Removal of inorganic arsenic from water using metal organic frameworks

It has been estimated that between 94 million and 220 million people around the world are at risk of consuming drinking water that contain arsenic concentrations higher than 10 μg/L (Podgorski and Berg, 2020), the World Health Organization (WHO) guideline level. The vast majority (94%) of the population at risk are in Southeast Asia (Uppal et al., 2019a; Yan, 2020), although there are also concerns over water arsenic in rural communities in many parts of the world.

The Agency for Toxic Substances and Disease Registry has consistently ranked arsenic on top of its Substance Priority List. The International Agency for Research on Cancer has classified inorganic arsenic as a human carcinogen. Chronic exposure to high concentrations of inorganic arsenic increases the risk of developing cancers and various non-cancerous effects in humans (Naujokas et al., 2013). Ingestion of arsenic from water and food is the major route of human exposure to inorganic arsenic. Therefore, it is critical to minimize arsenic concentrations in drinking water.

1.   Removal of arsenic from drinking water

A number of approaches and technologies have been developed to remove arsenic from drinking water. Community water treatment plants typically incorporate arsenic removal into the overall processes of water treatment that usually include coagulation, flocculation, filtration, and disinfection (to minimize microbial risk). Feasible and successful methods for the removal of arsenic at the point of entry or point of use (e.g., individual homes and water wells) most commonly involve some combinations of adsorption and filtration. A variety of materials, ranging from the natural sand and zeolite to the synthetic adsorbents and ion exchanges, have been used to remove arsenic from drinking water (Baskan and Pala, 2011; Kanel et al., 2005; Mohan and Pittman, 2007; Oehmen et al., 2011). Some of recent examples include the use of activated carbons, activated alumina, ion exchange resins, modified or synthetic carbons, clay minerals, sand, biomaterials, natural/synthetic oxides, and nanomaterials (Bessaies et al., 2020; Guo et al., 2019; Jacobson and Fan, 2019; Jung et al., 2018; Nieto-Delgado et al., 2019; Qiu et al., 2019; Sha et al., 2020; Song et al., 2019; Uppal et al., 2019b; Xie et al.,

2020). There has been much recent effort devoted to exploring the removal of arsenic using metal-organic frameworks (MOFs) as highly efficient adsorbents (Sun et al., 2019; Wang et al., 2015, 2019; Zhang et al., 2019a, 2019b; Zhu et al., 2012).

2.   Use of metal-organic framework (MOF) materials to remove arsenic from water

A relatively new class of porous materials, MOFs are built from metal ions or clusters and organic linkers (Li et al., 1999; Cavka et al., 2008; Zhou et al., 2012). MOF materials typically have high porosities, large surface areas, designable functional architectures, high chemical stability, and good regeneration ability (Eddaoudi et al., 2002; Furukawa et al., 2013). Because of these useful features, MOFs have been successfully tested for many potential applications, such as drug delivery, gas storage, catalysis, and capture of organic and inorganic compounds (Eddaoudi et al., 2002; Kreno et al., 2012; Horcajada et al., 2010; Lee et al., 2009; Lv et al., 2019; Rowsell and Yaghi, 2005; Wang and Astruc, 2020; Zhou et al., 2012).

Representative types of MOFs used for removing arsenic are summarized in Table 1. The removal efficiency of arsenic species using MOFs depends on the specific surface area, pore size, adsorption capacity, and the framework structure. The surface area and adsorption capacity of these MOF materials are generally higher than those of traditional adsorbents, such as those mentioned above.

3.   Synthesis and performance of polymetallic MOF adsorbent

A common approach of synthesizing MOFs is referred to as the solvothermal method. It typically includes heating a mixture containing a solvent (e.g., N,N-dimethylformamide, DMF), organic linkers, and inorganic salt of the chosen metals (Yu et al., 2019; Zhou et al., 2012). A modification to this method includes the addition of a modulator ligand that can compete with the linker for the coordination sites of metal ion(s). Such ligands are referred to as modulators, which promote crystal growth and increase material stability (Prabhu et al.,

Table 1 – Representative MOFs adsorbents explored for the removal of arsenic from water.

MOFs	Framework (Metal ions and linkers)	Specific surface area (m^2/g)	Adsorption capacity (mg/g)	Arsenic species	Reference
ZIF-8	Zinc ions and 2-methylimidazole linkers	1388	76	As^V	Li et al. (2014)
Zr-MOF (UiO-66)	$Zr_6O_4(OH)_4$ clusters and terephthalate linkers	569	303	As^V	Wang et al. (2015) He et al. (2017)
MIL-53(Fe)	Iron ions and terephthalate linkers	920	21	As^V	Vu et al. (2015)
Fe-BTC	Iron ions and 1,3,5-benzenetricarboxylic (BTC) linkers	-	12	As^V	Zhu et al. (2012)
MOF-76(Y)-Ac	Yttrium ions and BTC linkers; sodium acetate modulated	980	201	As^V	Li et al. (2020)
MIL-101 (Fe)	Iron ions and 1,4-benzenedicarboxylic acid (BDC) linkers	1172	232	As^V	Li et al. (2019)
HCl-UiO-66(SH)$_2$	$Zr_6O_4(OH)_4$ clusters thiol-containing BDC linkers; HCl modulated	1150	40	As^{III}	Audu et al. (2016)
Fe$_3$O$_4$@ZIF-8	Zinc ions and 2-methylimidazole linkers, core-shell structures	1133	100	As^{III}	Huo et al. (2018)
FeMn-MOF-74	Fe/Mn=~2 and 2,5-dihydroxyterephthalic acid (H$_4$DHTA) linkers	45	161	As^{III}	Zhang et al. (2019b)
UiO-66(NH$_2$)	$Zr_6O_4(OH)_4$ clusters and NH$_2$ group-containing terephthalate linkers	113	36/22	As^V & As^{III}	He et al. (2019)
Fe-MIL-88B @PGC20%	Iron ions and terephthalate linkers, covered with porous graphitic carbon (PGC) structure	134	212/321	As^V & As^{III}	Pandi et al. (2020)
Zn-MOF-74	Zinc ions and H$_4$DHTA linkers	604	325/211	As^V & As^{III}	Yu et al. (2019)
MIL-100(Fe)	Iron ions and 1,3,5-benzenetricarboxylic acid (H$_3$BTC) linkers	657	192/162	As^V & As^{III}	Polychompoo et al. (2020)
CoFe$_2$O$_4$@MIL-100(Fe)	Iron ions and H$_3$BTC linkers (core-shell structure)	292	114/143	As^V & As^{III}	Yang and Yin (2017)
Fe$_2$Co$_1$ MOF-74	Fe/Co=2 and terephthalate linkers	148	267/292	As^V & As^{III}	Sun et al. (2019)

ZIF= Zeolitic Imidazolate Framework; MIL= Materials of Institute Lavoisier; UiO=University of Oslo.

2019). Modulators also facilitate the formation of coordinative unsaturation of metal sites available for As^V adsorption. Audu et al. (2016) reported significant increases in capture of As^{III} by incorporating thiol (-SH) containing linkers. This approach is based on the strong affinity of As^{III} to thiol groups (Shen et al., 2013). Another recent modification is combining salts of different metals in order to obtain bimetallic or polymetallic MOF adsorbents. Combination of multiple metals into a MOF material may enable synergetic effects and increase the efficiency of arsenic removal (Gu et al., 2019; Sun et al., 2019).

Recently, Sun et al. (2019) showed promising results of removing arsenic from tap water, river water, and lake water samples using synthetic polymetallic MOF adsorbents (Fig. 1). They synthesized the Fe/Co MOF using a simple one-pot reaction by mixing solvents (DMF, methanol, water), an organic ligand (terephthalic acid), and metal sources (iron and cobalt inorganic salts) under magnetic stirring and subsequent heating at 120 °C in an autoclave for 24 h.

On the basis of previous reports showing effects of the metal ratio on the adsorbing efficiency of MOFs, Sun et al. (2019) tested five ratios of Fe to Co in their synthetic procedures. They found that the highest adsorption capacity for both As^{III} and As^V was achieved at the Fe:Co ratio of 2:1, which was associated with the highest MOF specific surface area at this Fe:Co ratio.

The high specific surface area of the Fe$_2$Co$_1$ MOF-74 material (148 m^2/g) in combination with a wide pore size distribution provided the availability of active adsorption sites on the particle and favored transport kinetics of arsenate and arsenite in the pores. The key active adsorption sites were revealed by X-ray photoelectron spectroscopy (XPS) and FT-IR analysis to be C-OH, M-O and M-OH. Resulting maximum adsorption capacities reached 267 mg/g and 292 mg/g for As^{III} and As^V, respectively, which are among the highest reported to date for arsenic removal using MOFs (Haldar et al., 2020).

Sun et al. (2019) showed that Fe$_2$Co$_1$ MOF-74 was capable of removing more than 80% of arsenic after 1 hour of contact time under high initial arsenic concentration of 2 mg/L. However, adsorption rate declined after the first hour. As a consequence, 12 hours in total were needed to reach 90% of arsenic removal.

Fe$_2$Co$_1$ MOF-74 possessed high sorption capacities to remove As^{III} and As^V in the pH range of 3-7. Sorption behaviors of As^{III} and As^V followed different trends with changes of pH, which was attributed to the effect of pH on the surface charge of the adsorbent and the deprotonation of arsenic species (Fig. 2). Interestingly, similar tendencies followed by pH change were reported for the removal of
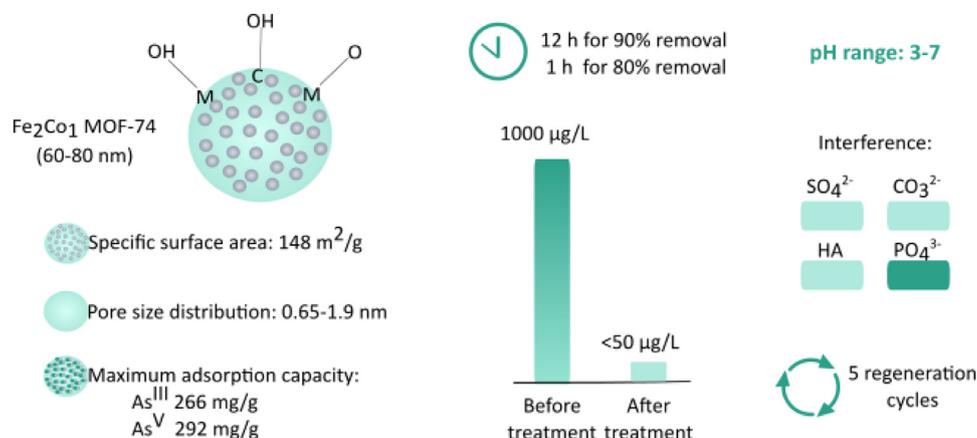
Fig. 1 – A summary of the characteristics of Fe_2Co_1 MOF-74 relevant to the adsorption of As^{III} and As^V in water. Data are based on the report of Sun et al. (2019).
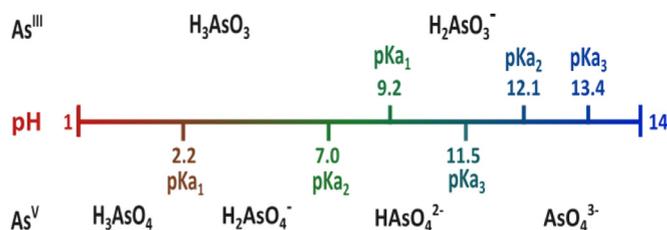

Fig. 2 – The predominant chemical species of inorganic As^{III} (top) and As^V (bottom) under different pH conditions. The pK_a values were obtained from Reid et al. (2020).

Sb^{III} and Sb^V using another Fe based MOF (Zhang et al., 2019b).

Sun et al. (2019) tested the performance of Fe_2Co_1 MOF-74 in the presence of common natural water components. Sulfate (SO_4^{2-} and HSO_4^-), carbonate (CO_3^{2-} and HCO_3^-) and humic acid (representing organic matter) had minimum effect on the removal of arsenic using Fe_2Co_1 MOF-74. However, phosphate ($H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}) caused a significant interference, lowering the removal efficiency from about 80% (no phosphate) to about 20% (10 mmol/L phosphate). Phosphate interference is commonly observed in studies of arsenic removal due to chemical similarities between arsenate and phosphate. However, the concentrations of phosphate in natural waters are usually lower than the concentration of phosphate that causes interference.

Sun et al. (2019) further assessed the performance of Fe_2Co_1 MOF-74 for adsorbing arsenic in deionized water and three types of real water samples (tap water, lake and river water). All the samples were spiked with 1 mg/L of As^{III} and As^V to achieve similar initial arsenic concentrations. Capture of arsenic by Fe_2Co_1 MOF-74 resulted in a reduction of arsenic concentrations to lower than 50 µg/L in all the water samples. Overall, the performance of ar-

senic removal from the three real water samples did not differ significantly from deionized water.

Sun et al. (2019) demonstrated that the Fe_2Co_1 MOF-74 adsorbent was of high durability and could be regenerated and reused for 5 times without significant loss in the ability of removing arsenic. The efficiency of arsenic removal decreased by less than 10% for both As^{III} and As^V, after reuse of the fifth time regenerated Fe_2Co_1 MOF-74 adsorbent.

4. Factors influencing the efficiency of arsenic removal

Removal of arsenic species from water using MOFs depends on various adsorption mechanisms on the specific MOF materials. Generally, the hydroxyl groups in MOFs is vital for arsenic coordination, leading to the formation of M-O-As (M: metal) bonds. Additional functional groups, such as thiols (–SH), improve adsorption capacity by capturing As^{III} with thiolated organic linkers and capturing As^V oxyanions at the hydroxylated node of MOF (Audu et al., 2016). Alternatively, As^{III} can be oxidized to As^V and subsequently captured by MOF materials (Zhang et al. 2019b). In addition, various mechanisms of arsenic interaction with MOFs, including donor-

acceptor interaction, electrostatic attraction, acid-base interaction, size-exclusion, hydrophobic interaction, breathing effect, and unsaturated sites, can influence adsorption behaviours of arsenic species on MOFs (Lv et al. 2019).

One of the major factors influencing the efficiency of arsenic removal is pH of the solution. pH affects the surface charge of MOFs and the degree of deprotonation of arsenate (As^V) and arsenite (As^{III}) simultaneously. Speciation of arsenate (As^V) and arsenite (As^{III}) in water is governed by their pK_a values and pH conditions (Fig. 2), whereas surface charge of MOFs depends on acid/base properties of the functional groups. The overall surface charge of adsorbents can be represented by zeta potential. MOF materials that can maintain positive surface charges at pH above 2.2 are useful for the removal of As^V and at pH above 9.2 are beneficial for the capture of both As^V and As^{III} species. For example, both Zr- and Y-based MOFs were shown to have an increase of arsenic removal efficiency at alkaline pH but a decrease of efficiency at pH>11 (He et al., 2019; Li et al., 2020). Removal of As^V was achieved in the pH range of 3-11 using MIL-101(Fe) (Li et al., 2019). These results suggest the complicated effects of pH on the speciation of arsenic and surface properties of MOFs, resulting in the overall effect on the adsorption processes.

On the removal of As^{III} species, reported effects of pH include: (1) low efficiency at highly acidic pH due to inactivation of surface OH groups caused by protonation (Sun et al., 2019); (2) low adsorption efficiency at pH lower than 9 as As^{III} exists mainly in the neutral form and has no electrostatic interaction with the adsorbent (He et al., 2019); (3) low adsorption at highly alkaline pH related to the decrease of electrostatic attraction (He et al., 2019; Sun et al., 2019); and (4) enhanced adsorption for Fe-based adsorbent with lower pH point of zero charge (Yang and Yin, 2017). Notably, Yang and Yin (2017) demonstrated high arsenic removal efficiencies using $CoFe_2O_4$@MIL-100(Fe) composite, with efficiencies close to 100% for both As^{III} and As^V over a pH range from 2 to 12. This high removal efficiency was attributed to the abundant OH groups and the lower pH point of zero charge achieved via combination of $CoFe_2O_4$ and MIL-100(Fe).

Effects of the co-existing ions have been shown to differ depending on their ability to form inner sphere or outer sphere complexes as well as on the type of interactions between the adsorbent and electrolytes of interest. Inert electrolytes generally form outer sphere complexes and do not influence adsorption as long as arsenic removal is based on the formation of inner sphere complexes (Li et al., 2019). Among the ions commonly found in drinking water, SO_4^{2-}, NO_3^- and Cl^- were generally reported to have only a slight effect on the adsorption process (Atallah et al., 2018; Georgiou et al., 2020; Yu et al., 2019). In contrast, ions capable of forming inner-sphere complexes can significantly inhibit arsenic adsorption. A typical example is phosphate, which acts as a competitor with arsenate and presents strong interference due to its chemical similarity with arsenate anion (Yu et al., 2019; Ploychompoo et al., 2020). Notably, Yang and Yin (2017) combined mesoporous nanoparticles with Fe-based MOF MIL-100(Fe), resulting in core-shell $CoFe_2O_4$@MIL-100(Fe) adsorbent, and showed minimum interference from phosphate, sulfate, carbon-

ate, and silicate anions. Results of good performance were attributed to size exclusion effect and the repulsion between anions and negatively charged MIL-100(Fe) shell while for arsenic anions adsorption was induced by inner-sphere complexes formation (Yang and Yin, 2017). Interestingly, other reports of using different MOFs showed that carbonate ion either decreased (Huo et al., 2018) or enhanced arsenic removal efficiency (Atallah et al., 2018).

Ionic strength may vary considerably between water samples as it depends on the concentration and type of ions present in the water. Change of ionic strength is expected to affect predominantly non-specific adsorption, which is driven by electrostatic interactions (Rencou et al., 2009; Yang and Yin, 2017).

Natural organic matter (NOM) commonly present in environmental water could affect the adsorption of As^{III} and As^V by competing for the sorption sites (Redman et al., 2002). Humic acid (HA) at high concentrations was found to moderately decrease adsorption of arsenic onto MIL-100(Fe) (Wang et al., 2018). In the study of Li et al. (2020) both humic acid and fulvic acid had little effect on the efficiency of As^V adsorption on the yttrium-based MOF adsorbent.

Because the adsorption efficiency of As^{III} is lower than that for As^V, researchers have explored oxidation of As^{III} to increase overall efficiency of arsenic removal. Wang et al. (2018) tested the effect of elevated oxygen concentrations and the applied voltage on the efficiency of removing arsenic using MIL-100(Fe). They found that supplying additional oxygen in the system increased the efficiency of As^{III} removal. When combined with a voltage to induce Joule heating, the enhanced As^{III} oxidation kinetics resulted in a 100% overall efficiency of arsenic removal. Effect of increased temperature showed decreased adsorption efficiency for both As^{III} and As^V (He et al., 2019). Birnessite (δ-MnO_2) coating was also used to enhance oxidation of As^{III}, resulting in improved removal of arsenic from water (Ploychompoo et. al., 2020).

5. Concluding remarks and future perspectives

A number of MOF materials have been synthesized and tested for the removal of arsenic species from water. Some of the recent improvements in the design and synthesis of MOFs include the use of new modulators, incorporation of linkers with functional groups capable of enhancing adsorption, adjusting the pore size, developing bi- and poly-metallic MOFs, and constructing hybrid materials.

One of the major advantages of MOFs is their significantly higher adsorption capacity for arsenic species than that of traditional adsorbents. However, a number of studies have reported dramatic decrease in adsorption efficiency caused by changes in pH and the presence of interfering substances. Thus, development of MOF materials with ability to maintain high adsorption efficiency over a wide range of conditions is an area of active research. Promising results have been achieved by combining magnetic nanoparticles with Fe-based MOF into hybrid core-shell $CoFe_2O_4$@MIL-100(Fe) adsorbent, which could maintain efficiencies of higher than 90% for removing both As^{III}

and As^V over a pH range from 2 to 12 (Yang and Yin, 2017). Increases of arsenic removal efficiency have also been demonstrated after incorporation of reduced graphene oxide support into MOFs (Ploychompoo et al., 2020).

A lack of knowledge about potential toxicity of MOFs is an important challenge on the way to broad applications of MOFs. Previous studies have shown that toxicity of MOF nanoparticles can range from low to highly toxic (Ruyra et al., 2015). Observed toxicity was mainly attributed to the leaching of metal ions from MOFs. Releasing of metal ions and linker molecules from some MOFs has also been suggested as a possible cause of toxic effects (Kumar et al., 2019). Therefore, metal ions, linkers, modulators, and solvents used during synthesis must be considered. The reagents could be trapped inside the pores of MOFs during synthesis and potentially be released into water.

Substitution of toxic organic solvents, e.g., DMF and methanol used for the synthesis of Fe$_2$Co$_1$ MOF-74, with environmentally friendly alternatives would advance applications of MOFs. Non-solvent or aqueous methods of synthesis of MOFs minimize toxicological and environmental concerns (Kumar et al., 2019; Lin et al., 2011; Stassen et al., 2016). Huo et al. (2018) have described successful attempts to replace DMF with ethanol for the synthesis of MIL-88B. Successful green synthesis in water was developed for producing MOF-74, MOF-5 and X-MIL-53-(Al) (Sánchez-Sánchez et al., 2014). A recent report described an environmentally friendly method of synthesis for MIL-100(Fe) bacterial cellulose composite where the only organic solvent used was acetone during a washing step (Ashour et al., 2020). There remains great potential for arsenic removal using new MOFs produced by green synthesis.

Further research is needed to scale up the synthesis and production of cost-effective MOF materials that offer high efficiency and capacity as well as rapid kinetic of arsenic removal. It is necessary to test the removal of arsenic from diverse water samples, with different concentrations of arsenic species, pH conditions, ionic strength, and co-existing ions and natural organic matter. The ultimate goal should be complete removal of arsenic from drinking water, or with residual arsenic concentrations below the WHO guideline level of 10 μg/L.

Tetiana Davydiuk**, Xiaojian Chen**
Department of Chemistry, University of Alberta, Alberta T6G 2G3, Canada

Lijin Huang*, Qin Shuai
Faculty of Material Science and Chemistry, China University of Geosciences, Wuhan 430074, China

X. Chris Le*
Department of Chemistry, University of Alberta, Alberta T6G 2G3, Canada
Department of Laboratory Medicine and Pathology, University of Alberta, Edmonton, Alberta T6G 2G3, Canada

*Corresponding authors at: Department of Laboratory Medicine and Pathology, University of Alberta, Edmonton, Alberta T6G 2G3, Canada.
E-mails: huanglj@cug.edu.cn (L. Huang), xc.le@ualberta.ca (X.C. Le)
** These authors contributed equally.

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