






Review

# Heavy Metal Removal from Aqueous Solutions Using Biomaterials and/or Functional Composites: Recent Advances and the Way Forward in Wastewater Treatment Using Digitalization

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**Abstract:** Due to its low cost, over the past decades, biosorption technology has been extensively carried out to treat heavy metal-laden wastewater using biosorbents. Recent studies on heavy metal biosorption mechanisms and the simulation of mathematical modeling on the biosorption process have enhanced scientific understanding about the binding between target metal cations and the functional group on different surfaces of biomasses as a biosorbent. However, so far, none have provided an overview of mechanistic studies on heavy metal removal from aqueous solutions using inexpensive biosorbents. To close this knowledge gap, this article discusses the applicability of the surface complexation (SC) model for biosorption of a target pollutant. Insightful ideas and directions of future research in wastewater treatment using digital technologies are also presented. It was conclusive from a literature survey of 115 articles (1987–2023) that *Aspergillus niger*, *Penicillium chrysogenum*, and *Rhizopus nigricans* represent biomaterials that have substantial adsorption capacities, up to 200 mg of Au(I)/g, 142 mg of Th/g, and 166 mg of Pb(II)/g, respectively. The metal-binding mechanisms involved include ion exchange, surface complexation, and micro-precipitation. Ion exchange is the only mechanisms that play key roles in sequestering heavy metal using fungal cells with chitin and chitosan. X-ray energy dispersion (XED) and scanning electron microscopy (SEM) analysis were used to evaluate biosorption mechanisms of the inorganic pollutants using physico-chemical characterization on the cell surfaces of the biomass. As metal removal by the biosorbent is affected by its surface properties, surface complexation also occurs. The affinity of the surface complexation depends on the type of functional groups such as phosphate, carboxyl, and amine.

**Keywords:** adsorption; ion exchange; surface complexation; micro-precipitation; water pollution

## 1. Introduction

Environmental sustainability has become one of the key goals in the UN's 2030 Agenda [1]. However, as for one of its Sustainable Development Goals (SDGs), a sustainable access to clean water is not achievable due to water pollution from industrial activities that generate effluents with toxic heavy metals [2]. Consequently, this matter undermines the world's economic growth and public health. In developing countries, serious water pollution takes place due to the limitation of appropriate water technologies that result in a low removal of heavy metals [3]. As a result, treated water does not meet the requirements of the drinking water standard. Currently, about 2 billion people worldwide still lack of access to clean water for their drinking [4]. Out of these people, only 60% of the population have basic sanitation services [5].

In spite of the increasing efficiency of water utilization, improper wastewater treatment has contributed to deteriorating water quality in the developing world, worsening water pollution [6]. This problem results not only in the scarcity of water resources, but also in the decreasing supply of clean water for public consumption [7]. This is attributed to the presence of heavy metals such as Cr, Cu, and Fe in municipal wastewater that contributes to water pollution.

Kurniawan et al. [8] reported heavy metals such as Cr(III), Cd(II), Cu(II), and Zn(II) in wastewater discharged from the electroplating industry. They seriously threaten public health and the environment [9,10]. Therefore, the industrial effluent needs to be treated thoroughly to meet the effluent limits set by legislation prior to its discharge to a water body (Table 1). Otherwise, the effluents not only contaminate the environment, but also threaten public health, limiting productive activities [11].

**Table 1.** Maximum contaminant level (MCL) of heavy metals in aqueous solutions.

Heavy Metals	Potential Health Effects	MCLs (mg/L)		
		WHO [12]	HK EPD [13]	China's EPA [14]
Cr(VI)	Kidney, liver damage	0.05	0.05–0.1	0.05–0.01
Cr(III)	Skin rashes			
Hg(II)	Teratogenesis, liver, neural damage	0.006	0.001	0.001
Cd(II)	Anemia, emphysema, heart disease	0.003	0.001	0.005–0.01
Cu(II)	Diarrhea, kidney, liver damage	2	0.05–0.1	1
Pb(II)	Anemia, constipation, hypertension	0.01	0.1	0.05–0.1
Ni(II)	Cancer, diarrhea, insomnia	0.07	0.1–0.2	0.05–0.1

*Remarks:* WHO: World Health Organization. EPD: Environmental Protection Department of Hong Kong SAR. EPA: Environmental Protection Agency of PR China.

To comply with the effluent limits set by national legislation, a variety of water technologies such as chemical precipitation and ion exchange have been applied to eliminate heavy metals from contaminated water [15–17]. However, chemical precipitation possesses bottlenecks such as the excessive generation of sludge that needs to be disposed of in local landfills. This adds to the operational cost for sludge disposal [18].

To overcome the limitations, the search for novel technologies has intensified recently [19]. Recently, due to its low cost, heavy metals removal has been extensively tested by using biomass through biosorption. This process binds a target metal from aqueous solutions using certain biomaterials [20]. The sorption can be described as 'active' or 'passive'. Active sorption such as phytoremediation involves metabolic activities of living biomass, while passive sorption is non-metabolic, as metal binding is undertaken using functional groups and surface characteristics of cell walls on dead biomass [21]. Phytoremediation is widely used to accumulate target pollutants in constructed wetlands [22]. For this treatment, metallothioneins and phytochelatin have been identified as the active units that contribute to heavy metals' binding by plants [23]. The active metal binding is more complex than passive sorption in terms of removal mechanisms by biomaterials [24].

Recently, passive sorption using algae, bacteria, and fungi biomasses has been employed to sequester metals [25–27]. Their works have been carried out at a laboratory scale for batch studies. In a few cases, the investigations were scaled up using column operations [28]. Although biosorbents have demonstrated high affinity for metals [29,30], not many studies have reviewed heavy metal-binding mechanisms by biosorption technology [31].

Preliminary works have dealt with biosorption using plant-derived biomass [32–35]. In spite of their novelty, their reviews did not provide a complete mechanistic study of biosorption for heavy metal removal. In addition, how to optimize biosorption performance using mathematical modelings and the elucidation on metal-binding mechanisms were not elaborated. Despite the widespread applications of the Langmuir and Freundlich isotherm models for wastewater treatment, only a few studies have employed the surface complexation model (SCM) to study the effects of pH changes on heavy metal removal using certain functional groups [36–38]. Therefore, there is a growing need to simulate mathematical modeling for scaling up the application of biosorption in water treatment.

To bridge the knowledge gap in the field of study, this work provides a comprehensive overview of mechanistic studies of heavy metal removal from aqueous solutions using various modeling methods. This article also analyzes and discusses the applicability of the surface complexation model for biosorption. Insightful ideas on nanomaterials and the way forward for wastewater treatment applications using digitalization are presented.

## 2. Heavy Metal Removal Using Biomaterials

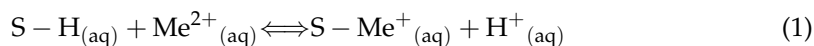
### 2.1. Passive Metal-Binding Mechanisms

Passive metal binding can be attributed to various mechanisms of metal uptake by the biosorbents based on ion exchange, surface complexation, electrostatic attraction, or micro-precipitation [39,40]. It is essential to note that the biosorption mechanism of certain metal cations by a biomass can be complicated. The metal uptake depends on the surface property of the biomass, types of target metals, and the pertinent conditions of reactions such as pH, temperature, and metal ion concentration [41].

To better understand the mechanism of metal binding on the surface of biomass, a variety of instruments such as Fourier transform infrared spectroscopy (FT-IR), transmission electron micrographs (TEM), atomic forces microscopy (AFM), X-ray diffraction (XRD), SEM, and EDX have been employed [42–44]. A surface analysis technique based on X-ray photoelectron spectroscopy (XPS) has also been used to quantitatively determine the binding energy of electrons and the elemental composition of biomass surface [45]. By integrating the instruments, results of mechanistic investigations demonstrated that biosorption involves ion exchange and surface complexation in metal biosorption by a biomass.

#### 2.1.1. Ion Exchange

During the biosorption process, ion exchange between metal ions and the biosorbent commonly occurs on the cell walls of a biomass with extracellular polymers [46]. Heavy metal removal from solutions using olive pomace was studied [47]. The ion exchange mechanism is proposed as follows :



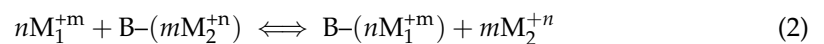
where  $S-H$  and  $Me$  represent the protonated binding site of the biomass and heavy metal, respectively. Equation (1) was also applied to another biosorption study [48]. The biosorption of Pb(II) from synthetic wastewater was performed using filamentous fungi *Mucor rouxii*. The scientists [48] reported that pH change affected Pb(II) biosorption capacity, implying the contribution of the ion exchange mechanism. Fewer metal ions were bound to the biomaterial at acidic pH due to the competition between protons and metal cations for the same binding sites of biomaterials. The EDX spectra showed a  $Pb^{2+}$  signal, while those of  $K^{+}$  and  $Ca^{2+}$  did not appear. This reveals that  $Pb^{2+}$  was substituted with  $K^{+}$  and  $Ca^{2+}$  on the cell wall of *Mucor rouxii*, which contained chitin and chitosan.

Yan and Viraraghavan [49] also investigated the removal of heavy metals by *Mucor rouxii*. They suggested that Pb(II), Cd(II), Ni(II), and Zn(II) removal by biosorption was attributed to the amine groups of chitin and chitosan. Apart from them, fungal cell walls consist of other macro-molecules such as proteins and lipids [50,51]. The carboxyl and phosphate groups present in proteins and lipids are also involved in the metal uptake by the fungi.

The release of K<sup>+</sup> into solutions was also reported using fungi *Rhodotorula glutinis* to remove Pb(II) from solutions [52]. Before biosorption, K<sup>+</sup> was identified by the EDX spectra of the biomass. However, it disappeared after the adsorption process. This could be due to the ion exchange mechanism as the predominant metal that binds the biomass surface.

Ion exchange was also the key mechanism in algal biosorption [53]. The cell walls of brown algae consist of alginate and fucoidan. Alginate consists of mannuronic and guluronic acids, while fucoidan contains sulfated esters and fucose [54]. The extracellular polysaccharides provide acidic functional groups for metal binding. Alkaline ions such as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> are naturally bound to carboxyl, sulfonic, and other acidic groups on the cell wall of algae. Consequently, the alkaline metals in untreated biomass can be substituted when reacting with other heavy metals and protons in aqueous solutions [55].

Metal sorption of Cd(II) was also explored using brown seaweeds *Durvillaea*, *Laminaria*, *Ecklonia*, and *Homosira* saturated with Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, and Na<sup>+</sup> [39]. To study their biosorption in a binary ion exchange system, a classical ion exchange model based on its equilibrium was applied. The ion exchange reaction is described as follows:

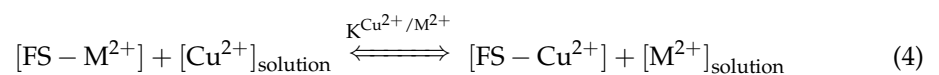


where *B* represents the biomass, *M*<sub>1</sub> is the metal ion with valence <sup>+m</sup>, and *M*<sub>2</sub> is the exchanging ion with valence <sup>+n</sup>. Ideally, the ion exchange ratio is 1:1 in both phases. The equilibrium constant *K*<sub>M<sub>1</sub>M<sub>2</sub></sub> is defined as:

$$K_{M_1M_2} = \frac{q_{M_1}^n C_{fM_2}^m}{C_{fM_1}^n q_{M_2}^m} \tag{3}$$

where *q*<sub>M<sub>1</sub></sub><sup>n</sup> and *q*<sub>M<sub>2</sub></sub><sup>m</sup> are the equilibrium uptakes of *M*<sub>1</sub> and *M*<sub>2</sub> based on the Langmuir sorption isotherm, and *C*<sub>fM<sub>1</sub></sub><sup>n</sup> and *C*<sub>fM<sub>2</sub></sub><sup>m</sup> are the equilibrium concentrations of *M*<sub>1</sub> and *M*<sub>2</sub> in solutions, respectively. The equilibrium constant *K*<sub>M<sub>1</sub>M<sub>2</sub></sub> quantitatively expressed the relative ionic compositions in the ion exchanger and solution phases. As a result, the relative binding preference is different for the two competing ions. Presumably, all binding sites are occupied and the free sites remain unchanged.

Based on the ion exchange mechanism, the ion selectivity of Ca<sup>2+</sup> and Mg<sup>2+</sup> in the biosorption of Cu(II) was examined using *Fucus serratus* (FS). Under ambient temperature, pH 5.5, and 6 h of reaction time, the ion exchange reaction is presented as [56]:



The apparent selectivity constant is expressed as:

$$K^{Cu^{2+}/M^{2+}} = \frac{[FS - Cu^{2+}][M^{2+}]}{[FS - M^{2+}][Cu^{2+}]} \tag{5}$$

$$[M^{2+}]_{\text{Total}} = [M^{2+}]_{\text{Solution}} + [FS - M^{2+}] \tag{6}$$

$$[Cu^{2+}]_{\text{Total}} = [Cu^{2+}]_{\text{Solution}} + [FS - Cu^{2+}] \tag{7}$$

where [M<sup>2+</sup>] and [FS - M<sup>2+</sup>] are the exchangeable cation concentrations in the solutions and in the solid, respectively. It was found that Mg<sup>2+</sup> was preferable to Ca<sup>2+</sup> for ion exchange with Cu<sup>2+</sup> on the biomass surface, as the selectivity constant for Mg<sup>2+</sup> (3.88) was higher than that of Ca<sup>2+</sup> (3.37).

This finding was in agreement with that reported by [57], who found the order of binding affinity ( $\text{Cd}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$ ) using Gram-positive *Bacillus megaterium* and *Streptococcus metans*. However, their binding efficiency varied due to the type of biomass. Metal sequestering using spruce sawdust found that the efficiency of ion exchange followed  $\text{Ca}^{2+} = \text{Mn}^{2+} > \text{Mg}^{2+} \gg \text{K}^+$ . This implies that  $\text{Ca}^{2+}$  was a key contributor to the ion exchange [58].

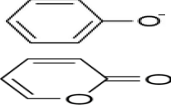
The non-uniformities in biomass surface could inaccurately estimate ion selectivity. In most cases, the distribution of binding sites was uniform in biomaterials [59]. This implies that an ion selectivity constant is applicable to biomass with a surface that has an even distribution of binding units. Stoichiometry is also used to investigate the relationship between target metal ions and a substituting ion exchanger [60].

The degree of exchange between target metal ions and the heavy metal can be indicated by a reaction stoichiometry. It is found that Co(II) was adsorbed onto *Ascophyllum nodosum* by releasing  $\text{Ca}^{2+}$ . The  $\text{Ca}^{2+}$  pretreated algal biomass had a 2:3 stoichiometric ratio for  $\text{Ca}^{2+}$  release to Co(II) uptake [61]. A ratio approaching one could be estimated if protons were included in the charge balance. Kuyucak et al. [62] explained that a non-stoichiometric ion exchange indicates that the ion exchange mechanism might not solely contribute to the metal binding. Surface complexation and microprecipitation might also be involved [63].

### 2.1.2. Surface Complexation

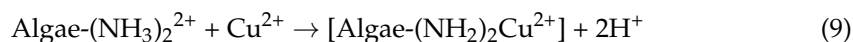
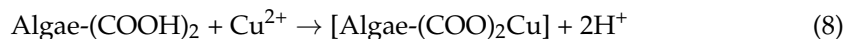
In adsorption, surface complex (SC) formation is widely known as the combination of cations with molecules or anions with lone pairs of electrons. Electrostatic interactions may be involved, in which metal cations are bound to anions or molecules to form coordination compounds [64]. The SC mechanism can be used to understand the physico-chemical interactions between heavy metal ions and the surface of a biomaterial. A possible binding associated with functional groups was tested using FTIR, EDX, or XPS analysis [65–67]. Functional groups such as amine, caboxyl, ester, ether, and pyronic groups were identified as the binding sites (Table 2), while the carboxyl group played roles in complexing metal cations.

**Table 2.** Surface complexation between metal cations and functional groups.

Metal Ions	Biosorbents	Functional Groups	References
Cr(II)	<i>Ecklonia</i> sp.	$-\text{COO}^-$	[68]
	<i>Ecklonia</i> sp.	$-\text{COO}^-$	[69]
Cd(II)	<i>Sargassum fluitans</i>	$-\text{COO}^-$	[70]
	<i>Padina</i> sp. and <i>Sargassum</i> sp.	$-\text{COO}^-$	[66]
	Activated sludge	$-\text{COO}^-$	[71]
Cd(II) & Ni(II)	Aerobic granules	$-\text{COO}^-$	[62]
Cd(II) & Pb(II)	<i>Lactobacillus fermentum</i> and <i>Bifidobacterium longum</i>	$-\text{COO}^-$	[72]
	<i>Pinus sylvestris</i>	$-\text{COO}^-$	[73]
Pb(II)	<i>Ganoderma carnosum</i>	$-\text{PO}_4^{2-}$	[74]
	<i>Mucor rouxii</i>	$-\text{COO}^-$	[75]
	<i>Padina</i> sp. and <i>Sargassum</i> sp.	R–O–R	[66]
Cu(II)	Activated sludge	$-\text{R}_3\text{N}$	[71]
	Olive pomace	$-\text{COO}^-$	[76]
	Olive pomace (thermally treated)		[76]
Cu(II) & Zn(II)	<i>Atriplex canescens</i>	$-\text{COO}^-$	[77]
Zn(II)	<i>Padina</i> sp. and <i>Sargassum</i> sp.	$-\text{COO}^-$	[66]
	Activated sludge	$-\text{COO}^-$ $-\text{R}_3\text{N}$	[71]



Carboxyl groups on the algae surface were identified as the main binding site for the biosorption of Cu(II) and Ni(II) using *Sargassum*, *Colpomenia*, and *Petalonia* at pH 4 [78]. A complex formation of Cu(II) with adjacent carboxylic acid and ammonium groups was proposed on the surface of *Vaucheria* as [79]:



A favorable binding site between Cu(II) and the amine group was also identified [71], while Cd(II) was preferentially bound with the carboxylic group on activated sludge. By studying the biosorption of divalent cations using bacteria *Pseudomonas pseudoalcaligenes* isolated from activated sludge at pH 5, it was found that metal adsorption was attributed to the extracellular polymers of the bacteria surface [36]. The extracellular polymers provide binding sites such as carboxyl groups for the metal removal based on surface complexation.

The pH changes caused profound effects in the association and dissociation of acidic functional groups, affecting the availability of sequestering metal in adsorption. For cation complexation, the biosorption capacity increases with pH since negatively charged functional groups are bound with metal cations. Theoretically, pHs higher than 8 contribute to metal precipitation in the form of hydroxides. However, the removal of Cr(VI) using brown seaweed *Ecklonia* contradicts this theory. Its removal decreased with an increasing pH in the solution due to the Cr(VI) uptake [69]. The predominant target metal was affected by pH during uptake.

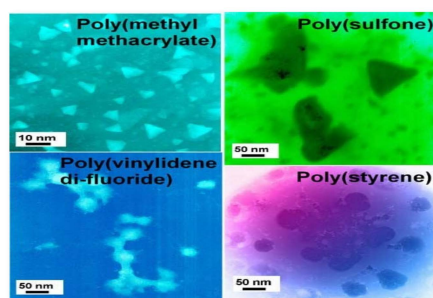
A polyethenimine-modified fungal biomass of *Penicillium chrysogenum* was employed to remove Cr(VI) ions ( $\text{CrO}_4^{2-}$ ,  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$ ). The major forms of ion species were dependent on pH, where  $\text{CrO}_4^{2-}$  was abundant at pH levels higher than 6.5, while  $\text{HCrO}_4^-$  is predominant in pH levels ranging from 2 to 5. As a result, the metal species binds to various surface functional groups, depending on the surface charge of the biomass and the type of target metal present in the solution [80].

### 3. Advances in Water Treatment Using Functional Composites

#### 3.1. Nanomaterials for Water Treatment

The need for water technologies, which do not lead to the production of toxic by-products, has resulted in the applications of nanoscale materials as adsorbents for environmental remediation. In recent years, cutting-edge research has been undertaken to synthesize and develop cost-effective and environmentally benign nanomaterials for environmental remediation [81]. When the nanomaterials are manufactured at atomic scales, they show better properties than starting materials due to enhanced structures and additional functionalities relevant for degradation or for sequestration [82]. In the next few years, adsorbents will not only play leading roles in the new generation of environmental technology but also revolutionize the world in which we live [83]. It is expected that low-cost and eco-friendly nanomaterials capable of detecting contaminants at an atomic level may substantially help improve public health and protect the environment.

Since existing treatment options are unable to maximize the removal of target contaminants in aqueous solutions, there is a growing consensus to develop other cost-effective technologies to enhance their treatment performance. The diverse applications of nanomaterials across a number of disciplines in recent years have responded to the need for an efficient and effective water treatment [84]. According to [85], any material can be categorized as nanoscale if it can meet any one of the following criteria: (1) Development at an atomic scale with length from 1 to 100 nm, (2) the technology creates and uses structures and/or systems with certain characteristics and functions because of their small sizes, and (3) the technology has the capability of being controlled or manipulated on a nanoscale level. The requirements underlie the principle that the properties of matter change at small scales (Figure 1).



**Figure 1.** Functional nanocomposites for wastewater treatment.

### 3.2. Technological Strengths of Nanomaterials

Due to their high porosity and active surface, not only can nanomaterials sequester target pollutants with different molecular sizes, but they also facilitate the manufacturing process to utilize raw materials efficiently [86]. Nanomaterials work rapidly and have high metal-binding adsorption capacities, and are regenerated after being saturated [87].

Currently, the design of environmentally friendly materials, products, and processes with tailor-made properties is based on the enhanced understanding of their synthesis, physico-chemical properties, and structure–property relationships. This understanding is essential at a molecular and nanoscale level. For this reason, nanomaterials can be manufactured by generating small structures from larger pieces of materials (‘top down’ techniques) such as etching to create circuits on the surface of a silicon microchip. They may be constructed by the arrangement of atom-wise additions into a nanostructure through physico-chemical interactions between the units (‘bottom up’ techniques). This technique results in nanomaterials with properties which vary from one to another [88].

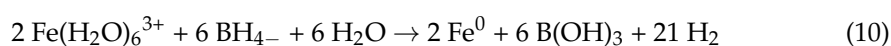
To manufacture nanomaterials with various levels of quality, different methods can be applied to exploit certain properties of the matter at atomic levels. Because of their tiny framework, the manipulation techniques under certain pH and doses enable the self-assembly of molecules to form fibrous nanostructures [89]. Because of their nano size, ranging from 1 to 100 nm, the nanoparticles have a substantial surface area to mass ratio, unlike bulk particles such as activated carbon [90]. Structures such as core/shell nanoparticles and multi-components, resulting from the proximity of nano-structured components, can demonstrate enhanced properties and new functionality. These properties allow the nanoparticles to stay suspended for a period of time, allowing them to eliminate target pollutants effectively. For example, a carbon nanotube was found to effectively eliminate inorganic contaminants [91].

Apart from their large surface area, due to the electronic density, certain functional groups can be easily attached to nanoparticles to improve their reactivity toward inorganic pollutants in contaminated water [92]. The key properties enable nanomaterials to be a powerful precursor to improve environmental sustainability through environmental remediation. Nanoscale materials provide indirect strategies for water pollution control through enhanced catalytic processes that not only generate minimum waste, but also produce improved sensors for effective separations.

### 3.3. Types of Nanomaterials

#### 3.3.1. *n*ZVI

One of the nanomaterials that is commercially available in market is the *n*ZVI particle. With its diameters ranging from 1 to 200 nm, *n*ZVI particles represent the novelty of nanoiron technology for wastewater treatment. Several studies have reported that iron-based nanoparticles can effectively reduce a large number of recalcitrant contaminants such as heavy metals [93]. By reacting  $\text{NaBH}_4$  with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , Fe(III) is reduced to Fe(0) according to the equation below:



Quinn [93] reported that *n*ZVI particles had a larger surface area (19 m<sup>2</sup>/g) than Fe(0). It was reported that the presence of boron and the shell thickness enhanced the reactivity of the particles toward target compounds. For this reason, *n*ZVI could dechlorinate polychlorobiphenyl (PCB) at a removal rate higher than that of Fe(0) powder.

### 3.3.2. Dendrimer

Advanced progress in material sciences has also enabled the manipulation of tiny structures called dendrimers to address water quality problems due to aquatic pollutants. Dendrimers are core-shell nanostructures with a certain composition and an architecture consisting of nanoscale features [94]. The particle comprises three covalently bonded elements, a core, and terminal branch cells. Due to its reactivity, this polymer has the ability to serve as a ligand for inorganic pollutants. Metal–dendrimer complexes can be removed from wastewater by pH adjustment. This enables the particles to be reused and allows metal recovery for polymer-supported ultrafiltration.

### 3.3.3. Metal Organic Framework (MOF)

Metal-organic frameworks (MOFs), widely known as porous coordination polymers, as a new class of porous hybrid materials with reticular structure, have demonstrated promising applications for water treatment such as adsorption, catalysis, and detection. However, there are still technical barriers to their practical application such as blockage of pipes, difficulty in recovery, high cost, and potential environmental toxicity [95].

### 3.3.4. Nanoporous Materials

Nanoporous materials are another emerging class of nanomaterials used in environmental applications. The materials were classified according to pore size (diameter) under microporous (less than 2 nm), mesoporous (between 2 and 50 nm), and macroporous materials (more than 50 nm), based on the IUPAC convention [96]. The materials with a diameter less than 100 nm could be categorized as nanoporous materials, useful in environmental applications. Zeolites are used in catalytic converters in car exhaust systems, which can filter and degrade harmful exhaust gases [97]. Energy efficiency and energy saving could be achieved with the application of zeolite, metallic foam, and activated carbon in a heat pump [97].

Spherical, well-defined core-shell PEI/PMMA (polyethyleimine/polymethyl methacrylate) nanoparticles represent a specific molecular type of particles that can be developed for wastewater treatment. In a preliminary work, nanoparticles were developed from PEI and PMMA, as well as PMMA and chitosan through graft copolymerization [89] (Figure 2). This method is not directly employed to immobilize monomers with amine chelating groups. Instead, a two-stage modification was conducted by involving the grafting of an epoxide-containing glycidyl methacrylate followed by the immobilization of PEI (Figure 3). The PEI not only improved the dispersion of the nanoparticles, but also brought new properties to the nanocomposite. Grafted PMMA provided support for the PEI chains in the adsorbent [98]. Further variations in the structure and functionality of the polymers can be achieved by altering the properties and synthesis techniques for the precursor chains.

The applications of PEI/PMMA for water treatment may revolutionize the ways in which we deal with environmental pollution sustainably. Industries may shift their paradigm in dealing with contaminated water, using less costly and more eco-friendly products while improving resource efficiency. As nano-adsorbents facilitate a powerful removal of target pollutants from contaminated water, it is anticipated that they may no longer apply physico-chemical treatments that cost half of the total treatment cost.

Overall, the applications of the TiO<sub>2</sub> nanocatalyst, *n*ZVI, or polymeric nanoparticles for treatment of contaminated wastewater are only the starting point of nanomaterial applications in water pollution control [99]. To advance their development for water treatment, research collaborations and scientific exchanges among interdisciplinary researchers need



to be undertaken not only to foster mutual partnership across industries and borders, but also to enable the sharing of tools, knowledge, and techniques [100].

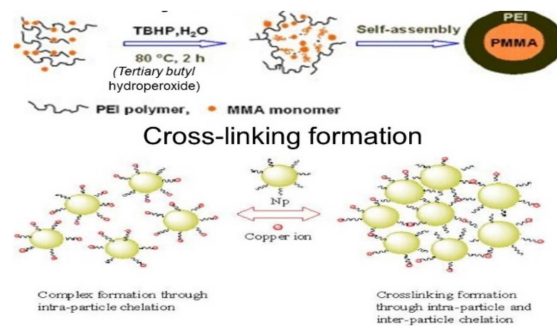


Figure 2. Synthesis route to PEI/PMMA composites.

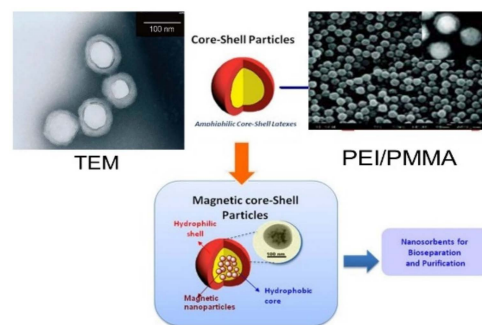


Figure 3. PEI/PMMA adsorbents for wastewater treatment.

#### 4. Prospect and Ways forward for Digitalization in Water Treatment Industry

Water pollution problems are increasingly complex and the answers to them are not clear. Mitigating these risks ultimately circles back to people's motivation to develop artificial intelligence (AI) and machine learning (ML) [101]. As an anchor in the water industry, water quality is subjected to regulations and must meet strict discharge requirements. There is no room for errors when complying with legislative requirements. However, digitalization can assist industry to remove potentials for error. For instance, digitalization makes real-time information and data become practical. Digital application benefits from information being stored safely and being accessible instantly [102].

To ensure the quality of the water, water treatment facilities vary in the way they maintain a common sequence of water treatment stages from water intake, pre-treatment stage, coagulation, filtration, and final discharge. Each stage is important in the water treatment process. The challenge includes monitoring and operating measurement points during daily operation. If there is no back up to the measuring points, disruptions to wastewater treatment can bring impacts on finance, regulatory aspects, and the environment [103]. Whether they are driven by regulation to deal with climate change or not, water companies need to consider this matter carefully.

To improve treatment efficiency, water companies seek ways to do more with fewer resources. Smart instruments enable rapid connectivity onsite using AI or ML. Remote communication is possible wirelessly, as data retrieval from the instrument is practical, regardless of distances. Although artificial intelligence (AI) and machine learning (ML) are not silver bullet solutions, new technicians in the water industry are trained fundamentally to absorb information using AI and ML. They are adept at utilizing information technology (IT) when gathering data differently. They do not retain information, as digitalization allows instrument manufacturers to obtain experiential skills and build them into devices. If an instrument is at fault, workers can scan the QR code into their cell phone to access diagnostic information on what will happen, and instantly alert workers of manufacturers

with their base in different countries by email. This enables communication reporting to be proactive, while removing any guesswork [104].

Digitalization also offers services such as early warning via email. If a threshold limit approaches, workers can obtain an email alert ahead of time, enabling them to address the problem earlier. This ensures that the water industry does not fall out with authorities [105]. The applications comprise a digital device with software to improve the functionality of the device, while making the measurement process practical. This can be conducted without spending any expenses, as the systems integrate the company's existing IT infrastructure (where resource planning systems are based) and the company's operational technology (its instruments in the field) [106].

Another development in digitalization is augmented reality (AR). This technique provides a practical way of training new operators. As water companies are working with limited resources, they focus on doing more with fewer resources [107]. Any solution that increases efficiency and reduces downtime is vital. Any *apps* on phones that allow e-manuals to be downloaded instantly can make differences with respect to an instrument's daily operations. At an advanced level, processes such as verification take out guesswork by enabling workers to address the problem earlier, minimizing downtime. This represents practicality, in which digitalization makes a difference [108]. Every application makes use of digital technology to maximize their assets without investing resources.

Cloud computing is another use of digital capabilities delivered via the internet for water industries to operate, innovate, and serve customers. It eliminates the need for companies to host digital applications on their own servers [109]. With cloud computing, companies can provide a range of services offered by cloud service providers (CSPs) [110]. The CSPs' servers host all the company's applications. This can enhance its computing power quickly and cost-effectively via the cloud rather than by purchasing, installing, and maintaining their own servers. This model helps water companies to scale up digital solutions with faster speed and agility, while creating value [111]. Industries use cloud services to build and run custom applications and to maintain water infrastructure and networks for companies. CSPs offer services, such as analytics, to handle and manipulate vast amounts of data [112].

Cloud computing came on the scene well before the global pandemic hit, but the ensuing digital dash helped demonstrate its power and utility. A water company can use a common cloud platform that serves 124 plants and 1500 customers to consolidate real-time data from machines and systems, track logistics, and offer insights on the processes [111]. Use of the cloud could shave 30% off operational costs by 2025, while sparking innovation simultaneously [113].

Today, the next generation of cloud computing, including capabilities such as serverless computing, makes it easier for software developers to tweak software functions independently, accelerating the pace of release and doing so efficiently [114]. Water industries can serve customers and launch services in an agile fashion, while the cloud continuously evolves [115].

## 5. Concluding Remarks

This review has demonstrated the feasibility of biomaterials and functional materials for heavy metal removal from aqueous solutions using unused biomaterials and/or functional nanomaterials. It was conclusive from a literature survey of 115 articles (1987–2023) that *Aspergillus niger*, *Penicillium chrysogenum*, and *Rhizopus nigricans* represent biomaterials that have substantial adsorption capacities, up to 200 mg of Au(I)/g, 142 mg of Th/g, and 166 mg of Pb(II)/g, respectively. The metal-binding mechanisms include ion exchange, surface complexation, and micro-precipitation. Ion exchange is the only mechanism that play key roles in sequestering metal using fungal cells with chitin and chitosan. X-ray energy dispersion (XED) and scanning electron microscopy (SEM) analysis were used to evaluate biosorption mechanisms of heavy metals using physico-chemical characterization on the cell surfaces of the biomass. As metal removal by the biosorbent is affected by its sur-

face properties, surface complexation also occurs. The affinity of the surface complexation depends on the type of functional groups present, such as phosphate, carboxyl, and amine.

Apart from biomaterials, nanomaterials have helped users shift their old paradigm in treating wastewater laden with heavy metals. They no longer employ physico-chemical treatments that cost almost half of the total treatment cost. Nanotechnologies have opened a way for industrial users to effectively remove target pollutants from contaminated water by using renewable and eco-friendly products. In the next few years, the diverse application of nanotechnologies will inspire researchers in the field of water treatment not only in treating contaminated water, but also in dealing with knowledge gaps in other sectors.

Due to their ability to minimize the generation of secondary waste using fewer resources and their capability of removing any type of pollutant from contaminated water effectively, it is anticipated that the nano-adsorbents would play roles in protecting the aquatic environment in the future. By addressing the long-term sustainability of resources through the applications of nanomaterials for water treatment, the world will have a green and clean environment, in which humans can co-exist with nature.

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