5, which means that the majority of these groups will be deprotonated in this pH range and that an increased number of negatively-charged sites will be available for adsorption (Torab-Mostaedi et al., 2013). Fig. 3.5 demonstrates this mechanism by showing the interactions between –OH groups and Mn(II).

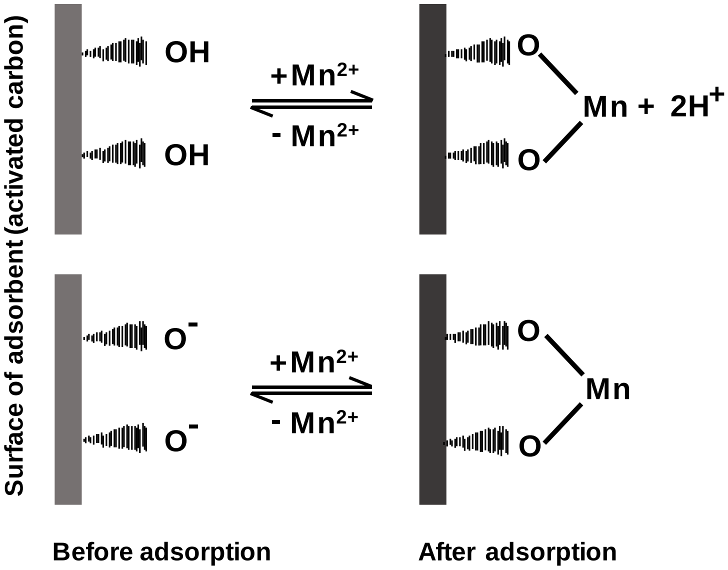

Figure 3.5: Adsorption of Mn(II) by –OH functional group (Sulyman et al., 2017)

The operation of this mechanism during the removal of heavy metals has been demonstrated by increasing the overall adsorption by modifying various adsorbents. Shukla and Rai (2005) modified the adsorbents used in their study using reactive dye to expose the metal ions to –OH groups to enhance removal (Shukla & Pai, 2005). As shown in Fig. 3.6, the –OH groups on the modified dye-loaded adsorbent are positioned to allow for better chelation and subsequent heavy metal removal.

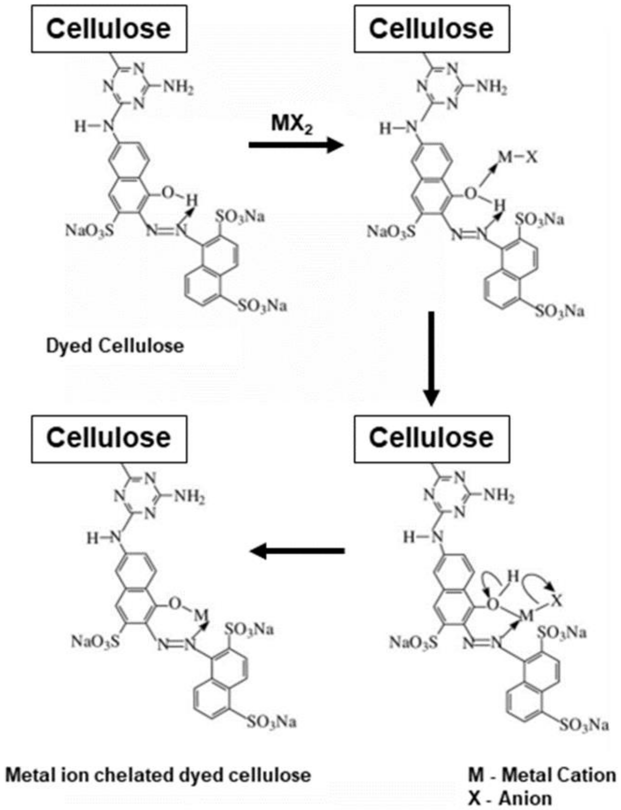

Figure 3.6: Heavy metal removal mechanism using dyed adsorbent (Shukla & Pai, 2005)

3.5 Conclusions

In the developing world, increased water scarcity and pollution contribute to a significant lack of access to clean drinking water. While various forms of water pollution exist, heavy metal contamination in drinking water sources is a growing concern. Moreover, developing countries do not have access to common water treatment methods that would remove heavy metals. As a result, a significant amount of research has been conducted to investigate the use of low-cost adsorbents to remove heavy metals from water sources. The low-cost adsorbents that have been investigated include different types of agricultural waste, soil and mineral deposits, aquatic and terrestrial biomass, and various abundant materials. Researchers have reported that these materials can effectively remove heavy metals. When evaluating each category outlined in this review paper, agricultural waste and byproducts appear to be the most effective at removing heavy metals, while natural soil and mineral deposits appeared to be the least effective. Though chemical modifications to the adsorbents increased the overall adsorption capacities of the materials tested, these methods are not typically available to communities in the developing world.

However, the effectiveness of these materials at removing heavy metals depends heavily on the water quality conditions, such as pH, ionic strength, and temperature, along with the characteristics of the material (*e.g.*, specific surface area, surface chemistry, *etc*.). These conditions can affect the speciation and stability of the heavy metals, along with the adsorptive characteristics of the adsorbent. Furthermore, in terms of the manner in which heavy metals are removed, ion exchange is the most cited mechanism, along with the influence of electrostatic forces. The efficiencies of these mechanisms are heavily influenced by water quality conditions.

Overall, these low-cost adsorbents are viable, cost-effective materials that can be used to remove heavy metals from water. In the developing world, these materials are readily available in large quantities, and limited technology and expertise would be required to integrate these materials into a water treatment process. Future research in this area should continue throughout the developing world to identify additional low-cost materials that are effective at removing heavy metals. Special attention should be given to the waste materials and other residual byproducts that are abundant in these countries, along with countries with significant industrial activities, which most often contribute to increases in heavy metal contamination. The implementation of these types of materials in water treatment processes in these locations is potentially environmentally-sustainable as it will reduce the disposal of waste while simultaneously improving the quality of the local water sources. Furthermore, future research should evaluate the capabilities of these materials with true, local water sources, such as industrial effluent, river and lake sources, and domestic wastewater, using bench-scale testing. Future research in this area should also determine the full impact of varying water conditions on heavy metal removal and assess the true viability of the proposed low-cost materials in developing countries through pilot-scale studies.

CHAPTER 4

REMOVAL OF CONTAMINANTS OF EMERGING CONCERN BY METAL-ORGANIC FRAMEWORK NANOADSORBENTS: A REVIEW[2]

Abstract

Over the last two decades, various contaminants of emerging concern (CECs), such as endocrine disrupting compounds, along with pharmaceuticals and personal care products (PPCPs), have been of interest to the water industry because of their incomplete removal during the typical water and wastewater treatment processes. Recently, the potential environmental applications of metal-organic frameworks (MOFs) and MOF-based nanoadsorbents (MOF-NAs) have been widely studied. In particular, the use of these nanoadsorbents for CECs in water and wastewater treatment processes has been a rapidly growing area of interest in the recent literature due to their unique physicochemical properties. Therefore, it is necessary to understand the adsorption phenomena of various CECs by MOF-NAs, particularly because the physicochemical properties of various CECs create unique challenges for the removal of these compounds from water. In addition, the adsorption of CECs on MOF-NAs is significantly influenced by the physicochemical

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[2] Joseph, L. et al., 2019. Removal of contaminants of emerging concern by metal organic framework nanoadsorbents: A review. *Chemical Engineering Journal* 369: 928-946. Reprinted here with permission of publisher.

properties of the MOF-NAs and the water quality conditions. Therefore, this review provides a comprehensive assessment of recent studies on the removal of various CECs (e.g., analgesics, antibiotics, antiepileptics, antiseptics, and etc.) with different physicochemical properties by various MOF-NAs under various water quality conditions (e.g., pH, background ions/ionic strength, natural organic matter, and temperature). In addition, this review briefly discusses the recent literature on the synthesis of MOF-NAs, regeneration of MOF-NAs, and removal of CECs during water and wastewater treatment processes.

4.1 Introduction

Over the last two decades, various contaminants of emerging concern (CECs), such as endocrine-disrupting compounds (EDCs) and pharmaceuticals and personal care products (PPCPs), have been a major issue in the water industry (Bolong, Ismail, Salim, & Matsuura, 2009; Y. Yoon, J. Ryu, J. Oh, B. G. Choi, & S. A. Snyder, 2010). Numerous CECs, including analgesics, antibiotics, antiepileptics, antiseptics, hormones, plasticizers, stimulants, and sunscreens, have frequently been detected in wastewater treatment plant effluents, indicating that these micropollutants are inadequately removed during the typical wastewater treatment processes (J. Ryu, J. Oh, S. A. Snyder, & Y. Yoon, 2014). Although some difficulty exists in explicitly defining the term “EDCs,” exogenous agents that inhibit the behavior of natural hormones in the body are generally classified as EDCs by the United States Environmental Protection Agency (USEPA, 1997). Stumm-Zollinger and Fair (1965) and Tabak and Bunch (1970) raised the first alarms regarding the possible adverse effects of various pharmaceuticals in municipal wastewater (Chu et al., 2017; Heo et al., 2016; C. Jung, A. Son, et al., 2015; Stumm-Zollinger & Fair, 1965; Tabak & Bunch, 1970; Y. Yoon et al., 2010).

Numerous studies have examined the fate and transport of EDCs and PPCPs in water and wastewater treatment processes because several of these compounds have been detected in drinking water sources and wastewater effluents (Mark J. Benotti et al., 2009; H. W. Chen et al., 2013; Conn, Barber, Brown, & Siegrist, 2006; Z.-h. Liu, Kanjo, & Mizutani, 2009; Luo et al., 2014; C. Park, Fang, Murthy, & Novak, 2010; Jaena Ryu, Jeill Oh, Shane A. Snyder, & Yeomin Yoon, 2014; Sui, Huang, Deng, Yu, & Fan, 2010; Vieno & Sillanpaa, 2014; B. Yang et al., 2012; Y. Yoon, J. Ryu, J. Oh, B.-G. Choi, & S. A. Snyder, 2010). The fate and transport of EDCs and PPCPs vary greatly depending on the treatment processes that are used, including coagulation-flocculation-sedimentation-filtration (L. Joseph et al., 2013; C. Jung, Oh, & Yoon, 2015), activated carbon treatment (C. Jung, L. K. Boateng, et al., 2015), ozonation (Westerhoff, Yoon, Snyder, & Wert, 2005), chlorination (C. Li et al., 2017), sonodegradation (Al-Hamadani et al., 2016; Al-Hamadani et al., 2017), and biodegradation (J. Park et al., 2017; Staniszewska, Graca, & Nehring, 2016). Among these commonly used technologies, adsorption is typically considered the most promising method for drinking water and wastewater treatment due to its adaptability, extensive applicability, and cost-effectiveness (Chowdhury & Balasubramanian, 2014). While granular or powdered activated carbon is commonly used in water and wastewater treatment, relatively new adsorbents such as carbon nanotubes, graphenes or graphene-based adsorbents, and metal-organic frameworks (MOFs) have been investigated recently for the removal of EDCs/PPCPs (Heo et al., 2012; Nam et al., 2015; Sarker, Bhadra, Seo, & Jhung, 2017).

MOFs are an emerging class of porous materials fabricated from metal-containing nodes and organic linkers (Zhou & Kitagawa, 2014). Over the past two decades, several hundred different MOFs have been studied for different applications, including gas purification, gas separation, gas storage, energy storage, and environmental applications (*e.g.*, adsorption, membrane preparation, and catalysis) (Bhadra, Seo, & Jhung, 2016; Hasan, Jeon, & Jhung, 2012; Rui et al., 2018; P. W. Seo, Khan, Hasan, & Jhung, 2016; M. Zhang, Ma, Wan, Sun, & Liu, 2018). Particularly in the environmental area, MOFs and MOF-based nanoadsorbents (MOF-NAs), such as Zr-benzenedicarboxylate (UiO-66), Zr-biphenyldicarboxylate (UiO-67), metal-benzenetricarboxylate (MIL-100; metal = Fe^{3+}, Cr^{3+}, or Al^{3+}), metal-benzenetricarboxylate (MIL-96; metal = Al^{3+}, Cr^{3+}, Ga^{3+}, or In^{3+}), Zn-2-methylimidazolate (ZIF-8), MIL-101-graphene oxide (GO), UiO-67/GO, Fe_3O_4@MIL-100(Fe), and urea-MIL-101(Cr), have been widely studied for the removal of various EDCs and PPCPs in water (Akpinar & Yazaydin, 2017; Embaby, Elwany, Setyaningsih, & Saber, 2018; Hasan et al., 2012; C. H. Liang, Zhang, Feng, Chai, & Huang, 2018; Moradi, Shabani, Dadfarnia, & Emami, 2016; Sarker, Song, & Jhung, 2018a; P. W. Seo, Khan, & Jhung, 2017). In addition, due to the unique physicochemical properties of MOF-NAs, the use of these nanoadsorbents for EDCs and PPCPs in water and wastewater treatment processes has been an area of rapidly growing interest in the recent literature. While a few recent review studies have documented the removal of organics and heavy metals using various MOFs (Z. Hasan & S. H. Jhung, 2015; Khan, Hasan, & Jhung, 2013), it remains critical to develop an understanding of the adsorption phenomena of various EDCs and PPCPs by MOF-NAs because their physicochemical properties create unique challenges for the removal of these compounds in water. In particular, it is essential to develop an understanding of the mechanisms of removal, such as by electrostatic interactions, metal effects, acid-base interactions, π-π interactions, and H-bonding. Additionally, the adsorption of EDCs and PPCPs on MOF-NAs is significantly influenced by the physicochemical properties of the compounds (*e.g.*, size/shape, hydrophobicity, functional group, and charge), as well as the physicochemical properties of the adsorbent itself (*e.g.*, surface area, hydrophobicity, charge, and functional group) and water quality properties (*e.g.*, pH, temperature, solute concentration, natural organic matter (NOM), and background anions/cations). It is very important to understand the problems that we have been faced for the potential use of MOF-NAs in the adsorptive removal of various EDCs and PPCPs from aqueous systems.

Therefore, the primary goal of this review is to provide a comprehensive assessment of the removal of various EDCs and PPCPs that have different physicochemical properties by various MOF-NAs under different water quality conditions. To accomplish this goal, this review briefly surveys recent literature on the synthesis of MOFs, regeneration of MOF-NAs, and removal of EDCs and PPCPs during water and wastewater treatment processes.

4.2 Synthesis of MOFs

Tomic (1965) first introduced materials that have metal–organic polymers or supramolecular structures, which are currently called MOFs (Tomic, 1965); however, the term "MOF" was widely disseminated by Yaghi *et al*. in 1995 (Yaghi, Li, & Li, 1995). Detailed historical developments in the synthesis of MOFs are described in Fig. 4.1.

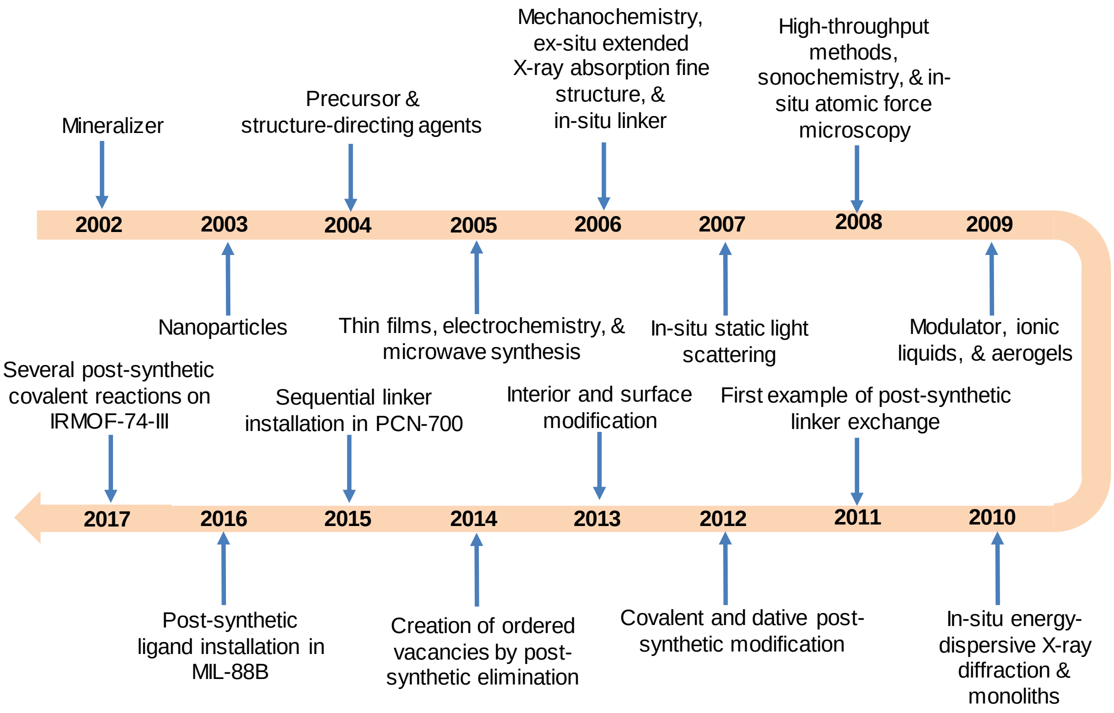

Figure 4.1: Historical developments in the synthesis of various MOFs (Stock & Biswas, 2012; Yin, Wan, Yang, Kurmoo, & Zeng, in press)

Since both nonflexible and flexible porous MOFs (*i.e.*, MIL-47 and MIL-53) were first reported in 2002 (Barthelet, Marrot, Riou, & Ferey, 2002; Serre et al., 2002), studies have shown that the synthesis of MOFs coupled with functionalization (*i.e.*, post-synthetic modification) may be an effective and practical tool for the modification of their structure and other properties (Yin et al., in press). Bi- and trivalent aromatic carboxylic acids have already been employed for fabrication of frameworks with Al, Fe, Ni, U, Th, and Zn, resulting in interesting features, such as high metal content and thermal stability (Czaja, Trukhan, & Muller, 2009). For various applications, the main purpose of MOF fabrication is to determine the optimal synthesis conditions to result in distinct inorganic building blocks without decay of the organic linker, while the kinetics of crystallization must be suitable to permit nucleation and growth of the desired phase (Kitagawa, Kitaura, & Noro, 2004). Fig. 4.2 provides an overview of synthesis methods (*e.g.*, conventional heating, electrochemistry, microwave-assisted heating, mechanochemistry, and sonochemistry), possible reaction temperatures (*e.g.*, room temperature, elevated temperatures, and solvothermal conditions), and final reaction products (*e.g.*, thin films, membranes, and composites) of MOF synthesis based on the various synthesis methods that have been applied in the last two decades (Stock & Biswas, 2012).

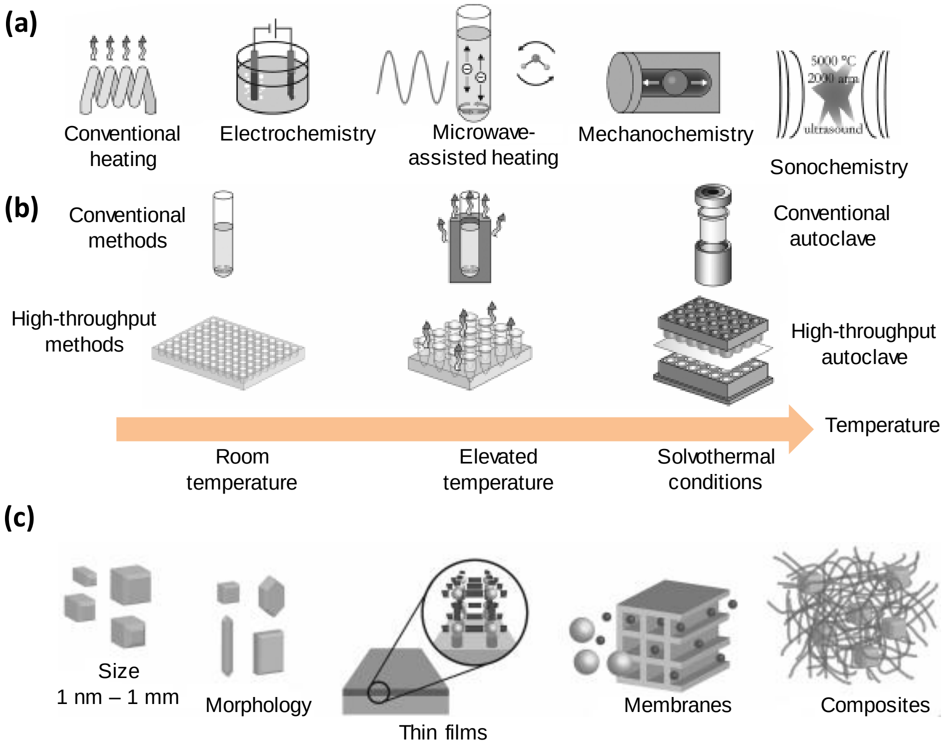

Figure 4.2: Overview of (a) synthesis methods, (b) possible reaction temperatures, and (c) final reaction products in MOF synthesis (Stock & Biswas, 2012)

While conventional synthesis includes reactions associated with conventional electric heating, excluding any parallelization of reactions, the two temperature ranges that include the solvothermal and non-solvothermal are generally distinguished from these (Waitschat, Wharmby, & Stock, 2015). Solvothermal reactions occur above the boiling point of the solvent at autogenous pressure in closed vessels, whereas non-solvothermal reactions take place below the boiling point of the solvent at room or elevated temperatures (Rabenau, 1985).

Systematic examination of the synthesis of MOFs is important because the properties of MOFs are greatly influenced by the synthetic methods employed. Detailed descriptions of these synthetic methods have been published previously (Stock & Biswas, 2012; Yin et al., in press). Briefly, a high-throughput method was first employed in the late 1990s for zeolites using solvothermal synthesis (Klein, Lehmann, Schmidt, & Maier, 1998). This method is a powerful tool that enables the use of solvothermal synthesis to accelerate the discovery of new MOFs and to enhance synthesis procedures (Stock, 2010). Optimal conditions by which new compounds are fabricated can be determined by time-resolved examination of MOF crystallization, which can be used to detect crystalline intermediates, determine reaction parameters (*i.e.*, reaction rate constants and activation energies), and provide insight into the mechanisms of crystallization (Surble, Millange, Serre, Ferey, & Walton, 2006). Different measurement methods are used in *ex situ* and *in situ* studies of MOF crystallization: Extended X-ray absorption fine structure, electron spray ionization-mass spectrometry, and X-ray powder diffraction are commonly used for *ex situ* studies, whereas energy-dispersive X-ray diffraction, atomic force microscopy, small-angle X-ray scattering, wide-angle X-ray scattering, static light scattering, and surface plasmon resonance are commonly employed for *in situ* studies (Stock & Biswas, 2012). The degree of MOF crystallization varies depending on the *ex situ* and *in situ* methods. In the *ex situ* method, the reaction is allowed to proceed for limited time intervals, which can result in changes in the composition of the sample and non-reliable outcomes; however, this method is advantageous because it can be conducted in a laboratory using relatively easy and uncomplicated methods (Haque, Jeong, & Jhung, 2010). In the *in situ* method, specific equipment and synchrotron radiation are often required to monitor the reactions continuously; however, this results in relatively better time-resolution data (X. L. Li et al., 2016). Overall, it is important to examine the mode of synthesis when comparing results because different methods of synthesis can affect the adsorption properties of MOFs.

4.3 Removal of CECs in conventional and advanced wastewater and water treatment processes

4.3.1 Removal in wastewater processes

Numerous studies have described the occurrence of various EDCs and PPCPs at different stages during wastewater treatment processes, which implies that the effectiveness of the removal of these micro-contaminants is significantly influenced by the physicochemical properties of the contaminants (*e.g.*, p*K*a, functional groups, and hydrophilicity) and the type of wastewater treatment method employed (*e.g.*, methods involving biological treatment, dilution of wastewater effluent or combined sewer overflow, or variations in rainfall or temperature) (M. J. Benotti & Brownawell, 2007; Phillips et al., 2012; Weyrauch et al., 2010). However, it is difficult to determine the exact transport and fate mechanisms of various EDCs and PPCPs during the processes of biodegradation (anaerobic/anoxic/aerobic), sorption to sludge, or oxidative degradation by chlorine or ozone (J. Ryu et al., 2014). Ryu *et al*. found that the approximate degradation rates of four antibiotics during wastewater treatment processes were as follows: triclocarban (85%) > sulfamethoxazole (70%) ≥ triclosan (65%) > trimethoprim (20%) (J. Ryu et al., 2014). Different degradation mechanisms can be employed. For example, for triclocarban and triclosan, sorption to sludge is a main method of degradation due to the relatively high hydrophobicity of these compounds (log K_{OW} = 4.90 and 4.76, respectively) (Hyland, Dickenson, Drewes, & Higgins, 2012), whereas biodegradation of these chemicals is relatively difficult (Heidler, Sapkota, & Halden, 2006). During the degradation processes, some degree of removal may also result from oxidation of these compounds by chlorine (Westerhoff et al., 2005). In particular, relatively high removal efficiency was observed for hydrophilic sulfamethoxazole (log K_{OW} = 0.89), probably due to the oxidation of the compound during chlorination (Nam, Jo, Yoon, & Zoh, 2014). However, hydrophilic trimethoprim (log K_{OW} = 0.91) demonstrated a very low degree of removal due to its low biodegradability (Alexy, Kumpel, & Kummerer, 2004) and limited adsorption to sludge (S. Kim, Eichhorn, Jensen, Weber, & Aga, 2005), whereas oxidation by chlorine may have an insignificant influence (Westerhoff et al., 2005). The removal efficiencies of analgesics and anti-inflammatories can be elucidated by investigating the various mechanisms by which they are degraded, such as biodegradation, sorption to sludge, and oxidation (J. Ryu et al., 2014). Diclofenac was significantly removed during chlorination (Noutsopoulos et al., 2015) but exhibited minimal biodegradability and adsorption to sludge (Buser, Poiger, & Muller, 1998; Carballa, Fink, Omil, Lema, & Ternes, 2008). A separate study revealed that compounds such as diclofenac, sulfamethoxazole, and trimethoprim, which contain primary or secondary amines, can be significantly oxidized by chlorine, which mainly occurs when the amines form heterocyclic ring structures (Westerhoff et al., 2005). In addition, chlorine was found to enhance naproxen removal, whereas removal of ibuprofen was relatively insignificant, presumably due to the electron-capturing functional group on its aromatic ring (Westerhoff et al., 2005). High concentrations of artificial sweeteners (sucralose and acesulfame) were detected in raw wastewater at levels of approximately 5,300 and 3,900 ng/L, respectively, and relatively low removal of these compounds (<25%) was achieved during wastewater treatment processes (J. Ryu et al., 2014). Similarly, it was found that degradation of these compounds through both aerobic and anaerobic biological processes was insignificant (Buerge, Buser, Kahle, Muller, & Poiger, 2009; Torres et al., 2011). Sucralose and acesulfame also appeared to be poorly oxidized by chlorine under typical wastewater treatment plant operating conditions and demonstrated negligible partition coefficients in activated sludge due to their high hydrophilicity (log K_{OW} = -1.00 for sucralose and -1.33 for acesulfame) (J. Ryu et al., 2014). Table 4.1 describes the degree of removal for selected CECs in wastewater treatment plants under dry-weather conditions using a representative sample of the existing literature regarding biodegradability, along with trends concerning adsorption to sludge and oxidation by chlorination.

4.3.2 Removal in water treatment processes

The majority of the population of the United States (approximately 95%) has access to drinking water from community water systems that employ conventional water treatment processes (coagulation-flocculation, sedimentation, filtration, and disinfection) (Agency, 2018). However, numerous studies focusing on various CECs, such as EDCs, PPCPs, herbicides, pesticides, and polyaromatic hydrocarbons, have shown that conventional processes can remove these compounds at only minimal levels (S. A. Snyder, Westerhoff, Yoon, & Sedlak, 2003; Y. Yoon et al., 2010).

Table 4.1: Removal efficiencies of selected CECs at wastewater treatment plant under dry weather conditions with examples of previously published literature related to biodegradability, tendency of adsorption to sludge, and tendency of oxidation by chlorination

Compound	Use	MW (g/mol)	pK_a^b	Log K_{OW}^c	Inf. (ng/L)	Eff. (ng/L)	Rem (%)	Bio.	Ads.	Oxi.	Ref.
Acesulfame	Sugar substitute	201.2	2.0	-1.33	3863	3705	4	L	L	L	(Buerge et al., 2009) [B,A]; (Mawhinney, Young, Vanderford, Borch, & Snyder, 2011)[O]
Atrazine	Herbicide	215.1	<2 (1.6)	2.61	ND	ND	NA	L	M	L	(S. Snyder et al., 2004)[B,A]; (Lei & Snyder, 2007)[O]
Atenolol	Oral beta blocker	266.3	9.6	-0.03	1040	529	49	M	L	L	(Bueno et al., 2012) [B,A]; (Huerta-Fontela, Galceran, & Ventura, 2011)[O]
Benzophenone	Ultraviolet blocker	182.2	<2	3.18	88	47	47	L	M	L	(Kasprzyk-Hordern, Dinsdale, & Guwy, 2009)[B]; (Z. F. Zhang et al., 2011)[A];

Benzotriazole	Heterocyclic	119.2	8.2	1.44	88	47	47	M	L	L	(Stackelberg et al., 2007)^{O} (Reemtsma, Miehe, Duennbier, & Jekel, 2010)^{B,A}; (Sichel, Garcia, & Andre, 2011)^{O}
Caffeine	Stimulant	194.2	6.1	-0.07	8810	236	97	H	H	M	(S. Snyder et al., 2004)^{B}; (Blair et al., 2013)^{A}; (Westerhoff et al., 2005)^{O}
Carbamazepine	Analgesic	236.3	<2	2.45	188	156	17	L	L	H	(Clara, Strenn, & Kreuzinger, 2004)^{B}; (Carballa et al., 2008)^{A}; (Westerhoff et al., 2005)^{O}
DEET	Insect repellent	191.3	<2	2.18	47	46	2	M	L	L	(S. Snyder et al., 2004)^{B,A}; (Westerhoff et al., 2005)^{O}
Diltiazem	Calcium channel blockers	414.5	12.9	2.79	ND	ND	NA	M	M	L	(Domenech, Ribera, & Peral, 2011)^{B}; (Blair et al., 2013)^{A};

											(Huerta-Fontela et al., 2011)[O]
Diclofenac	Arthritis	318.1	(4.2)	0.7	6897	359	95	L	L	H	(Buser et al., 1998)[B]; (Carballa et al., 2008)[A]; (Westerhoff et al., 2005)[O]
Diphenhydramine	Antihistamine	255.5	9.0	3.27	171	142	17	L	M	NF	(C. X. Wu et al., 2010)[B]; (Hyland et al., 2012)[A]
E1	Steroid	270.4	10.3	3.13	ND	ND	NA	H	M	H	(S. Snyder et al., 2004)[B,A]; (Westerhoff et al., 2005)[O]
Gemfibrozil	Anticholesterol	250.2	4.7	4.72	45	33	27	H	M	H	(S. Snyder et al., 2004)[B,A]; (Westerhoff et al., 2005)[O]
Ibuprofen	Analgesic	206.1	4.5 (4.9)	3.97	2724	241	91	H	M	M	(Buser, Poiger, & Muller, 1999)[B]; (Carballa et al., 2008)[A]; (Lei & Snyder, 2007)[O]
Iohexol	Contrast agent	821. 1	11.7	-3.05	14432	16008	-11	L	L	L	(Deblonde, Cossu-Leguille, & Hartemann, 2011)[B,A]

Iopamidol	Contrast agent	777.1	10.7	-2.42	8518	10091	-18	L	L	NF	(Deblonde et al., 2011)[B,A]
Iopromide	Contrast agent	790.9	<2 and >13	-2.10	11133	12895	-16	L	L	L	(S. Snyder et al., 2004)[B,A]; (Lei & Snyder, 2007)[O]
Meprobamate	Anti-anxiety	218.3	<2	0.70	ND	ND	NA	M	L	L	(S. Snyder et al., 2004)[B,A]; (Lei & Snyder, 2007)[O]
Naproxen	Analgesic	230.1	4.5 (4.2)	3.18	5113	482	91	M	M	H	(S. Snyder et al., 2004)[B]; (Hyland et al., 2012)[A]; (Lei & Snyder, 2007)[O]
Primidone	Anticonvulsant	218.3	11.5	0.73	100	40	60	M	L	H	(J. W. Kim et al., 2012)[B]; (Ternes et al., 2002)[A]; (Huerta-Fontela et al., 2011)[O]
Propylparaben	Preservative	180.2	8.5	3.04	520	7	99	H	H	H	(Kasprzyk-Hordern et al., 2009) [B,A]; (Andersen, Lundsbye, Wedel, Eriksson, & Ledin, 2007)[O]
Simazine	Herbicide	201.7	1.62	2.18	ND	ND	NA	H	M	M	(Bueno et al., 2012)[B,A];

											(Ormad, Miguel, Claver, Matesanz, & Ovelleiro, 2008)^{O}
Sucralose	Sweetener	397.6	NA	-1.00	5289	4043	24	L	L	L	(Torres et al., 2011)^{B,A,O}
Sulfamethoxazole	Antibiotic	253.1	2.1 & <2 (5.7)	0.89	400	117	71	L	H	H	(S. Snyder et al., 2004)^{B,A}; (Westerhoff et al., 2005)^{O}
TCEP	Fire retardant	285.5	NA	1.44	439	348	21	L	M	L	(Meyer & Bester, 2004)^{B,A}; (S. Snyder et al., 2004)^{A}; (Lei & Snyder, 2007)^{O}
Triclocarban	Antibiotic	315.6	NA	4.90	198	33	83	L	H	NF	(Heidler et al., 2006)^{B}; (Hyland et al., 2012)^{A}
Triclosan	Antibiotic	289.6	8 (7.9)	4.76	190	63	67	L	H	H	(S. Snyder et al., 2004)^{B,A}; (Westerhoff et al., 2005)^{O}
Trimethoprim	Antibiotic	290.1	6.3, 4.0, <2 (7.1)	0.91	150	118	21	L	L	H	(Alexy et al., 2004)^{B}; (S. Kim et al., 2005)^{A}; (Westerhoff et al., 2005)^{O}

Source: Modified from (J. Ryu et al., 2014).

Inf. = influent; Eff. = effluent; Rem. = overall removal; Bio. = biodegradation (^{B}); Ads. = adsorption to sludge (^{A}); Oxi. = oxidation by chlorine (^{O}); Ref. = references; H = high; M = medium; L = low; ND = not determined because under detection limit (ND values = 15 ng/L for E1, 50 ng/L for diltiazem, 5 ng/L for atrazine, 1.5 ng/L for simazine, and 0.5 ng/L for meprobamate) ; NA = not available or not applicable; NF = not found.

The potential fate and transport of EDCs/PPCPs in conventional drinking water treatment processes are described in Fig. 4.3.

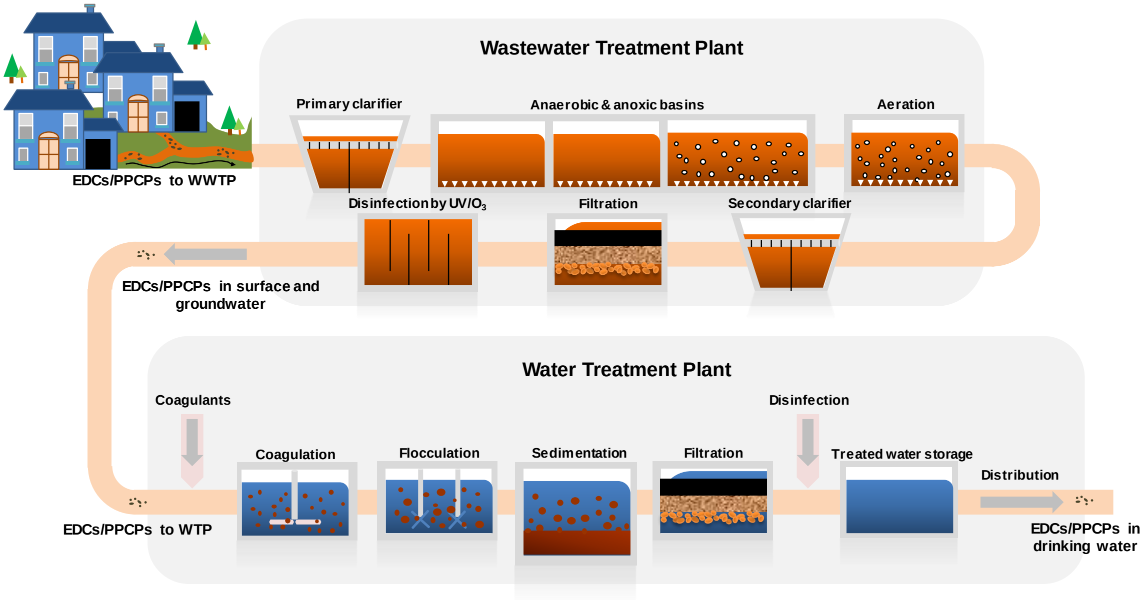

Figure 4.3: Possible fate and removal of EDCs and PPCPs in conventional wastewater treatment and drinking water treatment processes modified from (C. M. Park et al., 2017)

Aluminum- or iron-based salts are commonly used to precipitate compounds as metal hydroxides during the chemical coagulation processes used in drinking water treatment. Westerhoff *et al*. reported that 26 of 28 EDCs and PPCPs exhibited < 20% removal during coagulation using aluminum sulfate, whereas slightly more removal (> 20%) was achieved for herbicides, pesticides, and polyaromatic hydrocarbons (10 of 25 compounds) (Westerhoff et al., 2005). This is presumably because the compounds with higher removal efficiencies are considered relatively hydrophobic (based on their log octanol-water partition coefficients; log K_{OW} = 2.16-6.13) and partitioned either onto particulate matter or onto precipitated solids that contained adsorbed NOM during removal.

Adsorption with activated carbon has been widely used to remove various organic and inorganic contaminants in aqueous solutions (Chanil Jung et al., 2013). Activated carbon treatment is a cost-effective process, and activated carbon is a popular adsorbent for water treatment due to its strong interactions, particularly with hydrophobic organic contaminants. However, the physicochemical properties of activated carbon, including its pore size, shape, and charge, prevent the adsorption of large molecules (Kilduff, Karanfil, Chin, & Weber Jr, 1996). Jung *et al*. showed that the degree of adsorption of three EDCs and four active pharmaceutical compounds was in the following order: ibuprofen > EE2 > atrazine > bisphenol A > carbamazepine > sulfamethoxazole > diclofenac; this order is presumably due to varying degrees of competitive adsorption, particularly based on π–π bonding and hydro-bonding interactions in the mixture (C. Jung et al., 2013). A separate study conducted a linear regression analysis to assess the adsorption of 22 EDCs and PPCPs by a commercially available powdered activated carbon, arriving at the following equation: [percentage removal] = 15×[log K_{OW}] + 27% (n = 22; $R^2 = 0.88$) (Westerhoff et al., 2005). Overall, the findings implied that protonated bases are substantially removed by powdered activated carbon, whereas EDCs and PPCPs with relatively low log K_{OW} values or deprotonated acid functional groups were the most challenging to remove with powdered activated carbon.

Membrane processes such as forward osmosis, reverse osmosis, nanofiltration, and ultrafiltration have been widely used in water and wastewater treatment processes (Al-Obaidi, Li, Kara-Zaitri, & Mujtaba, 2017; Corzo, de la Torre, Sans, Ferrero, & Malfeito, 2017; Lee, Ihara, Yamashita, & Tanaka, 2017; Soriano, Gorri, & Urtiaga, 2017). However, the removal of EDCs and PPCPs using these membranes varies depending on their physicochemical properties (*e.g.*, solute size/shape, pK_a, and hydrophilicity), water quality conditions (*e.g.*, pH, temperature, background anions/cations, and NOM), and membrane properties (*e.g.*, membrane pore size/density, porosity, charge, hydrophobicity) (S. Kim,

K. H. Chu, et al., 2018). Heo *et al*. reported the removal of several selected organic compounds by forward osmosis: sulfamethoxazole (65–90%) ≈ carbamazepine (65–85%) >> atrazine (35–50%) > 4-chloraphenol (30–40%) > phenol (20%) (Heo et al., 2013). The forward osmosis process uses an osmotic pressure difference produced by a concentrated draw solution to transport water from a feed solution to the draw solution through a membrane (Xie, Nghiem, Price, & Elimelech, 2012). Conversely, reverse osmosis, nanofiltration, and ultrafiltration processes use hydraulic pressure difference as the main driving force to permeate water through a semipermeable membrane (Cartinella et al., 2006). Removal by reverse osmosis exhibited different retention trends compared to those observed with forward osmosis for selected organic compounds, as follows: 4-chloraphenol (94%) > EE2 (90%) >> phenol (70%) > atrazine (55%) > carbamazepine (32%) >> sulfamethoxazole (6.2%) (Heo et al., 2013). In a separate study, removal of neutrally charged carbamazepine (p*K*a = 2.3) by two nanofiltration membranes (NF-90 and NF-270) was fairly constant because removal is governed completely by steric exclusion in the absence of charged functional groups (Nghiem, Schafer, & Elimelech, 2005). The removal of seven different pharmaceuticals using an ultrafiltration membrane was relatively low (<50%) in a pilot-scale municipal wastewater reclamation system, although the findings indicated that molecular weight, log *D*, and the charge of the molecules were key factors influencing their retention (Chon, Cho, & Shon, 2013).

In drinking water treatment systems, the addition of free chlorine and ozone causes oxidation of reduced metals and organic compounds, as well as the inactivation of microorganisms (Gallard & Von Gunten, 2002; von Gunten, 2003). In addition, the presence of nucleophilic sites (*e.g.*, carbon-carbon double bonds), the electron density degree of functional groups, and the amount of protonation influence the reactivity of organic matter with these oxidants (J. Y. Hu & Aizawa, 2003). For instance, free chlorine reacts quickly with phenolic compounds, primarily through the reaction between hypochlorous acid and the deprotonated phenolate anion, which causes repeated addition of chlorine to the aromatic ring, followed by ring cleavage (Faust & Hoigne, 1987). This reactivity of the phenolic functional group is likely the mechanism of the oxidation that occurs during chlorination of various estrogenic hormones that contain phenolic moieties (*e.g.*, ethynylestradiol, estriol, estradiol, and estrone) (Pinkston & Sedlak, 2004). Of approximately 60 EDCs and PPCPs, the concentrations of some residual EDCs and PPCPs (*e.g.*, sulfamethoxazole, diclofenac, estradiol, ethynylestradiol, estriol, naproxen, estrone, acetaminophen, oxybenzone, triclosan, and several polyaromatic hydrocarbons) were below the detection limit of 10 ng/L, demonstrating a high degree of oxidation with chlorine, whereas ozone had much stronger oxidation reactivity with these compounds (Westerhoff et al., 2005). In particular, steroids containing phenolic moieties (*e.g.*, estradiol, ethynylestradiol, and estrone) were oxidized more effectively by ozone compared to those without benzene or phenolic moieties (*e.g.*, androstenedione, progesterone, and testosterone). This is presumably because the OH functional groups lose electrons to the benzene rings, which leads to increased reactivity with ozone compared to non-aromatic ring structures or conjugated bonds with COOH functional groups (Huber, Canonica, Park, & Von Gunten, 2003). Table 4.2 summarizes the expected performances of various technologies used in both water and wastewater treatment plants based on literature reports characterizing particular classes of compounds or their similarities to other EDCs and PPCPs that have been investigated in detail.

Table 4.2: Unit processes and operations used for CEC removal.

Group	Classification	AC	BAC	MOFs/MOF-NAs	O_3/ AOPs	UV	Cl_2/ ClO_2	Coagulation/ flocculation	Softening/ metal oxides	NF	RO	Degradation {B/P/AS}*
EDCs	Pesticides	E	E	F - E	L - E	E	P - E	P	G	G	E	E {P}
	Industrial chemicals	E	E	F - E	F - G	E	P	P - L	P - L	E	E	G - E {B}
	Steroids	E	E	F - E	E	E	E	P	P - L	G	E	L - E {B}
	Metals	G	G	F - E	P	P	P	F - G	F - G	G	E	P {B}, E {AS}
	Inorganics	P - L	F	F - E	P	P	P	P	G	G	E	P - L
PhACs	Antibiotics	F - G	E	F - E	L - E	F - G	P - G	P - L	P - L	E	E	E {B} G - E {P}
	Antidepressants	G - E	G – E	F - E	L - E	F - G	P - F	P - L	P - L	G - E	E	G - E
	Anti-inflammatories	E	G – E	F - E	E	E	P - F	P	P - L	G - E	E	E {B}
	Lipid regulators	E	E	F - E	E	F - G	P - F	P	P - L	G - E	E	P {B}
	X-Ray contrast media	G - E	G – E	F - E	L - E	F - G	P - F	P - L	P - L	G - E	E	E {B and P}
	Psychiatric control	G - E	G – E	F - E	L - E	F - G	P - F	P - L	P - L	G - E	E	G - E
PCPs	Synthetic scents	G - E	G – E	F - E	L - E	E	P - F	P - L	P - L	G - E	E	E {B}
	Sunscreens	G - E	G – E	F - E	L - E	F - G	P - F	P - L	P - L	G - E	E	G - E

Antimicrobials	G - E	G – E	F - E	L - E	F - G	P - F	P - L	P - L	G - E	E	F {P}
Surfactants/detergents	E	E	F - E	F - G	F - G	P	P - L	P - L	E	E	L - E {B}

Source: Modified from (S. A. Snyder et al., 2003).

PhACs = pharmaceuticals; PCPs = personal care products; BAC = biological activated carbon; AOPs = advanced oxidation processes; UV = ultraviolet NF = nanofiltration; RO = reverse osmosis; *B = biodegradation, P = photodegradation (solar); E = excellent (> 90%), G = good (70-90%), F = fair (40-70%), L = low (20-40%), P = poor (< 20%).

4.4 Removal mechanisms of various CECs by MOF-NAs

4.4.1 Removal influenced by the adsorption properties of MOF-NAs

4.4.1.1 *MOF-NA Properties*

The physicochemical properties of MOF-NAs can significantly influence removal of EDCs and PPCPs (R. M. Abdelhameed, Abdel-Gawad, Elshahat, & Emam, 2016; Bayazit, Danalioglu, Salam, & Kuyumcu, 2017; Bhadra & Jhung, 2017). The porosity structure of MOF-NAs is one of the main factors affecting the adsorption performance, particularly when no specific adsorption mechanism exists, excluding van der Waals interactions (Ahmed, Khan, & Jhung, 2013). For example, a Cu–benzene-1,3,5-tricarboxylic acid-cotton composite was reported to have a high sorption capacity for ethion insecticide due to the accessible binding sites on the cellulose in the composite (R. M. Abdelhameed et al., 2016), which are particularly associated with chemical interactions and physical adsorption. Two factors may contribute to this effect. First, the physical adsorption can be significant because the pores of Cu–benzene-1,3,5-tricarboxylic acid may act as binding sites for the target molecules. Second, the anticipated chemical interactions between the solute and the composite may occur by H-bonding between cellulose functional groups and the oxygen of ethion. In a separate study, nitrogen-doped porous carbons were prepared from MOF (ZIP-8) combined with ionic liquid via a ship-in-bottle method (Ahmed et al., 2017). While ionic liquid@MOF-derived carbons are less porous than MOF-derived carbons, the ionic liquid@MOF-derived carbons showed better adsorption performance than the MOF-derived carbons. This finding indicates that ionic liquid loading in ZIF-8 combined with the increased nitrogen content of carbonaceous materials significantly influences adsorption. Fig. 4.4 illustrates a plausible adsorption mechanism for six different compounds (atrazine, dibenzothiophene, sodium diclofenac, diuron, indole, and quinoline) over ionic liquid@MOF-derived carbons.

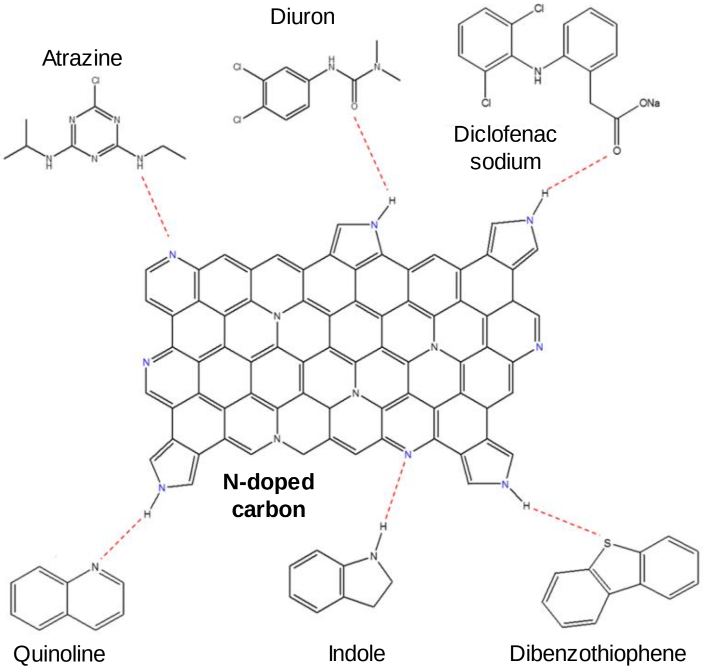

Figure 4.4: Plausible adsorption mechanism of the six adsorbates over ionic liquid@MOF-derived carbons through H-bonding (dotted lines) (Ahmed et al., 2017)

Of three different major forms of doped nitrogen on the surface of the material (N-6, N-5, or N-Q) (H. M. Jeong et al., 2011), N-6 and N-5, which are primarily observed at the edge of the graphite sheet, are the most chemically active nitrogen sites (Ahmed & Jhung, 2016). In addition, H-bonding and acid-base interactions readily occur at the N-6 and N-5 nitrogen sites due to basic and H-bonding functionality (Yan, Kuila, Kim, Lee, & Lee, 2015).

Pyrolysis temperature was found to be a significant factor influencing the porosity, surface area, and pore volume of MOF-derived carbons. For example, highly porous MOF-derived carbons at 1000°C (total pore volume = 1.32 cm^3/g) showed approximately 2.5 times higher porosity than that of the pristine MOF (ZIF-8; total pore volume = 0.51 cm^3/g) employed to fabricate it, and thus the adsorption capacity of MOF-derived carbons was almost twenty times greater than that of the pristine ZIF-8 for the pharmaceutical compound sulfamethoxazole (Ahmed, Bhadra, Lee, & Jhung, 2018). Three MOFs (ZIF-8, UiO-66, and UiO-67) that have different properties showed different adsorptive removal trends for atrazine (I. Akpinar & A. O. Yazaydin, 2018). The removal efficiencies of atrazine aqueous solution at pH 6.9 using the MOFs were as follows (mg atrazine/g adsorbent): UiO-67 (11.0) > ZIF-8 (6.78) > UiO-66 (2.57). These findings can be explained by their pore size, pore volume, and surface area: the higher adsorption capacity of UiO-67 is presumably due to its larger total pore volume (1.249 cm^3/g) and surface area (2,345 m^2/g) than those of ZIF-8 (0.714 cm^3/g and 1,875 m^2/g, respectively) and UiO-66 (0.656 cm^3/g and 1,640 m^2/g, respectively). The relatively small pore size of UiO-66 compared to that of UiO-67 may make it difficult for atrazine to access its pores, and while ZIF-8 also has relatively small pore size, almost all atrazine is still removed by ZIF-8, presumably due to the relatively high hydrophobic attraction between the hydrophobic ZIF-8 (Ghosh, Colon, & Snurr, 2014) and atrazine (log K_{OW} = 2.67). However, the less hydrophobic UiO-66 does not enable effective adsorption of atrazine from aqueous solution even by surface interactions (X. Y. Zhu et al., 2015).

The adsorption performance for several CECs was compared between metal-azolate frameworks, porous carbon-derived metal-azolate frameworks, and commercial activated carbon (Bhadra & Jhung, 2017). The findings for the CECs revealed that adsorption values on these adsorbents were partly reliant on the adsorbents' surface areas when few specific interaction sites existed. Overall, the porous carbon-derived metal-azolate frameworks had greater adsorption capacities than did the metal-azolate frameworks. This was presumably because adsorption over metal-azolate frameworks occurs mainly due to simple filling resulting from hydrophobic interactions, π-π interactions, and van der Waals interactions (Bhadra & Jhung, 2016). However, additional mechanisms, such as electrostatic attraction, acid-base interactions, and H-bonding, which occur in porous carbon-derived metal-azolate frameworks, could enhance adsorption (Delgado, Charles, Glucina, & Morlay, 2015). Moreover, further study of the detailed mechanisms is necessary due to the complex chemistry of adsorption and the numerous functional groups of different CECs (Z. Hasan & S. H. Jhung, 2015).

4.4.1.2 *Environmental parameters that influence MOF-NA adsorption properties*

Influence of pH: One of the most important parameters that affects adsorption capacity is solution pH, because both inorganic/organic speciation and adsorbent surface functional groups vary depending on solution pH (Q. Z. Li, Chai, & Qin, 2012). Adsorption of sulfamethoxazole on porous MOF-derived carbons varies within a wide range of pH values, from 2 to 12 (Ahmed et al., 2018), which can be explained by the electrostatic interactions between the solute and adsorbent (pH point of zero charge, $pH_{pzc} = 4.9$) (Khan et al., 2013). At pH <1.6, the sulfamethoxazole is positively charged, whereas at pH > 5.7 it is negatively charged due to its two pK_a values associated with the protonated $-NH_3^+$ and acidic NH groups (Vidal, Seredych, Rodriguez-Castellon, Nascimento, & Bandosz, 2015). Therefore, at pH > 5.7, where the acidic -NH group of the sulfamethoxazole molecule becomes deprotonated, electrostatic repulsion is expected because, at pH > 4.9, the surface charge of the adsorbent also becomes negative (Ahmed et al., 2018). In a separate study, the adsorption of atrazine on different MOFs was found to be insignificantly influenced by solution pH, because the electrostatic interactions that occur between the MOFs and the neutral form of atrazine are negligible (*i.e.*, the neutral form is dominant over the protonate form in water) (Salvestrini, Sagliano, Iovino, Capasso, & Colella, 2010). A copper-based MOF demonstrated varying adsorption trends for sulfonamide antibiotics under different pH conditions (Azhar et al., 2016). Sulfonamide exists in cationic and neutral forms at pH < 5.5 and in an anionic form at pH > 5.5 due to its pK_a value of 5.5 (Braschi et al., 2016), whereas the copper-based MOF is positively charged at pH < 4 and negatively charged at pH > 4 (Lin et al., 2014). In general, the adsorption capacity of the copper-based MOF decreased with increasing solution pH (ranging from 3.5 to 11.5). The highest adsorption was achieved at pH 3.5, at which a cationic form of sulfonamide is more likely to be dominant based on the protonation of heterocyclic nitrogen (in the strongest basic form of the sulfonamide molecule, sulfonamide$^+$). Therefore, the greater adsorption capacity of sulfonamide at this pH is due mainly to electrostatic attraction associated with H-bonding and π-π interactions (Azhar et al., 2016).

Sarker *et al*. reported that triclosan adsorption was significantly influenced by carboxylic-acid-functionalized UiO-66-NH_2 at different pH conditions in aqueous solutions (Sarker, Song, & Jhung, 2018b). Of various adsorption mechanisms, such as electrostatic interactions, acid-base interactions, coordination, π-π interactions, and hydrophobic interactions, electrostatic interactions were irrelevant as a possible main mechanism at pH < 8.1. The adsorption of triclosan is expected to be very low because triclosan is neutral under this pH condition, and thus no electrostatic interactions could occur with any species. However, a relatively high adsorption capacity (approximately 120-140 mg/g) was achieved at pH 2-8, mainly due to H-bonding interactions between triclosan and the functionalized MOF, which had positive ($-NH_2^+$) and negative ($-COO^-$) ions in its structure (Sarker et al., 2018b). The adsorption capacity for triclosan increased with increasing pH from 2 to 8 and decreased rapidly with further increases in solution pH (from 8 to 12). Thus, the H-bond interactions might occur between triclosan (H-bond donor = H of the phenolic group) and the MOF (H-bond acceptor = O and N species). The increase in adsorption capacity with increasing pH (from 2 to 8) could be because the ability of the $–NH_2^+–CO-COO^-$ group to act as an H-bond acceptor is greater than that of $–NH_2^+-CO-COOH$. While the H-bond accepting ability of $–NH-CO-COO^-$ (*i.e.*, the group produced on the MOF at a high pH) is high, no hydrogen (H-bond donor) is present on the phenolic group of triclosan at pH > 8.1 due to deprotonation (Sarker et al., 2018b).

It should be noted that the choice of pH during adsorption from water might result in severe degradation of certain MOF structures, sometimes to the point of complete destruction or transformation of the original phase and resulting in loss of most if not all adsorption capacity. For instance, Bezverkhyy *et.al*. found that the structural stability of iron-containing MOFs, MIL-100(Fe) and MIL-53(Fe) that were synthesized under fluoride-free conditions is severely degraded when these materials are exposed to water and the pH was brought to neutral using buffer solutions (Bezverkhyy, Weber, & Bellat, 2016). This process yields hydrated iron oxide species and, therefore, a structural collapse in both MOFs. In general, the check for stability of a specific MOF to acidic or alkaline conditions should be considered paramount prior to considering it effective for water purification. In acidic conditions, the degradation may be driven by competition of a proton and a metal ion for the coordination with the ligand, while in alkaline conditions decomposition may take place due to replacement of linkers by hydroxide (Yuan et al., 2018). This should be considered guidance and not certainty since there are other factors that may inhibit these processes to take place. In fact, there are several ways to improve stability of MOFs under certain pH conditions, some even capable of eliminating any detrimental effects on the structure (ul Qadir, Said, & Bahaidarah, 2015).

Influence of background ions and ionic strength: Porous carbon derived from metal azolate framework-6 demonstrated various degrees of adsorption for different CECs, such as bisphenol-A, clofibric acid, sodium diclofenac, oxybenzone, and salicylic acid (Bhadra & Jhung, 2017). The presence of background ions (NaCl, 0-40 mM) had almost no effect on the adsorption of these CECs by the MOF, indicating that the MOF would be usable in the presence of various salts. Chen *et al*. reported the effects of ionic strength based on NaCl on the adsorption of the antibiotic gatifloxacin on Zr(IV)-based porphyrinic MOFs (J. J. Chen, Wang, Xu, Wang, & Zhao, 2018). The adsorption was found to be enhanced with increasing NaCl concentration (from 0 to 0.75 mol/L). This increase is presumably due to the decrease in gatifloxacin solubility by the salting out effect, which may impel the diffusion of gatifloxacin onto the hydrophobic surface of the MOF and increase the adsorption capacity. However, different results were observed for the removal of ciprofloxacin by ZIF-67-derived hollow $C_{O3}S_4$, particularly in the presence of $CaCl_2$ (C. H. Liang et al., 2018). The adsorption capacity of ciprofloxacin decreased from 118 to 83.2 mg/g and 118 to 18.6 mg/g with increasing NaCl and $CaCl_2$ concentrations (0 to 1 mol/L), respectively. This finding is presumed to be attributed to the competition of Na^+ or Ca^{2+} with ciprofloxacin for the active adsorptive sites, while the presence of salt also negatively influenced electrostatic interactions for adsorption between ciprofloxacin and the MOF (C. H. Liang et al., 2018).

Zhang *et al*. employed two-tailed cationic MOFs (*i.e.*, α,β-ethanebbbdisulfonic-Cu-(4,4′-bipy)$_2$ and sulfamic-Cu-(4,4′-bipy)$_2$) to remove ClO_4^- in the presence of coexisting anions in aqueous solution (H. G. Zhang et al., 2017). For the removal of ClO_4^-, two potential mechanisms were investigated: electrostatic attraction and ion exchange. SO_3H groups on these MOFs were found to act as selective anion displacers in solutions containing ClO_4^- and/or PO_4^{3-}, and the receptors exhibited favorable selection of tetrahedron oxoanions. Therefore, the MOFs were capable of trapping both ClO_4^- and PO_4^{3-} due to interactions with the cationic MOFs and exchange with SO_4^{2-} groups. Anions with properties comparable to SO_3H groups can be removed using cationic MOFs. These findings are consistent with previous research for the removal of arsenic by MOFs, in which the mechanism of removal was found to operate primarily due to electrostatic interactions and ion-exchange (C. H. Wang, Liu, Chen, & Li, 2015). Additionally, the free-energy change (ΔG^0) of ClO_4^- was lower than the ΔG^0 values of PO_4^{3-} and the mixture of ClO_4^- and PO_4^{3-}, which also indicates that ClO_4^- may be more favorably adsorbed onto MOFs than PO_4^{3-} and the mixture of ClO_4^- and PO_4^3. Although as an anionic species, SO_4^{2-} has similar physicochemical properties to those of ClO_4^- and PO_4^{3-}, the R-SO_4, which is the main functional group of the MOFs, may create difficulties for the direct swap of ClO_4^- and PO_4^{3-} with SO_4^{2-} (H. G. Zhang et al., 2017).

Influence of NOM: Various types of NOM are found widely in natural water and wastewater at different levels. It is therefore necessary to evaluate the effects of NOM on the removal of CECs by MOF-NAs. Liang *et al*. examined the effects of humic acid (0-30 mg/L) on ciprofloxacin removal by ZIF-67-derived hollow $C_{O3}S_4$ at an initial concentration of 10 mg/L at pH 7 (C. H. Liang et al., 2018). The results revealed that the adsorption capacity of the MOF-NA for ciprofloxacin was barely influenced by the presence of humic acid, whereas the presence of humic acid decreased adsorption for the removal of ciprofloxacin by a magnetic carbon composite (Mao, Wang, Lin, Wang, & Ren, 2016). Nanoporous carbons derived from carbonization of zeolitic imidazolate framework-8 were employed to remove ciprofloxacin in the presence of humic acid in water (S. Q. Li, Zhang, & Huang, 2017). The results did not support the original assumption that adsorption of ciprofloxacin would decrease in the presence of humic acid due to competition between ciprofloxacin and humic acid for the adsorption sites of the MOF-NA. The findings instead revealed that adsorption of ciprofloxacin on the MOF-NA was enhanced as humic acid concentration increased (from 0 to 5 mg/L), and then remained nearly constant at high humic acid levels (5–40 mg/L), presumably due to various interactions between humic acid, ciprofloxacin, and MOF. The initial enhancement in the degree of adsorption may be due to adsorption of humic acid on MOF-NA carbon materials (Daifullah, Girgis, & Gad, 2004), which may provide additional adsorption sites by creating hydrogen bonds between multiple hydroxyl groups and the amine of ciprofloxacin. However, due to the limitation of the adsorption capacity of carbon materials for humic acid (J. P. Chen & Wu, 2004), the additional increase in humic acid concentration would be unfavorable to the adsorption behavior of the MOF-NA, particularly under the more neutral pH condition (pH 6) (S. Q. Li et al., 2017).

Influence of temperature: Thermodynamic assessments in terms of ΔG^0, the standard enthalpy change (ΔH^0), and the standard entropy change (ΔS^0) provide detailed information on the internal energy variations associated with adsorption (S. Kim, C. M. Park, et al., 2018). A copper-based MOF was reported to demonstrate different adsorption capacities for sulfonamide at varying solution temperatures (Azhar et al., 2016). In that study, a linear relationship was observed between ln ΔG^0 and 1/temperature for the ΔH^0 and ΔS^0

calculations at various temperatures (from 298 to 318 K), indicating that the positive ΔH^0 (4.0 kJ/mol) and ΔS^0 (110.3 J/mol·K) values imply an endothermic process and increased randomness for the adsorption of sulfonamide, respectively. Additionally, the ΔH^0 and ΔS^0 values imply negligible desorption of pre-adsorbed H_2O molecules (Haque, Lee, et al., 2010). This finding also provides support for the presence of unsaturated metal sites in the copper-based MOF that occur as a result of the removal of H_2O molecules (Ke et al., 2011). Chen *et al*. observed that the adsorption capacities of both carbamazepine and tetracycline hydrochloride increase with increasing temperature, indicating that endothermic reactions are dominant for the process of adsorption (C. Q. Chen et al., 2017). During the adsorption process of ClO_4^- onto the cationic MOF, the negative value of ΔH^0 (-38.2 kJ/mol) indicated that the adsorption on MOF is exothermic, while the negative entropy change ΔS^0 (-0.113 J/mol·K) indicated that the free energy was reduced at the solid-solution interface throughout the adsorption process (T. Li, Yang, Zhang, Zhu, & Niu, 2015). In addition, the decreasingly negative ΔG^0 values (from -6.29 to -1.67 kJ/mol) with increasing temperature (from 283 to 323 K) indicate that the adsorption is unfavorable at high temperatures and occurs spontaneously.

4.4.2 Removal of selected CECs by MOF-NAs

4.4.2.1 *EDCs*

Bisphenols: Bisphenol A is an EDC. Bhadra *et al*. synthesized Bio-MOF-1-derived carbons that were employed as an adsorbent to remove bisphenol A (Bhadra, Lee, Cho, & Jhung, 2018). The adsorption results implied that an important parameter in the adsorption of bisphenol A is the porosity or surface area of the adsorbent. Electrostatic interactions may be minimal between neutral bisphenol A at pH < its pK_a and Bio-MOF-1-derived carbons

(pH_{pzc} = 4.3) (Ahmed et al., 2018). H-bonding interactions may be the applicable adsorption mechanism, because the Bio-MOF-1-derived carbons have some acidic functional groups, as well as N-containing basic groups, and bisphenol A has two –OH groups, providing H-bond donors and acceptors (Ahmed & Jhung, 2017). Two findings support the conclusion that the H atom of the phenol group of Bio-MOF-1-derived carbons also acts as an H donor for the oxygen atom of bisphenol A at pH < 9.6: the variation in the total concentrations of nitrogen and oxygen between different Bio-MOF-1-derived carbons was minimal, even when the adsorption rates were very different; and the phenol groups of both bisphenol A and the MOF should be similar in terms of chemical properties (Bhadra et al., 2018).

Pesticides and herbicides: Organophosphate pesticides are commonly used to control various pests in different crops by preventing acetyl cholinesterase enzyme activity (Pope, 1999). Several billion United States dollars are spent every year on these types of pesticides, indicating that an enormous quantity of pesticide is used (Conrad et al., 2018). Over 97% of ethion (an insecticide, maximum adsorption capacity = 182 mg/g) was removed by adsorption to the stable and readily recyclable Cu–benzene-1,3,5-tricarboxylic acid that was effectively composited with cotton materials (R. M. Abdelhameed et al., 2016). Sarker *et al*. employed ion liquid@ZIF-8 adsorbent to remove two herbicides (diuron and 2,4-dichlorophenoxyacetic acid (2,4-D)) (Sarker, Ahmed, & Jhung, 2017). Their removal phenomena were described as having occurred mainly through the mechanism of H-bonding. While electrostatic attraction was considered a factor in the removal, the influence of these interactions appeared to be minimal based on their properties (ion liquid@ZIF-8, pH_{pzc} = approximately 3.0; 2,4-D, pK_a = 2.7-2.8). For the removal of diuron and 2,4-D by liquid@ZIF-8, H-bonding was found to be very strong between target compounds having a polar nature and the adsorbent, which possesses several surface functional groups (lactonic, carboxylic, and phenolic groups) along with its surface pyridinic and pyrrolic species (Ahmed et al., 2017). While the adsorbents and adsorbates may contribute as H-bond donors or acceptors, the degree of H-bonding varies depending on the pH conditions. For example, the adsorption of diuron was relatively constant between pH 4 and 7, while it decreased at pH < 4 and pH > 7, which can be explained by the influence of electrostatic interactions (*i.e.*, repulsion) between protonated diuron and the positively charged liquid@ZIF-8 surface (pH < 3) and a reducing contribution of H-bonding caused by protonated diuron when the compound acts as an H-acceptor (Sarker, Ahmed, et al., 2017).

Yang *et al*. fabricated a UiO-67/graphene oxide hybrid nanocomposite, which was employed to remove glyphosate in water (Q. F. Yang et al., 2017). The dominant mechanisms of glyphosate adsorption on UiO-67/graphene oxide were revealed through Fourier-transform infrared (FTIR) spectroscopy analysis to be the formation of surface/inner-complexes between the various functional groups and the UiO-67/graphene oxide surface. The FTIR analysis data revealed that the spectra of UiO-67/graphene oxide had clear differences in bonds before and after glyphosate adsorption due to interactions between the target compound and the adsorption sites of UiO-67/graphene oxide (Q. F. Yang et al., 2017). In particular, the glyphosate adsorption exhibited a new transmittance band at 941 cm^{-1} based on the spectrum of UiO-67/graphene oxide, which indicates a Zr-O-P stretching vibration (Daou et al., 2007). Additionally, new bands were observed at 1,157 and 1,075 cm^{-1}, which appeared to be P = O and P - O bonds, respectively, indicating that the Zr-OH of UiO-67/graphene oxide may be an active node for the binding of the target compound molecules, thus enhancing the removal efficiency of glyphosate. Moreover, after the adsorption of glyphosate, the vibration intensity of C-O-Zr (1,500–1,650 cm^{-1}) reduces significantly due to the influences of the generation of C-O-Zr-O-P, which implies that chemical integration is the key parameter affecting glyphosate removal by UiO-67/graphene oxide (Q. F. Yang et al., 2017).

Perchlorate: Perchlorate (ClO_4^-) is an EDC (Sharma, Grabowski, & Patino, 2016). Colinas *et al*. reported removal of a high concentration of ClO_4^- (initial concentration = 35 mg/L) through complete anion exchange using cationic MOF (silver 4,4′-bipyridine nitrate, adsorption capacity = 354 mg/g, with a contact time of 90 min). In a separate study, a cationic MOF based on amino sulfonic acid ligand linked with Cu-4,4′-bipyridyl chains was fabricated using the solvothermal method and was used as an adsorbent for efficient removal of ClO_4^- in water (T. Li et al., 2015). The findings demonstrated that the maximum sorption amount of ClO_4^- was approximately 135 mg/g at pH 7 and that the ClO_4^- could be removed effectively at a wide range of pH values (2-11). For ClO_4^- removal, one of the primary mechanisms is ion exchange, presumably because SO_3^- groups in the MOF are exchanged with ClO_4^- after adsorption (Fei et al., 2010). In addition, electrostatic adsorption cannot be ignored because the stretching vibration of N-H in the $-NH_2$ groups was not present after the adsorption process, indicating that the $-NH_2$ groups may be surrounded by ClO_4^- due to its positive charge (T. Li et al., 2015).

4.4.2.2 *PPCPs*

Analgesics: H-bonding and electrostatic interactions were previously discussed to describe the adsorption of organic compounds on MOF-NAs (Ahmed et al., 2013; P. W. Seo, Bhadra, Ahmed, Khan, & Jhung, 2016). However, recent findings have revealed that the adsorption of carbamazepine on UiO-67 is not significantly influenced by electrostatic interactions at varying pH conditions, and the influence of H-bonding is anticipated to be minimal (Akpinar & Yazaydin, 2017). Unlike H-bonding and electrostatic interactions, the study observed that the hydrophobic and π-π interactions between the benzene rings of carbamazepine molecule and the MOF linkers were dominant mechanisms of the adsorption. The benzene rings of carbamazepine, which have a strong electron-donating group (*i.e*., $-NH_2$; π donor), can form a strong bond with the oxygen-containing functional group on the surface of the UiO-67 (electron acceptor; π acceptor) (Akpinar & Yazaydin, 2017). An *et al*. observed that porous metal azolate framework-6 carbon (a subclass of MOFs; $q_{\max}$ = 408 mg/L) was significantly more effective for removal of ibuprofen than commercially available activated carbon (q_{max} = 168 mg/L) (H. J. An, B. N. Bhadra, N. A. Khan, & S. H. Jhung, 2018). This is presumably because hydrophobic interactions play an important role in the adsorption between the hydrophobic adsorbate (ibuprofen, log K_{OW} = 3.97) and the hydrophobic adsorbent, i.e., the hydrophobicity of metal azolate framework-6 carbon is much higher than that of activated carbon (Bhadra, Cho, Khan, Hong, & Jhung, 2015)). Additionally, π-π interactions should also be considered for adsorption, because the ibuprofen and metal azolate framework-6 carbon have an aromatic benzene ring and a graphitic layer, respectively (H. J. An et al., 2018).

Diclofenac is one of the most commonly detected pharmaceuticals in drinking water sources (Huerta-Fontela et al., 2011). Zr-based functionalized MOFs (UiO-66/SO_3H-NH_2) were tested to remove diclofenac in aqueous solutions (Hasan, Khan, & Jhung, 2016). The removal mechanisms can be explained based on the properties of diclofenac and UiO-66/SO_3H-NH_2. For example, at a pH of approximately 4 to 5.5, electrostatic attraction is expected to be favorable between negatively charged diclofenac (pH_{pzc} = 4 (Bajpai & Bhowmik, 2010)) and positively charged UiO-66/SO_3H-NH_2 (pH_{pzc} = 5.5 (Y. S. Seo, Khan, & Jhung, 2015)). However, both diclofenac and UiO-66/SO_3H-NH_2 exist in negatively charged states at a pH > 5.5, resulting in a rapid decrease in diclofenac adsorption with pristine UiO-66. Thus, the influence of electrostatic interactions would be minimal under high-pH conditions. A similar influence of pH was observed in adsorption of *p*-arsanilic acid and phthalic acid (B. K. Jung, Jun, Hasan, & Jhung, 2015; Khan, Jung, Hasan, & Jhung, 2015). The adsorption of diclofenac at varying pH conditions (4.5, 7.5, and 10.5) may be due to π–π stacking between the diclofenac benzene rings and the pristine UiO-66 (F. M. Cao et al., 2009).

Antibiotics: For various hazardous compounds, one of the main adsorption mechanisms is H-bonding (Song & Jhung, 2017). Ahmed *et al*. observed that the extraordinary adsorption of sulfamethoxazole on highly porous MOF-derived carbons was due mainly to H-bonding because the MOF-NA has several acidic groups, such as carboxylic and phenolic groups, that engage in H-bonding (Ahmed et al., 2018). The findings also indicated that both sulfamethoxazole and MOF-NA act as H-bonding donors and acceptors. Increased attention has been given to ciprofloxacin (a second-generation fluoroquinolone antibiotic) due to its extensive use in both humans and animals (Q. Q. Zhang, Ying, Pan, Liu, & Zhao, 2015). Liang *et al*. demonstrated the effective adsorption performance of ZIF-67-derived hollow $C_{O3}S_4$ for the removal of ciprofloxacin (C. H. Liang et al., 2018). Of four different kinetic models (intra-particle diffusion, liquid-film diffusion, pseudo-first-order kinetic, and pseudo-second-order kinetic), the fitted results exhibited the highest correlation coefficient (0.999) when using a pseudo-second-order kinetic model. In addition, the findings indicated chemisorption behavior of ciprofloxacin on the hollow $C_{O3}S_4$ on the ZIF-67 surface, which was verified by FTIR measurements. After adsorption by the MOF, two bands shift to 1,269 and 1,710 cm^{-1} (assigned to stretching of C-O and O-H deformation of the carboxyl group, and C-O stretching in the carboxyl group, respectively (Jalil, Baschini, & Sapag, 2015)) and their peaks are reduced. This phenomenon is presumably due to surface complexation between the -COOH of ciprofloxacin and the hollow $C_{O3}S_4$ on the ZIF-67 surface (W. T. Jiang et al., 2013).

Seo *et al*. reported removal of nitroimidazole by MIL-101(Cr) modified with urea, melamine, and O_2N (P. W. Seo et al., 2017). While electrostatic interactions were considered as a potential mechanism for the removal of nitroimidazole, they do not appear to be the main mechanism for the effective adsorption of nitroimidazole by these modified MOF-NAs. The adsorption capacity values for nitroimidazole by the MOF-NAs are in the following order: MIL-101-urea > MIL-101-melamine > MIL-101 > MIL-101-O_2N; however, the surface area values of each adsorbent are as follows: MIL-101 (3,030 m^2/g) > MIL-101-urea (1,970 m^2/g) > MIL-101-O_2N (1,620 m^2/g) > MIL-101-melamine (1,350 m^2/g). The results suggest that the influence of the $-NH_2$ group (in melamine and urea) on the adsorption of nitroimidazole needs to be evaluated to verify the adsorption mechanisms. H-bonding interactions between MIL-101 and nitroimidazole can be considered as a possible mechanism due to their -NH_2 and -NO_2 groups, respectively (Ahmed & Jhung, 2017). In particular, effective H-bonding through the solid six-membered ring takes place between the -NO_2 and -NH_2 groups, which is comparable to the interactions between sweeteners and the -NH_2 group on MIL-101 (P. W. Seo, Khan, et al., 2016). MIL-101-O_2N demonstrated unfavorable adsorption of nitroimidazole, presumably due to the lack of possible H-bonding between the two -NO_2 groups in MIL-101 and nitroimidazole. Thus, the -NO_2 on nitroimidazole and the -NH_2 groups on MIL-101-urea or MIL-101-melamine would be the H-acceptor and H-donor, respectively (P. W. Seo et al., 2017).

Antiepileptics: Several possible mechanisms were evaluated for the adsorption of carbamazepine by UiO-66 (C. Q. Chen et al., 2017). Adsorption due to hydrophobic interactions can be explained mainly by the hydrophobicity of carbamazepine (log K_{OW} = 2.77); however, the influences of electrostatic attraction and π-π interactions/stacking should also be considered. The intermolecular electrostatic attraction between carbamazepine and UiO-66 is relatively weak because both are negatively charged at pH > 5 based on their pH_{pzc} values (4.81 for UiO-66 and 2.45 for carbamazepine). π-π interactions/stacking are commonly found in the absence of electrons or in electron-rich chemicals (Z. Hasan & S. H. Jhung, 2015). π-π electron donor-acceptor interactions readily occur between carbamazepine, which possesses NH_2 groups (*i.e.*, electron donor), and UiO-66, which possesses a benzene ring (*i.e.*, electron acceptor) (Oleszczuk, Pan, & Xing, 2009). Moreover, π-π stacking (aromatic-aromatic interactions) was found to occur between the benzene rings in carbamazepine and in the organic ligands of UiO-66 (C. Q. Chen et al., 2017). Fig. 4.5 describes the potential adsorption mechanisms that occur with carbamazepine and tetracycline hydrochloride.

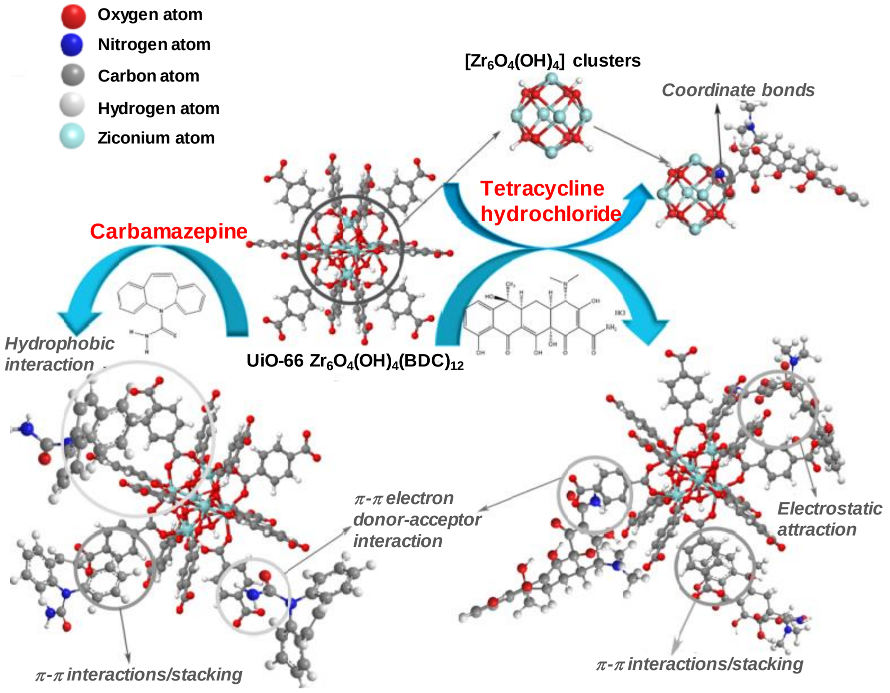

Figure 4.5: Adsorption mechanism between zirconium MOF UiO-66 and carbamazepine/tetracycline hydrochloride (C. Q. Chen et al., 2017)

Akpinar and Yazaydin compared the removal efficiencies of carbamazepine with UiO-67 and commercial activated carbon (F400) (Akpinar & Yazaydin, 2017). Significant removal of carbamazepine was demonstrated by UiO-67 (95%), whereas F400 removed only 35% of the compound within a contact time of 2 min, which may have been due to UiO-67's relatively small particle size/pore volume and the very active adsorption sites generated by the missing-linker defects. Twelve linkers are found in defect-free samples of UiO-67 nodes, while binding around the node can be changed to have less than twelve carboxylates. The sites that are missing carboxylate are covered with -OH and H_2O groups. Thus, carbamazepine may create particular interactions with these functional groups on nodes (Akpinar & Yazaydin, 2017). In addition, some missing-linker defects result in improved porosity, which may expedite quicker adsorption and higher adsorption capacity (D. Yang et al., 2016).

Antiseptics: Triclosan is a broad-spectrum bacteriostatic germicide that is used widely in a number of PPCPs (Adolfsson-Erici, Pettersson, Parkkonen, & Sturve, 2002). Structure-directing agent-modified mesoporous MIL-53(Al) was examined for removal of triclosan at various initial concentrations (0-60 mg/L) (Dou, Zhang, Chen, & Feng, 2017). The modified MOF with relatively high meso-porosity and total pore volume demonstrated greater adsorption capacity (488 mg/g) than that of microporous MIL-53(Al) (447 mg/g), and the triclosan adsorption was approximately 4.5 times faster with the modified MOF. In addition, the adsorption capacity values for different compounds by the modified mesoporous MIL-53(Al) were in the following order: triclosan > bisphenol A > 1-naphthol > phenol, which was proportional to their hydrophobicity (log K_{OW} = 4.84, 2.84, 2.76, and 1.46, respectively). This implies that higher selectivity for triclosan adsorption on the modified MOF occurs in the presence of coexisting compounds with relatively low hydrophobicity. FTIR measurements provide more insights into the interactions between triclosan and the MOF. Bands were observed at 3,660 and 995 cm^{-1}, which were assigned to the asymmetric/symmetric stretching of the hydroxyl groups of $AlO_4(OH)_2$. The band at 3660 cm^{-1} moved to a lower frequency and an extra vibrational band at 3540 cm^{-1} was detected after triclosan adsorption, implying H-bond interactions between triclosan and $AlO_4(OH)_2$ groups, which indicates that H-bond interactions are an additional parameter affecting triclosan adsorption. Additionally, adsorption of triclosan on the modified MOF was confirmed by the presence of both a vibrational band at 660 cm^{-1} (–C–Cl) and small stretching bands at 1,025-1,245 cm^{-1} (aromatic C–O–C) (Dou et al., 2017). Sarker *et al.*

reported effective adsorption performance for the removal of triclosan by carboxylic-acid-functionalized UiO-66-NH_2 (Sarker et al., 2018b). While UiO-66-NH-CO-COOH has the smallest porosity (0.37 cm^3/g) of the tested adsorbents, including activated carbon, UiO-66, UiO-66-NH_2 (0.56, 0.53, and 0.48 cm^3/g, respectively), it demonstrated better adsorption performance for triclosan compared to the other adsorbents, implying that the functional groups on the MOF may play an important role in the adsorption of triclosan. The potential mechanisms that may be important for the adsorption of CECs on MOF-NAs are summarized in Fig. 4.6.

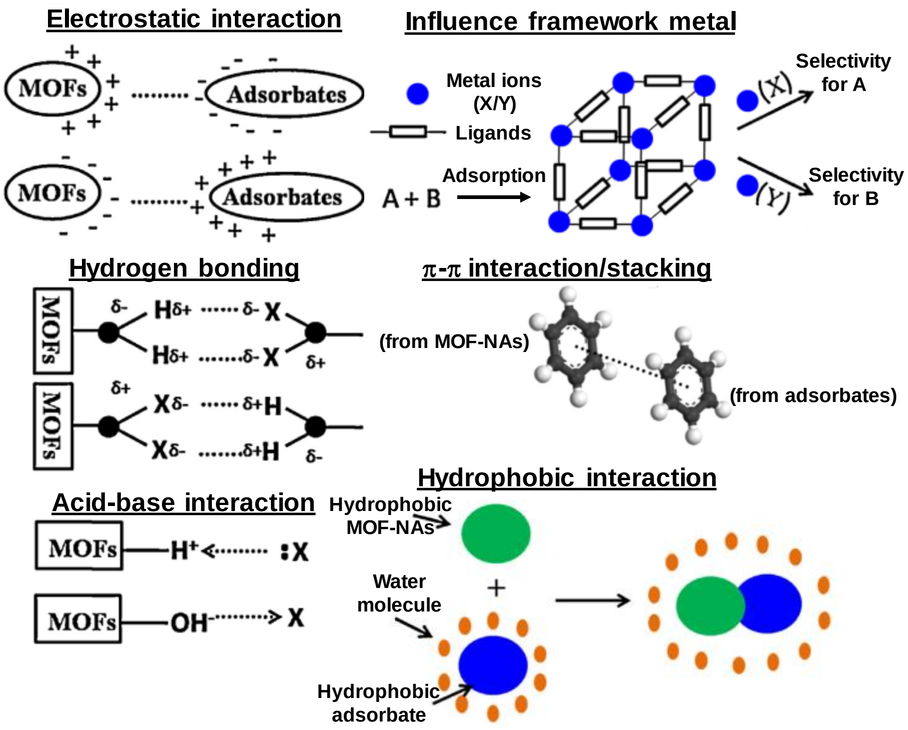

Figure 4.6: Possible mechanisms for adsorptive removal of CECs on MOFs or MOF-NAs (Z. Hasan & S. H. Jhung, 2015)

4.5 Regeneration of MOF-NAs

The regeneration capacity of MOF-NAs is a factor of concern because extraordinary reusability may result in improved environmental sustainability and cost efficiency in the treatment of various CECs. The desorption degree of the CECs during regeneration of MOF-NAs is an essential parameter for evaluation of the reusability of the MOF-NAs. Successful regeneration was achieved for a Cu–benzene-1,3,5-tricarboxylic acid/cotton composite, because ethion is well-dissolved in a solvent (*i.e.*, acetonitrile) (R. M. Abdelhameed et al., 2016). An effective removal efficiency (> 85%) of ethion was observed during a consecutive regeneration/reuse (desorption/adsorption) process after five cycles. Ahmed *et al*. observed that the adsorption capacity of atrazine by ionic liquid@MOF-derived carbons was not significantly reduced even after four cycles of washing with ethanol (Ahmed et al., 2017). Acetone was employed to regenerate MOF (UiO-67) after the adsorption of carbamazepine (Akpinar & Yazaydin, 2017). During the regeneration process, the used MOF was shaken at room temperature and reactivated under vacuum at 90^{o}C; it demonstrated a minor reduction in adsorption capacity after five recycles. After sulfonamide adsorption, the regeneration capacity of an MOF (UiO-66) was evaluated with NaOH (0.01 M) (Azhar et al., 2017). While the MOF retained greater than approximately 80% removal efficiency after three cycles, the N_2 adsorption-desorption isotherm was not significantly affected by the adsorption of sulfonamide, which indicates that the structure of the MOF was stable after adsorption. Bhadra *et al*. used simple solvent washing (water (v):methanol (v)) under ultrasonic irradiation to regenerate used Bio-MOF-1-derived carbons after bisphenol A adsorption (Bhadra et al., 2018). After four cycles, almost no reduction in the porosity of the recycled adsorbent occurred compared to the pristine one. In a separate study, used MOF (UiO-66) after adsorption of carbamazepine and tetracycline hydrochloride was regenerated by soaking in chloroform for 24 h to desorb the target compounds (C. Q. Chen et al., 2017), washing with methanol, and drying at 80°C for 24 h. While the regeneration was relatively unsuccessful, the findings are useful because they indicate that the adsorption of carbamazepine on UiO-66 is primarily physical adsorption, and that the absorbed carbamazepine in the micropores of the MOF was desorbed only during the degassing process. However, after the adsorption of tetracycline hydrochloride, the BET surface area and total pore volume of the MOF reduced significantly from 592 to 285 m^2/g and from 0.323 to 0.183 cm^3/g, respectively, which indicates that tetracycline hydrochloride may be adapted to the micropore inner surface by strong interactions, including H or chemical bonding (C. Q. Chen et al., 2017).

In a separate study, ethanol washing was employed for regeneration of used liquid@ZIF-8 after diuron adsorption (Sarker, Ahmed, et al., 2017). The FTIR spectra revealed peaks at 1,740 and 1,291 cm^{-1} for fresh liquid@ZIF-8, pure diuron, diuron-adsorbed liquid@ZIF-8, and recycled liquid@ZIF-8; the stretching bands were detected for both diuron and diuron-adsorbed liquid@ZIF-8, implying the presence of adsorbed diuron on liquid@ZIF-8. The disappearance of these bands in the recycled liquid@ZIF-8 confirmed that it was effectively regenerated by ethanol washing (Sarker, Ahmed, et al., 2017). After the adsorption of ciprofloxacin on ZIF-67-derived hollow $C_{O3}S_4$, ethanol was employed as a washing agent to desorb ciprofloxacin and regenerate the hollow $C_{O3}S_4$ MOF (C. H. Liang et al., 2018). However, ethanol removed only a limited amount of ciprofloxacin (approximately 5%) from the MOF. An additional cleaning agent (HCl, 0.1 mol/L) was therefore used for desorption of ciprofloxacin from the used MOF. Consequently, a mixture of ethanol and HCl was adopted as the cleaning agent. While the adsorption capacity was slightly reduced after the first use of the MOF, the removal efficiency for ciprofloxacin was retained at > 80% after five regeneration cycles, implying that the ZIF-67-derived hollow $C_{O3}S_4$ MOF has high adsorption capacity for ciprofloxacin and is readily regenerated for acceptable reusability (C. H. Liang et al., 2018). The maximum regeneration performance for used structure-directing agent-modified mesoporous MIL-53(Al) was using 90% methanol at pH 11 (Dou et al., 2017). This was presumably because triclosan entirely dissociates into ionized forms at high pH conditions, disturbing each part of the adsorption process by splitting the H-bonds between $(AlO_4)OH_2$ and triclosan species adsorbed on the modified MOF, which reduces the triclosan hydrophobicity and enhances the solvation of triclosan molecules in water, therefore resulting in more favorable desorption of triclosan from the modified MOFs (Dou et al., 2017). It is strongly recommended that in addition to adsorption and desorption performance, the stability of MOF-NAs should also be monitored throughout reusability/regeneration studies over prolonged periods.

4.6 Conclusions and areas of future study

Over the last two decades, several hundred different MOFs and MOF-NAs have been studied for different applications, including gas purification, gas separation, gas storage, energy storage, and environmental applications. Of the various environmental applications, numerous recent studies have reported that MOF-NAs are effective for removal of organics and heavy metals, including different CECs. These findings have shown that the removal/adsorption efficiency of CECs by MOF-NAs is significantly influenced by the properties of the CECs and MOF-NAs, as well as the water quality conditions. The porosity volume and structure of MOF-NAs appears to be a major factor in adsorption performance, particularly when no specific adsorption mechanism excluding van der Waals interactions exists. However, once MOF-NAs are modified with different functional groups, the removal may be explained by more complex mechanisms, such as electrostatic interactions, metal effects, acid-base interactions, π-π interactions/stacking, hydrophobic interactions, and H-bonding, which also vary greatly depending on water chemistry conditions. In general, one of the most important parameters affecting adsorption capacity is pH, because both the speciation of CECs and the functional groups of MOF-NAs vary depending on solution pH. Significant electrostatic interactions can occur only when CECs and MOF-NAs have different negative/positive charges. Moreover, the adsorption of CECs may vary depending on the type and concentration of background anions and cations. Unlike activated carbon, NOM appears to enhance the adsorption of some CECs as a result of various interactions among NOM, CECs, and MOF-NAs. The increased adsorption is presumably due to adsorption of NOM on the surface of MOF-NAs, which may provide additional adsorption sites.

The research has shown that it is relatively difficult to determine common trends for the effects of CEC properties on their removal by MOF-NAs, because CECs have varying physicochemical properties. However, of the potential mechanisms for the selected CECs and MOF-NAs, the dominant mechanisms are influential in the following order: electrostatic interactions > H-bonding > π-π interactions/stacking > hydrophobic interactions ≈ acid-base interactions ≈ metal effects; however, these factors may vary depending on water chemistry conditions. In the adsorption processes, one of the main concerns for environmental sustainability is the regeneration capacity of the MOF-NAs, because extraordinary reusability may improve their cost efficiency in the treatment of various CECs. The findings demonstrate that most MOF-NAs can be regenerated effectively using different solvents, such as acetonitrile, acetone, NaOH, methanol,

ethanol, and HCl. Regeneration capacity can be enhanced by combined use of these cleaning agents.

More comprehensive assessments of different synthesis methods for MOF-NAs are necessary because the physicochemical properties of MOF-NAs can vary significantly depending on the reaction time used, particle size, and morphology, particularly for their application in large-scale processes. Additionally, the adsorption of different CECs varies significantly depending on the physicochemical properties of the compounds, the physicochemical properties of the MOF-NAs themselves, and the water quality; this might require almost unlimited experiments to identify the adsorption properties all CECs. Therefore, quantitative structure-activity relationship studies may be needed to elucidate the adsorption mechanisms for CECs on different MOF-NAs, which may be useful in understanding interactions between the functional groups in the CEC molecules with the highest activity. Overall, to be competitive with other types of adsorbents that are currently used in water and wastewater treatment processes, MOF-NAs must be practical in terms of cost. While these emerging MOF-NAs are promising due to their high-performance adsorption, many challenges must still be overcome to develop homogeneous pores, structures, and functional groups with long-term stability. In addition, more research is needed to provide comprehensive life-cycle analyses and ecotoxicological assessments of MOF-NAs, particularly when considering its disposal. However, the use of MOFs and MOF-NAs for the adsorption of CECs remains a very promising avenue of research.

CHAPTER 5

REMOVAL OF SELECTED HEAVY METALS FROM WATER USING FABRICATED MIL-100(FE) AND MIL-101(CR): EXPERIMENTAL AND MOLECULAR MODELING STUDY

Abstract

Heavy metal contamination is a growing concern throughout the world, particularly as industrial and urban activities have increased. Recently, researchers have studied metal-organic frameworks (MOFs) as potential adsorbents for removing various water contaminants, including dyes, organic contaminants, and emerging contaminants of concern. In this study, MIL-100(Fe) and MIL-101(Cr) are fabricated and investigated to determine their ability to remove copper (Cu^{2+}), cadmium (Cd^{2+}), and lead (Pb^{2+}) from aqueous solution. MIL-100(Fe) and MIL-101(Cr) exhibited fast adsorption kinetics, achieving equilibrium in approximately 0.5 hours. To evaluate the adsorption capacities of MIL-100(Fe) and MIL-101(Cr), the experimental data was fit to the Linear, Freundlich, and Langmuir isotherm models. Based on the sum of the squared error (SSE) analysis, the experimental data fit most closely to the Freundlich model, followed closely by the Linear isotherm model. However, the values for the Freundlich parameter *n* were close to 1, which suggests that the adsorption followed the Linear isotherm model. The K_{LIN} coefficient [(mg/g)/(mg/L)] for the Linear isotherm model was the largest for Cu^{2+} ($K_{LIN,\ MIL\text{-}100(Fe)}$ = 14.9; $K_{LIN,\ MIL\text{-}101(Cr)}$ = 60.3), followed by Cd^{2+} ($K_{LIN,\ MIL\text{-}100(Fe)}$ = 12.9; $K_{LIN,\ MIL\text{-}101(Cr)}$ =

11.5) and Pb^{2+} ($K_{LIN,\ MIL\text{-}100(Fe)} = 4.44$; $K_{LIN,\ MIL\text{-}101(Cr)} = 8.33$). Characterization data of MIL-100(Fe) and MIL-101(Cr) showed high surface areas of 1,586 m^2/g and 2,505 m^2/g for MIL-100(Fe) and MIL-101(Cr), respectively, along with the presence of various functional groups, including carboxyl and phenyl groups. Considering this data alongside the local energy decomposition analysis that was performed using molecular modeling, electrostatic interactions were determined to be the dominant adsorption mechanism for the removal of Cu^{2+}, Cd^{2+}, and Pb^{2+} by MIL-100(Fe) and MIL-101(Cr), which is consistent with similar adsorption studies. This study shows that MIL-100(Fe) and MIL-101(Cr) are effective adsorbents for the removal of heavy metals from aqueous solution.

5.1 Introduction

Heavy metal contamination is a growing concern, particularly as industrial and urban activities have increased throughout the world. Sources of heavy metals, which are elements that are characterized by their high-density (> 5 g/cm^3), include various rock and soil formations that can enter into water sources via erosion or weathering (Kobielska, Howarth, Farha, & Nayak, 2018). Contaminated wastewater from various industries, including coal-fired power plants (Demirak et al., 2006) and mining (D. Archundia et al., 2017), along with waste recycling and solid waste disposal activities (S. Herat & P. Agamuthu, 2012; Olafisoye et al., 2013; Perkins et al., 2014; Q. Wu et al., 2015) also represents a major source of heavy metal pollution. Vehicle emissions and other urban activities also contribute to heavy metal contamination throughout the environment (J. Pandey & U. Pandey, 2009; Prasse et al., 2012). These contaminants have been shown to have harmful effects on human health (Järup, 2003). Table 5.1 provides various harmful health impacts related to heavy metal exposure.

Table 5.1: Health effects of common heavy metals (Lesley Joseph, Jun, Flora, Park, & Yoon, 2019).

Heavy metal	Common sources	Human health effects
Arsenic (As)	Naturally-occurring Electronics production	Skin damage Circulatory system issues
Cadmium (Cd)	Naturally-occurring Various chemical industries	Kidney damage Carcinogenic
Chromium (Cr)	Naturally-occurring Steel manufacturing	Allergic dermatitis Diarrhea, nausea, and vomiting
Copper (Cu)	Naturally-occurring Household plumbing systems	Gastrointestinal issues Liver or kidney damage
Lead (Pb)	Lead-based products Household plumbing systems	Kidney damage Reduced neural development
Mercury (Hg)	Fossil fuel combustion Electronics industries	Kidney damage Nervous system damage

Several water treatment technologies have been evaluated to remove heavy metals from water sources, including membrane filtration (Sewoon Kim et al., 2018), electrocoagulation (Al-Qodah & Al-Shannag, 2017), and microbial remediation (Ayansina Segun Ayangbenro & Olubukola Oluranti Babalola, 2017; P.-S. Li & H.-C. Tao, 2015). Along with these approaches, adsorption can also serve as a potential solution to the proliferation of heavy metal contamination due to its relative ease of use, versatility, and regenerative characteristics (Fallah TAlooki, Ghorbani, & Ghoreyshi, 2015). A wide variety of adsorbents have been examined to remove heavy metals for water sources, including activated carbon (Asimakopoulos et al., 2021; Nasseh et al., 2021; Z. Zhang, Wang, Zhang, Liu, & Xing, 2021), naturally-occurring soil (Satti et al., 2020; J. Wang & Zhang, 2021), and carbon nanotechnology (Aydin, 2021; C. Chen, Feng, & Yao, 2021; Egbosiuba et al., 2021).

Recently, researchers have studied metal-organic frameworks (MOFs) as potential adsorbents for removing various water contaminants. MOFs are crystalline porous materials that consist of inorganic components, such as metal ion clusters, and organic components, such as ligands. Due to their tunability and high porosity, the presence of coordinatively unsaturated sites, and varying pore architecture and composition, MOFs are effective in a wide variety of applications, including drug delivery (M. X. Wu & Yang, 2017; Zheng et al., 2016) and gas storage (Xia, Mahmood, Zou, & Xu, 2015; Yoo, Yoon, Bae, & Jhung, 2020). MOFs have also been shown to effectively remove a wide variety of contaminants, such as dyes (Haque et al., 2010; H. Wang et al., 2015), organic contaminants (Zubair Hasan, Jeon, & Jhung, 2012; Z. Hasan, Khan, & Jhung, 2016), and emerging contaminants of concern, including pharmaceuticals (Hyung Jun An, Biswa Nath Bhadra, Nazmul Abedin Khan, & Sung Hwa Jhung, 2018) and pesticides (Isil Akpinar & A Ozgur Yazaydin, 2018). The unique characteristics of MOFs, along with their effective removal of a wide range of contaminants, suggest that they may be effective in the removal of heavy metals from water sources.

To evaluate the adsorption mechanisms involving MOFs, researchers have employed ab initio modeling. For instance, Mavrandonakis et al. (2015) performed a computational study on the binding of H_2O, H_2, CO, and CO_2 molecules for a variety of trimetallic oxo-centered $M_3^{III}(\mu_3\text{-}O)X(COO)_6$ building units of MOF with M = Al^{3+}, Sc^{3+}, V^{3+}, Cr^{3+}, Fe^{3+}, Ga^{3+}, Rh^{3+}, In^{3+}, and Ir^{3+}, using wave function theory and density functional theory (DFT). They found that the binding free energies were dependent on the metal composition of the trimetallic oxo-centered unit due to the change in orbital interactions, dispersion, and charge back donation with the change in metal composition. Simons et al. (2019) demonstrated through an experimental and computational study that mononuclear high spin Fe(II) sites situated in the nodes of MOF MIL-100(Fe) convert propane by reacting with N_2O oxidant. They reported that the energy barrier associated with reactions of N_2O with Fe(II) sites was lower for the high spin state than an intermediate or low spin state. Canepa et al. (2013) also performed a computational study using DFT on the adsorption of H_2O, CH_4, H_2, and CO_2 by MOF-74 with different metal compositions. The study concluded that metal species to the left of periodic table displayed larger affinities for H_2O and lower affinities for CO_2. However, the interaction of CO_2 with MOF-74 was stronger for noble metals, such as Rh, Pd, Os, Ir, and Pt, while their affinity for water was weaker. Many additional studies have been conducted using ab initio modeling to evaluate the adsorption of various molecules by MOFs, including an assessment of the binding affinities of M-MOF-74 for CO_2 ,where M = Mg, Ca, and the first transition metal series using DFT (J. Park, Kim, Han, & Jung, 2012) and the binding between CO_2 and the open metal sites of two MOFs, BTT and MOF-74, for different metal cations using DFT with van der Waals dispersion corrections (Poloni, Lee, Berger, Smit, & Neaton, 2014). While these studies have provided insight into the interactions between various molecules and different MOFs, modeling studies that examine the adsorption of heavy metals on MOFs in aqueous solution have not been reported to date.

In this study, MIL-100(Fe) and MIL-101(Cr) are fabricated and examined to determine their ability to remove copper (Cu^{2+}), cadmium (Cd^{2+}), and lead (Pb^{2+}) from aqueous solution. Although a significant amount of research has been conducted on the adsorption capabilities of MOFs, little information is available on its removal of heavy metals. Therefore, characterization studies of MIL-100(Fe) and MIL-101(Cr) are performed to understand the properties of these MOFs. The adsorption behavior associated with the removal of these heavy metals are investigated by kinetic, equilibrium, and thermodynamic analysis. Finally, molecular modeling will be utilized to enhance our understanding of the possible interactions and adsorption mechanisms between the heavy metals and the MOFs that are used in this study. Evaluating the adsorption of these heavy metals by MIL-100(Fe) and MIL-101(Cr) via characterization analysis, experimental studies, and computational analysis using molecular modeling provide a comprehensive understanding of the interactions and potential removal mechanisms.

5.2 Materials and Methods

5.2.1 Materials

High purity $Pb(NO_3)_2$, $CdSO_4$, $CuSO_4$, HNO_3, and HCl acid were purchased from Sigma-Aldrich (St. Louis, MO, USA). Approximately 0.25 g of $Pb(NO_3)_2$, $CdSO_4$, and $CuSO_4$ were each dissolved in deionized water (500 mL) to produce stock solutions of 500 mg/L.

5.2.2 Synthesis of MIL-100(Fe) and MIL-101(Cr)

MIL-100(Fe) and MIL-101(Cr) were fabricated in the laboratory prior to being used in this study. To prepare MIL-100(Fe), iron chips (99.98%) and trimesic acid (BTC, 95%) were purchased from Sigma-Aldrich. To prepare MIL-101(Cr), chromium(Ш) nitrate nonahydrate ($Cr(NO_3)_3{\cdot}9H_2O$, > 99%) and terephthalic acid (TPA, 98%) were purchased from Sigma-Aldrich. Nitric acid (HNO_3, 60%), hydrofluoric acid (HF, 40%), and reagent alcohol (CH_3CH_2OH, ≤ 0.003%) were also obtained from Sigma-Aldrich.

MIL-100(Fe) and MIL-101(Cr) were synthesized using the solvothermal method with procedures that have been reported in the literature (Férey et al., 2005; Horcajada et al., 2007) with some modifications. For MIL-100(Fe), 1.0 Fe^0:0.67 BTC:1.2 HNO_3:2.0 HF:280 DI water was loaded in a Teflon-lined steel autoclave and then placed in an electric oven at 150°C for 12 h. After cooling to room temperature, the orange-colored solid material was recovered by filtration using a 10-µm glass filter. The synthesized MIL-100(Fe) was then purified using DI water at 90°C for 3 h, followed by reagent alcohol at 65°C for 5 h. After filtration, the purified MIL-100(Fe) was dried at 100°C overnight and stored in a desiccator for future use.

For MIL-101(Cr), 1.0 $Cr(NO_3)_3\cdot 9H_2O$:1.0 TPA:1.0 HF:300 DI water was loaded in a Teflon-lined autoclave and then placed in an electric oven at 210°C for 8 h. After cooling to room temperature, the green-colored solid material was recovered by filtration using a 25-µm glass filter, followed by a 10-µm glass filter. Then, to further purify the products, the synthesized MIL-101(Cr) was then purified using reagent alcohol at 100°C for 20 h, filtered, and dried overnight at 100°C. After drying, the purified MIL-101(Cr) was then stored in a desiccator for future use.

5.2.3 Adsorption experiments

Adsorption kinetic experiments were prepared using 200 mL solutions in glass beakers with initial heavy metal concentrations of 10 mg/L. These concentrations were confirmed by measuring control samples prior to experimentation. Small amounts of MIL-100(Fe) and MIL-101(Cr) weighed and placed in the solutions to achieve a concentration of 200 mg/L. At time intervals of 0, 0.5, 1, 2, 4, and 8 h, aliquots of the heavy metal solutions were withdrawn from the beakers and passed through 0.2 µm membrane filters (Millipore, Ireland). The heavy metal concentrations were measured by inductively coupled plasma-mass spectrometry (ICP-MS) (Model 7900; Agilent Technologies, Santa Clara, CA, USA).

Adsorption isotherms were investigated using a batch adsorption technique under varying conditions. Heavy metal stock solutions were diluted to initial concentrations ranging from 0-50 mg/L. MIL-100(Fe) and MIL-101(Cr) was weighed and applied to the heavy metal samples to achieve a concentration of 200 mg/L. The samples containing the heavy metals were placed in 50-mL centrifuge tubes, spiked with the MOFs, and sealed with Teflon-lined screw caps. The tubes were then placed in a shaker for 24 h at 13.9 rpm to ensure that equilibrium is reached. Each sample was then filtered through a 0.2 µm membrane filter and analyzed using ICP-MS. Duplicates of the experiments were conducted to ensure the reproducibility of the results. The removal efficiency (%) and the amount of heavy metal adsorbed were calculated using the following equations:

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{3}$$

$$q = (C_0 - C_t)\frac{V}{m} \tag{4}$$

where q is the amount of heavy metal adsorbed onto the MOFs (mg/g), C_0 and C_t are the concentrations at the beginning and end of a time period (mg/L), V is the volume of the initial solution (L), and m is the mass of MOFs (g).

The adsorption isotherm data obtained in the experiments was fitted to three different isotherm models to determine the maximum adsorption capacity of the MOFs: Langmuir, Freundlich, and Linear. The Langmuir model assumes a single layer adsorption process in which the ions only interact with the surface of the MOFs (Langmuir, 1918). However, the Freundlich model assumes multi-layer adsorption on the surface of the adsorbent (Freundlich, 1907). As the Freundlich parameter *n* approaches 1, the multi-layer adsorption more closely represents the Linear isotherm. The equations for these isotherm models are as follows:

$$\text{Langmuir model: } q_e = \frac{q_m b C_e}{1 + b C_e} \tag{5}$$

$$\text{Freundlich model: } q_e = K_f {C_e}^{1/n} \tag{6}$$

$$\text{Linear isotherm: } q_e = K_{LIN} C_e \tag{7}$$

where q_e is the solid phase concentration (mg/g), C_e is the equilibrium solution phase concentration (mg/L), K_{LIN} is the linear coefficient associated with adsorption capacity [(mg/g)/(mg/L)], K_f is the Freundlich affinity coefficient [(mg/g)/(mg/L)$^{1/n}$], n is the dimensionless number related to surface heterogeneity, q_m is the Langmuir maximum adsorption capacity (mg/g), and b is the Langmuir equilibrium constant (L/mg).

In many instances, the use of linearization to determine the isotherm parameters can result in significant errors (Badertscher & Pretsch, 2006; El-Khaiary & Malash, 2011). Therefore, the original, non-linear model equations were used to analyze the equilibrium data. To fit these models, the sums of the squares of the errors (SSE) between the experimental data and the modeled predictions were minimized by varying the isotherm coefficients. The solver add-in for Microsoft Excel was used to perform the minimization. Eq. 8 provides the equations for the SSE function:

$$SSE = \sum_{i=1}^{n} \left(q_{cal} - q_{exp}\right)_i^2 \tag{8}$$

5.2.4 Adsorption thermodynamic studies

The effect of temperature on the adsorption of Cu^{2+}, Cd^{2+}, and Pb^{2+} was investigated at 20°C, 30°C, and 40°C with an absorbent dose of 100 mg/L and an initial concentration of 50 mg/L. These studies were conducted at a pH of 6 with a contact time of 24 h to ensure that equilibrium was achieved. Thermodynamic parameters, which included Gibbs free energy ($\Delta G°$) (kJ/mol), enthalpy ($\Delta H°$) (kJ/mol), and entropy ($\Delta S°$) (kJ/mol-K), were calculated with the following equations:

$$K_L = \frac{q_e}{C_e} \tag{8}$$

$$\ln K_L = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{9}$$

$$\Delta G° = -RT\ln(K_L) \tag{10}$$

where K_L is the adsorption equilibrium constant, q_e is the amount of the heavy metal ion adsorbed on the adsorbent at equilibrium (mg/g), and C_e is the equilibrium concentration of the heavy metal in the solution (mg/L). R is the universal gas constant (0.008314 kJ/mol-K), and T is the temperature (K). The $\Delta H°$ and $\Delta S°$ values are determined from the slope and the intercept of the plots of ln K_L vs. $1/T$, respectively. The $\Delta G°$ values are calculated using Eq. 10.

5.2.5 Characterization of MIL-100(Fe) and MIL-101(Cr)

The structures of MIL-100(Fe) and MIL-101(Cr) were determined by X-ray diffraction (XRD) patterns, which were collected with an UTIMA Ш X-ray diffractometer (Rigaku, Tokyo, Japan). The diffractometer used Cu Kα radiation (λ = 1.5418 Å) and operated at 40 kV and 44 mA. Fourier transform-infrared (FT-IR) spectra were obtained using a Frontier spectrometer (PerkinElmer, Waltham, MA, USA), which utilized the KBr pellet technique to detect functional groups. X-ray photoelectron spectroscopy (XPS) measurements were obtained using a Quantera SXM (Physical Electronics, Inc., Chanhassen, MN, USA) with Al Kα X-ray as the excitation source, which confirmed the surface electronic states of the synthesized MOFs. Nitrogen adsorption and desorption equilibrium data were gathered at -196 ˚C using a Micromeritics ASAP 2020 static volumetric adsorption unit (Micromeritics Inc., Norcross, GA, USA). This data were used to estimate the textural properties of the MOFs. Prior to each analysis, the MOFs were degassed at 150˚C under high vacuum for 12 h. Surface area was estimated using the Brunauer-Emmett-Teller (BET) and Langmuir models. Pore diameter and pore volume were evaluated using the Barrett-Joyner-Halenda (BJH) method. Pore size distributions (PSDs) were obtained using Horvath-Kawazoe (H-K) and BJH analyses methods to cover micropore and mesopore regions, respectively (Lowell, Shields, Thomas, & Thommes, 2012; Rege & Yang, 2000).

5.2.6 Molecular modeling – Computational methods

The size of the basic building blocks of MIL-100(Fe) and MIL-101(Cr) did not allow for accurate levels of quantum chemical calculations. As a result, the approach that was taken in this study was to use fragments of the organic linker and the Fe/Cr trimers to calculate the binding free energies of the heavy metals onto these fragments. All calculations were performed with Version 4.2 of the Orca quantum chemistry software (Neese, 2012, 2018).

Geometries of the fragments with and without the metal ions were optimized using density functional theory with the PBE0 functional (Adamo & Barone, 1999), Grimme's D3 dispersion corrections with Becke-Johnson damping (Grimme, Antony, Ehrlich, & Krieg, 2010; Grimme, Ehrlich, & Goerigk, 2011), and the ma-def2-tzvp basis set (Weigend & Ahlrichs, 2005; Zheng, Xu, & Truhlar, 2011) using the RIJCOSX method for SCF acceleration (Neese, Wennmohs, Hansen, & Becker, 2009) and the def2/J auxiliary basis set (Weigend, 2006). Additional discussion of the rationale for using the PBE0 functional can be found in Supplemental Information (SI). Default effective core potentials def2-ECP were specified for Cd^{2+} and Pb^{2+}. The grid5 setting was used for the integration grids during optimization and final energy calculations, while the gridx5 setting was used with RIJCOSX. Frequency calculations were performed to verify the absence of imaginary frequencies and to calculate Gibb's free energies. Stability analysis was performed to ensure that the wavefunction was minimized. Solvation energies in water were calculated using the SMD model (Marenich, Cramer, & Truhlar, 2009). Final single point energies were calculated using DLPNO-CCSD(T) (Hansen, Liakos, & Neese, 2011; Liakos, Guo, & Neese, 2019) with the ma-def2-QZVPP basis set (Weigend & Ahlrichs, 2005; Zheng et al., 2011) and the def2-qzvpp/c auxiliary basis set (Hellweg, Hättig, Höfener, & Klopper, 2007). Final water phase binding energies were calculated as follows:

$$\Delta G_{binding} = \Delta G_{complex} - \Delta G_{fragment} - \Delta G_{Metal} \tag{11}$$

where $\Delta G_{\mathrm{binding}}$ represents the binding free energy of the interaction between the heavy metal and the modeled fragment, $\Delta G_{\mathrm{complex}}$ represents the free energy of the combined heavy metal/MOF complex, $\Delta G_{\mathrm{fragment}}$ represents the free energy of modeled fragment, and $\Delta G_{\mathrm{metal}}$ represents free energy of the heavy metal. The free energy for the product complex and the reactants in solution are calculated using the following equation:

$$\Delta G = E_{DLPNO-CCSD(T)}^{gas} + \left(E_{DFT}^{SMD} - E_{DFT}^{gas}\right) + \Delta G_{corrections}^{gas} + 1.89\,\frac{kcal}{mol}$$

where ΔG is Gibb's free energy, $E_{DLPNO-CCSD(T)}^{gas}$ is the gas phase energy calculated using DLPNO-CCSD(T) local correlation method, E_{DFT}^{SMD} is the solvation energy using SMD continuum solvation model, E_{DFT}^{gas} is the gas phase energy using density functional theory, $\left(E_{DFT}^{SMD} - E_{DFT}^{gas}\right)$ is the solvation correction, $\Delta G_{corrections}^{gas}$ is free energy corrections, and 1.89 kcal/mol is used to convert standard state free energies at 1 atm of gas phase pressure to 1 M of liquid phase concentration at 298 K.

5.3 Results and Discussion

5.3.1 Characterization of MOFs

The synthesized MOFs were characterized by XRD, FT-IR, and XPS. The XRD patterns indicate that, by matching well with the simulated patterns, MIL-100(Fe) and MIL-101(Cr) were successfully synthesized under the applied conditions (Fig. 5.1).

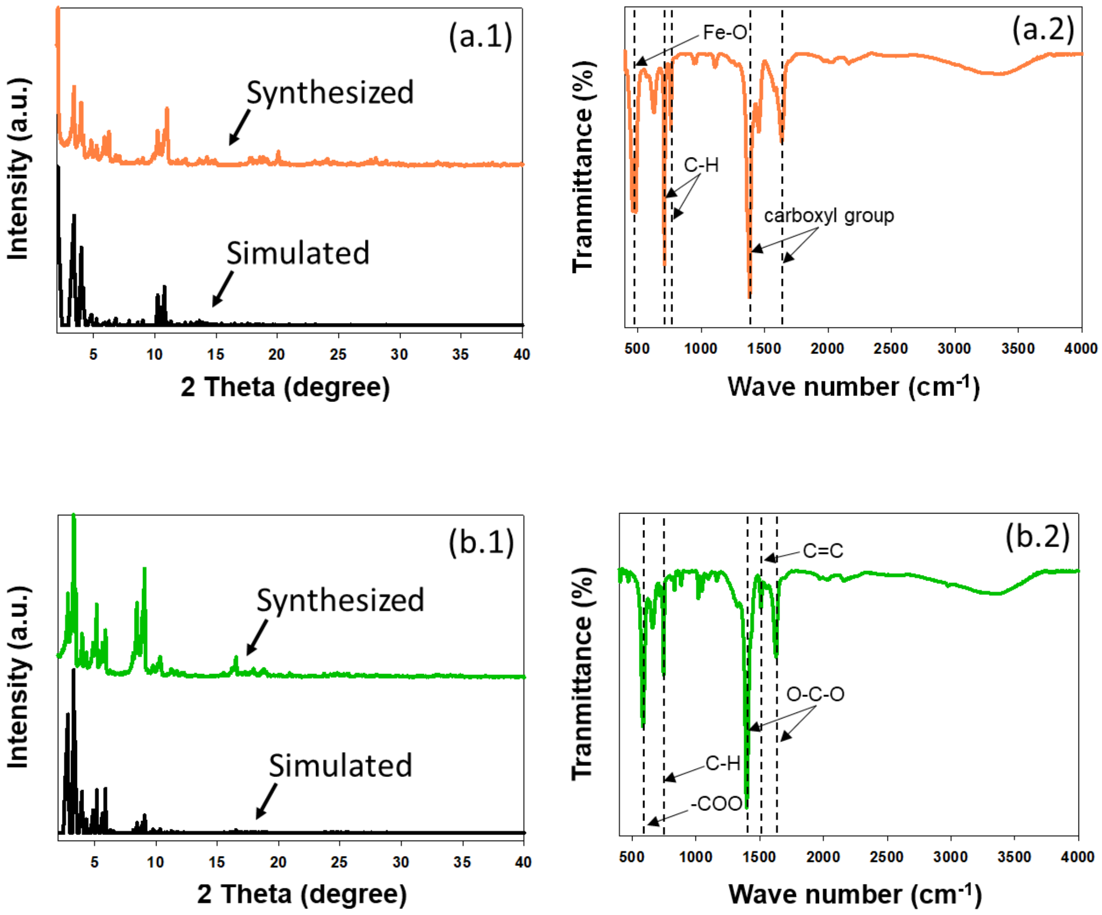

Figure 5.1: Characteristics of (a) MIL-100(Fe) and (b) MIL-101(Cr) using (1) XRD analysis and (2) FT-IR spectra.

Furthermore, as shown in Fig. 5.1(a.2), the FT-IR spectrum of MIL-100(Fe) clearly exhibited peaks at 1,635, 1,383, 762, 711, and 485 cm^{-1}, in excellent agreement with the corresponding functional groups of this structure from previous work (Horcajada et al., 2007; P. Wang, Zhao, Sun, Yu, & Quan, 2014). The peaks at 1,635 and 1,383 cm^{-1} can be assigned to the carboxyl groups of organic ligands within MIL-100(Fe). The peaks of C-H bending are at 762 and 711 cm^{-1}. Fe-O is indicated by the peak at 485 cm^{-1}. The FT-IR spectrum of MIL-101(Cr) is similar to that obtained in previous studies (Fig. 5.1(b.2) (Férey et al., 2005; Y. Hu, Song, Liao, Huang, & Li, 2013). The vibrational stretching frequencies of O-C-O are at 1,620 and 1,400 cm^{-1}, indicating the presence of dicarboxylate linkers within the MIL-101(Cr) structure. The peaks between 500 and 1,600 cm^{-1} can be assigned to the vibrations of benzene rings, including C=C at 1,510 cm^{-1}, C-H at 746 cm^{-1}, -COO at 587 cm^{-1}. The XPS spectrum shows the surface chemical states of MIL-100(Fe) (Fig. 5.2) and MIL-101(Cr) (Fig. 5.3). For both MIL-100(Fe) and MIL-101(Cr), the XPS spectrum of C 1s contains two peaks at 284.8 and 288 eV, which correspond to phenyl and carboxyl signals, respectively (M.-G. Jeong et al., 2016; B.-J. Zhu et al., 2012). The O 1s peaks at 531.7 and 532 eV correspond to the Fe-O-C and Cr-O-C species in the XPS spectra of MIL-100(Fe) and MIL-101(Cr), respectively (R. Liang et al., 2015; Vu et al., 2014). The Fe 2p spectrum for MIL-100(Fe) can be deconstructed into two peaks centered at 712.3 and 724.8 eV, corresponding to the peaks of Fe 2p3/2 and Fe 2p1/2, respectively (F. Zhang et al., 2015). The spectrum of Cr 2p for MIL-101(Cr) was assigned to two peaks at 577 and 587 eV, corresponding to the Cr 2p3/2 and Cr 2p1/2 signals, respectively (M.-G. Jeong et al., 2016).

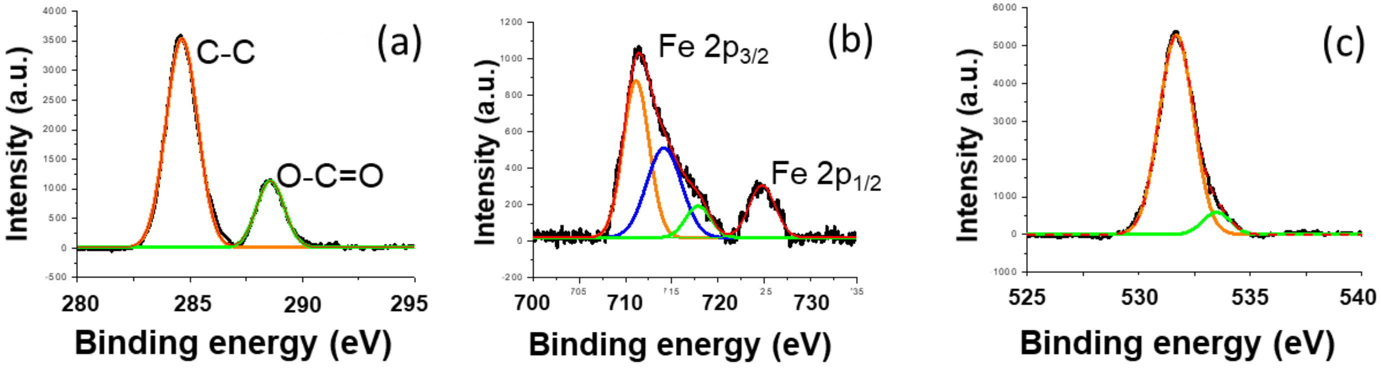

Figure 5.2: XPS spectra of MIL-100(Fe) for (a) C 1s, (b) Fe 2p, and (c) O 1s

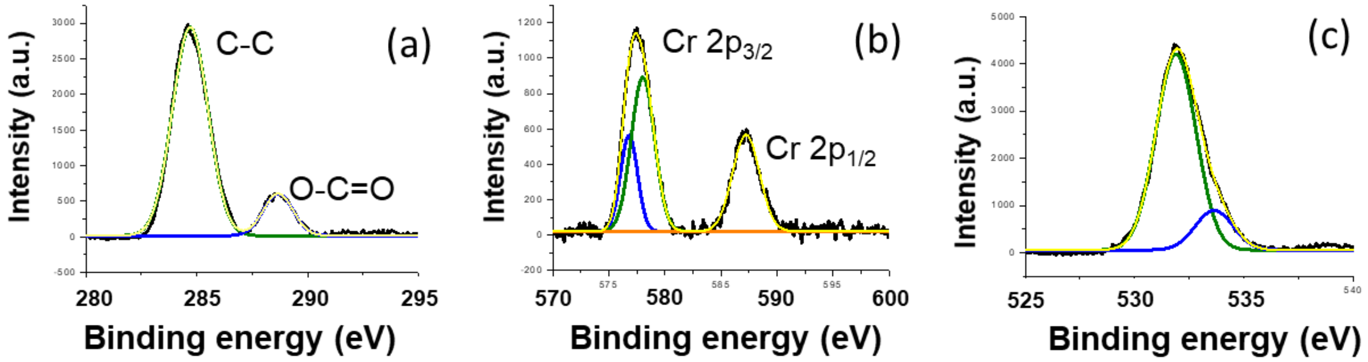

Figure 5.3: XPS spectra of MIL-101(Cr) for (a) C 1s, (b) Cr 2p, and (c) O 1s

MIL-100(Fe) and MIL-101(Cr) exhibited large surface areas and pore volumes, as expected from highly microporous frameworks. The calculated BET surface areas for MIL-100(Fe) and MIL-101(Cr) were 1,586 and 2,505 m^2/g, respectively. Moreover, the Langmuir surface areas for MIL-100(Fe) and MIL-101(Cr) were 2,637 and 3,966 m^2/g, respectively. Furthermore, a stack of PSD profiles for MIL-100(Fe) and MIL-101(Cr) shows the presence of pores with windows of the 9 and 12 Å, along with spherical cavities ranging from 23-28 Å for MIL-100(Fe) and 26-36 Å for MIL-101(Cr), respectively (Fig. 5.4).

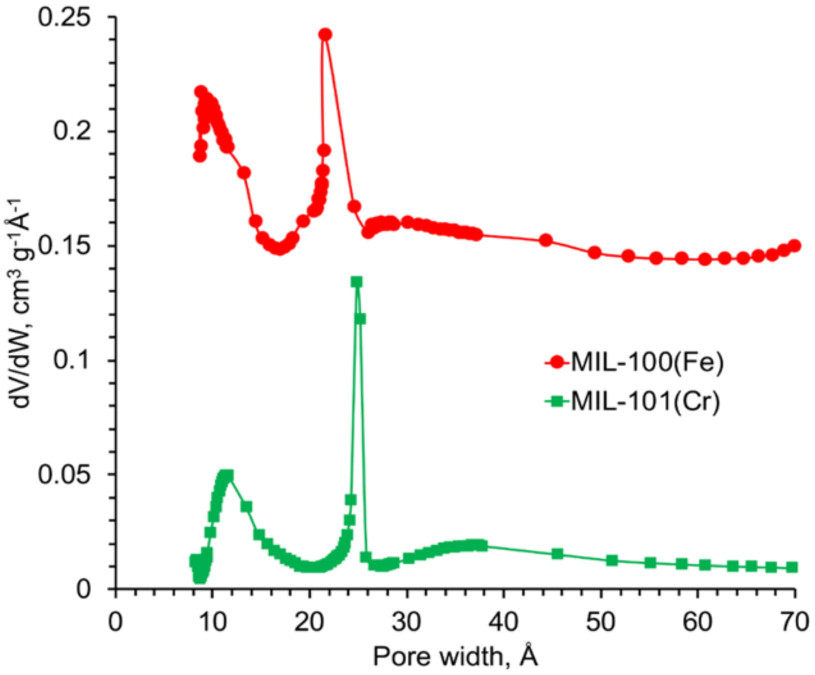

Figure 5.4: Pore size distribution profiles based on Horvath – Kawazoe's (H-K) and Barrett-Joyner-Halenda (BJH) analyses of the N_2 equilibrium adsorption data gathered at -196°C

These values agree with data previously reported elsewhere (Férey et al., 2005; Huo & Yan, 2012). Therefore, the XRD, FT-IR, XPS, and N_2 isotherms demonstrate that lab-made MIL-100(Fe) and MIL-101(Cr) were successfully synthesized and can now be evaluated for heavy metal adsorption applications.

5.3.2 Adsorption kinetic studies

Adsorption kinetic studies were conducted to gain an understanding of the controlling mechanism of the adsorption process. Fig. 5.5 provides the removal of the heavy metals by the MOFs over an 8-h period.

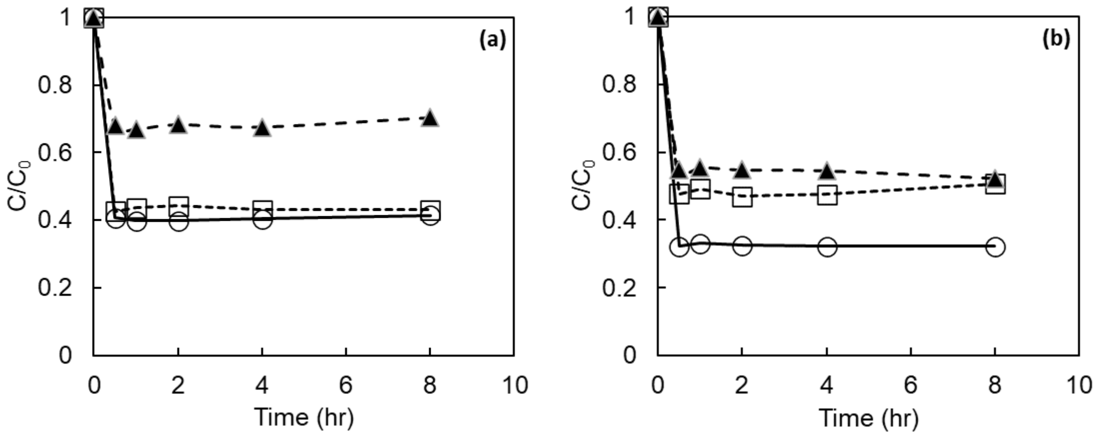

Figure 5.5: Effect of contact time on the adsorption of heavy metals onto (a) MIL-100(Fe) and (b) MIL-101(Cr) (C_0 = 10 mg/L; adsorbent dose = 100 mg/L; temperature = 20°C). Cd^{2+}(□); Cu^{2+}(○); Pb^{2+}(▲).

Equilibrium concentrations of the heavy metals appeared to be achieved after 0.5 h, which was consistent with the equilibrium times observed in similar studies (Thanh et al., 2018; B.-L. Zhang et al., 2020). For both MOFs, higher amounts of Cu^{2+} were adsorbed, followed by Cd^{2+} and then Pb^{2+}. MIL-101(Cr) provided higher removal efficiencies than MIL-100(Fe) for Cu^{2+} (68% vs. 59%) and Pb^{2+} (46% vs. 33%), while MIL-100(Fe) provided higher removal efficiencies for Cd^{2+} (57% vs. 49%). With the rapid removal of the heavy metals by MIL-100(Fe) and MIL-101(Cr), the kinetic models were could not be applied to this set of data. Thus, kinetic parameters were not obtained for this study.

5.3.3 Adsorption isotherm studies

Adsorption isotherm studies were performed to determine the adsorption capacities of the MOFs for the removal of heavy metals. Fig. 5.6 provides the adsorption isotherm data for the removal of Cu^{2+}, Cd^{2+}, and Pb^{2+} by MIL-100(Fe) and MIL-101(Cr) using the Langmuir, Freundlich, and Linear isotherm models. Table 5.2 provides the isotherm parameters for the Linear and Freundlich models.

Table 5.2. Isotherm fitting parameters for removal of heavy metals using MOFs

Adsorbent	Heavy Metal	Linear		Freundlich		
		K_{LIN} (mg/g)/(mg/L)	SSE	K_F (mg/g)/(mg/L)$^{1/n}$	n	SSE
MIL-100(Fe)	Cu^{2+}	14.9	86.84	12.6	0.94	16.48
	Cd^{2+}	12.9	7.714	13.1	1.01	7.324
	Pb^{2+}	4.44	31.89	3.49	0.93	5.485
MIL-101(Cr)	Cu^{2+}	60.3	6475	28.8	0.70	1600
	Cd^{2+}	11.5	141.7	11.3	0.99	141.1
	Pb^{2+}	8.33	1040	9.77	1.18	1040

Based on the error analysis using the SSE function, the Freundlich and Linear isotherm models provided the best fit to the experimental data. However, the Freundlich parameter *n* is close to 1, which suggests that adsorption is most effectively explained by the Linear isotherm. Both of these isotherm models suggest that the adsorption processes in this study are multi-layered and that the surface of the adsorbent is heterogenous (Thanh et al., 2018). While the Langmuir isotherm model appeared to provide a good fit to the experimental data (Fig. 3), the flatter portion of the standard Langmuir curve that is used to determine the maximum adsorption capacity, q_{max}, occurs outside of the range of the experimental data and cannot be reliably obtained through extrapolation.

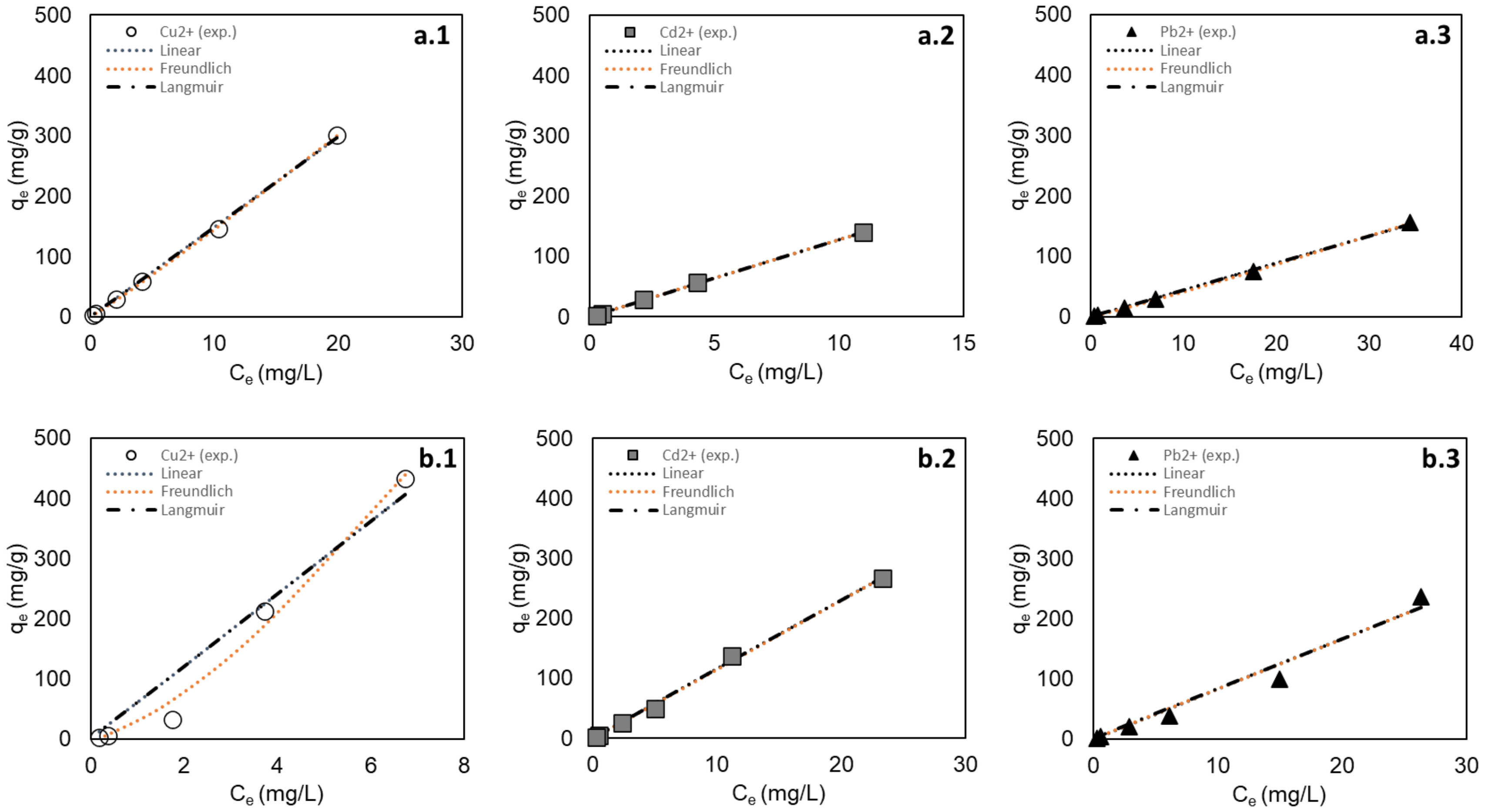

Figure 5.6: Adsorption isotherms for heavy metal removal onto (a) MIL-100(Fe) and (b) MIL-101(Cr) (C_0 = 0 – 50 mg/L; adsorbent dose = 100 mg/L; temperature = 20°C; contact time = 24 h). Heavy metals: (1) Cu^{2+}, (2) Cd^{2+}, and (3) Pb^{2+}.

The K_{LIN} and K_F parameters for the Linear and Freundlich isotherm models, respectively, are often understood to represent the adsorption capacity of the adsorbents, which varied based on the heavy metal ion and the adsorbent. For MIL-100(Fe) and MIL-101(Cr), the K_{LIN} values were highest for Cu^{2+} ($K_{LIN,\ MIL\text{-}100(Fe)}$ = 14.9; $K_{LIN,\ MIL\text{-}101(Cr)}$ = 60.3), followed by Cd^{2+} ($K_{LIN,\ MIL\text{-}100(Fe)}$ = 12.9; $K_{LIN,\ MIL\text{-}101(Cr)}$ = 11.5) and Pb^{2+} ($K_{LIN,\ MIL\text{-}100(Fe)}$ = 4.44; $K_{LIN,\ MIL\text{-}101(Cr)}$ = 8.33). The K_F values for MIL-101(Cr) followed the same pattern, with the highest value for Cu^{2+} (K_F = 28.8), followed by Cd^{2+} (K_F = 11.3) and Pb^{2+} (K_F = 9.77). However, for MIL-100(Fe), the K_F values for Cu^{2+} (K_F = 12.6) and Cd^{2+} (K_F = 13.1) were similar, followed by Pb^{2+} (K_F = 3.49). Table 5.3 provides a comparison of the Freundlich isotherm parameters for the adsorption of Cu^{2+}, Cd^{2+}, and Pb^{2+} using various MOFs. The data provided in this table suggests that MIL-100(Fe) and MIL-101(Cr) achieved good adsorption in this study when compared to other MOFs.

5.3.4 Molecular modeling

The molecular structures of MIL-100(Fe) and MIL-101(Cr) are complex, which creates challenges when developing the molecular model and performing computational analysis. Therefore, in this study, model fragments that could be found in the organic linker sections of MIL-100(Fe) and MIL-101(Cr), such as benzoate, phenol, and benzene, and Fe/Cr trimetallic oxides, were linked with formate and terminated with hydroxide to represent the metal centers. Fig. 5.7 provides an example of the entire molecular structure of the MOF and its corresponding model fragment, which was used in the analysis. Supplemental Information (SI) provides additional discussion regarding the rationale for the use of the hydroxide terminated trimetallic oxide structure.

Table 5.3 Comparison of the Freundlich fitting parameters for the adsorption of Cu^{2+}, Cd^{2+}, and Pb^{2+} using various MOFs.

Heavy Metal	MOF	Freundlich			Reference
		K_F	n	R^2	
Cu^{2+}	Fe_3O_4@MOF@COF	1.76	1.36	0.95	(W.-T. Li et al., 2020)
	Ln(BTC)(H_2O)(DMF)$_{1.1}$	2.799	2.328	0.99	(Jamali, Tehrani, Shemirani, & Morsali, 2016)
	Fe_3O_4@MOF	3.78	1.24	0.99	(W.-T. Li et al., 2020)
	MIL-100(Fe)	**12.36**	**0.93**	**0.99**	**This study**
	MIL-101(Cr)	**26.06**	**0.715**	**0.98**	**This study**
	UiO-66-EDA	26.08	2.14	0.85	(Ahmadijokani et al., 2021)
	NH_2-MIL-125	30.7	6.77	0.77	(Reda M Abdelhameed et al., 2019)
Cd^{2+}	MOF-5	0.405	1.58	0.84	(J. Zhang, Xiong, Li, & Wu, 2016)
	Co-Gly	4.47	1.94	0.94	(Visa, Maranescu, Lupa, Crisan, & Borota, 2020)
	Ni-Gly	5.54	2.01	0.94	(Visa et al., 2020)
	MIL-101(Cr)	**9.44**	**0.93**	**0.99**	**This study**
	MIL-100(Fe)	**10.14**	**0.87**	**0.99**	**This study**
	UiO-66-EDA	35.01	2.40	0.89	(Ahmadijokani et al., 2021)
	HS-mSi@MOF-5	37.08	3.54	0.88	(J. Zhang et al., 2016)
Pb^{2+}	MOF-5-CMC	1.75	3.22	0.96	(Jin et al., 2019)
	MIL-100(Fe)	**2.26**	**0.81**	**0.99**	**This study**
	Ln(BTC)(H_2O)(DMF)$_{1.1}$	3.857	4.307	0.98	(Jamali et al., 2016)
	MIL-101(Cr)	**5.76**	**0.91**	**0.99**	**This study**
	MIL-101	14.12	3.48	0.90	(Thanh et al., 2018)
	PFe_3O_4@NH_2-MIL-125	19.44	3.41	0.97	(Venkateswarlu, Panda, Kim, & Yoon, 2018)
	Fe-MIL-101	24.02	3.53	0.99	(Thanh et al., 2018)
	MIL-125	27.53	1.12	0.95	(X.-X. Liang et al., 2018)
	UiO-66-EDA	69.04	3.04	0.89	(Ahmadijokani et al., 2021)
	MMMT@Zn-BDC	110.1	3.03	0.92	(Shen, Wang, Wang, Yu, & Ouyang, 2018)

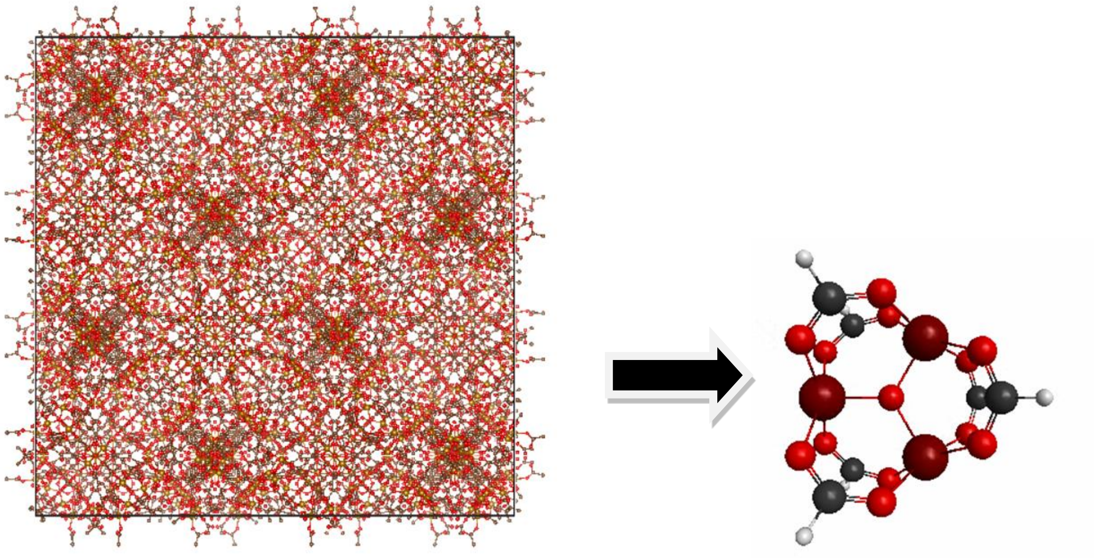

Figure 5.7: Complete molecular structure of MIL-100(Fe) reduced to model fragment used for molecular modeling and analysis.

Table 5.4 provides the binding free energies of the heavy metals onto the organic fragments of MIL-100(Fe) and MIL-101(Cr).

Table 5.4 Binding free energies of heavy metals on the organic fragments associated with MIL-100(Fe) and MIL-101(Cr).

Heavy Metal	Multiplicity	ΔG, Binding free energy, kcal/mol			
		Benzoate	Phenolate	Phenol	Benzene
Cu^{2+}	2	-92.9	-120	-74.8	-64.6
	4	-15.4	-54.9	no complex	13.6
Cd^{2+}	1	-91.0	-83.8	-52.6	-51.4
	3	-44.1	-86.9	no complex	no complex
Pb^{2+}	1	-34.2	-33.6	-10.7	-14.2
	3	47.2	14.1	no complex	no complex

Based on these calculations, the heavy metals interact and bind to the organic model fragments. Lower multiplicities resulted in greater binding of the heavy metals to the organic fragments, with the exception of the interaction of Cd^{2+} and phenolate. For each heavy metal, the Δ*G* values were more negative for interactions associated with benzoate and phenolate, which are negatively charged. This result suggests that electrostatic interactions are the dominant adsorption mechanism for heavy metal removal. However, the Δ*G* values for interactions with phenol and benzene suggest that binding can also occur between the heavy metal ions and neutral organic fragments, which may be the result of π-orbital interactions between the heavy metals and the neutral fragments. Electrostatic interactions (Kobielska et al., 2018; Xing Li et al., 2018; C. Yu, Shao, Liu, & Hou, 2018) and π-orbital interactions (Z. Hasan & S. Jhung, 2015; C. Yu et al., 2018) have often been cited as potential removal mechanisms for heavy metals by MOFs. Moreover, for each organic fragment, the Δ*G* values were more negative for Cu^{2+}, followed by Cd^{2+} and Pb^{2+}, which suggests that Cu^{2+} has the greatest affinity for the organic portions of the MOFs. This finding is consistent with the experimental data, which shows the higher adsorption capacity for Cu^{2+}, followed by Cd^{2+} and Pb^{2+}.

Table 5.5 provides the binding free energies of the heavy metals on the trimetallic oxide fragments.

Table 5.5: Binding free energies of heavy metals on the trimetallic oxide fragments.

Heavy Metal	Multiplicity	MIL-100(Fe) $(OH)_3$ ΔG, kcal/mol	Multiplicity	MIL-101(Cr) $(OH)_3$ ΔG, kcal/mol
Cu^{2+}	13	-57.5	7	-69.1
	15	-77.2	9	-89.8
	17	-88.0	11	-85.7
	19	-33.5	13	-29.2
Cd^{2+}	14	8.6	8	-39.6
	16	-16.2	10	-56.3
	18	-56.4	12	-52.4
	20	54.4	14	17.3
Pb^{2+}	14	55.1	8	67.4
	16	26.1	10	-29.4
	18	115.6	12	49.3

For the instances with the lowest binding free energies, broken symmetry DFT calculations were performed with the flipspin feature of the Orca software using the same conditions as geometry optimization. The spin of each of the trimetallic centers of MIL-100(Fe) and

MIL-101(Cr) were flipped, after which a converged DFT solution was obtained. Geometry optimization was then performed using the converged solution. A broken symmetry solution was not found in most cases, and the DFT energies at the optimum geometry were always higher, which indicates that the calculations at the high spin level represents the binding free energies of heavy metals onto MIL-100(Fe) and MIL-101(Cr).

With the exception of Pb^{2+} on MIL-100(Fe), the heavy metals interacted with these fragments based on their preferred multiplicities near the trimer high spin. The interactions among the trimetallic oxide fragments were the strongest with Cu^{2+}, followed by Cd^{2+} and Pb^{2+}, which followed the same pattern as the interactions with the organic fragments. In general, each heavy metal experienced the highest binding free energy with the negatively-charged organic fragments and lowest binding free energy with the neutral organic fragments. For Pb^{2+}, the binding free energy with the MIL-101(Cr) trimetallic oxide fragment was similar to that of the negatively-charged organic fragment. For Cu^{2+}, the binding free energies with the trimetallic oxide fragments were higher than that of the neutral organic fragment while for Cd^{2+}, the binding free energies with the trimetallic oxide fragments were similar to that of the neutral organic fragment. These results show that interactions exist between the heavy metals and the trimetallic oxide fragments, which suggest that these fragments may also contribute to the adsorption of heavy metals.

5.3.5 Adsorption thermodynamic studies

Thermodynamic parameters were calculated to assist in determining whether the adsorption process is endothermic or exothermic, along with whether or not the adsorption occurs spontaneously. Fig. 5.8 provides a plot of $\ln K_L$ vs. $1/T$ to determine the relevant thermodynamic values, as outlined in Eq. 9.

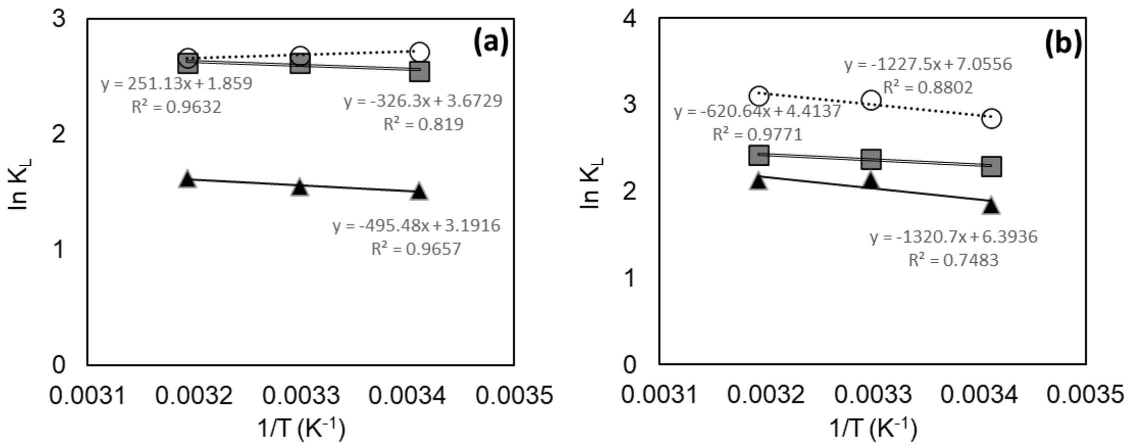

Figure 5.8: Plot of ln K_L vs. 1/T for adsorption of heavy metals by (a) MIL-100(Fe) and (b) MIL-101(Cr) Heavy metals: Cd^{2+}(■); Cu^{2+}(○); Pb^{2+}(▲).

Table 5.6 provides the values for Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) for the adsorption of Cd^{2+}, Cu^{2+}, and Pb^{2+} onto the MOFs.

Table 5.6: Thermodynamic parameters for the adsorption of heavy metals by MIL-100(Fe) and MIL-101(Cr).

MOF	Heavy Metal	ΔG° (kJ/mol)			ΔH° (kJ/mol)	ΔS° (J/mol-K)	R^2
		293 K	303 K	313 K			
MIL-100(Fe)	Cu^{2+}	-6.63	-6.76	-6.94	2.09	15.5	0.963
	Cd^{2+}	-6.22	-6.59	-6.82	-2.71	30.5	0.819
	Pb^{2+}	-3.67	-3.90	-4.21	-4.12	26.6	0.966
MIL-101(Cr)	Cu^{2+}	-6.92	-7.72	-8.08	-10.2	58.7	0.880
	Cd^{2+}	-5.58	-5.99	-6.32	-5.16	36.7	0.977
	Pb^{2+}	-4.49	-5.38	-5.54	-11.0	53.2	0.748

For the adsorption of Cd^{2+}, Cu^{2+}, and Pb^{2+} onto MIL-100(Fe) and MIL-101(Cr), the $\Delta G°$ values are negative at each temperature, which suggests that adsorption is feasible and spontaneous. Moreover, in each scenario, the $\Delta G°$ values decrease as the temperature increases, which suggest that adsorption is more efficient at higher temperatures.

When considering the enthalpy and entropy for the adsorption of the heavy metals onto MOFs, the $\Delta H°$ and $\Delta S°$ values were investigated for each adsorption process. These values were determined by plotting the values of ln K_c versus $1/T$, as shown in Fig. 5.8, and the findings are shown in Table 5.6. For MIL-100(Fe), the Δ*H*° values for the adsorption of Cd^{2+} and Pb^{2+} were both negative, which suggests that these processes are exothermic. However, for the adsorption of Cu^{2+}, the Δ*H*° values were positive, which suggests that this process is endothermic. For MIL-101(Cr), the Δ*H*° values were negative for each heavy metal. When evaluating entropy, the Δ*S*° values were positive, which suggest that high affinity for the heavy metal ions and the surfaces of the MOFs is present during adsorption (Özsin, Kılıç, Apaydın-Varol, & Pütün, 2019; B.-L. Zhang et al., 2020).

5.3.6 Adsorption mechanism

To gain further insights into the potential adsorption mechanism between the heavy metal ions and the MOFs in this study, additional computational analysis was conducted. Local energy decomposition analysis (Altun, Saitow, Neese, & Bistoni, 2019; Schneider et al., 2016) was performed on the lowest energy complexes in Tables 5.4 and 5.5 to evaluate the nature of the interaction between the heavy metal ions and the MOFs. These results are shown in Table 5.7.

Table 5.7: Gas phase local energy decomposition of adsorbate-metal ion complex.

Complex	Multiplicity	ΔE(geo-prep)	ΔE(ref-int)	ΔE(corr-int)	ΔE
Benzoate-Cu	2	18.4	-421.9	-37.1	-440.7
Benzoate-Cd	1	6.7	-357.9	-22.7	-374.0
Benzoate-Pb	1	10.6	-346.2	-9.5	-345.1
Phenolate-Cu	2	3.3	-413.7	-62.1	-472.5
Phenolate-Cd	3	3.2	-365.4	-16.1	-378.3
Phenolate-Pb	1	6.9	-327.7	-11.5	-332.4
Phenol-Cu	2	8.3	-158.9	-64.0	-214.6
Phenol-Cd	1	14.9	-130.2	-20.7	-136.0
Phenol-Pb	1	4.2	-101.8	-16.1	-113.7
Benzene-Cu	2	3.2	-120.1	-72.3	-189.1
Benzene-Cd	1	7.2	-112.7	-19.8	-125.4
Benzene-Pb	1	0.5	-94.9	-13.7	-108.1
MIL100Fe-Cu	17	33.4	-580.2	-41.9	-588.8
MIL100Fe-Cd	18	30.4	-532.9	11.9	-490.7

MIL100Fe-Pb	16	42.5	-548.0	61.4	-444.1
MIL101Cr-Cu	9	13.8	-426.7	-181.4	-594.2
MIL101Cr-Cd	10	17.0	-386.2	-127.4	-496.6
MIL101Cr-Pb	10	32.2	-490.4	-13.0	-471.2

ΔE(geo-prep) represents the energy penalty due to the deformation of the complexes from their optimum energy geometry to the complex geometry. ΔE(ref-int) occurs due to static interaction terms and accounts for the electronic preparation penalty, along with the electrostatic and exchange interactions. ΔE(corr-int) accounts for dynamic corrections to the static terms and dispersive interactions, which is often associated with diffusion. In all cases, the static ΔE(ref-int) predominantly accounted for the favorable interaction between the MOFs and the heavy metals, with the electrostatic term accounting for the largest magnitude within ΔE(ref-int).

These results suggest that electrostatic interactions represent the dominant adsorption mechanism for heavy metal removal by MIL-100(Fe) and MIL-101(Cr). This finding is not surprising because the heavy metals are positively charged (+2), while these MOFs are negatively charged at neutral pH values (Thanh et al., 2018; B.-L. Zhang et al., 2020). Moreover, electrostatic interactions have often been cited as the dominant removal mechanism for heavy metals by MOFs (M. Feng, Zhang, Zhou, & Sharma, 2018; Hakimifar & Morsali, 2019; C. Liu et al., 2019). In this study, ΔE(corr-int) contributions to the interaction are relatively small compared to $\Delta \mathrm{E}$(ref-int) and even repulsive for the MIL100Fe-Cd and MIL100Fe-Pb complexes. For each of the organic adsorbates, both ΔE(ref-int) and ΔE(corr-int) consistently followed the relative trend where the interactions favored Cu^{2+}, followed by Cd^{2+} and Pb^{2+}, This trend is supported by the experimental results found in this study, where Cu^{2+} experienced the largest removal, followed by Cd^{2+}

and Pb^{2+} (Table 1). While no specific trend was associated with ΔE(geo-prep), the trend for the overall ΔE was not affected. However, trends for the specific energy terms were not observed for the heavy metal complexes with MIL-100(Fe) and MIL-101(Cr), which suggests that the relative contributions of the various adsorption mechanisms between the heavy metals and each trimer may be more complicated. Additional research is required to determine if trends can be identified that are related to different metals and MOFs.

5.4 Conclusions

In this study, MIL-100(Fe) and MIL-101(Cr) were fabricated and employed to investigate their ability to remove Cu^{2+}, Cd^{2+}, and Pb^{2+} from aqueous solution. Fragments of the molecular structures of MIL-100(Fe) and MIL-101(Cr) were also modeled to investigate the interactions between the adsorbents and the heavy metals, as well as understand the potential adsorption mechanisms associated with heavy metal removal. When evaluating various adsorption isotherm models, the experimental results had the best fit the Linear and Freundlich isotherm models. The K_{LIN} values, which are often representative of adsorption capacity, of Cu^{2+}, Cd^{2+}, and Pb^{2+} for adsorption onto MIL-100(Fe) were 14.9, 12.9, and 4.44, respectively. Meanwhile, K_{LIN} values of Cu^{2+}, Cd^{2+}, and Pb^{2+} for adsorption onto MIL-101(Cr) were 60.3, 11.5, and 8.33, respectively. These adsorption capacities are similar to those found for other MOFs in the literature. MIL-100(Fe) and MIL-101(Cr) also exhibited fast adsorption kinetics, achieving equilibrium in approximately 0.5 h. The adsorption studies suggest that MIL-101(Cr) appeared to remove Cu^{2+} and Pb^{2+} more efficiently, while MIL-100(Fe) appeared to remove Cd^{2+} more efficiently. The adsorption mechanism for heavy metal removal by MIL-100(Fe) and MIL-101(Cr) was evaluated using molecular modeling. Local energy decomposition analysis was conducted to evaluate the various binding free energies. The results of this analysis suggest that electrostatic interactions represent the dominant adsorption mechanism for heavy metal removal by MIL-100(Fe) and MIL-101(Cr), which is consistent with other, similar adsorption studies. Overall, this study demonstrates that MIL-100(Fe) and MIL-101(Cr) can effectively remove heavy metals from aqueous solution.

CHAPTER 6

OVERALL CONCLUSIONS

Increased water scarcity and pollution contribute to a significant lack of access to clean drinking water. While various forms of water pollution exist, heavy metal contamination in drinking water sources is a growing concern. As a result, a significant amount of research has been conducted to investigate the use of novel adsorbent materials to remove heavy metals from water sources. These novel adsorbents include low-cost adsorbents, such as agricultural waste, soil and mineral deposits, aquatic and terrestrial biomass, and various waste materials, along with MOFs. Researchers have reported that the low-cost adsorbents can effectively remove heavy metals, while MOFs have been shown to effectively remove CECs. For the removal of heavy metals using low-cost adsorbents, ion exchange is the most cited mechanism, along with the influence of electrostatic forces. However, the efficiencies of these mechanisms are heavily influenced by water quality conditions. For the removal of selected CECs by MOFs, the dominant mechanisms are influential in the following order: electrostatic interactions > H-bonding > π-π interactions/stacking > hydrophobic interactions ≈ acid-base interactions ≈ metal effects.

To further evaluate the ability of MOFs to remove heavy metals from water sources, MIL-100(Fe) and MIL-101(Cr) were fabricated and employed to investigate their ability to remove Cu^{2+}, Cd^{2+}, and Pb^{2+} from aqueous solution. Fragments of the molecular structures of MIL-100(Fe) and MIL-101(Cr) were also modeled to investigate the interactions between the adsorbents and the heavy metals, as well as understand the potential adsorption mechanisms associated with heavy metal removal. MIL-100(Fe) and MIL-101(Cr) exhibited fast adsorption kinetics, achieving equilibrium in approximately 0.5 h. The adsorption studies suggest that MIL-101(Cr) appeared to remove Cu^{2+} and Pb^{2+} more efficiently, while MIL-100(Fe) appeared to remove Cd^{2+} more efficiently. The results of the molecular modeling analysis suggest that electrostatic interactions represent the dominant adsorption mechanism for heavy metal removal by MIL-100(Fe) and MIL-101(Cr), which is consistent with other, similar adsorption studies. Overall, MIL-100(Fe) and MIL-101(Cr) were shown to effectively remove heavy metals from aqueous solution.

The results found in this study demonstrate the effectiveness of low-cost adsorbents and MOFs to remove heavy metal contamination from water sources. Low-cost adsorbents are viable, cost-effective materials that often available in large quantities and can be used to remove heavy metals from water. For future research, researchers should continue to identify additional low-cost materials that are effective at removing heavy metals and evaluate their effectiveness in true, local water sources, such as industrial effluent, river and lake sources, and domestic wastewater, using bench-scale and pilot testing. MOFs are also promising materials due to their high-performance adsorption. However, many gaps remain in our understanding of their application in water and wastewater treatment systems. For instance, more research needs to be conducted to determine its ability to remove heavy metals in aqueous solution with varying water quality. Moreover, more research is needed to provide comprehensive life-cycle analyses and ecotoxicological assessments of MOFs, particularly when considering its disposal. However, the use of MOFs for the heavy metal adsorption remains promising. Overall, low-cost adsorbents, along with MOFs, can potentially be implemented into the water treatment process to remove heavy metals.

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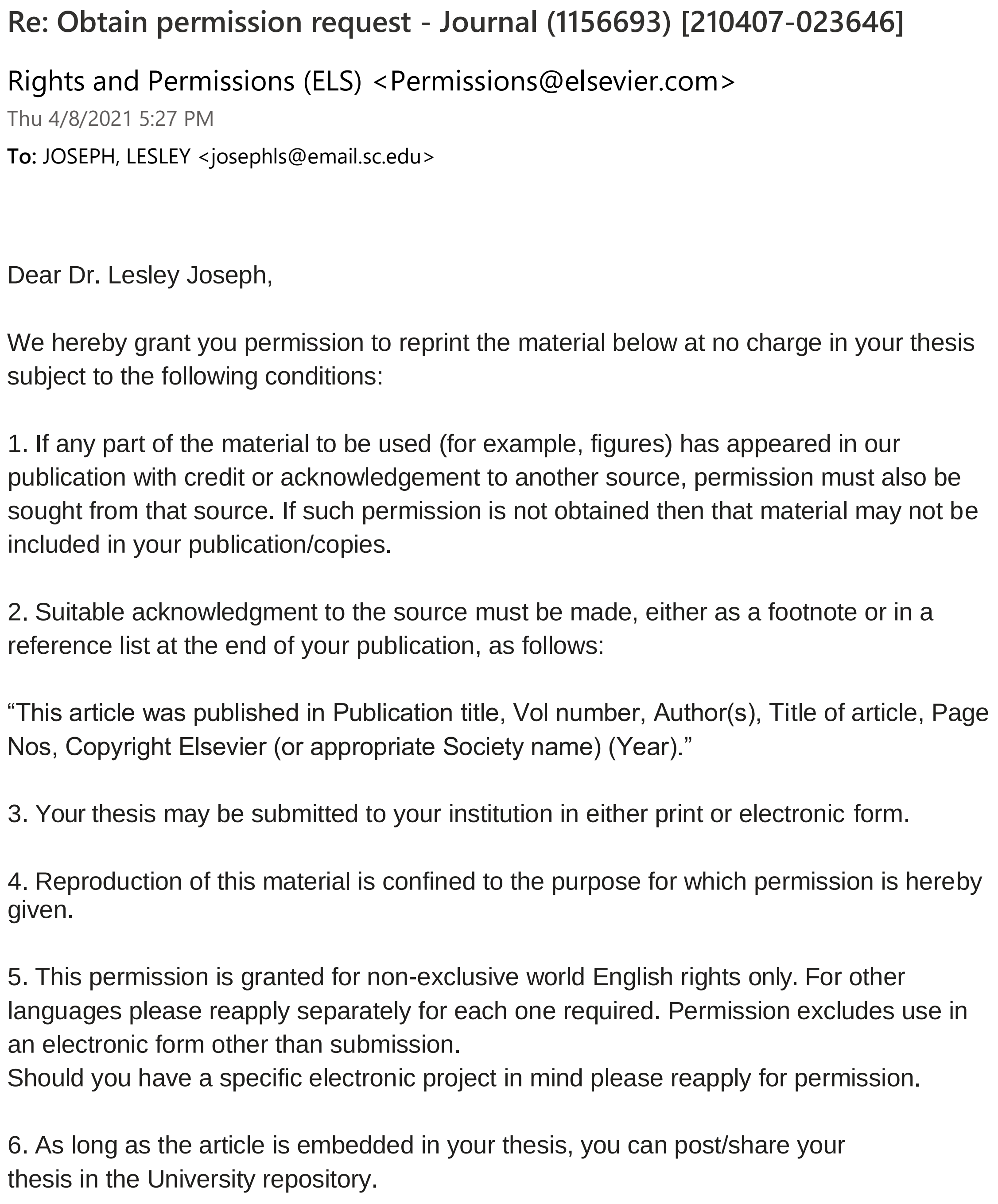

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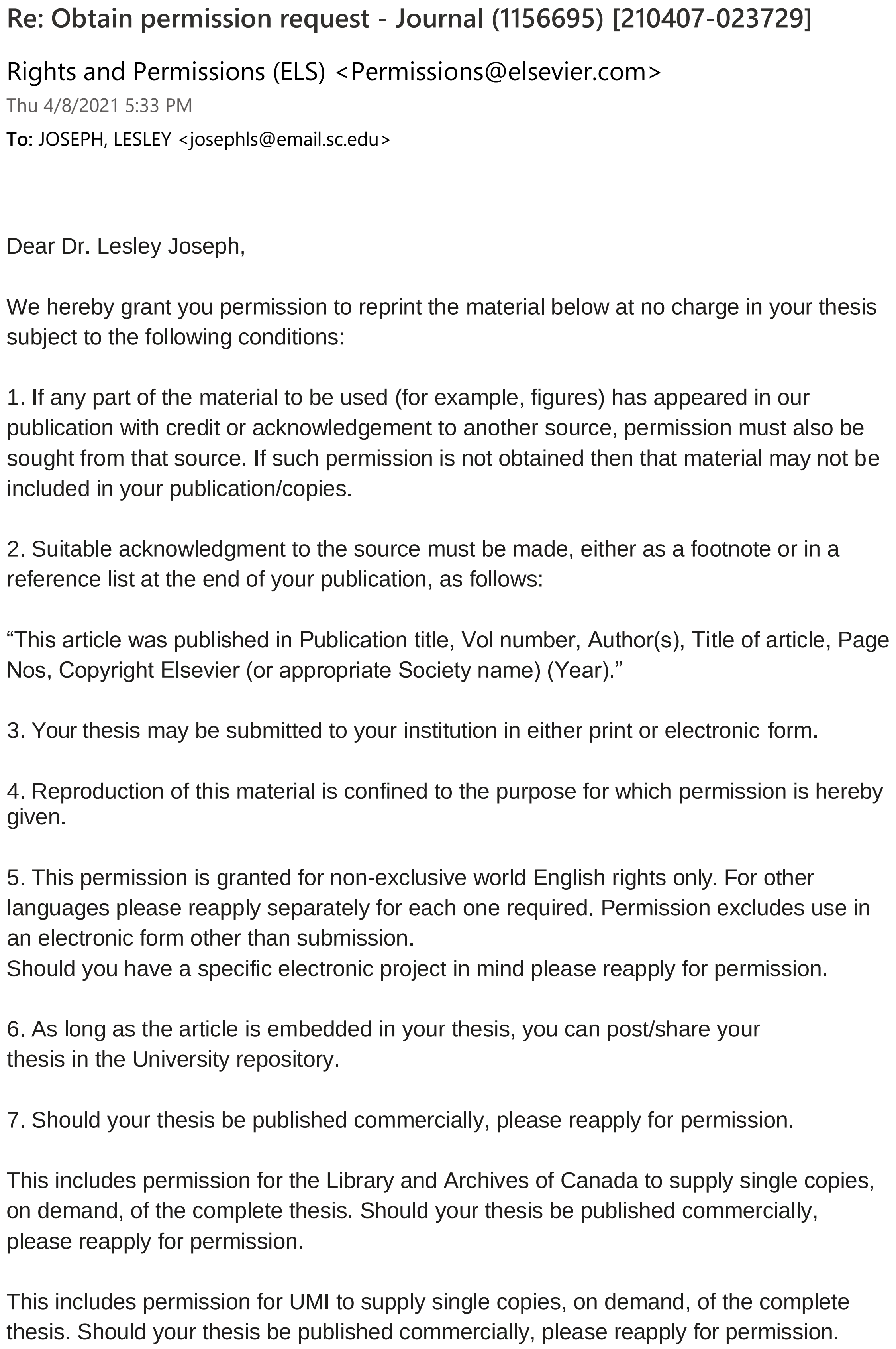

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