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Review

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Progress and challenges in heterocyclic polymers for the removal of heavy metals from wastewater: a review

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Abstract

Water contamination by heavy metals has emerged as a global environmental problem. Their toxicity, non-degradability, and persistent nature make them a serious threat to human health, flora, and fauna. Therefore, several techniques have been developed for the removal of these pollutants from wastewater. Recently, linear aromatic polymers have received increasing attention for wastewater treatment due to the presence of various heterocyclic moieties containing electron-donating atoms such as nitrogen, oxygen, or sulfur on their backbone, which can be easily coordinated with metals, resulting in excellent affinity for heavy metals. This review article is specifically devoted to providing an overview of the various linear-architecture heterocyclic polymers that have been synthesized to be used as adsorbent phases for the removal of heavy metals from wastewater over the past fifteen years. The importance of incorporating heterocyclic units as efficient chelating sites for ion binding is

highlighted. The adsorption mechanisms of different aromatic polymers are presented; their adsorption isotherms can primarily be modeled with the Langmuir model and their kinetics follow a pseudo-second-order kinetic model. The ways to improve the adsorption capacities of the linear aromatic polymers by increasing their specific surface area are discussed in the perspective paragraph, along with strategies to improve their reusability by choosing the proper acidic washing step.

Keywords: Adsorption, heterocyclic linear polymers, polyimides, polyamides, heavy metals, wastewater

INTRODUCTION

In recent years, water pollution caused by heavy metal contamination has become a global concern[1]. Due to the rapid growth of industrialization and anthropogenic activities including metal plating, mining operations, tannery, batteries, chemical, automobile radiator manufacturing, and other industries, a dramatic increase in heavy metal pollution has occurred in the aquatic environment[2,3]. Extensive use of heavy metals in the above industries results in industrial wastewater rich in heavy metals that mix with lakes, rivers, oceans, and other drinking water sources, leading to water pollution[4,5]. There are various kinds of heavy metals, but the most predominant in industrial effluents are copper (Cu) (1.45 ± 1.22 mg/L), chromium (Cr) (65.81 ± 40.01 mg/L), lead (Pb) (21.28 ± 6.85 mg/L), iron (Fe) (90.52 ± 32.08), zinc (Zn) (62.90 ± 8.63 mg/L), cadmium (Cd) (25.65 ± 6.60 mg/L), mercury (Hg) (6.78 ± 3.36 mg/L), and nickel (Ni) (0.74 ± 0.80 mg/L)[6,7]. These heavy metal compounds are extremely toxic, persistent, non-biodegradable, and highly soluble in aqueous media[8,9]. They, therefore, rapidly penetrate into food chains and accumulate in living organisms, causing severe threats to humans and aquatic ecosystems[10,11]. Although the consumption of limited amounts of certain heavy metals is extremely essential for human beings due to their unique role in the human metabolic system, excessive intake can lead to harmful health effects[12]. For example, nickel (Ni) can be useful at non-hazardous levels; it functions as an enzyme activator and is involved in many important metabolic processes. However, the excessive ingestion of Ni may cause lung and kidney damage, gastrointestinal disorders, dermatitis, and breathlessness[13,14]. Zn is a versatile element that plays critical roles in various cellular processes, making it indispensable for all living organisms[15,16]. At excess levels, Zn can cause serious health problems such as neuronal and respiratory disorders, vomiting, nausea, anemia, and prostate cancer[17]. Although Cu is an essential metal for humans, it is also potentially toxic above supra-optimal levels[18]. Cobalt (Co) serves as a metal component of vitamin B12 (cyanocobalamin), but can be hazardous to the human body following excessive exposure[19]. Heavy metal levels in drinking water are strictly controlled by powerful organizations such as the World Health Organization (WHO) and the US Environmental Protection Agency (USEPA)[20] [Table 1].

Therefore, efforts have been devoted to researching effective technologies for removing toxic metals from wastewater[5]. Numerous water decontamination techniques have been applied, including chemical precipitation[21], ion exchange[22], membrane filtration[23], and electrochemical processes[24,25]. However, these techniques are difficult to remove heavy metals in low concentrations[26]. Up to now, adsorption has been considered the best process for removing damaging metals from water resources, thanks to its higher efficiency, simplicity, ease of accessibility, cost-effectiveness, and environmentally-friendly nature[27,28]. The additional advantage of adsorption is that adsorbents can be easily regenerated using an appropriate desorption process[29-31]. Many adsorbents are employed to trap heavy metals in wastewater. The conventional adsorbents are activated carbons, activated clays, zeolites, and silica gels[32-37]. In recent decades, many efforts have been made to remove heavy metals, using several types of organic linear polymers bearing heterocyclic moieties in their main or lateral chains. Heterocyclic polymer based-adsorbents are one of the best alternatives for heavy metal adsorption due to the presence of heteroatom groups on their chains that can be chelating sites for metals, thus making the resulting polymers effective

Table 1. Acceptable heavy metal levels according to WHO and USEPA

Heavy metals	WHO	USEPA
Cd	3 µg/L	5 µg/L
Hg	6 µg/L	2 µg/L
Cr total	50 µg/L	100 µg/L
Cu	2,000 µg/L	1,300 µg/L
Pb	10 µg/L	15 µg/L
Ni	70 µg/L	100 µg/L
Fe	1,000-3,000 µg/L	300 µg/L
Zn	3,000 µg/L	5,000 µg/L

WHO: World Health Organization; USEPA: US Environmental Protection Agency.

adsorbent phases to remove different metals from wastewater. Moreover, the incorporation of heteroaromatic rings on the polymer chains is the most common approach for increasing the chemical and thermal stability of the resulting polymers and their hydrophilicity, which is a necessary property to extract inorganic pollutants from water media[38,39]. The recent developments in synthesized heterocyclic polymers-based adsorbents for the extraction of various toxic metals from wastewater are reviewed here. This review was based on the querying of the scientific database (Web of Science, Scopus, and Google Scholar) through the main keywords: Adsorption, heterocyclic linear polymers, polyimides (PIs), polyamides, heavy metals, wastewater, and through a selection of the published papers in the last 15 years. To our knowledge, no other review specifically oriented to the use of heterocyclic polymers for the removal of heavy metals from wastewater has been published until now. The published reviews, such as the one by Malik *et al.*, have cited all types of adsorbents used for heavy metal removal, but only a few examples of polymers have been mentioned[5].

HEAVY METALS AND THEIR IMPACT ON HUMAN HEALTH

Heavy metals are part of the natural environment, and their traces are essential for human health. However, their excessive use on an industrial scale generates considerable pollution in water systems, due to their discharge through industrial wastewater, posing a severe threat to the ecological environment and public health. Many heavy metals, including Hg, Cd, Pb, Zn, Cr, As, Cu, Fe, Mn, Ag, Co, and Ni, have been identified as the most abundant in water and soil[40]. These metals are highly soluble in water and easily accumulate in plants and the human body through the food cycle[41]. Long-term exposure to heavy metals leads to serious diseases and an increased risk of some cancers[42,43]. Exposure to high levels of Hg affects the central nervous system and can damage the functionality of the brain, kidneys, and liver[44-46]. Cd is known as a carcinogenic metal and can cause kidney dysfunction, cardiovascular diseases, lung cancer, hypertension, and testicular atrophy[47,48]. Pb is another heavy metal with negative effects on human health, such as Alzheimer's disease, kidney damage, mental retardation, reproductive system dysfunction, and cancers[49,50]. Chronic exposure to Zn has been reported to cause fertility disorders, cancer, and cholesterol imbalance[51,52]. Arsenic exposure has been linked with heart disease, bronchitis, dermatitis, mental disorders, and lung and skin cancers[53,54]. Cr exists as a trivalent ion [Cr(III)] and as a hexavalent ion [Cr(IV)], which is the form most harmful to humans, plants, and animals. It can cause lung tumors, digestive tract cancer, mutagenicity and embryotoxicity, hemorrhage, and skin irritation[55,56]. Cu toxicity has been associated with kidney disorders, vomiting, diarrhea, gastroenteritis, liver damage, and even death[57,58]. Excessive silver consumption causes serious toxicological issues, such as changes in blood cells, and liver and kidney damage[59].

ADSORBENTS

Several adsorbents have been used for the adsorption method that can be sorted into three main families: industrial adsorbents, bioadsorbents, and polymeric adsorbents. Industrial adsorbents generally present specific surface areas greater than 100 m^2/g, up to 1,000 m^2/g. The most popular industrial adsorbents are activated carbons, zeolites, silica gels, and activated clays. Approximately 150.000 t/year of activated zeolites, 400.000 t/year of activated carbons, 400.000 t/year of activated clays, and 25.000 t/year of silica gels have been produced[60]. The most popular industrial adsorbents are activated carbons, zeolites, silica gels, and activated clays, all of which demonstrate excellent adsorption capacities for metal removal. Zeolites consist of micropores and aluminosilicate compounds that form a network of SiO_4 and AlO_4^- tetrahedra, linked by common oxygen atoms[61]. These materials present a large specific surface area, high cation exchange capacity, non-emission of toxic compounds, and excellent heat resistance, which make them suitable for the removal of undesired heavy metals[62]. Due to the low ion exchange capacities of natural zeolites, chemical or physical methods are frequently used to enhance their adsorption performance[63]. Álvarez *et al.* compared the adsorption efficiency of activated zeolite with that of natural zeolite for removing Cr (VI)[64]. They reported that adsorption capacity depended on the type of activation and decreased in the following order: activated zeolite with NaOH (82%) > natural zeolite (34%) > activated zeolite with HCl (13%). Mehdi *et al.* also prepared an activated zeolite as an adsorbent material for Ni^{2+} removal from an aqueous solution[65]. The study revealed that the adsorption process was temperature-dependent. The maximum adsorption capacity expected from Langmuir isotherm was found to be 28.79 mg/g at 20 °C. In addition, the values of Freundlich constant n relating to the adsorption intensity were increased from 2.52 to 3.11, with increasing temperature of solution from 20 to 60 °C, indicating better adsorption at a higher temperature.

Adsorption onto activated clay can also constitute an efficient technique for decontaminating water polluted by toxic metals. Khalfa *et al.* studied the removal of several metals Cu^{2+}, Pb^{2+}, Zn^{2+}, and Cd^{2+} using natural and activated clay to assess the effectiveness of these abundant materials in treating wastewater[66]. The authors reported that the heavy metal adsorption properties of natural and activated clay were $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$. They also noted that activated clay has eliminated greater amounts of metals than pure clay. In fact, after sulfuric acid treatment of clay, the adsorption capacity of Pb^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+} was found to increase from 29.11, 22.30, 21.93, and 20.86 mg/g to 50.94, 33.66, 26.74, and 26.44 mg/g, respectively. Dim *et al.* treated the natural clay using hydrochloric acid for Cr (VI) and Fe (III) adsorption from a wastewater medium[67]. The study revealed that the highest removal recorded on activated clay for Cr (VI) and Fe (III) was 18.15 and 39.80 mg/g, respectively. Based on the value of *n*, activated clay showed a greater affinity to Cr (VI) (n = 1.76) than Fe (III) (n = 0.356).

Activated carbon is the most commonly used and widely produced adsorbent for wastewater treatment. It has recently received significant interest for the removal of heavy metals due to the large surface area, suitable surface functional groups, and appropriate pore diameter[68]. Numerous researchers have examined the adsorption capacity of activated carbon as a function of changes in preparation factors [Table 2]. It has been shown that the nature of raw material, the preparation conditions (temperature, heating rate, and duration), and the type of activation method (physical or chemical) have a significant influence on the physicochemical properties of activated carbon and therefore on adsorption performance[69-74].

However, the use of activated carbon is limited by its high production cost, poor selectivity, difficult functionalization, and low regeneration. Its regeneration requires high energy (500-900 °C) with a 10%-15% loss of the carbonaceous material and a limited adsorption capacity. The recovery of the adsorbed heavy metals decreases the process cost; nevertheless, eluents should not damage the adsorbent and should be cost-effective and eco-friendly. Diluted HCl solutions were used to recover the heavy metals[75]. Therefore,

Table 2. Adsorption behavior of activated carbon prepared under different conditions

Used raw material	Temperature of preparation (°C)	Time of preparation (min)	Surface area (m^2/g)	Heavy metal	Adsorption capacity (mg/g)	1/n[(a)]	Ref.
Rape straw	300	120	699.9	Pb (II)	253.2	0.181	[69]
Sugar beet bagasse	450	120	748	Cr (VI)	52.8	0.592	[70]
Rice straw	400	240	4.39	Cd (II)	37.14	-	[71]
Gingko leaf	800	90	310	Cu (II)	59.90	0.3785	[72]
Rice husk	600	10	768.98	Hg^0	0.016	-	[73]
Pine bark	600	24	-	Cd (II)	85.8	0.3364	[74]

[(a)]1/n: The correction factor related to the intensity of adsorption (Freundlich isotherm).

the adsorption onto economic sorbents such as bio-based materials has been the subject of numerous studies, due to their availability, inexpensiveness, biodegradability, biocompatibility, and renewability. These parameters have a great impact on environmental practices. There are several agricultural by-products, such as banana peel[76], green tea waste[77], rice husk[78], and treated olive pulp[79], that have been employed as bio-adsorbents to remove heavy metals in water.

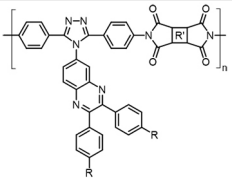
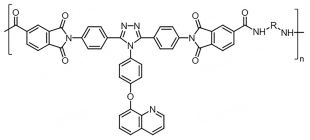
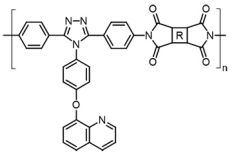
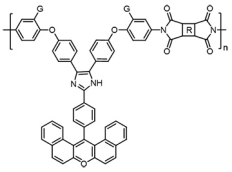
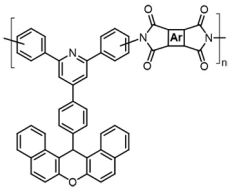
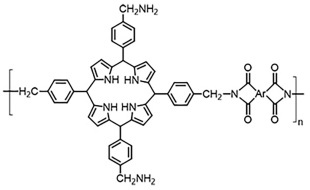
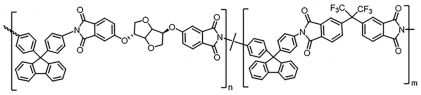
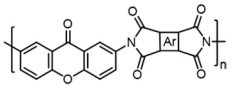
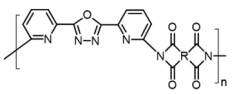
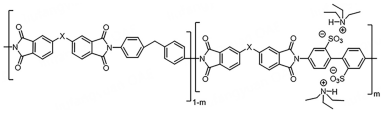
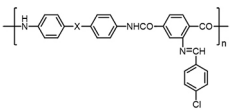
Polysaccharides are the most abundant carbohydrate and possess excellent properties for use as bio-based adsorbents for metals[80-82]. These natural polymers, such as cellulose, carrageenan, alginate, starch, cyclodextrin, chitin, and its derivative chitosan, have obtained vast attention as practical and low-cost adsorbents as opposed to activated carbons. Many attractive properties of polysaccharides, such as their specific structure, high reactivity, chemical stability, and excellent selectivity for metals, have made them such smart alternative adsorbents. Moreover, the chemistry of their surface can be modified by grafting functional groups onto chains to acquire new adsorption properties. Yu *et al.* proposed the grafting of amino-terminated hyperbranched polyamide (HP) onto the surface of cellulose-bearing aldehyde groups for efficient removal of metals[83]. This material shows excellent adsorption performance for Cu^{2+} with an adsorption capacity of 138 mg/g. Guleria *et al.* developed a poly-(acrylamide-co-acrylic acid) functionalized cellulose adsorbent to improve its heavy metal adsorption performance[84]. Triazole groups have also been grafted onto cellulose chains by Yin[85] to eliminate Gd(III) and by Mahalakshmi[86] to adsorb efficiently Pb^{2+}, Co^{2+}, Ni^{2+}, and Cd^{2+}. This study revealed that incorporating heteroatoms as chelating units in the cellulose backbone plays a major role in the adsorption process with the coordination reaction between nitrogen atoms in triazole and metals.

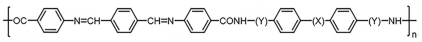
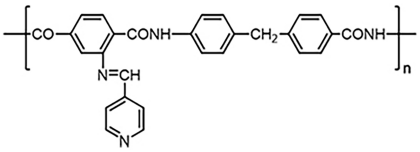
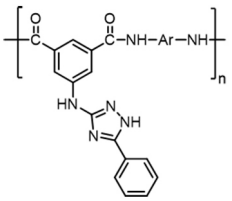
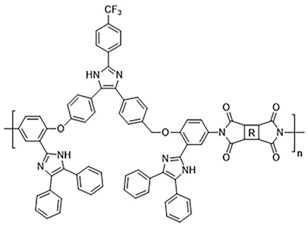
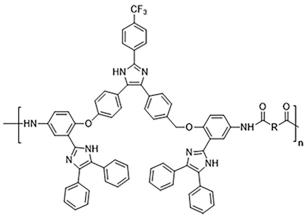
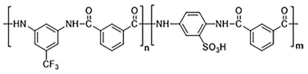
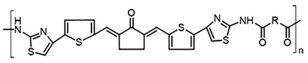
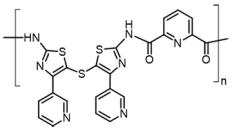
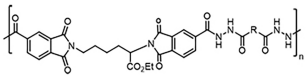
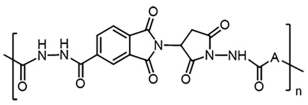
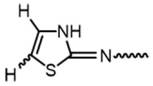
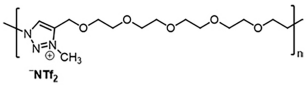
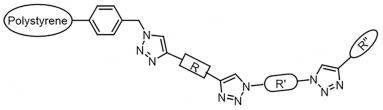
Polymeric adsorbents including ion exchange resins, molecularly imprinted polymers (MIPs), and porous organic polymers (POPs) have been utilized extensively in the remediation of metals from water[87-89], but the usage of linear organic polymers as adsorbents is less reported. Over the last few years, heterocyclic polymer-based adsorbents, such as polypyrroles, polyamides, PIs [Table 3], have received increasing attention from researchers because of their potential applications in the uptake of various heavy metals and the fact that the incorporation of different functional groups in polymer matrices enables them to be used as adsorbents capable of efficiently absorbing numerous organic and inorganic pollutants. In addition, these polymers can easily be regenerated under mild conditions.

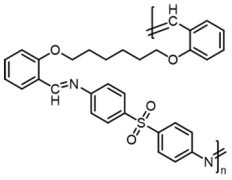
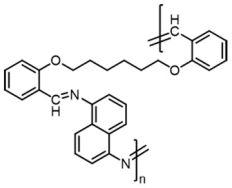
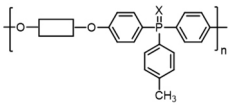
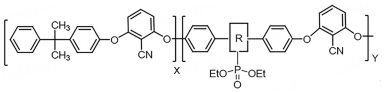
HETEROCYCLIC LINEAR POLYMER-BASED ADSORBENTS

A review of recent adsorbents used in metal removal from contaminated wastewater is presented here, with a focus on linear functional polymeric adsorbents. These polymers can be produced from different polymerizations of heterocyclic monomers. Furthermore, the impact of different factors such as the pH of

Table 3. Heavy metal ions adsorption using various linear aromatic polymers

Polymer adsorbent	Repetitive unit	Metal ion	Adsorption capacity (mg/g) or %	Affinity Parameter (1/n)	Ref.
Quinoxaline-based PTIs		$Cr_2O_7^{2-}$, Pb^{2+}, Hg^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}, Cr^{3+}	28%, 33%, 40%, 44%, 50%, 60%, 85%, 89% (pH = 8)	-	[90]
Phenoxy quinoline-based PTAIs		F^-, $Cr_2O_7^{2-}$, Cr^{3+}, Cd^{2+}, Pb^{2+}, Hg^{2+}	9.50, 8.56, 6.60, 6.66, 7.97, 8.76 mmol/g (pH = 3). 5.96, 4.99, 7.99, 7.90, 8.94, 9.2 mmol/g (pH = 10)	-	[91]
Phenoxy quinoline-based PTIs		F^-, $Cr_2O_7^{2-}$, Cr^{3+}, Cd^{2+}, Pb^{2+}, Hg^{2+}	8.91, 7.55, 5.0, 4.2, 5.5, 5.71 mmol/g (pH = 3) 5.0, 4.0, 6.1, 7.0, 8.38, 8.8 mmol/g (pH = 10)	-	[92]
Polyimides containing imidazole and xanthene pendants		Hg^{2+}, Cr^{3+}, Cd^{2+}, Co^{2+}, Pb^{2+}	37.9, 32.65, 28.6, 21.15, 19.80 mmol/g	-	[93]
Polyimides containing pyridine and xanthene pendants		Cr (VI)	91%	-	[94-96]
Porphyrin-based PIs		Cd^{2+}, Hg^{2+}	28.59, 27.73 mmol/g	-	[97,98]
Biosourced polyimides		Pb^{2+}, Ni^{2+}, Cd^{2+}, Hg^{2+}	0.726, 0.818, 0.488, 0.084	0.096, 0.064, 0.102, 0.181	[99]
PXIs		Cd^{2+}, Pb^{2+}, Cu^{2+},Ni^{2+}, Co^{2+}, Cr (VI)	57.3%, 47%, 45.2%, 42%, 41.1%, 39%	-	[100]
Polyimides bearing1,3,4-oxadiazole and pyridine units		Co^{2+}, Ni^{2+}	110.4, 100.5 mmol/g	-	[101]
Sulfonated copolyimides		Pb^{2+}	99%	-	[102]
Chlorobenzylidine-based polyamides		Pb^{2+}, Cr^{3+}	274.6, 255.2 mmol/g	-	[103]

PAMAs		Cu^{2+}, Cd^{2+}, Pb^{2+}	470.7, 462.3, 452.1 mmol/g	0.345, 0.393, 0.413	[104]
Pyridine-containing polyamides		Cu^{2+}, Pb^{2+}	389.9, 403.1 mmol/g	-	[105]
1,2,4-triazole-based polyamides		Hg^{2+}	99%	-	[106]
Imidazole-based polyimides Imidazole-based polyamides	 	Cr^{3+}, Co^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}	38.45, 26.20, 20.5, 18.40, 13.30 mmol/g 43.90, 30.80, 25.10, 21.60, 19.60 mmol/g	-	[107]
Sulfonated polyamides		Pb^{2+}, Hg^{2+}	11.87, 5.17 mmol/g	-	[108]
PAS	 	Hg^{2+} Pb^{2+}	47.95 mmol/g 714 mmol/g	0.14 0.059	[109] [110-113]
Poly(amide-hydrazide-imide)s	 	Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+} Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}	0.99, 075, 0.47, 0.31, 0.037 mmol/g 1.70, 0.71, 0.54, 0.29, 0.43 mmol/g	-	[114] [115]
Poly(2-aminothiazole)		Ag^{+}	336.98	0.233	[116]
1,2,3-triazole based-poly(ionic liquid)		Cr (VI)	13.545	0.289	[117]
1,2,3- triazole containing polystyrene		Mg^{2+}, Zn^{2+}	3, 30%	-	[118]

Polyazomethines		Co^{2+}, Cu^{2+}, Au^{3+}	21.28, 31.25, 35.71	- [119]
		Ni^{2+}, Cu^{2+}, Co^{2+}	25.64, 15.38, 31.25	[120]
Poly(etherphosphine)s		Pb^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+}	-	- [121]
Diethylphosphonate-containing poly(arylene ether nitrile)s		Pb^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+}	-	- [122]

PTIs: Poly(triazole-imide)s; PTAIs: poly(triazole-amide-imide)s; PTIs: poly(triazole-imide)s; PIs: polyimides; PXIs: poly(xanthone-imide)s; PAMAs: poly(azomethine amide)s; PAS: polyamide-sulfide.

the solution, the adsorbent dosage, the initial concentration of heavy metals, and the contact time on the adsorption capacity of polymers-based adsorbents are studied.

PIs

PIs are one of the most important aromatic polymer classes, offering excellent thermal stabilities, sufficient chemical resistance, and high mechanical and electrical properties. However, they present very poor hydrophilicity, and therefore, many efforts have been undertaken to incorporate heterocyclic functional groups into their backbone or side groups to generate new PIs with enhanced thermal properties and improved chelating properties.

Among various heterocycle structures, 1,2,4-triazole has been the subject of numerous studies, mainly due to its stability under diverse conditions and the well-established role of triazole units as binding sites for metals. Therefore, insertion of the triazole ring into the main chains produces materials with high hydrophilicity, enabling them to interact with metals. Bazzar *et al.* synthesized a series of PIs bearing 1,2,4-triazole moiety in the principal chain and quinoxaline as a pendant group, according to a two-step procedure that involves the condensation of diamines with dianhydrides followed by the imidization process[90]. The obtained poly(triazole-imide)s were used as adsorbents of Cr^{3+}, Co^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Hg^{2+}, Cr^{VI}, and Mn^{2+} individually or in mixtures, at a range of pH values (1-14). The removal percentage of metals was increased in the order of $Cr^{3+} > Mn^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+} > Hg^{2+} > Pb^{2+}$, which is contrary to the order of their ion radii. The maximum adsorption of 98% was given to the smallest metal ion (Cr^{3+}), while 35% removal was observed for the largest metal ion (Pb^{2+}) [Figure 1A].

A series of solutions at different pH values ranging from 1.0 to 14.0 was prepared to study the effect of initial solution pH on metal ion removal. As shown in Figure 1B, the percentage of Cr^{3+} removal was low in the pH zone between 1 and 5, and increased with increasing pH, reaching a maximum of 98% at a basic pH of 10. While the adsorption efficiency of $Cr_2O_7^{2-}$ anion was 80% at pH 1.0 and decreased as pH increased [Figure 1C]. This finding can be explained by the fact that in the acidic pH range, nitrogen atoms of the

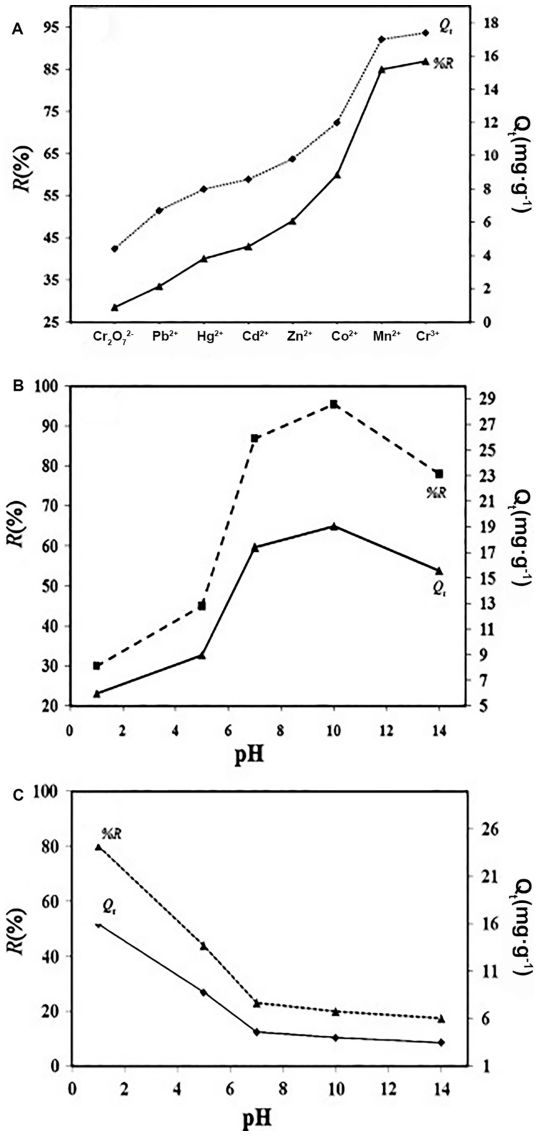


Figure 1. (A) The quantity of adsorbed metals (Qt) and adsorption efficiency (%R) at pH = 8 by poly(triazole-imide); (B) effect of pH variation on the adsorption amount of Cr^{3+} cation; (C) effect of pH variation on the amount of adsorption of $Cr_2O_7^{2-}$ anion. From[90] with permission.

triazole and quinoxaline cycles are protonated, resulting in a repulsive interaction between the positive ions and the positively charged polymer surface that reduces the adsorption of the Cr^{3+} cation. On the other hand, the negative-charged $Cr_2O_7^{2-}$ is electrostatically attracted to positive bonding groups on the PI surface. The solution pH is an important parameter as it can affect the adsorbent's functional group ionization and can determine the attractive or repulsive interaction between the adsorbent and the metals to enhance or reduce adsorption efficiency. Ghaemy *et al.* also reported the influence of pH on metal adsorption ability using triazole-based poly(amide-imide) bearing a pendant phenoxy quinoline unit[91]. The polycondensation reaction was performed between a diimide-diacid and three commercial diamines in the presence of thiamine pyrophosphate as an activator in NMP (N-méthyl-2-pyrrolidone)/Pyridine mixture containing LiCl and $CaCl_2$. At acidic media pH = 3, the highest extraction percentages of 95% and 85% were found for F^- and $Cr_2O_7^{2-}$ anions, respectively, and the adsorption of Cr^{3+} and Cd^{2+} cations showed the lowest value of 66% at this pH. The adsorption study revealed that polymer removal performance depended mainly on the

structure and hydrophilic character of the diamine moiety in the polymer backbone. The highest adsorption percentage was observed with the polymer containing two hydrophilic triazole rings in the repeating unit, increasing its hydrophilic character and adsorption capacity. The same authors[92] reported the design of another family of phenoxy quinoline-based poly(triazole-imide)s for the efficient removal of metals. The triazole and phenoxy quinoline groups were identified as effective chelating and host units for heavy metals. According to this research, structural modification of PI by incorporating heterocyclic rings can be an interesting approach to improving their adsorption capacity.

Flexible ether linkages, imidazole rings, and xanthene as a pendant group have been successfully added to PIs by Amininasab *et al.*[93]. The use of Imidazole heterocyclic rings and their derivatives is advantageous due to their high electron affinity and good thermal stability. The prepared PIs showed an enhanced adsorption capacity for adsorbing heavy metals due to the increased presence of –NH and –O groups along the adsorbent's backbone. The adsorption capacities for Hg^{2+}, Cr^{3+}, Cd^{2+}, Co^{2+}, and Pb^{2+} were 37.90, 32.65, 28.60, 21.15, and 19.80 mg/g, respectively. For efficiently removing Cr (VI) from wastewater, PIs were functionalized with pyridine and xanthene groups[94].

The pyridine heterocyclic ring has been reported to improve the processability, solubility, and adsorption performance of PIs due to its aromaticity and polarizability resulting from nitrogen heteroatoms[95], which are recognized as the main adsorption sites and effective binding sites for heavy metals to form metal complexes which are known as the main adsorption site and as an effective binding site of heavy metals to form a metal complex[96]. The adsorption behavior of these polymers at different Cr (VI) concentrations (1, 5, and 10 mg/L) showed that the adsorption capacity (91%) was higher when the concentration of hexavalent Cr in aqueous solution was 5%. Rafiee *et al.*, in turn, described the development of new PIs having porphyrin units utilizing four tetracarboxylic dianhydrides and tetramine through a two-step imidization technique for the adsorption of Cd^{2+} and Hg^{2+}[97]. Porphyrins are regarded as an attractive class of heterocyclic materials with a high capacity to bind with a diverse array of metals and create stable complexes. The nitrogen atoms in the tetrapyrrolic core, due to their electron-donating properties, can serve as ligand sites to adsorb various metals, allowing their efficient extraction[98]. Adsorption tests were performed by dissolving 5 mg of a single PI in 25 mL of individual aqueous metal ion solutions at pH 7 and stirring for 3 days. The results showed that the utilized PI had an excellent adsorption capacity toward Cd^{2+} > Hg^{2+}.

Bio-sourced coPIs were used as adsorbent films which is similar to the order

f Pb^{2+}, Ni^{2+}, Cd^{2+}, and Hg^{2+} from aqueous solution[99]. These polymers were synthesized by combining, from 100% to 0%, three monomers (isosorbide-based dianhydride, petroleum-based dianhydride, and cardo diamine). It was noted that adsorption efficiency increased as the proportion of isosorbide moieties in the PI backbones increased. Thus, the homopolyimide, obtained from 100% of biobased dianhydride and diamine, exhibited the highest adsorption efficiency toward metals. This rise is mainly due to the incorporation of isosorbide into the polymer structure, which can generate attractive hydrophilicity and wettability, increasing their tendency to remove contaminants from water. Comparing the adsorption capacity of metals on this polymer, the order was as follows: $Pb^{2+} \approx Ni^{2+} > Cd^{2+} > Hg^{2+}$. Based on the 1/n values, the adsorption of Ni^{2+} (0.064) and Pb^{2+} (0.096) is deemed to be more advantageous, while the adsorption of Hg^{2+} (0.181) is less favorable. In addition, the proposed adsorption mechanism was mainly based on oxygen-heavy metal interactions [Figure 2].

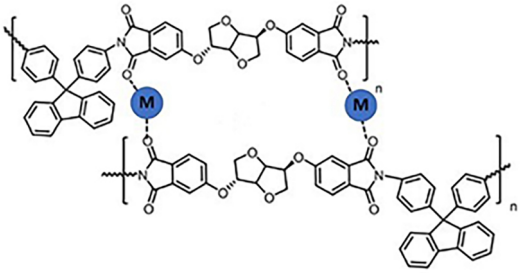


Figure 2. The metal-polyimide complex formed via oxygen-heavy metal interaction. From[99] with permission.

Lakouvaj *et al.* also investigated the extraction of metals including Cr (VI), Co (II), Ni (II), Cu (II), Pb (II), and Cd (II) from aqueous solutions using a new class of poly(xanthone-imide)s (PXIs)[100]. The authors revealed that the adsorption efficiency (%) increased in the order of Cd^{2+} > Pb^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Cr(VI), which is similar to the order of their ionic radii. They stated that the carbonyl functional groups in PI chains act as coordination sites for chelation with metals [Figure 3].

Mansoori *et al.*, in a similar research, reported the synthesis of PIs containing 1,3,4-oxadiazole and pyridine moieties for removing Co^{2+} and Ni^{2+}[101]. It has been demonstrated that variations in solution pH impact the coordination capabilities of PIs toward metals. Consequently, the highest metal uptake capacities for Co (II) and Ni (II) were 110.4 and 100.5 mg/g, respectively, at pH 7.0. This finding was reported by Manzoor *et al.* It was shown that variations in solution pH affect the coordination capacities of PIs toward metals[102]. Thus, the highest metal uptake capabilities of Co^{2+} and Ni^{2+} were 110.4 and 100.5 mg/g, respectively, at pH 7.0. Manzoor *et al.* prepared two aromatic sulfonated copolyimides (SPIs), FBM and OBM, using two distinct dianhydrides FDA [4,4'-(hexafluoroisopropylidene)-diphthalic anhydride] and ODPA (4,4'-oxydiphthalic anhydride), along with stoichiometric amounts of sulfonated [BDSA (Benzidine-2,2'-disulfonic acid)·TEA (triethylamine)] and non-sulfonated [MDA (4,4′-methylenedianiline)] diamines as comonomers, aiming for effective Pb adsorption from aqueous solutions[102]. They reported that incorporating anionic sulfonate groups into the PI backbone improved hydrophilicity, resulting in enhanced Pb^{2+} adsorption.

The authors employed quantum chemical simulations using Molecular Operating Environment software (MOE) to identify the structural factors affecting the sorption efficiency of Pb^{2+} onto SPI adsorbents. It was observed that OBM has a hydrophilic surface area larger than that of FBM, as shown in Figure 4. The enhanced hydrophilicity of the OBM copolyimide contributes to its increased adsorption capacity, which is consistent with experimental results, with data showing higher adsorption of Pb ions on the OBM surface (99%) compared to FBM (30%).

Polyamides

Heterocyclic polyamides represent one of the most important classes of high-performance materials, which are ideal candidates for use as heavy metal ion adsorbent from aqueous solutions. Significant attention has been drawn to the synthesis of polyamides containing –CONH–, –CSNH–, –N=CH–, and heterocyclic groups that can serve as metal-complexing ligands. The presence of these chelating functionalities in an aromatic polyamide backbone is expected to enhance metal ion adsorption capacity and stability for reuse.

Ravikumar *et al.* synthesized aromatic polyamides and polythioamides incorporating pendant chlorobenzylidine rings via direct polycondensation of a dicarboxylic acid with diamines and thioamines, respectively, for the removal of toxic metals from water[103].

Figure 3. Chelation of metals with PXIs[100]. PXIs: Poly(xanthone-imide)s.

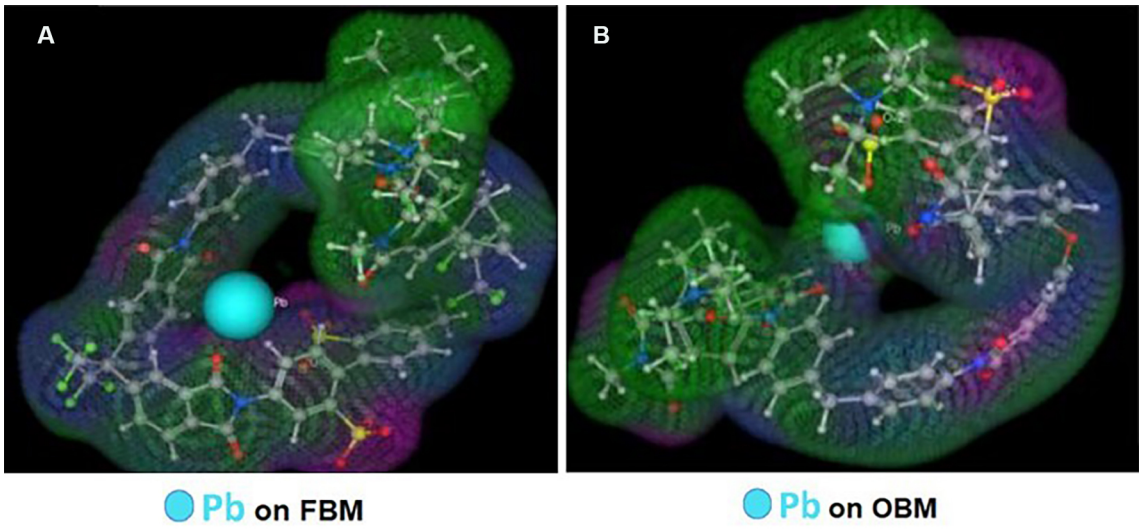


Figure 4. Hydrophobic regions (depicted as green dots) and hydrophilic regions (represented by blue and purple areas) of two sulfonated aromatic copolyimides, the sulfonated FBM (A) and non-sulfonated OBM (B) complex with Pb. From[102] with permission.

They reported that the amide, carbonyl, and azomethine groups in the polymer backbone enhanced the adsorption capacity of Pb^{2+} and Cr^{3+} from water. The highest adsorption capacity for Pb^{2+}, 274.6 mg/g, was achieved at pH 10, while the maximum adsorption for Cr^{3+}, 255.2 mg/g, occurred at pH 6.

Murugesan *et al.*, on the other hand, examined the elimination of Pb^{+2}, Cu^{+2}, and Cd^{+2}, using aromatic poly(azomethine amide)s[104]. Their results showed that the removal of metals varied with pH, peaking at pH 6. They also reported an increase in adsorption efficiency as the contact time increased and equilibrium was observed in 60 min. The polyamide exhibited maximum adsorption capacities of 470.7 mg/g for Cu^{2+}, 462.3 mg/g for Cd^{2+}, and 452.1 mg/g for Pb^{2+}. In an additional study[105], they investigated the adsorption efficiency of newly developed polyamides incorporating pyridyl and azomethine pendant groups for the removal of Cu (II) Pb (II) metals. The highest adsorption capacities of Cu (II) and Pb (II) ions, determined by Langmuir models, were determined to be 389.9 and 403.1 mg/g, respectively. Gómez-Valdemoro *et al.* fabricated aromatic polyamides bearing pendant 1,2,4-triazole groups to extract Hg cations from aqueous media[106]. The study demonstrated that the polar triazole unit significantly enhanced the hydrophilicity of polyamides, rendering these polymers effective solid phases for the high extraction (99%) of Hg^{2+} from aquatic environments. Soleimani *et al.* have also highlighted the importance of incorporating a heterocyclic imidazole ring into polyamide backbones as a hydrophilic chelating agent for heavy metals[107]. They reported high percentage removal of 87.80%, 61.60%, 50.20%, 43.09%, and 39.30% for Cr^{3+}, Co^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}, respectively. Santiago *et al.* prepared a series of sulfonated aromatic polyamides and evaluated their uptake performance to eliminate Pb and Hg ions[108]. It was found that the polyamides exhibited higher adsorption capacities for Pb^{2+} compared to Hg^{2+}.

Albukhari *et al.* synthesized a series of four heteroaromatic sulfur-containing polyamides by polycondensation of diamine with diacid chlorides for the selective removal of heavy metals from wastewater[109]. The obtained polymers demonstrated a remarkably high selectivity for Hg (II) ions, with the maximum adsorption capacity reaching 47.95 mg/g by the Langmuir model. The effect of pH (ranging from

1 to 9) on the adsorption of Hg^{+2} was also studied. It has been reported that the highest percentage of Hg^{+2} extraction, 98.75%, was achieved at pH 1. This increase was explained by the electrostatic attraction forces that can occur between protonated sites formed at pH 1, such as secondary amine groups and carbonyl groups in the polymer backbones, with the negatively charged species including $HgCl_4^{-2}$, neutral $HgCl_2$, and another chloroanionic complex $HgCl_3^{-1}$. In another study, Rezania *et al.* prepared a polyamide-sulfide (PAS) incorporating pyridine and thiazole heterocycles for Pb removal from water[110]. They observed that the synthesized polymer is an excellent adsorbent of Pb(II) ions, demonstrating a significant adsorption capacity of around 714 mg/g.

Replacing polyamides with copolyamides such as poly(amide-imide)s (PAIs) may be beneficial for increasing the polarity of the polymer chain to extract heavy metals with more affinity. Due to the presence of both amide and imide units in their polymer repeating units, PAIs exhibit properties that are different from those of polyamides and PIs. As a result, this class of polymers provides a good combination of excellent thermal stability, processability, and high uptake of heavy metals[111-113].

The adsorption of PAIs was enhanced by incorporating hydrazide functional groups in their backbone. This improvement is attributed to the polar characteristics of the hydrazide group (–CO–NH–NH–CO–), which readily engages with metals to create complexes[114]. These heterocyclic polymers were prepared by polycondensation of a diacid monomer containing imidic rings with various dihydrazides for the extraction of heavy metal cations such as Pb, Cd, Cu, and Zn. Among heavy metals, Pb demonstrated the highest adsorption capacity at 0.99 mmol/g, while Cd ions were adsorbed with a capacity of 0.75 mmol/g. A comparative study was carried out using another family of poly(amide-hydrazide-imide) obtained from the reaction of an acid chloride-anhydride monomer with dihydrazides, which resulted in more efficient adsorption of Pb^{2+} (1.70 mmol/g)[115].

Other heterocyclic polymers

Powerful adsorption of silver ions was obtained utilizing a poly(2-aminothiazole)P-2AT prepared via the polymerization of 2-aminothiazole with benzoyl peroxide (BPO) as an initiator in 1,4-dioxane at 80 °C for 24 h[116]. The adsorption tests were performed at different pH levels (3-6), contact times (15-90 min), and initial Ag^+ concentrations (100-1,200 mg/L) to study the effect of these parameters on adsorption capacity. It revealed that adsorption efficiency increased with the increasing initial concentrations and the contact time. The maximum adsorption capacity of Ag^+ on P-2AT was found to be 336.98 mg/g for 1,200 mg/L Ag (I) solution at pH 5 after 90 min of contact. An attractive heavy metal adsorbent based on a poly(ionic liquid) bearing 1,2,3-triazole moiety was developed by Puguan and Kim for Cr (VI) extraction[117]. It was prepared by Cu-catalyzed cycloaddition CuAAC of α-azide-ω-alkyne monomer in the presence of $CuIP(OEt)_3$ followed by quaternization and anion exchange. The Langmuir isotherm model described the adsorption of Cr (VI) on the poly(ionic liquid) as monolayer adsorption with an adsorption capacity of 13.545 mg/g at room temperature and pH 2. The adsorption was the result of van der Waals and electrostatic forces between the amines in the triazole ring and the dissociated Cr (VI) in water. The 1,2,3-triazole unit has also been grafted into polystyrene chains [Figure 5] to be tested as sorbents for the removal of Mg and Zn present in wastewater[118]. These polymers showed a low selectivity for Mg, with an extraction percentage of below 3%, while for Zn, the removal percentage was around 30%.

Qureshi *et al.* synthesized polyazomethine through a polycondensation reaction of dialdehyde and diamine for the adsorption of Co^{2+}, Cu^{2+}, and Au^{3+} from wastewater[119]. The sorption process followed the Langmuir monolayer adsorption model, and the adsorption capacities for Co^{2+}, Cu^{2+}, and Au^{3+} were 21.28, 31.25, and 35.71 mg/g, respectively. The results indicated a chemisorption/ion-exchange nature of adsorption. The

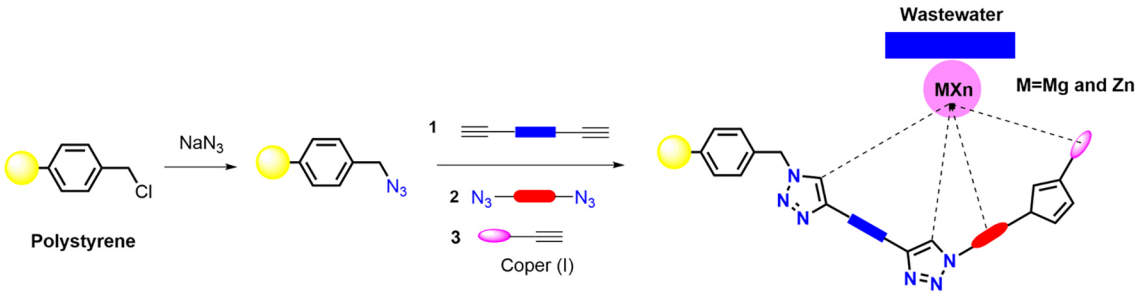


Figure 5. Synthetic Scheme of 1,2,3-Triazoles-Based Polystyrene and its application in the Extraction of Zn and Mg from Wastewater. From[118] with permission.

authors varied several parameters, including initial ion concentration (10-50 mg/L), pH levels (2-8), the quantity of polymer adsorbent (10-50 mg), and the contact time (10-180 min), to obtain maximum adsorption capacity from the optimum adsorbent. The ideal conditions obtained for the highest adsorption capacity of Co^{2+}, Cu^{2+}, and Au^{3+} are at a pH value of 8 for Co^{2+} and Cu^{2+} and 2 for Au^{3+}. The corresponding adsorption capacities were 4.32, 51.8, and 41.32 mg/g, respectively.

Likewise, a polyazomethine derived from another diamine[120] was also prepared and used for the efficient extraction of Ni^{2+}, Cu^{2+}, and Co^{2+}. This material removed up to 77% of Ni^{2+}, 98% of Cu^{2+}, and 72% of Co^{2+} from wastewater. Chabbah *et al.* developed phosphorous polymers for the detection of Pb^{2+}, Cd^{2+}, Hg^{2+}, and Ni^{2+} heavy metals[121,122]. Their results showed that the synthesized polymers display a performing ability for the decontamination of water.

ADSORPTION MECHANISMS

The Langmuir adsorption model assumes that a polymer has a fixed number of binding sites. All the binding sites show the same affinity for the adsorbent. Therefore, each site adsorbs only one molecule and forms a single monolayer.

The linear form of the Langmuir model can be written as:

$$1/q_e = 1/bq_m\,(1/C_e) + 1/q_m \quad \text{(Eq. 1)}$$

Where q_e (mg/g) is the amount of heavy metals adsorbed onto the polymer at equilibrium, Ce (mg/L) is the equilibrium concentration, q_m (mg/g) denotes the maximum adsorption capacity, and b (L/mg) is the Langmuir constant related to free energy. The Langmuir constants q_m and b were calculated from the slope and the intercept of the Langmuir plot of $1/q_e$ *vs.* $1/C_e$.

The linear form of the Freundlich model is given as:

$$\ln q_e = 1/n\,\ln C_e + \ln k_F \quad \text{(Eq. 2)}$$

Where q_e (mg/g) represents the amount of heavy metals adsorbed per unit mass of adsorbent, C_e (mg/L) is the equilibrium concentration of heavy metals, and n and k_F are Freundlich constants. These constants can be determined from the linear plot of $\ln q_e$ *vs.* $\ln C_e$.

The Redlich-Peterson isotherm combines Langmuir and Freundlich models. At higher concentrations, it approximates the Freundlich model, while at lower concentrations, it aligns with the Langmuir equation. The equation is given as:

$$q_e = (K_R C_e)/(1 + a_R C_e^b) \quad \text{(Eq. 3)}$$

where K_R is the Redlich-Peterson isotherm constant (L/g), α_R is the Redlich-Peterson isotherm constant (L/mg), and β is the exponent that lies between 0 and 1. The constant β can characterize the isotherm as: if β = 1, the Langmuir will be the preferable isotherm, while if β = 0, the Freundlich isotherm will be the preferable isotherm.

The Temkin isotherm model contains a factor that explicitly takes into account the adsorbing species - adsorbate interactions. This model assumes the following conditions: (1) the heat of adsorption of all the molecules in the layer decreases linearly with the coverage due to adsorbent-adsorbate interactions; and (2) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied by the Freundlich equation. The Temkin isotherm has commonly been applied in the following form:

$$q_e = B \ln (AC_e) \quad \text{(Eq. 4)}$$

where B = RT/b and A is Temkin constant.

The kinetics of heavy metal adsorption onto the different fabricated polymers were analyzed at various time intervals using the pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order kinetic model is expressed as:

$$\ln (q_e - q_t) = -k_1 t + \ln q_e \quad \text{(Eq. 5)}$$

where q_t and q_e (mg/g) are the amount of heavy metals adsorbed at time *t* (min) and equilibrium time, respectively. The parameter k_1 (min^{-1}) denotes the rate constant of the pseudo-first-order kinetic model. The rate constant of the pseudo-first-order kinetic model and q_e values are derived from the slope and the intercept of the linear plots of $\ln(q_e - q_t)$ *vs.* time (min), respectively. The pseudo-first-order kinetic model assumes that one heavy metal ion is sorbed onto one sorption site on the surface of a polymer.

The pseudo-second-order kinetic model can be written as:

$$1/q_t = t/q_e + 1/k_2 q_e^2 \quad \text{(Eq. 6)}$$

where k_2 (g/mg/min) is the rate constant of the pseudo-second-order kinetic model. This model assumes that one heavy metal ion is sorbed onto two sorption sites on the surface of an adsorbent. The rate constant of the pseudo-second-order kinetic model and q_e are estimated from the intercept and the slope of the linear plots of t/q_t *vs.* time (min), respectively.

The adsorption isotherms were best fitted with Langmuir model for the adsorption of heavy metals on biosourced PI[99], polyamide sulfide[109], 1,2,3-triazole based-poly(ionic liquid)[117], and polyazomethines[119].

Redlich-Peterson model allowed the best fitting of the adsorption isotherms of heavy metals on poly(azomethine amide)s[104]. This point suggests that the polymer surface presents a homogeneous surface with specific adsorption sites.

The pseudo-second-order kinetic model allowed the best fitting of the adsorption of heavy metals on poly(azomethine amide)s[104], 1,2,3-triazole based-poly(ionic liquid)[117], and polyazomethines[119], suggesting that the rate-limiting step of heavy metal adsorption is mainly chemisorption process.

PERSPECTIVES AND CHALLENGES

The main factors characterizing the adsorbent qualities are its affinity, represented by the factor 1/n (with a lower value indicating higher affinity), and its adsorption capacity. Some quantitative data for conventional adsorbents can be found in the literature [Table 4].

For zeolites[65], 1/n is equal to 0.39 and the adsorption capacity is 28.79 mg/g for Ni (II) ions at 20 °C. For activated clays[71], 1/n is equal to 0.56 for Cr (VI) and 2.80 for Fe (III), and adsorption capacities are 18.15 mg/g and 39.80 mg/g, respectively. For activated carbon, depending on the raw materials [Table 2], 1/n varies from 0.181 for Pb (II) to 0.592 for Cr (VI) and adsorption capacities vary from 37.14 mg/g for Cd (II) to 253.2 mg/g for Pb (II). The characteristics of heterocyclic linear polymers are compared to those of the conventional adsorbents to select the best of them. Biosourced PIs[99] present a value of 1/n equal to 0.064 for Ni (II) and PASs[110] has a value of 0.059 for Pb (II). Such low values were not obtained with conventional adsorbents. Moreover, certain heterocyclic linear polymers demonstrated selectivity for specific heavy metal ions; for example, poly(etherphosphine)[121] and diethylphosphonate-containing poly(arylene ether nitrile)[122] were selective for Pb(II). This selectivity is particularly relevant for the recovery of pure heavy metals in diluted acidic media or complexing media. Concerning the adsorption capacities of heterocyclic linear polymers for Pb (II), they could vary from less than 1 mg/g[121] to 403.1 mg/g[105] and 452.1 mg/g[104] with respectively a pyridine-containing polyamide and a poly(azomethine amide)s. To enhance the adsorption capacities of linear polymeric phases, inorganic compounds such as silica gel, graphene, graphene oxide (GO), clay, and monoliths can be coated with them. The resulting materials significantly present a larger specific surface area and then a higher adsorption capacity; an example shows that the capacity of adsorption of PI for Cu^{2+} ion increased by a factor of 77 after PI/silica coprecipitation[123]. Another way to increase the specific surface area is the electrospinning of the heterocyclic linear polymers. Amino-rich functionalized PIs-polyethyleneimine (PEI) fibers with a diameter of 13 μm and a surface roughness of Rq = 17.10 nm were successfully synthesized. These fibers present numerous amine groups at the surface and were able to adsorb Cr (VI) ions with a capacity of adsorption of 50 mg/g[124]. Electrospun Fe_3O_4/MWCNTs/polyamide 6 nanofibers with a diameter of 101 nm enabled the adsorption of Pb (II) ion through the OH groups at their surface; an adsorption capacity of 49.3 mg/g was obtained[125]. Electrospun PA6/CaO nanofibers presented an adsorption capacity of 39 mg/g for Pb (II) ions and 33 mg/g for Cr (VI) ions[126].

Adsorbent regeneration is important for repeated use in different applications, as well as for reducing the quantity of adsorbent material, which in turn lowers the cost of the adsorbent. Studies have shown that adsorbents based on aromatic linear polymers can be reused for numerous cycles without significant loss of adsorption capacity.

Pyridine-based polyamide designed for removing Pb(II) and Cu(II) ions was successfully regenerated with various acids, including H_2SO_4, HCl, and CH_3COOH, and used for seven adsorption-desorption cycles [Figure 6][105]. Among these, aq. H_2SO_4 and aq. HCl proved more effective than aq. CH_3COOH for the

Table 4. Comparison of the characteristics of heterocyclic polymers to other popular heavy metal absorbents

Adsorbent	Heavy metal	Adsorption capacity mg/g	Affinity (1/n)	Ref.
Zeolite	Ni	28.79	0.39	[65]
Activated clay	Cr	18.15	0.56	[71]
	Fe	39.80	2.80	[71]
Activated carbon	Pb	253.2	0.181	[69]
	Cd	85.8	0.3364	[74]
Biosourced polyimides	Ni		0.064	[99]
Polyamide-sulfides	Pb		0.059	[110]
Poly(etherphosphine)	Pb	1		[121]
Poly(azomethine amide)	Pb	403.1		[105]
	Pb	452.1		[104]
Functionalized amino-rich PI-PEI fibers	Cr	50		[124]
Electrospun Fe_3O_4/MWCNTs/polyamide 6 nanofibers	Pb	49.3		[125]
Electrospun PA6/CaO nanofibers	Pb	39		[126]
	Cr	33		

PI: Polyimide; PEI: polyethyleneimine.

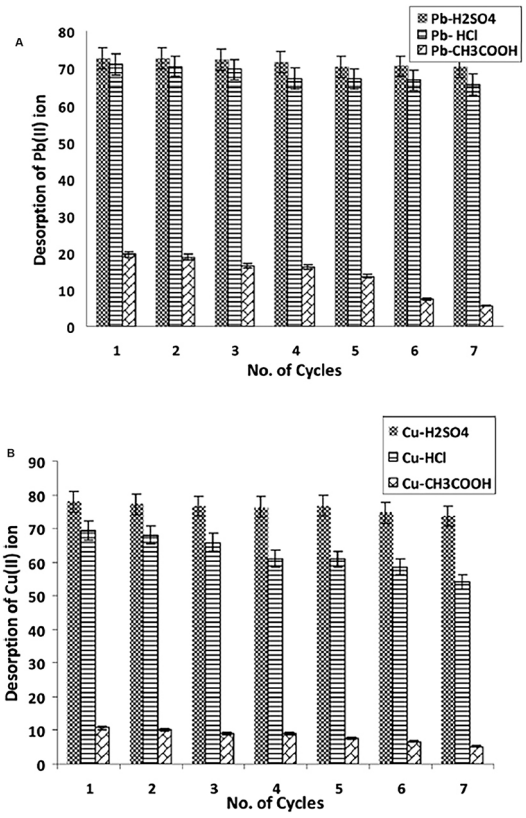


Figure 6. Adsorption-desorption of Pb^{2+} (A) and Cu^{2+} (B) onto adsorbent polyamide. From[105] with permission.

desorption of Cu (II) and Pb (II) ions. Additionally, the adsorbent demonstrated sustained efficiency in removing Cu (II) and Pb (II) ions, without considerable loss of efficiency even after seven adsorption-desorption cycles.

Similarly, polyamide and polythioamide bearing chlorobenzylidine moieties retain their original removal capacity for removing Cr^{2+}, Pb^{2+}, Cd^{3+}, and Cu^{2+} after four consecutive adsorption-desorption cycles[103]. Adsorbent regeneration was carried out using an aqueous solution of HCl (2N). The reusability results, presented in Table 5, revealed that the capacities of both polyamide P3 and polythioamide P5 remained practically unchanged for all metals, even after four cycles of adsorption-desorption.

Bıyıkoğlu *et al.* also examined the reusability of poly(2-aminothiazole) P-2AT after four adsorption-desorption cycles[116]. To remove the previously adsorbed Ag^+ ion, the P-2AT was treated with 0.1 M HNO_3 solution. As shown in Figure 7, the Ag^+ adsorption capacity was almost the same on the second use and decreased on the fourth cycle to 23.84 mg/g. This suggests that P-2AT can be used repeatedly to remove Ag (I) ions.

Table 5. Metal ion adsorption capacity of polyamide P3 and polythioamide P5 after four cycles of adsorption-desorption[103]

Cycle no.	Adsorption capacity (mg/g) of polyamide P3			
	Pb(II)	Cu(II)	Cr(II)	Cd(III)
1	108.7	102.5	91.8	60.1
2	106.4	102.4	71.1	58.2
3	104.9	100.9	65.7	53.8
4	99.7	98.1	64.7	49.6
	Adsorption capacity (mg/g) of polythioamide P5			
1	109.4	108.5	82.6	60.1
2	107.5	100.9	71.8	56.5
3	105.9	99.5	71.1	44.6
4	103.8	96.7	65.7	37.8

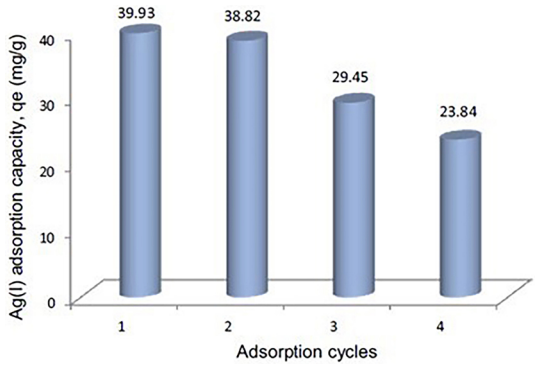


Figure 7. Adsorption capacity of Ag (I) onto poly(2-aminothiazole) after four adsorption cycles. From[116] with permission.

After selecting the best formula and configuration for the heterocyclic polymers, the further challenge is achieving large-scale production at a reduced cost.

CONCLUSION

This study aims to present an overview of heterocyclic polymer-based adsorbents for the extraction of heavy metals to reduce water pollution. The various parameters affecting the adsorption capacity of heavy metals are studied. The removal of heavy metals from wastewater through adsorption is a cost-effective alternative to conventional costly methods, making it an optimal choice for wastewater treatment. Heterocyclic linear polymers are effective adsorbents of toxic metals due to their chemical and physical stability, their specific affinity, their adsorption capacity that can be improved, and their easy regeneration. The heterocyclic functional groups contained in the polymer backbone are responsible for the increased adsorption efficiency and recyclability of heavy metal ions in aqueous media. These groups act as attractive chelating sites and tend to eliminate ions through electrostatic interactions. The regeneration of the adsorbent polymers showed that the adsorption-desorption process is reversible, indicating that aromatic linear polymers have a strong potential for reuse, as the active sites are physically bonded to the polymer backbone. The successful use of heterocyclic polymer-based materials also opens up new possibilities for eliminating hazardous organic pollution from wastewater.

DECLARATIONS

Authors' contributions

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Conflicts of interest

Jaffrezic-Renault N is an Editorial Board member of the journal *Water Emerging Contaminants & Nanoplastics*, while the other authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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