Review

Sustainable Application of ZIF-8 for Heavy-Metal Removal in Aqueous Solutions

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Abstract: Water is life, and clean-water demand is increasing daily as a result of rapid population growth and industrial evolution. Nevertheless, due to the inadequate supply and availability of new water sources, there is a need for effective, sustainable removal of contaminants for wastewater reuse. Several treatment approaches that include chemical, physical, and biological methods have been thoroughly tested, with biological treatment being regarded as the most cost-effective and environmentally friendly method. However, the presence of heavy metals and complicated chemicals that are nonbiodegradable limits the use of this cost-effective approach. In this paper, we review the sustainable application of a cheap, water-stable metal-organic framework, the zeolitic imidazolate framework (ZIF-8), with an easier synthesis approach for heavy-metal removal in aqueous solutions. In this review, we discuss the removal efficiency in terms of adsorption capacity, describe the underlying mechanism behind the adsorption capacity of ZIF-8, present a sustainable synthesis approach, and make vital suggestions to aid in the future application of ZIF-8 for the removal of heavy metals.

Keywords: zeolitic imidazolate framework; heavy metals; sustainable

1. Introduction

With the rapid increase in industrial activities, the disposal of industrial wastewater and municipal waste has become one of the mounting environmental issues worldwide for global public health [1,2]. Many industries, including electroplating, mining, battery-manufacturing, metallurgy, tannery, and metal furnishing, release effluents containing relatively large amounts of heavy metals such as copper, cadmium, nickel, mercury, lead, etc. Untreated sewage from these industries harms the environment and human health. Unlike organic contaminants, heavy-metal ions are nonbiodegradable and pose an extreme health risk when they enter the human food chain [3,4]. These metals cause multiple-organ damage, induce congenital defects, learning frailties, and are carcinogenic. These risks make the prevalence of heavy-metal ions in wastewater a significant global concern [5]. According to the World Health Organization (WHO), an estimated 1 billion people (approximately 1/7 of the world's population) do not have access to clean drinking water, a crisis that is anticipated to become worse with industrial processes increasing human exposure to these toxic materials [6–8].

Nevertheless, to ensure that environmental and human well-being is congruent with Sustainable Development Goals (SDGs) 3 and 6, we must find new remediation solutions that are cheap, environmentally friendly, and energy-efficient to remove trace contaminants

from water [8,9]. Commercial methods of heavy-metal remediation, such as chemical precipitation, sorbents, electrodialysis, photocatalysis, bio-electrochemical systems [BES] and membranes, have been found to have many disadvantages, including high economic and energy costs, low efficiency of removal, difficult regeneration and frequent fouling, as well as producing large quantities of chemical-sludge [4,7,10].

Several researchers have recently sought to address this environmental crisis in a more economically efficient and environmentally friendly way with materials called metal-organic frameworks (MOFs). Sun et al. [9] described MOFs as a network of metal nodes with an organic chemical 'strut' intended to extract things like water and gases from air or pollutants from aqueous solutions [9]. In addition to the wide surface area, chemical tunability, and adsorption capabilities of MOFs, this ability makes them a capable material to selectively remove heavy metals from water. They have been shown to be a promising material for overcoming the aforementioned drawbacks associated with commercial treatment processes [11]. In this study, we specifically review the use of the zeolitic imidazolate framework (ZIF-8), a type of MOF used for heavy-metal removal in aqueous solutions, as well as its application, adsorption mechanisms, and the factors that influence its adsorption mechanism. In addition, the prospects of ZIF-8 are discussed to aid researchers.

2. Metal-Organic Frameworks

Yaghi first introduced the term metal-organic framework [MOF] in 1995, when he developed a copper MOF with a layered structure using hydrothermal synthesis [12]. According to Yu et al. [13], MOFs became a research focus after Hoskins and Robson published their paper around 1990, anticipating the formation of a wide range of microporous, stable, crystalline solids with the potential to have catalytic, gas-sorption, and ion-exchange properties, and the prospect of postsynthetic modification by incorporating functional groups [13–15]. Metal-organic frameworks are porous coordination polymers that are highly ordered and crystalline. MOFs are hybrid materials formed by the union of organic ligands [linkers] and metal clusters [15]. These ligands are organic structures that comprise tricarboxylic acids, pyridyls groups, and imidazole [14]. This union of organic-metallic clusters offers many possible amalgamations of organic compounds and metals to form particles of various textural and chemical properties, which are typically very porous and versatile [14,16].

Unlike traditional porous materials, the crystalline nature of MOFs with their ultra-high porosity and high internal-surface-area characteristics, together with an extraordinary degree of organic and inorganic compositions, makes MOFs attractive for application in several fields such as membranes, catalysis, gas capture and storage, adsorption and energy, etc. [14,17]. There are different families of MOFs (Figure 1), and the distinction between families is based on the metal nodes or the organic linkers used in their synthesis. However, the prerequisite for using any MOF for contaminant removal in aqueous solutions is their water stability [18]. The ZIF-8 subcategory of MOFs is seen to exemplify this quality [19].

Zeolitic Imidazolate Framework [ZIF-8]

The zeolitic imidazolate framework (ZIF) is a subcategory of metal-organic frameworks with topologies and structures that are analogous to aluminosilicate zeolites [20]. Therefore, ZIFs combine the advantages of both MOFs and natural zeolite. They consist of tetrahedral cations as metal clusters and imidazole ligands as binding agents that emulate the role of oxygen and silicon in natural zeolite structures [13,21]. As a subcategory of metal-organic frameworks, ZIFs are often configured with cobalt (Co^{2+}) or zinc (Zn^{2+}) as the metal clusters (ions) and imidazole-derived ligands, which are all comparatively inexpensive [22,23]. Subsequently, the strong 145° bond angle between metal ions and imidazolates of ZIFs was shown to be comparable to that between silicon and oxygen molecules in natural zeolite [20,21]. Hence, they often possess isomorphic structures like zeolite, with a relatively strong and long bonding [22,24]. Therefore, like traditional ze-

olites, high surface areas, cage-like structures, and thermal, mechanical, and chemical stability are well represented within this class of materials [25,26]. Due to their unique properties consisting of ultrahigh porosity, hydrophobicity, satisfactory thermo-chemical stability, and easy synthesis, ZIF-8 MOF nanoparticles are great candidate materials for adsorption applications [20,27]. According to Cravillon et al. [25] and Yu et al. [13], the group of zeolitic imidazolate frameworks called ZIF-8 features large pore sizes, i.e., 11.6 Å, and the desired aperture size of 3.4 Å. In addition, it is known for its outstanding chemical, mechanical, and thermal stability due to the strong bond interaction between zinc(II) ions and 2-methylimidazolates, which are not very well represented in other classes of MOFs [22,28,29]. In a study conducted by Park et al. [19] to determine the chemical and thermal stability of ZIFs, twelve species were examined. The ZIF-8 species was found to possess exceptionally high thermochemical stability, with the largest surface area of 1947 m^2/g. Their experiment revealed that ZIF-8 and ZIF-11 were the only species that sustained their structures in water for seven days at a temperature of 50 °C [19]. However, after seven days, ZIF-8 was the only material found to have maintained its original structure in boiling water, while the ZIF-11 structure was transformed into another material after three days. Furthermore, ZIF-8 was also stable at 100 °C for up to 24 h in 0.1 and 8 M aqueous sodium hydroxide [19]. Wu et al. [30] also compared the removal capacity of arsenate (As(V)) to activated carbon, zeolite, and ZIF-8. ZIF-8 removed 90.92 mg/g of As(V) compared to 3 mgg^{-1} and 13.92 mgg^{-1} for active carbon and zeolite, respectively [30]. Similarly, Jie Li et al. [31] decorated polypyrrole (PPy) with ZIF-8 for the removal of uranium from wastewater. They obtained an adsorption capacity of 534mg^{-1}, which was higher than those of the other MOFs included in their study [31]. These examples demonstrate the remarkable resistance and removal effectiveness of ZIF-8 compared to other MOFs and other adsorbents. Researchers have investigated and extensively explored the use of ZIF-8 in catalysis, gas storage, membrane separations, and CO_2 sequestration because of its remarkably resilient framework. However, recently, more and more attention is being focused on the exploration of ZIF-8 for the removal of hazardous material from wastewater. This is largely due to factors such as ease of synthesis, the use of common materials, room-temperature reaction conditions, adsorption capability, and a relatively wide surface area [32]. The use of ZIF-8 in contaminant removal, especially heavy metals from wastewater, is a growing field of research [33]. This review focuses on the heavy metal removal efficiency, removal mechanisms, and limitations of ZIF-8, and provides an outlook for the potential application of ZIF-8 in the removal of heavy metals from wastewater. The common ZIF-8 synthesis methods are discussed in Table 1 below.
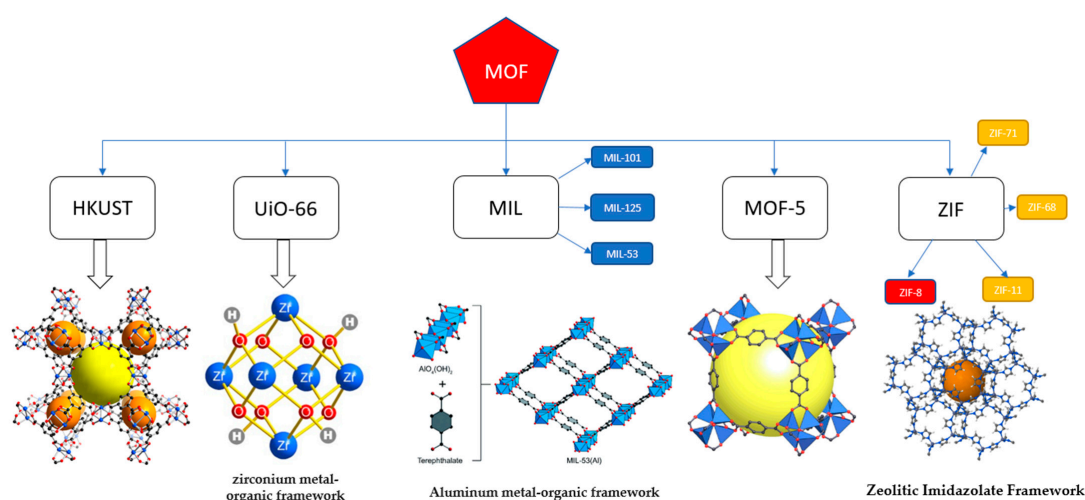

Figure 1. Schematic representation of varying classes of widely-used MOFs. MOF (metal organic framework); HKUST (hongkong university of science and technology); UiO-66 (Universitetet I Oslo); MIL (Matériaux de l'Institut Lavoisier); ZIF (zeolitic imidazolate framework).

Table 1. Different heavy metals and their adsorption capacity by zeolitic imidazolate framework (ZIF-8).

Metal	Surface Area of ZIF-8 [BET] m^2/g	Adsorption Capacity ($mg\ g^{-1}$)	Metal Ion Source	Adsorption Equilibrium Time (Mins)	Optimal pH	Reference
Copper (Cu^{2+})	1340	800	$Cu(NO3)_2$	30	4	[2]
	1065	224.3	$CuCl_2.2H_2O$	20		[32]
	1370	454.72	$Cu(NO_3) \cdot 3H_2O$	120	5.2 ± 0.2	[34]
	1072	1191.67	$Cu(CH_3COO)_2$	–	6	[35]
Arsenic [As (III)]	1063.5	49.49	$NaAsO_2$	780	7	[36]
		151.34	$NaAsO_2$			[37]
Arsenate [As(V)]	1063.5	60.03	$Na_3AsO_4 \cdot 12H_2O$	420	7	[36]
	1167	90.92	$Na_2HAsO_4 \cdot 7H_2O$	–	7	[30]
		197.26	$Na_3AsO_4.12H_2O$			[37]
Nickle (Ni^{2+})	1065	52.8	$NiCl_2 \cdot 6H_2O$	20	–	[32]
Cobalt (Co^{2+})	1065	33	$CoCl_2 \cdot 6H_2O$	20	–	[32]
Cadmium (Cd^{2+})	1065	77.56	$CdCl_2$	20	–	[32]
Lead (Pb^{2+})	1370	1119.80	$Pb(NO_3)_2$	120	5.1 ± 0.4	[34]
Chromium (VI)	719	2.34	$K_2Cr_2O_7$	80	7	[38]
	1072	43	$K_2Cr_2O_7$	–	6	[35]
Uranium	1300	534	$UO_2(NO_3)_2 \cdot 6H_2O$	90	3.5	[31]

3. ZIF-8 Synthesis Methods

UPTOHERE It is recognized and established that the parameters and conditions of synthesis have a major influence on the physicochemical properties of ZIF-8 [23]. Aside from alternative synthesis routes, such as sonochemical (which uses ultrasound radiations), mechanochemical, and microwave-assisted synthesis, there are two traditional approaches to ZIF-8 synthesis: the solvothermal method and room-temperature synthesis [15,18]. The solvothermal process is a well-recognized method for MOFs. In ZIF-8 synthesis, it involves the reactions of hydrated metal salt ($Zn(NO_3)_2 \cdot 6H_2O$) and an imidazole-type ligand (2-Methylimidazole) in an amide solvent such as methanol (CH_3OH) or N,N-dimethylformamide (DMF), placed in a closed and tight container at an autogenous pressure (often autoclaved) above the boiling point of the solvent, i.e., at 80–150 °C [18,24]. Under these conditions, amines resulting from the thermal degradation of the solvent causes deprotonation of the connecting imidazole1H (ImH). Usually, when cooled, moderate to high yields (50–90% yield) of ZIF-8 crystals are obtained. In 2006, Yaghi et al. reported the first ZIF-8 synthesis using the solvothermal method [15,19]. Several researchers have used the solvothermal method to produce a pure-phase, water-stable ZIF-8. However, when using this method, essential reaction parameters like concentration temperature, reaction volume, and time are crucial synthesis conditions that need to be controlled. When these parameters are left uncontrolled, it may lead to structural defects and the degradation of the resultant ZIF [24]. The influence of synthesis conditions on the development of ZIF-8 under the microwave-assisted solvothermal method was assessed by a study conducted by Lai et al. [29]. At various temperatures, ranging from 80 °C to 140 °C, they synthesized a series of ZIF-8 particles. Using scanning-electron microscopy (SEM) for a surface-morphology analysis of their resulting ZIF-8 samples, their findings showed that ZIF-8 formation can be largely affected by solvent expansion at higher temperatures and pressure [29]. Therefore, while the solvothermal approach has many advantages, time and temperature have to be strictly monitored. The temperature change, for instance, can affect the morphology of the particles, and the extension of the reaction time can lead to ZIF degradation [18].

However, because of the stringent conditions required and the intense heating of toxic, polar aprotic solvents at high temperature and pressure, which can pose dangerous health risks and other concerns, such as waste generation, high-energy demand, and safety problems, other, greener synthesis alternatives have been explored that are nonsolvothermal or room temperature. The room-temperature synthesis (RTS) of ZIF-8 in an aqueous solution has also been confirmed to be relatively sustainable [26,34]. Cravillon et al. [25] conducted RTS and further characterization of the resultant ZIF-8 by using zinc nitrate hexahydrate $(Zn(NO_3)_2 \cdot 6H_2O)$, 2-methylimidazole (Hmin), and methanol (CH_3OH) in a molar ratio of approximately 1:8:700 [25]. The characterization of the resultant ZIF-8 samples yielded a pure, well-shaped, stabilized ZIF-8 nanocrystal without any auxiliary stabilizing agents or activation (conventional heating, microwave, or ultrasound irradiation). This is shown to be more favorable than the solvothermal method in terms of energy usage, reaction time, and safety [14]. A comparative study by Malekmohammadi et al. [23] was carried out for ZIF-8 synthesis in methanolic and aqueous solutions. In their investigation, the influence of synthesis parameters on the crystallinity and textual characteristics of the resulting products was also evaluated. The outcome of their study was confirmed by Cravillon et al. [25], who found that the sort of solvent used, crystallization temperature, and content of the linker (molar ratio) significantly influence the phase purity of the synthesized ZIF. They obtained the highest yield of ZIF-8, at 97%, from a water solution as a solvent and at a room temperature of 25 °C (nonsolvothermal), which was even higher than the solvothermal method at 130 °C [25]. Therefore, for a stable formation of a pure-phase crystalline structure and the textual properties needed for practical application in contaminant removal, synthesis processes and conditions that are easy, economical, and environmentally friendly, with a high percent yield of ZIF-8, are essential to consider [39].

4. ZIF-8 Heavy-Metal Removal Mechanism

There is growing attention to the sustainable removal of heavy metals from aqueous solutions. Several technologies have been employed to ensure that heavy-metal concentrations in wastewater are lowered to meet the standards of the Environmental Protection Agency (EPA) [40]. Recently, the use of MOFs, especially ZIF-8, has caught the attention of most scientists because of its unique characteristics, such as the high surface area, high adsorption capacity, thermochemical stability, hydrophobicity, and sustainable room-temperature synthesis [41]. The primary mechanism underlying ZIF-8 efficiency in heavy-metal removal is its high adsorption capacity. Adsorption in wastewater treatment is a chemical or physical process that involves the accumulation of a compound (contaminant) at the surface of an adsorbent during a natural interaction between the adsorbate and the adsorbents [42]. In heavy-metal removal, the chemical and hydrothermal stability, and adsorption capacity of the adsorbent are crucial for optimal removal. The adsorption capacity and removal efficiency (%) of ZIF-8, like any other adsorbent, is usually determined by:

Adsorption Capacity

$$Q_\epsilon = \frac{(C_0 - C_e) \times v}{m} \tag{1}$$

Removal Efficiency

$$R_E = \frac{C_i - C_f}{C_i} \times 100\% \tag{2}$$

From Equation (1), C_0 is the initial concentration, C_e is the equilibrium concentration for the adsorbate in solution, v equals the volume of solution, m is the mass (mg) of the adsorbent, and Q_e is the equilibrium adsorption value, used to determine the adsorption capacity of the adsorbent [27]. From equation (2), C_i (mg/l) in the determination of removal efficiency is the initial concentration and C_f (mg/l) is the final concentration of metal ions in the treated effluent [27,38]. The efficiency of the adsorbent is typically described using adsorption-equilibrium isotherms as well as kinetic models. Whereas kinetic models, such as pseudo-first-order and pseudo-second-order kinetics, describe the adsorption rate, adsorption isotherms such as Freundlich and Langmuir isotherms

describe the amount of material adsorbed per unit mass of adsorbent as a function of the equilibrium concentration [32,39,43]. In an experiment conducted by Zhang et al. (2016) to assess the ZIF-8 adsorption mechanism and the removal efficiency of copper ions (Cu^{2+}) from aqueous solutions an unexpectedly high adsorption capacity of Cu^{2+} [800 mg/g] with fast kinetics at an adsorption time of less than 30 min was revealed, obtaining a removal efficiency of 97.2% [2]. The exceptional adsorption capacity of ZIF-8 is underpinned by adsorption mechanisms such as ion-exchange, coordination reaction, surface chemistry, and hydrophobic interactions as diagrammatically expressed in Figure 2 [33,36]. By comparing Fourier Transform Infra-Red (FTIR) spectra and X-Ray Photoelectron Spectroscopy (XPS) before and after adsorption, Zhang et al. [2] attributed the high Cu^{2+} adsorption of ZIF-8 to the strong coordination reaction and ion exchange between the nitrogen atoms on the Cu^{2+} surface of the ZIF connectors [2]. Liu et al. [20] also conducted a study using ZIF-8 for the removal of arsenite (As(III)) and arsenate (As(V)) in aqueous systems. They obtained a maximum adsorption capacity (Q_{max}) of 60 mg/g and 49 mg/g for As(III) and As(V), respectively, which was significantly higher than other adsorbents like iron chitosan flakes, iron-coated zeolite, CuO nanoparticles, etc. compared in their study [40,41]. Zhao et al. [32] also conducted an experiment assessing the removal of four binary heavy metal ions (Cu^{2+}, Ni^{2+}, Co^{2+}, and Cd^{2+}) from aqueous solutions by adsorption onto ZIF-8 nanocrystals. In their study, they used ZIF-8 both as bare nanocrystals and in the formation of a nanocomposite membrane to remove binary heavy metals. In both experiments, although ZIF-8 showed a distinctive selectivity towards Cu^{2+}, the adsorption capacity of ZIF-8 in the removal of these binary heavy metals was exceptionally high [32]. Begum et al. [38] also used ZIF-8 as a nanocomposite membrane with magnesium hydroxide ($Mg(OH)_2$), graphene oxide, and amine groups for Cr(VI). They obtained a maximum removal efficiency of 98% of Cr(VI) at an adsorption equilibrium of 4.88 mg g^{-1} [38].

In many cases, there will be more than one mechanism responsible for the high adsorptive capabilities of ZIF, such as diffusion, hydrogen bonding, and electrostatic interactions [2,44–46]. In a study by Begum et al. [38], the surface of ZIF-8 was positively charged because =N−, −NH− and −NH_2 groups of imidazolate ligands were protonated in an aqueous system, which provided an electrostatic interaction for Cr(VI) for adsorption. The bonding of hydroxyl groups to zinc and the presence of GO and Mg $(OH)_2$ also strengthened interactions with Cr(VI), further reducing it to Cr(III), partially. In addition, Mg^{2+}, which was positively charged, coordinated with oxyanion, triggering chemisorption, and provided a platform for species adsorption [38]. Zhou et al. (2019) also investigated the use of ZIF-8 for simultaneous removal of mixed contaminants, e.g., copper and norfloxacin from an aqueous solution. They obtained a high removal efficiency of 95.4% and 80.3% for copper and norfloxacin, respectively. Nevertheless, they noticed that the adsorption mechanism for the mixed contaminant was mainly due to the ion exchange for Cu (II) adsorption, whereas electrostatic interactions, π-π stacking between the imidazole ring of ZIF-8, and the benzene ring in norfloxacin were responsible for norfloxacin adsorption [46]. Hence, depending on conditions and constituent of wastewater, surface functional groups, surface charge, and coordination strength, one or more mechanisms may be found to interplay in the removal mechanism. In an experiment by Jian et al. [36], the ZIF-8 adsorption of arsenic from aqueous solutions was mainly controlled by pore diffusion (intraparticle diffusion), similar to the results of Huang et al. [34]. However, it is important to state that the effectiveness of these mechanisms is controlled by critical operating conditions such as pH, temperature, contact time, and adsorbent features [46].
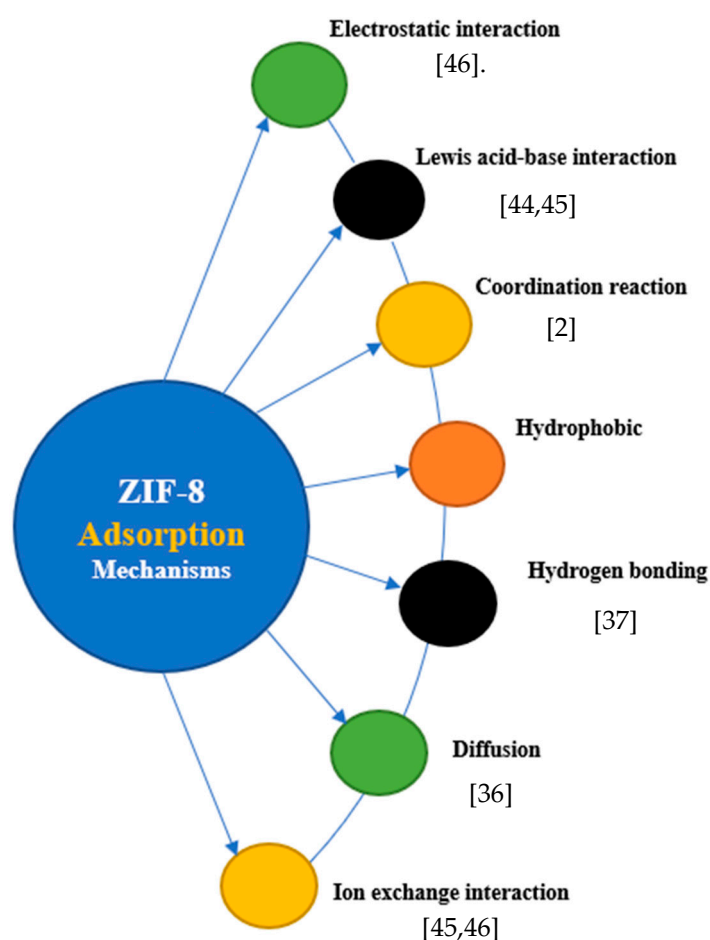
Figure 2. ZIF-8 adsorption mechanisms for heavy-metal removal. Electrostatic interaction [47]; Lewis acid-base interaction [45]; Coordination reaction [2]; Hydrogen boding [37]; Diffusion [36] Ion exchange interraction [45,46]

5. Factors that Influence ZIF-8 Metal-Adsorption Mechanisms

Adsorbent features such as porosity, pore-volume, and the surface area of the ZIF-8 play an essential role in determining interactive sites available for adsorption [34]. Generally, the larger the surface area and porosity of adsorbent, the more adsorption sites will be easily accessible and diffusion of contaminants through the framework will be enhanced. A couple of the crucial advantages of ZIF-8 responsible for its high kinetics and high adsorption capacity are its high surface area of 1000–2000 m^2/g and porosity [33,38]. In an experiment conducted by Begum et al. [38] to assess the adsorption capacity kinetics of Cr (VI) on ZIF-8, as shown in Table 1, they obtained an adsorption capacity of 2.34 mg/g and removal efficiency of 65%, which was primarily due to their small Brunuaer Emmet Teller [BET] surface area. In contrast, Zhang et al. [2] also attributed their high adsorption capacity of 800 mg/g of Cu^{2+} with a removal efficiency of 95% within 10 min to the high specific surface of ZIF-8 as shown in Table 1. Therefore, to enhance the adsorption capacity of ZIF-8, synthesis methods must aim at achieving a greater surface area and pore volume.

The solution pH is another sensitive parameter that either enhances or creates an unfavorable condition for the adsorption mechanism. Generally, pH affects the speciation of metal ions and influences the structural stability and surface charges of ZIF-8. In an experiment performed by Jian et al. [36] to assess arsenic removal from an aqueous solution by ZIF-8, they revealed that a large amount of Zn^{2+} from ZIF-8 was released into the water in an acidic condition [36]. This drastically destabilized the ZIF adsorbent and impeded the adsorption of arsenic. This result was practically consistent with the observations of

Zhang et al. [2]. As pH is reduced to more acidic levels, the atoms of an adsorbent are protonated, and adsorption cannot occur due to the repulsive forces. Begum et al. [38] also noticed in their study that as pH increases, the surface of ZIF-8 becomes negatively charged, which often causes an electrostatic repulsion between metal ions and ZIF-8 [31,41]. For an effective adsorption mechanism, a pH range of near-neutral is considered ideal for optimum adsorption capacity. In a study conducted by Begum et al. [38] and Zhang et al. [2], where they assessed the effect of pH on adsorption capacity by carrying out experiments at pH ranging between 2–14 and 2–6, respectively, while keeping all other parameters constant, they observed the highest adsorption capacity at neutral and near-neutral pH (6) for ZIF-8. Therefore, for any sustainable application of ZIF-8 in heavy-metal removal in an aqueous solution, the pH of wastewater is a crucial parameter to be considered [36]. Other essential parameters, in addition to pH and the surface area, that influence the adsorption mechanism, are the initial concentration and contact time. Contact time is the length of time allowed for an adsorbent surface to remain directly in contact with the adsorbate (wastewater). It is evident from several studies that adsorption increases with contact time. The shorter the time, the less contact between ZIF-8 and wastewater [2]. The ZIF-8 will then have less surface coverage, with more adsorption sites not accessed by contaminants to reach maximum adsorption capacity. It is therefore imperative that, for a sustainable application of ZIF-8 for heavy metal removal, these major factors need to be rightly considered, including temperature and the adsorbent dosage.

6. Future Perspective

ZIF-8 shows great promise for heavy-metal removal from wastewater and other forms of aqueous solutions. This study shows that a wide variety of heavy-metal ions can be extracted from aqueous solutions using ZIF-8, as shown in Table 1. Nevertheless, there is a need to explore the removal of other types of heavy metals such as mercury, zinc, iron, and thallium, which are similarly toxic to humans, even at low concentrations. Additionally, doping ZIF-8 with extra metal ions, such as nickel and cobalt, which have a similar structural and electron arrangements to zinc, to form heterometallic ZIFs during synthesis would substantially improve the structural properties of ZIF-8. For example, Wang et al. [47] used Fe-C groups as dopants on ZIF-8 to enhance the oxygen-reduction-reaction activities, whereas Shen et al. [35] doped ZIF-8 with cobalt and nickel and obtained a surface area greater than that of pure ZIF-8 while also achieving a 101% improvement in adsorption capacity for Ni@ZIF-8, i.e., more than pure ZIF-8 for Cr(VI) removal [43,46]. Doping ions help ZIF-8 surfaces to have more active sites for adsorption, and could also improve the photocatalytic ability of ZIF-8. This is an area that has rarely been explored in the use of ZIF-8 for heavy-metal removal.

In technological applications, it is evident that ZIF-8 has been used extensively for gas storage and capture, membrane technology, and energy storage. Nevertheless, ZIF-8 can also be used to complement some of the best biological approaches which are already considered ideal for wastewater treatment, with minor drawbacks. For example, most bio-electrochemical systems (BES), with little to zero environmental footprint, are considered sustainable technologies, but are limited in their capacity to attain optimum removal efficiency for heavy metals as heavy metals are not biodegradable. Therefore, by incorporating ZIF-8 as a pretreatment technology, or using ZIF-8 to form a composite membrane in BES through the phase-inversion process, the capacity of the technology to remove heavy metals would be significantly enhanced. This will be a significant breakthrough for BES systems, especially with the antifouling and antiscaling characteristics of ZIF-8. Nonetheless, there is a need for a Life Cycle Analysis (LCA) on ZIF-8 to assess its environmental footprint from synthesis to disposal. As far as sustainability is concerned, the regeneration and reuse of ZIF-8 and adsorbed heavy metals through appropriate desorption processes are also exciting areas that need further investigation. Niknam Shahrak et al. [48], in their experiment using ZIF-8 for efficient removal of Cr(VI) ions, used a 0.1 M solution of HCl to evaluate the regeneration and reusability of the nanomaterial after adsorption. They obtained four

cycles of desorption without any significant change in the adsorption capacity of ZIF-8 [48]. This is an area that has rarely been studied. We need to investigate the extent to which ZIF-8 can remain reusable, and what happens beyond that limit. Can it be recycled to attain the optimal level of sustainability? We need to find solutions to these questions.

Institutional Review Board Statement: "Not applicable" for studies not involving humans or animals.

Informed Consent Statement: "Not applicable" for studies not involving humans.

Data Availability Statement: The data presented in this study are openly available in [repository name e.g., FigShare] at [**doi**], reference number [reference number].

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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