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ORIGINAL PAPER

Investigating the efficacy of 1,2,4-oxadiazole decorated cross-linked polyamidoxime-based macromolecular networks in metal ions remediation

Manzar Zahra[1,2] · Sonia Zulfiqar[3,4,5] · Muhammad Ilyas Sarwar[1] · Eric W. Cochran[4]

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Abstract
Crosslinked polyamidoximes (PAOs) were synthesized using terephthaloyl chloride (TPC) as a crosslinking agent, which interacted with the pendant amidoxime groups on the polymer chains. The incorporation of a stiff 1,2,4-oxadiazole bridging unit was achieved by reacting TPC with PAOs in tetrahydrofuran (THF) under reflux. The linkage was verified using FTIR spectroscopy to identify the characteristic functional groups in the crosslinked polyamidoximes. X-ray diffraction (XRD) patterns indicated improved chain alignment due to crosslinking. Additionally, the thermal stability of crosslinked PAOs increased significantly to a range of 515–593 °C, compared to 426–489 °C for non-crosslinked PAOs. These crosslinked PAOs were tested for their effectiveness in removing metal ions through a batch process. Optimal conditions resulted in maximum adsorption efficiencies of 86% for Cd (II) and 88% for Pb (II) at pH 6, with a contact time of 3 h, a feed concentration of 40 mg/L, and 0.1 g of adsorbent. The adsorption mechanism conformed more closely to the Langmuir isotherm than the Freundlich model. In competitive adsorption, the order of metal uptake was Fe (II) > Pb (II) > Cd (II) > Cu (II). Consequently, this class of crosslinked polyamidoximes shows potential for use in water treatment applications for removing heavy metal ions.

Keywords Cross-linked polyamidoximes · Thermal stability · Metal ions remediation

Introduction

Crosslinked polymeric systems represent a significant category of macromolecules renowned for their robust attributes such as enhanced thermal stability, porosity, and versatile capability to sequester a diverse array of chemical species [1–4]. These materials are pivotal in many applications spanning various fields, owing to their innate qualities and operational efficiency. Their robust mechanical strength, coupled with a substantial surface area, enables effective adsorption of guest molecules, irrespective of the presence of specific active sites. Hydrogels [5–7] and interpenetrating polymeric networks (IPNs) [8–11] are prominent examples of interlinked systems within this class, each offering distinct characteristics and specialized functionalities tailored to specific application requirements. These structures not only enhance material durability and performance but also expand the potential for innovative solutions in fields ranging from biomedical engineering to environmental remediation.

In the context of wastewater treatment, a critical challenge involves reducing concentrations of dyes and heavy metal ions using methods that are both cost-effective and technologically feasible. Adsorption has emerged as a promising approach to address these challenges. Various adsorbents have been employed due to their high removal efficiency, ease of use, and selectivity in capturing cations [12–17]. Examples include activated carbon, biologically derived

✉ Sonia Zulfiqar
sonia.zulfiqar@osu.cz; zulfiqar@iastate.edu

✉ Eric W. Cochran
ecochran@iastate.edu

1 Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan

2 Department of Chemistry, Lahore Garrison University, Lahore 54920, Pakistan

3 Department of Chemistry, Faculty of Science, University of Ostrava, 30. Dubna 22, Ostrava 701 03, Czech Republic

4 Department of Chemical and Biological Engineering, Iowa State University, Sweeney Hall, 618 Bissell Road, Ames, IA 50011, USA

5 Department of Physical Sciences, Lander University, 320 Stanley Ave, Greenwood, SC 29649, USA

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adsorbents, chelating polymers, nanocomposites, and macromolecules such as interpenetrating networks, hydrogels, and crosslinked polymers [18–26]. These materials are chosen for their ability to effectively bind and immobilize target pollutants from aqueous solutions, making them pivotal in sustainable wastewater treatment strategies. Polymer-based adsorbents have recently become popular due to their superior mechanical properties, water insolubility, and ease of regeneration under gentle conditions [27]. Amberlite XAD-4 is notably the most frequently utilized polymeric resin, particularly for adsorbing phenol and related compounds from wastewater [28]. These resins, with their water-repellent surfaces and related interactions, work well for organic components. However, they are not suitable for capturing polar substances, be they inorganic ions or other polar entities [29]. The synthesis of polar adsorbents was intensively studied to optimize bonding and interactions with molecules. This involved modifying the macromolecular backbone by adding various pendant groups, such as modifying the nonpolar poly (styrene–divinylbenzene) (PS-DVB) with polar entities like benzoyl, acetyl, and hydroxymethyl etc. Another method for enhancing the adsorption of polar entities is copolymerization using an appropriate functional group [30, 31]. Some commercial sorbents like Amberlite XAD-7 from Room and Haas feature ester groups, while others like Porapak RDX and the poly(N-vinylpyrrolidone-divinylbenzene) (PVP-DVB) copolymer demonstrate this technique. DPA-6S, a Supelco sorbent based on polyamide, is another example, though its adsorption capacity is limited due to its linear polymeric structure [32]. Nitrile functionality has also been explored as a crucial chelating agent towards cationic species. Some noted block copolymers include cyanomethyl styrene (CMSt)/divinylbenzene (DVB) [33], acrylonitrile (AN)/DVB and methacrylonitrile (MAN)/DVB· [34] Divinylbenzene (DVB) has been reported as a crosslinking agent for several block copolymers, like 4-vinylpyridine-divinylbenzene (4VP-DVB) [35], 4-vinylimidazole-divinylbenzene (4VIm-DVB) [36] and N-vinylimidazole-divinylbenzene (NVIm-DVB) [37]. When evaluating their adsorption abilities, NVIm-DVB demonstrated superior adsorption of polar entities, attributed to its polar nitrogen components acting as nucleophilic agents [32]. Since the 1970s, research has been conducted on crosslinked macromolecular adsorbents, with early reports highlighting the hypercrosslinking of polystyrene using bifunctional structures for enhanced sorption qualities. Today, several companies, including Purolite International (UK and USA, Dow Chemical (USA), and the Chemical Plant of Nankai University in China, produce such structures commercially. While these adsorbents demonstrate superior binding capacities, concerns remain regarding their cost-effectiveness and the use of potentially carcinogenic crosslinking agents like chloromethyl methyl ether. Another approach for creating crosslinked polymers involves using unsaturated groups catalyzed by the Friedel–Crafts mechanism. Research by Zhou et al.'s [26] and Aleksieva et al.'s teams [38] looked into crosslinking the base copolymer, styrene-co-divinylbenzene, via pendant vinyl groups using anhydrous ferric chloride as the catalyst. However, the resulting crosslinked components come from non-polar precursors, making them unsuitable for industrial use due to their lack of compatibility with polar compounds. While there are few reports of polar sorbents, one example is a block copolymer with a polar ester group, crosslinked similarly, which has been used for uptake of aromatic substances like phenol. Other documented methods involve introducing polar monomers [39, 40] or using them as crosslinking agents [41, 42]. These types of macromolecules show enhanced affinity towards polar groups due to interactions like hydrogen bonding, dipole–dipole, acid–base, and electrostatic forces [43, 44].

Heavy metals, identified as pollutants in water sources, are primarily added through human activities. These metals are harmful due to their persistence and inability to degrade biologically. As a result, there are established limits for safe water consumption. Adsorption is recognized as a key technique to lower heavy metal ion concentrations [45]. This study uses Cd (II) and Pb (II) as model cations. Cadmium sources include pigments, fossil fuels, batteries, fertilizers etc. [46] whereas lead mainly comes from solders, plumbing fixtures, storage batteries, paints, and vehicles [47, 48]. Studies have explored the use of polymeric adsorbents for the capture of heavy metal ions. These can be chelating groups [15, 17, 49, 50] functionalized organic/inorganic supports [51–54] or interpenetrated polymer networks [8]. Our previous research has shown efficient metal ion adsorption using interconnected polyamide systems [55]. Despite the proven electrostatic interactions of cations with nucleophilic centers, very few attempts have been reported using crosslinked organic macromolecules.

Polyamidoximes have been extensively studied for their ability to chelate metal cations effectively through the amidoxime group. However, the potential enhancement of their thermal resistance through crosslinking has not been previously explored. Herein, polyamidoximes were subjected to crosslinking to attain a thermally stable network with metal binding ability. A bifunctional monomer was utilized to interlink the chains and introduce more basic centers. Polymer resins containing nucleophilic binding sites offer promising adsorptive capabilities, akin to other effective adsorbents such as polyamides, poly(ester-imide)s, polyetherketones polyaniline, iminodiacetic acid functionalized macromolecules and many more. Recent studies have shown that oxadiazoles [56] can adsorb Hg^{2+}, and similarly, crosslinked polymers incorporating 1,2,4-oxadiazole with improved thermal stability have been developed to assess their adsorption capacity for Cd(II) and Pb(II)

heavy metal ions. This research introduces a novel class of adsorbents with decent efficiency for metal ions uptake, proposing them as effective materials for water treatment to remove heavy metals.

Experimental

Materials

Chemicals used to synthesize polyamidoximes are given in our previous report [57]. Terephthaloyl chloride (TPC, ≥ 99%), Tetrahydrofuran (THF) and methanol were purchased from Sigma Aldrich and used as received.

Synthesis of crosslinked polyamidoximes

In this endeavor, pre-synthesized polyamidoximes (PAO-1, PAO-2 and PAO-3, Fig. 1) [57] were interlinked using terephthaloyl chloride as a crosslinking agent to yield crosslinked polyamidoximes respectively (CL-1, CL-2 and CL-3). In a typical synthesis, polyamidoximes (PAO 1–3) were taken in a round bottom flask in THF, into which separately prepared TPC solution in THF was added dropwise in stoichiometric amounts. The reaction mixtures were set to reflux at 65 °C till the completion of the reaction (monitored by thin layer chromatography (TLC)). The solid products with 1,2,4-oxadiazole bridging units, were collected after cooling followed by washing with MeOH: H_2O (1:1) mixture by volume and dried to constant weight (Figs. 2, 3, and 4).

CL-1 Yield: 96%; *FTIR* ($\bar{\upsilon}$, cm^{-1}) 1668 (amide N–H), 1340 (C-N stretch), 1659 (C = N ring stretch), 956 (N–O), 1602, 1495 (Ar C = C), 3068 (= C-H), 1237 (C-O).

CL-2 Yield: 98%; *FTIR* ($\bar{\upsilon}$, cm^{-1}) 1684 (amide N–H), 1353 (C-N stretch), 1663 (C = N ring stretch), 964 (N–O), 1600, 1491 (Ar C = C), 3108 (= C-H), 1212 (C-O).

CL-3 Yield: 97%; *FTIR* ($\bar{\upsilon}$, cm^{-1}) 1652 (amide N–H), 1338 (C-N stretch), 1687 (C = N ring stretch), 943 (N–O), 1600, 1494 (Ar C = C), 3086 (= C-H), 1197 (C-O).

Characterization

Structural elucidation of the synthesized crosslinked polyamidoximes (CL 1–3) was carried out using Thermo Nicolet 6700 FTIR spectrophotometer in the range of $4000 - 550\ cm^{-1}$. XRD patterns were recorded on 3040/60X′Pert PRO X-ray diffractometer using Ni-filtered Cu Kα radiation over the range of $2\theta = 5 - 40°$ with a scanning rate of 0.02°/sec. Thermal stability of crosslinked polyamidoximes (CL 1–3) was investigated using NETZSCH

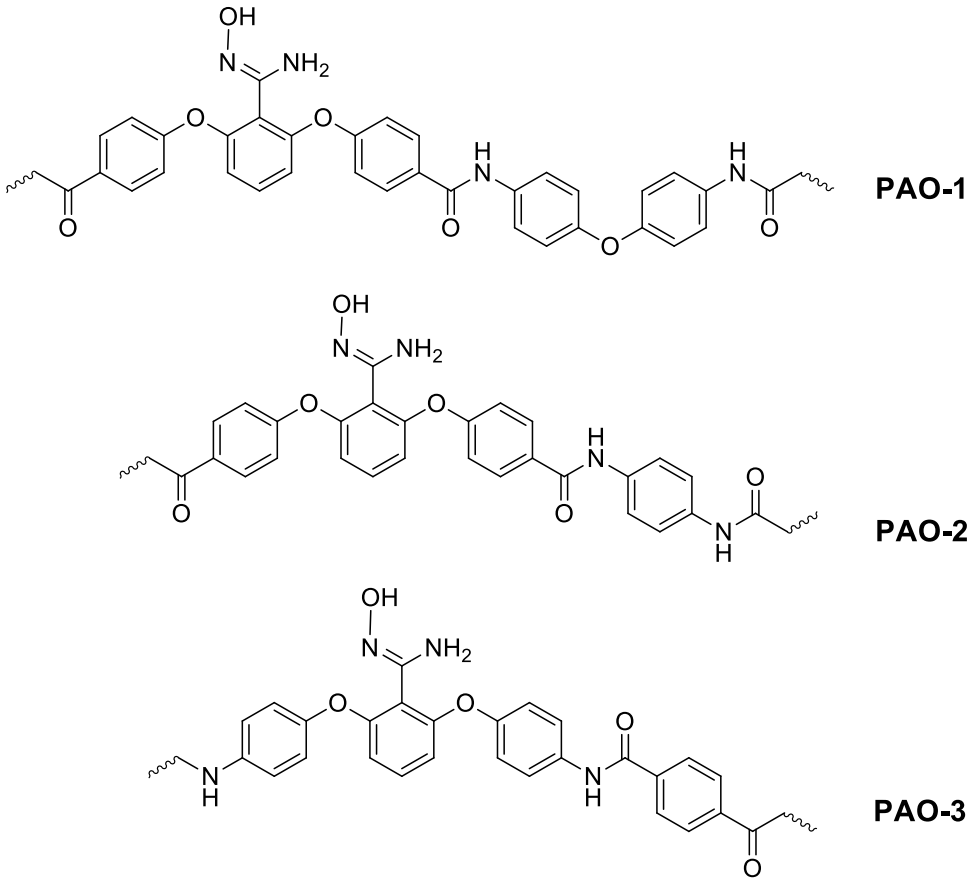


Fig. 1 Structures of various polyamidoximes employed for crosslinking [57]

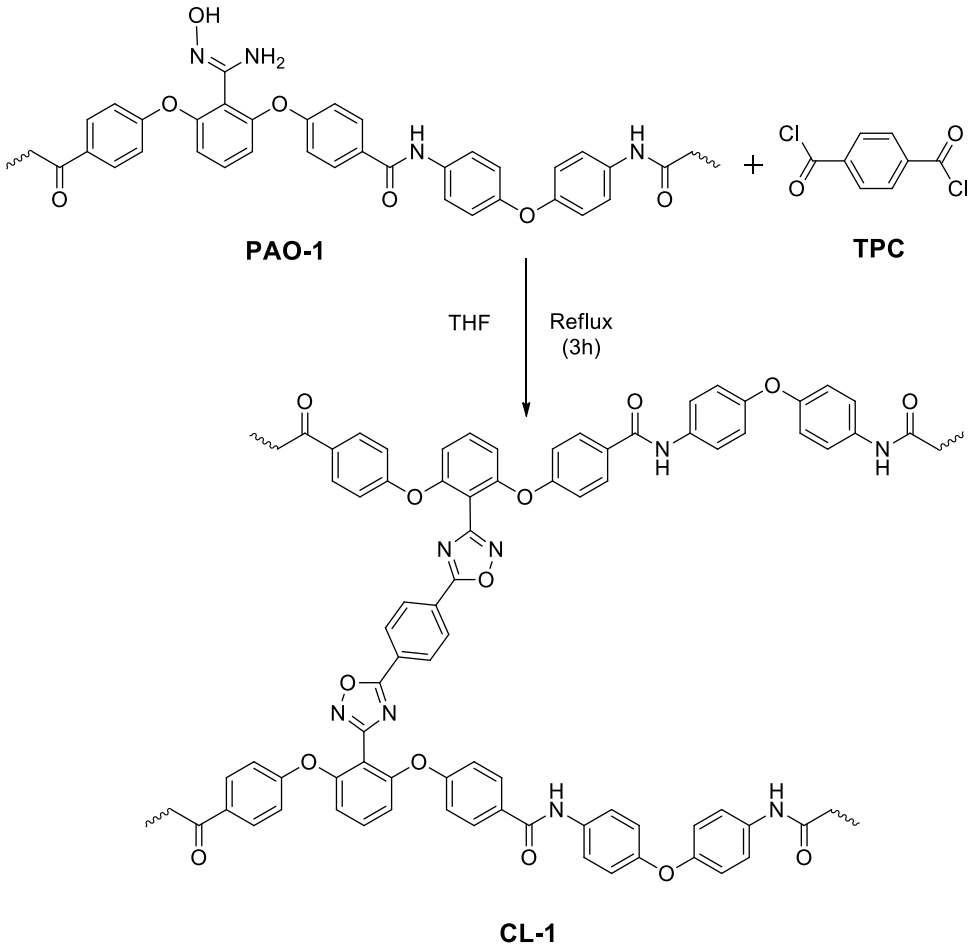


Fig. 2 Synthesis of cross-linked PAO-1 (CL-1)

TG 209 F3 thermogravimetric analyzer using 1 – 5 mg of the sample in an Al_2O_3 crucible heated from 25 to 1000 °C at a heating rate of 10 °C/min under a nitrogen atmosphere with a gas flow rate of 20 mL/min. A Shimadzu AA 670 flame atomic absorption spectrophotometer was employed to measure the uptake of metal ions.

Results and discussion

This research is focused on using pendant amidoxime groups to crosslink chains through diacid chloride and the creation of crosslinked macromolecular structures was confirmed using FTIR spectroscopy. The polyamidoximes (PAOs 1–3) initially dissolved well in polar aprotic solvents, including dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), and dimethyl acetamide (DMAc), but they became insoluble after undergoing crosslinking. This change in solubility served as an indicator that the crosslinking reaction had successfully taken place, resulting in a stiffer crosslinked structure. The cross-linked versions of these polyamidoximes, referred to as CL (1–3), were subsequently analyzed for their thermal stability and capacity to capture cations. These structures are useful in the adsorption of heavy metals; acrylonitrile polymers, in particular, are noted for their capacity to adsorb cations, and their thermal stability can be enhanced through interpenetrating or crosslinked polymer networks [8–10].

FTIR spectroscopic analysis

FTIR spectroscopic analysis verified the crosslinking of polyamidoximes (PAO 1–3), as evidenced by clear signals for the formation of new 1, 2, 4-oxadiazole linkages. Polyamidoximes are characterized by their hydrophilic properties, which facilitate further connections, leading to the formation of intertwined or crosslinked polymer chains. A new, more robust ring structure, oxadiazole, was successfully created with a notably higher yield, as verified by FTIR spectroscopy. The emergence of oxadiazole rings was evidenced by specific bands in the spectrum. The C = N stretching was observed between 1659–1687 cm^{-1}, which is characteristic for the 1, 2, 4-oxadiazole ring acting as a crosslinking segment. Furthermore, the C-N ring stretching appeared within 1338–1353 cm^{-1}, and the N–O stretching was detected between 943 to 964 cm^{-1}. The

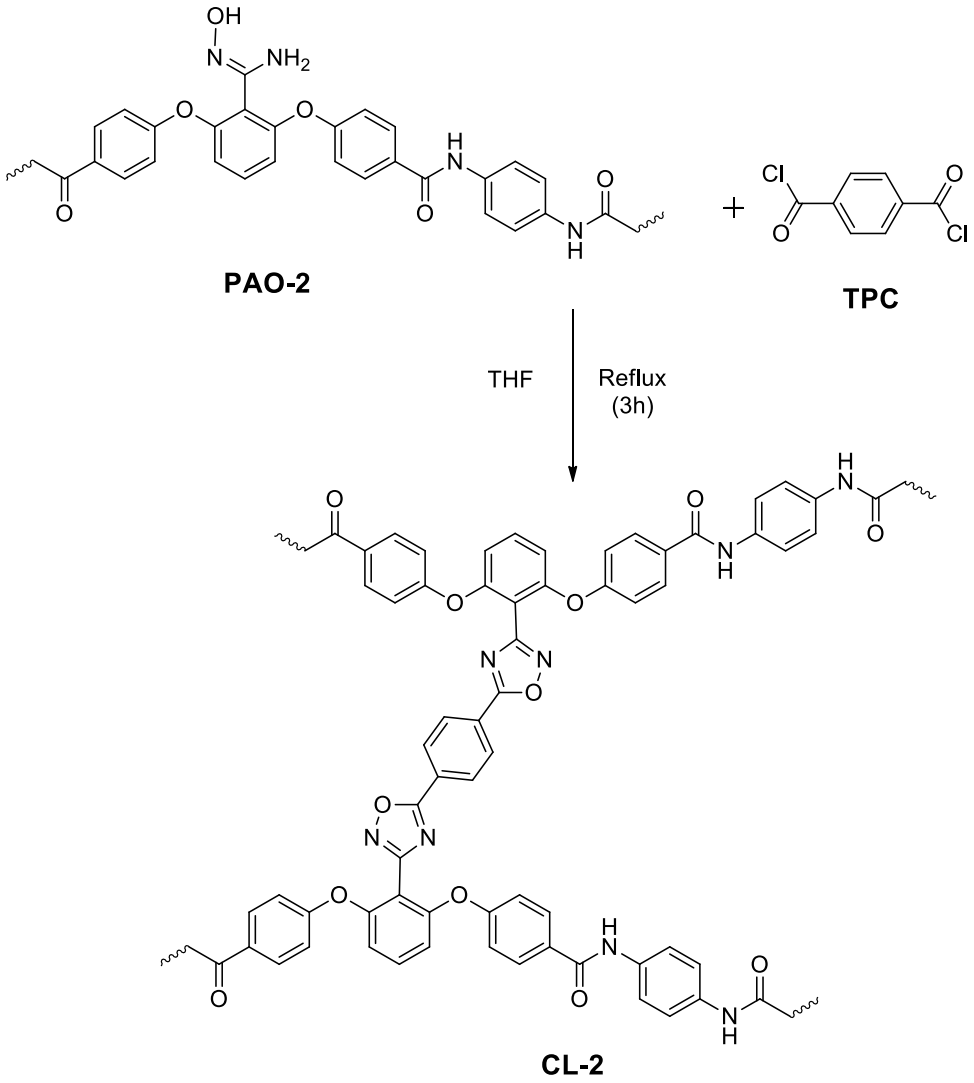


Fig. 3 Synthesis of cross-linked PAO-2 (CL-2)

absence of primary amine signals lent further proof to the formation of the ring structure. The presence of other signals, such as aromatic C = C, amide N–H, C-O, = C-H stretching, further confirmed the crosslinked polymer's structural framework.

X-ray diffraction analysis

X-ray diffraction (XRD) analysis was conducted to evaluate the crystalline structure and alignment of polymer chains resulting from the interlinking of polyamidoxime chains. Polyamidoximes (PAOs) are generally known for their amorphous characteristics, with PAO 1 exhibiting mild chain alignment attributed to a flexible ether linkage [57]. The combined XRD profiles of polyamidoximes PAO (1–3) and their crosslinked counterparts CL (1–3) demonstrated variations in crystallinity. According to the literature, increased crystallinity and orderly arrangement of macromolecular chains produces sharp peaks in XRD patterns, particularly notable in crosslinked forms of linear polymers [58–60]. The introduction of cross-links enhanced chain alignment, evident from distinct peaks in the XRD spectra. Crosslinking enhances the polymer crystallinity by aligning chains, reducing entanglements, and promoting ordered packing. Covalent bonds between chains restrict mobility and encourage a regular molecular arrangement characteristic of crystalline structures. Rigid crosslinking units like oxadiazoles stabilize the structure, increasing thermal stability and reducing amorphous regions. Incorporating a rigid oxadiazole group into each polymer repeat unit resulted in more pronounced and orderly chain structures with a semi-crystalline nature, as depicted in Fig. 5.

Among the crosslinked polymers, CL-3 exhibited the highest level of crystallinity, followed by CL-1 and CL-2. X-ray diffraction confirms sharper peaks in crosslinked polymers, indicating higher crystallinity and suitability for applications requiring durable materials with enhanced structural integrity.

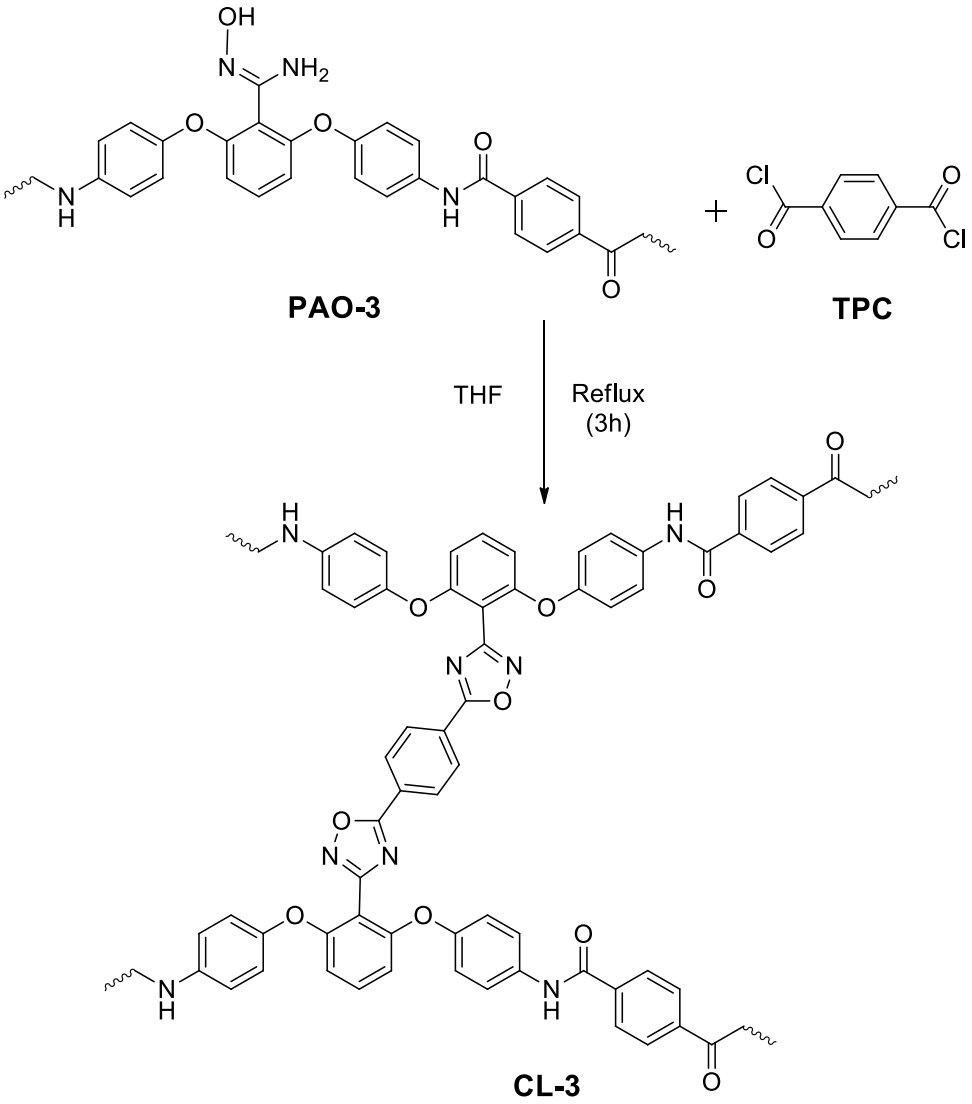


Fig. 4 Synthesis of cross-linked PAO-3 (CL-3)

Thermogravimetric analysis

Cross-linking improves thermal stability by adding bonds between polymer chains, limiting their movement and enhancing resistance to heat-induced degradation. Incorporating rigid rings, such as those found in aromatic compounds, enhances material durability and resistance to breakdown, high temperatures, chemicals, and wear. Polyamidoximes, with their reactive pendant groups, are ideal for cross-linking. In this study, oxadiazole linkages were introduced for the first time into adsorbents to assess their effectiveness in cation adsorption compared to non-cross-linked polyamidoxime molecules. This reinforcement with rigid cross-linking agents like oxadiazole groups prevents easy breakdown or melting at high temperatures, making these materials suitable for demanding applications requiring durability in extreme thermal environments. Thermal behavior investigation of cross-linked polyamidoximes CL (1–3) from 25 to 1000 °C under an inert environment revealed superior temperature resistance compared to original polyamidoximes (PAO 1–3) [57], as depicted in Fig. 6.

Original polyamidoximes decomposed rapidly between 426 and 489 °C. In contrast, the introduction of oxadiazole links increased chain rigidity and thermal stability, shifting peak decomposition between 515 and 593 °C (Fig. 7). These more robust chains maintained stability across a broad temperature range, with char yields for cross-linked polymers reaching 56% to 67%, compared to 2.6% to 37% for non-crosslinked polyamidoximes at approximately 1000 °C. Therefore, these cross-linked materials, as heavy metal ion adsorbents, are likely to exhibit greater stability over varying temperatures and potentially have a longer shelf life than pristine polyamidoximes.

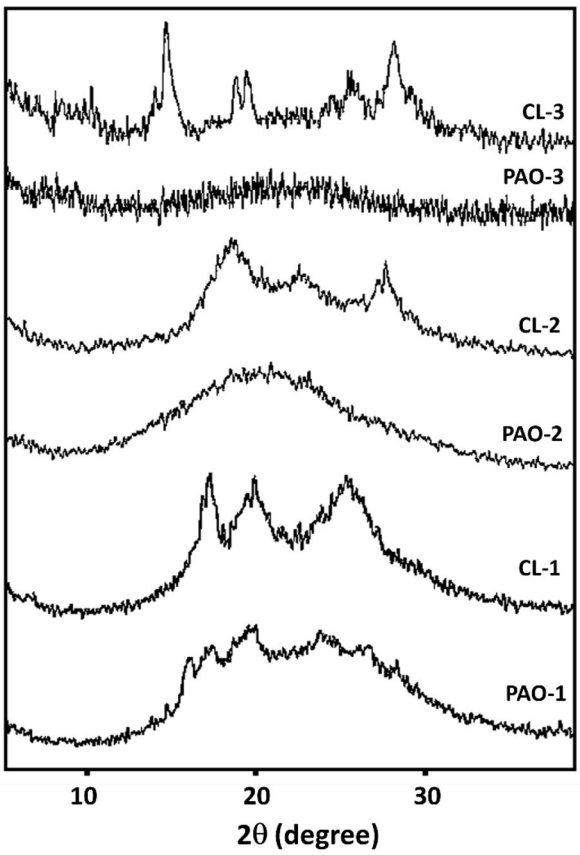


Fig. 5 XRD patterns of polyamidoximes [57] and their cross-linked counterparts

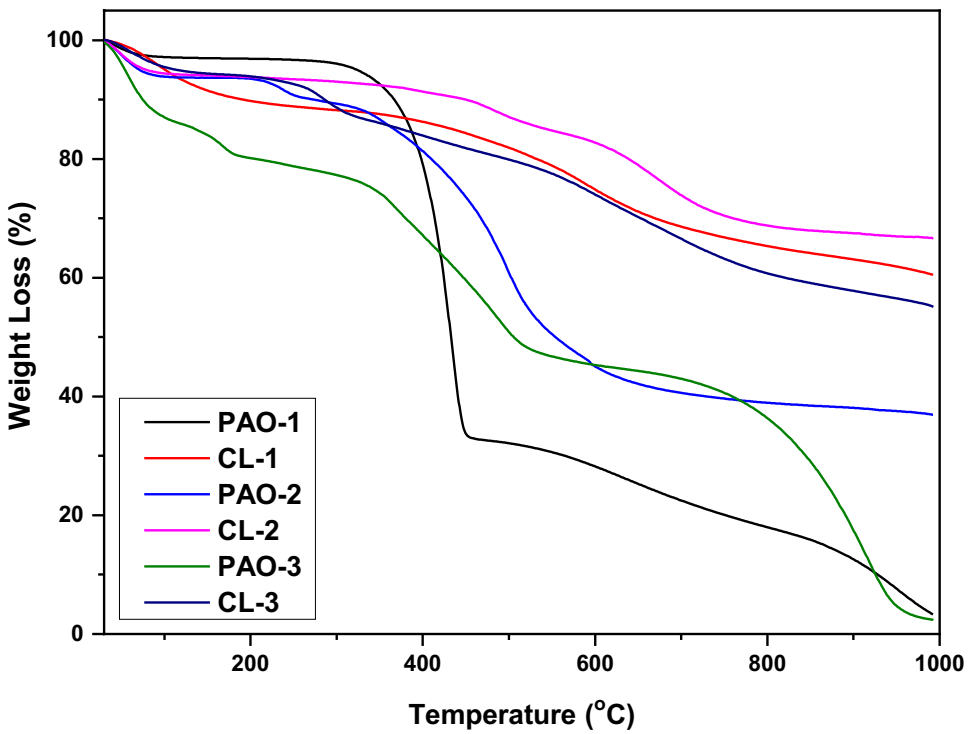
Adsorption of divalent cations

Polymeric networks are extensively studied for their ability to bind positively charged entities due to the presence of electronegative groups, which facilitate the capture of metal ions or nanoparticles. [5, 11, 55] Consequently, when a Lewis base is incorporated into the macromolecular network, it enhances the material's capability to attract and capture cations, rendering the resin highly effective for removing metal ions from water. The adhesion mechanisms in these polymers can be attributed to a combination of dipole–dipole interactions, electron transfer, and electrostatic forces [61]. The cross-linked resins synthesized in this study were examined through a batch process, during which the conditions for maximum metal ion uptake were optimized. These optimized conditions were then compared to those of the original, non-crosslinked polyamidoximes to evaluate the improvements in performance and efficiency.

pH

The adsorption of positively charged ions is closely linked to the presence of basic sites on the adsorbing material, and this process is heavily influenced by pH due to its effect on Lewis acid–base interactions. The increased basicity of Lewis bases is crucial for effective binding; however, in acidic environments, the basic sites are consumed by excess hydrogen ions. This competition results in reduced cation adsorption as hydrogen ions compete with the positively charged ions for binding

Fig. 6 TGA curves of of polyamidoximes [57] and their cross-linked counterparts



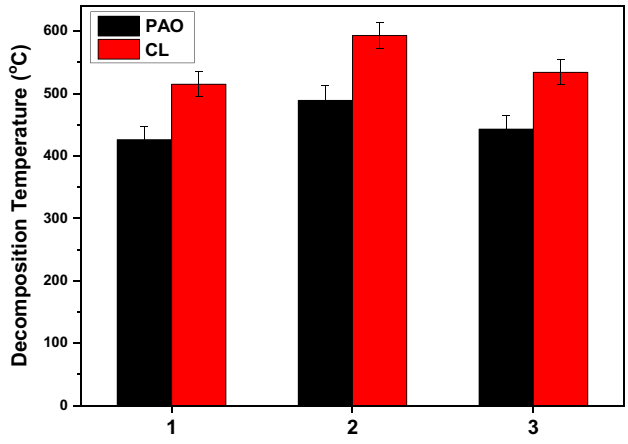


Fig. 7 Comparative Plot for Decomposition Temperatures before and after Crosslinking

sites on the electronegative groups. The binding of positively charged ions to the cross-linked polyamidoximes (CL 1–3) varies significantly with pH, as illustrated in Fig. 8. In an acidic medium, the abundance of hydrogen ions reduces the adsorption of cations. Conversely, as the pH increases, the basicity of the Lewis bases, or electronegative entities, is enhanced, leading to increased cation adsorption. The highest adsorption was observed at a pH of 6 for all cross-linked polyamidoximes (CL 1–3), beyond which the adsorption plateaued. Unlike metal ion complexation with amidoxime groups in PAOs, cross-linked polymers capture cations primarily through electrostatic attractions with electronegative entities. Therefore, the mechanism of metal ion capture within cross-linked polymeric structures is suggested to involve coordination or electrostatic interactions. This distinction highlights the unique adsorption behavior of cross-linked polyamidoximes and their effectiveness in removing metal ions from aqueous solutions.

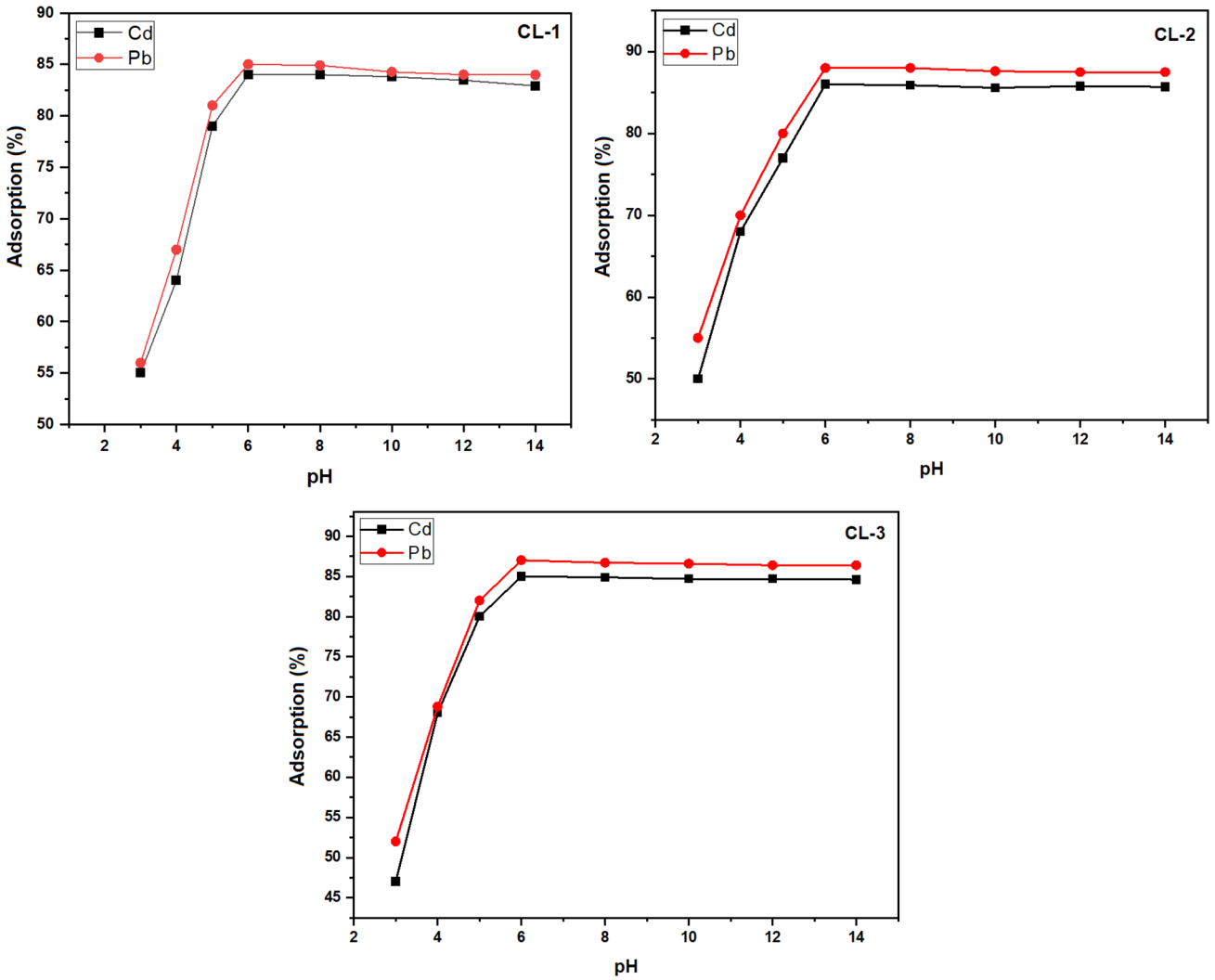


Fig. 8 Effect of pH on adsorption (%) by cross-linked polyamidoximes (CL-1, CL-2 and CL-3)

Contact time

The study investigated the adsorption mechanism by varying the interaction duration between the adsorbate and the adsorbent. The findings indicated that the adsorption rates for both cadmium and lead ions increased with longer contact times, reaching a maximum at 3 h for all the cross-linked polyamidoximes (CL 1–3), as depicted in Fig. 9. Beyond this point, the rate of adsorption plateaued, suggesting that further extension of the contact time does not enhance the adsorption capacity. This plateau indicates that 3 h is the optimal duration for effective coordination of the cations with the adsorbent's binding sites. At this point, it is inferred that all the available binding sites on the adsorbent have been occupied, and the adsorption process has reached equilibrium.

The initial increase in adsorption rate can be attributed to the availability of abundant vacant sites, which allows for rapid uptake of cations. As these sites become increasingly occupied, the rate slows down until no further significant adsorption occurs, signifying that the adsorbent's capacity has been fully utilized. This insight is crucial for optimizing the conditions for maximum metal ion removal in practical applications, ensuring efficient and effective use of the cross-linked polyamidoximes.

Concentration of adsorbate

This study investigated the impact of varying concentrations of Cd and Pb ions on their adsorption levels through a series of controlled experiments. The results indicated that the highest ion adsorption occurred at a concentration of 40 mg/L for both Cd and Pb ions. As the concentration increased from 20 mg/L to 40 mg/L, the adsorption rates correspondingly increased, reaching a peak at 40 mg/L. Beyond this concentration, the adsorption rates began to decline steadily, as illustrated in Fig. 10. At the lower concentration of 20 mg/L, it is

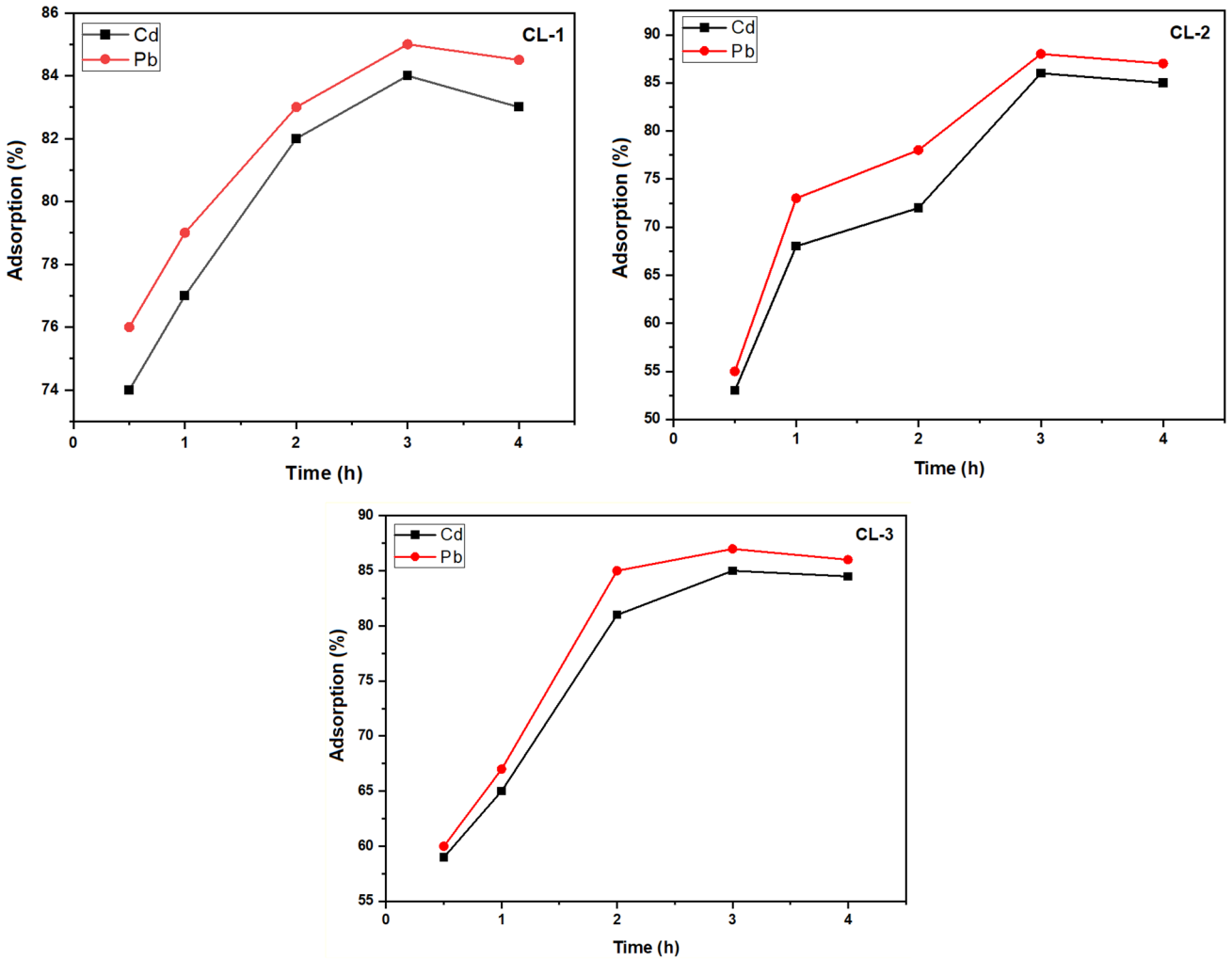


Fig. 9 Effect of contact time on adsorption (%) by cross-linked polyamidoximes (CL-1, CL-2 and CL-3)

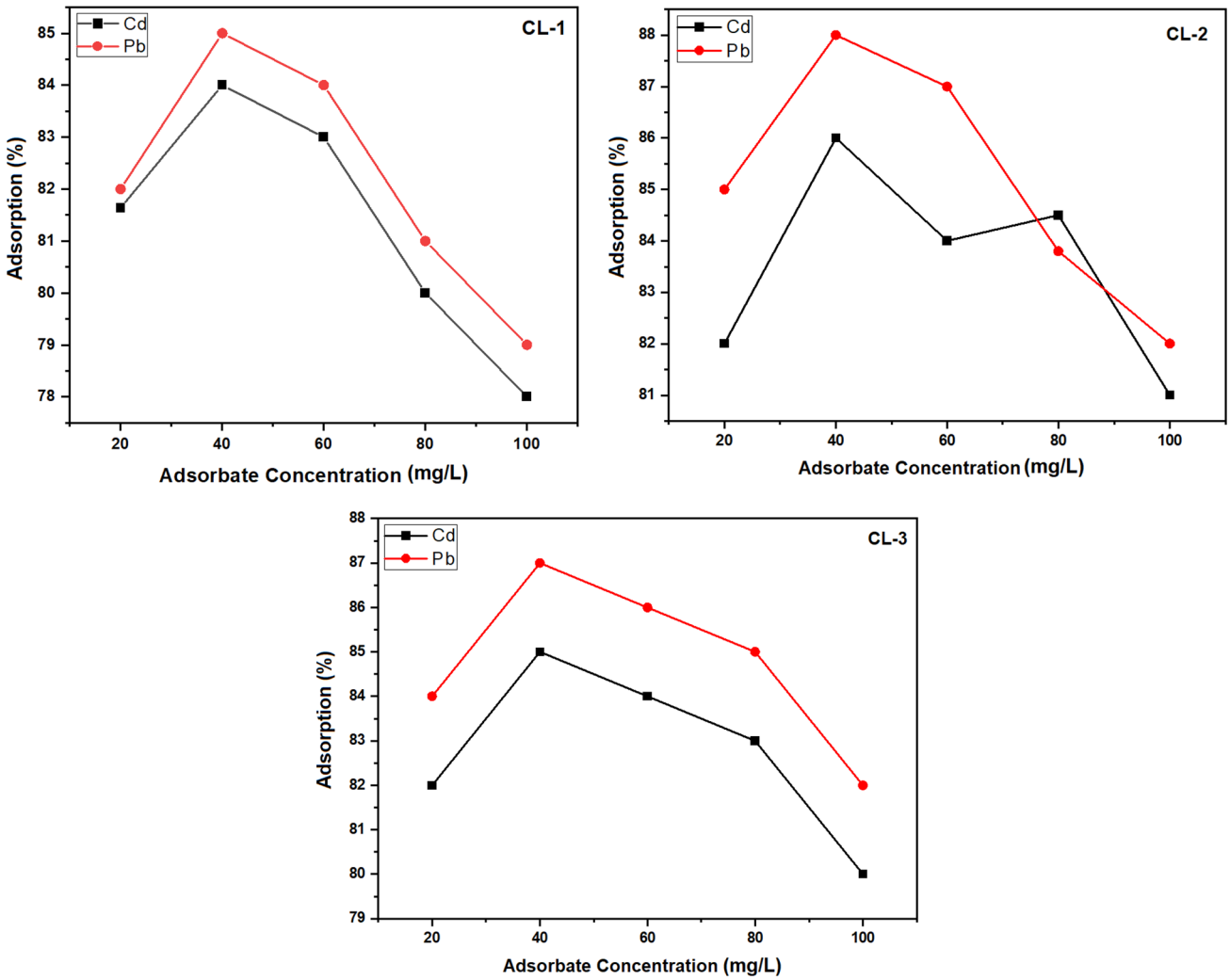


Fig. 10 Effect of adsorbate concentration on adsorption (%) by cross-linked polyamidoximes (CL-1, CL-2 and CL-3)

hypothesized that numerous binding sites on the adsorbent were available for cation interaction. As the concentration increased to 40 mg/L, these sites became fully occupied, maximizing the adsorption capacity. However, when the ion concentration exceeded 40 mg/L, the number of cations surpassed the available binding sites, resulting in an excess of ions in the solution and a subsequent decrease in adsorption capacity. This decline occurs because the adsorbent can no longer accommodate additional cations, having reached its saturation point. The observation of maximum percent uptake at 40 mg/L, followed by a decrease, underscores the importance of optimizing ion concentrations to achieve efficient adsorption. The consumption of all available binding sites at 40 mg/L signifies the peak adsorption capacity, beyond which no further significant adsorption can occur, leaving excess cations unbound in the solution. This finding is crucial for designing and optimizing practical applications for metal ion removal using cross-linked polyamidoximes.

Amount of adsorbent

The effectiveness of an adsorbent centers on its ability to selectively and efficiently adsorb cations. A highly efficient adsorbent can bind a substantial quantity of cations using a minimal amount of material. In this study, the impact of varying amounts of adsorbent (ranging from 0.1 g to 0.3 g) on the uptake of Cd and Pb ions was investigated under optimized conditions of pH, contact time, and initial solution concentration. The findings indicated that the maximum uptake of both Cd and Pb ions occurred with 0.1 g of adsorbent, demonstrating optimal adsorption efficiency. As the amount of adsorbent increased beyond 0.1 g, the percentage uptake of cations gradually decreased. This observation suggests that using excess adsorbent did not proportionally enhance adsorption capacity and may indicate surface saturation or competition for binding sites among multiple adsorbent particles. Under optimized parameters,

the adsorbent achieved significant removal efficiency, capable of adsorbing up to 88% of Pb cations using CL-2 polymer (as depicted in Fig. 11). This level of removal effectively reduces the concentration of heavy metals to safe levels, highlighting the practical efficacy of the adsorbent in environmental remediation applications. These results underscore the importance of optimizing adsorbent dosage to achieve maximum adsorption efficiency and minimize material usage in practical applications for water treatment and metal ion removal.

Comparative uptake of metal ions

The study focused on achieving the maximum adsorption capacity under optimized conditions: a contact time of 3 h, pH 6, adsorbate concentration of 40 mg/L, and adsorbent amount of 0.1 g. Results for the three cross-linked polyamidoximes (CL 1–3) demonstrated that Pb ions were adsorbed more efficiently than Cd ions, with adsorption rates ranging from 84 to 86% for Cd and 85% to 88% for Pb (see Fig. 12). In contrast, polyamidoximes PAO (1–3) exhibited greater efficiency, achieving > 99% adsorption [57] for both metal ions, a performance that declined in the cross-linked (CL 1–3) samples due to the cross-linking of polyamidoxime chains, which reduced the availability of amidoxime groups for chelation. Furthermore, Pb ions consistently exhibited higher adsorption rates compared to Cd ions across all cross-linked polyamidoximes tested. This differential performance underscores the influence of chemical structure and functional groups on adsorption efficiency, highlighting the potential trade-offs between structural modification (such as cross-linking) and adsorption capacity in designing effective adsorbents for heavy metal removal from aqueous solutions.

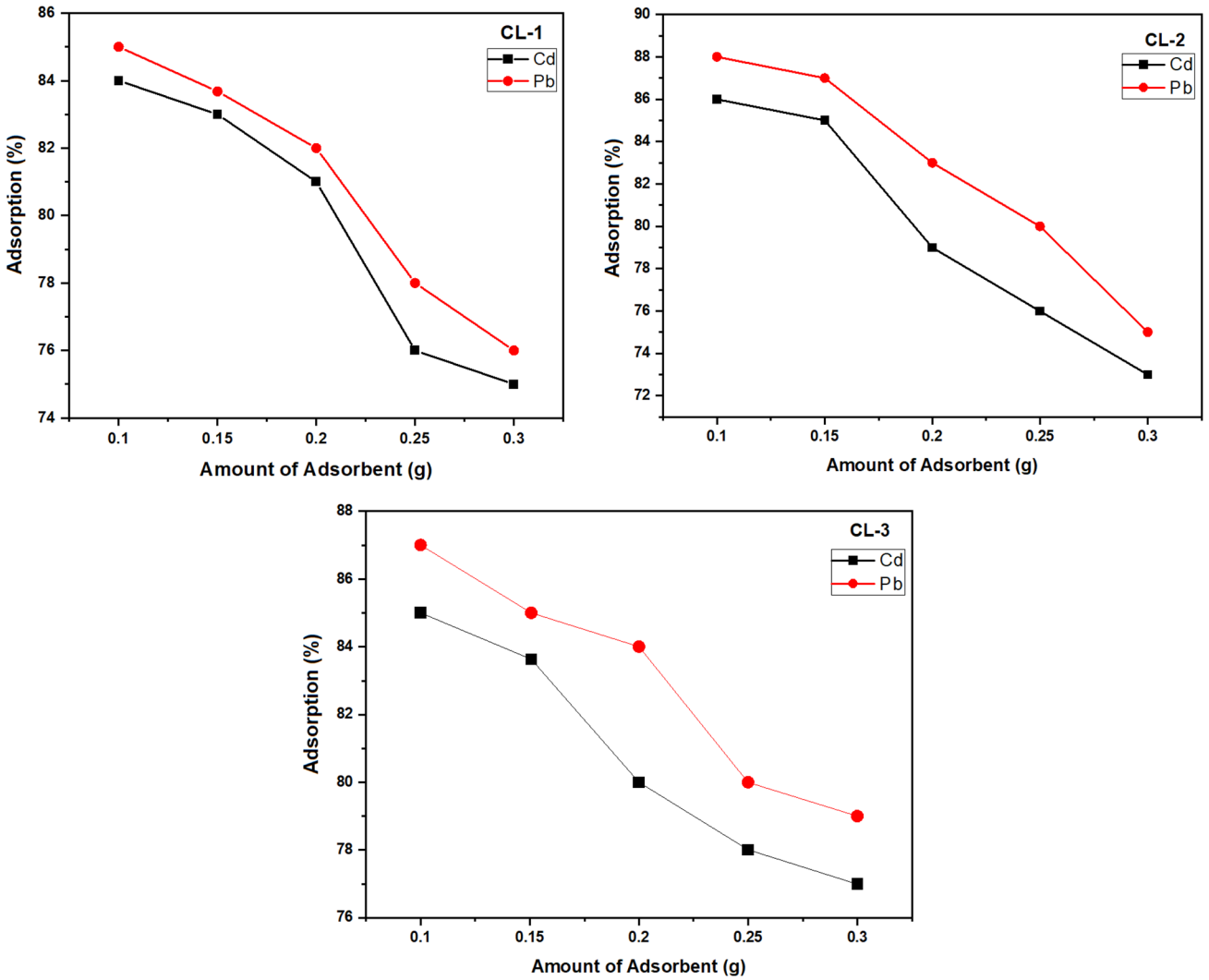


Fig. 11 Effect of amount of adsorbent on adsorption (%) by cross-linked polyamidoximes (CL-1, CL-2 and CL-3) at contact time = 3 h, pH = 6, and adsorbate concentration = 40 mg/L

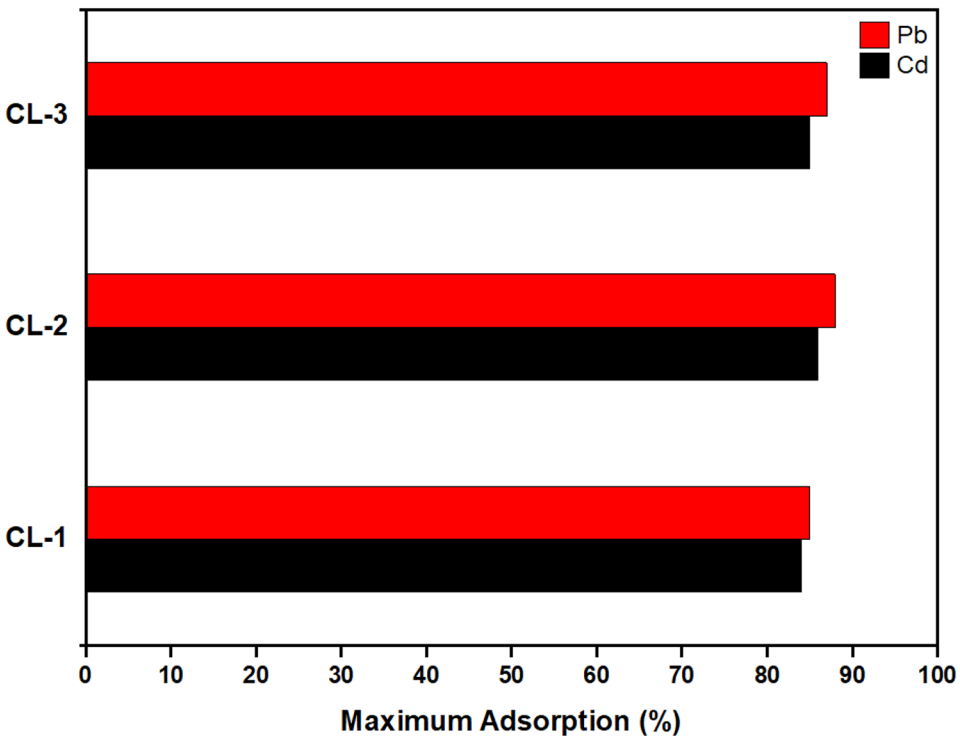


Fig. 12 Maximum adsorption (%) of Cd (II) and Pb (II) ions at optimized parameters by cross-linked polyamidoximes (CL-1, CL-2 and CL-3)

Equilibrium adsorption isotherms

The study of the adsorption isotherms was conducted using newly developed cross-linked PAO adsorbents, testing concentrations between 20 and 100 mg/L for Cd and Pb ions. A dynamic equilibrium was proposed to be established at the optimized contact time for the maximum uptake of cations. 'q_e' represents the concentration of adsorbed species onto the solid adsorbent, and 'C_e' is the concentration of cation in solution at equilibrium. These parameters were employed to assess the nature of cation adsorption based on adsorption isotherms. The adsorption behavior was analyzed using Freundlich and Langmuir models, as described by Eqs. 1 and 2 respectively.

$$ln\ q_e = ln\ K_F + \frac{1}{n} ln\ C_e \tag{1}$$

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_o\ C_e} \tag{2}$$

where Q_o is the maximum adsorption capacity, b is the binding constant calculated from Langmuir model, K_f and n are the Freundlich constants indicating adsorption capacity and adsorption intensity, respectively. The value of 'n' is of critical significance in determining the nature of the adsorption of metal ions on the polymeric resin. The Freundlich constant "n" is pivotal in characterizing adsorption intensity and surface heterogeneity of an adsorbent. A value of "n" greater than 1 indicates favorable adsorption, with increasing adsorption capacity at higher concentrations, while also suggesting a heterogeneous surface with diverse adsorption sites. Conversely, a lower "n" value points to a more uniform surface. This constant effectively models the non-linear adsorption typical in real-world scenarios and facilitates the comparative analysis of adsorbent efficiency under varying conditions, making it essential for optimizing adsorption processes. Figures 13 and 14 illustrate the Freundlich and Langmuir adsorption isotherms for all the crosslinked polyamidoximes CL (1–3) including the fitting parameters for both Cd and Pb ions. The findings show that the Langmuir model more accurately describes the adsorption process compared to the Freundlich adsorption model, indicating monolayer adsorption of cations (Table 1). This is further supported by electrostatic interactions between the nucleophilic sites and the cations, as well as coordination via NH groups [5, 62, 63], which prevent additional accumulation of adsorbate ions once the active sites are filled. The Langmuir isotherm introduces an additional parameter, the equilibrium or separation factor R_L, which quantifies the favorability of cation adsorption as given by the relation (3):

$$R_L = 1/(1 + bC_O) \tag{3}$$

The initial concentration is denoted by Co. Adsorption is considered favorable when the R_L value is between 0 and 1. The R_L values listed in Table 1 validate the favorable nature of adsorption, showing a uniform distribution of active sites

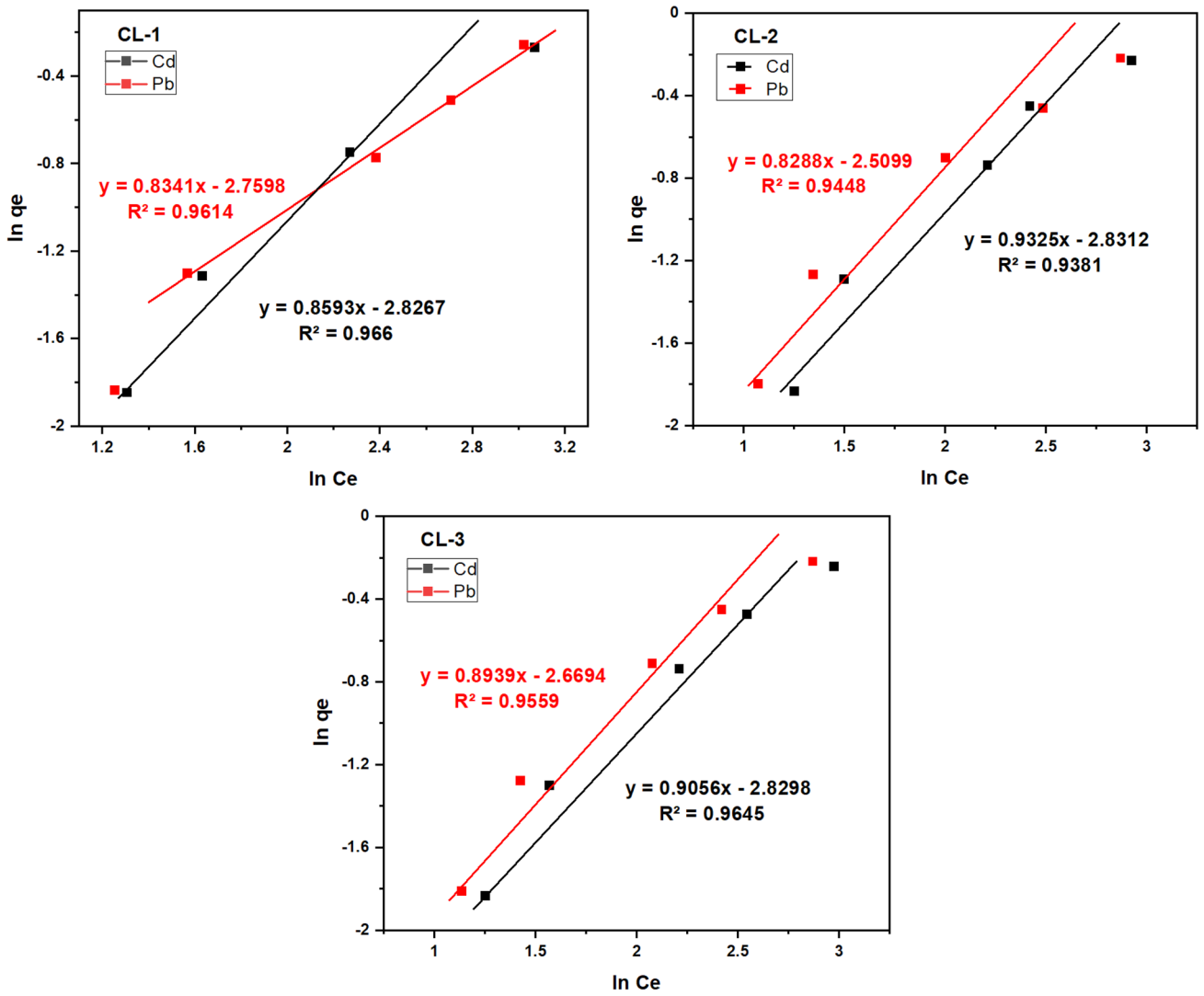


Fig. 13 Freundlich adsorption isotherms for various cross-linked polyamidoximes (CL-1, CL-2 and CL-3)

within the adsorbent's macromolecular structure. Groups containing nitrogen, oxygen, and sulfur are recognized as effective for adsorbing metals, making polyamides suitable owing to their abundant active sites for chelating cations through coordination or electrostatic forces [53, 64]. The adsorption efficiency of the cross-linked polyamidoximes CL (1–3) was slightly lowered compared to the pristine polyamidoximes PAO (1–3) [56], nonetheless, they still proved efficient for adsorbing heavy metal ions. The rigid and crystalline structure of these cross-linked polymers suggests they would exhibit superior performance at elevated temperatures due to their enhanced thermal stability. Detailed examination of cadmium and lead ion adsorption revealed that lead ions exhibited stronger interactions compared to cadmium ions. This difference can be attributed to lead's higher polarizability and larger ionic size, which enhance its affinity for the active sites within the crosslinked macromolecules. A representative mechanism for cationic binding with crosslinked polyamidoxime (CL-1) is presented in Fig. 15.

Competitive adsorption of cations

The nucleophilic sites on the adsorbent enable it to attract Lewis acids, which are cations. This interaction, encompassing both electrostatic forces and Lewis acid–base coordination, allows the adsorbent to capture electrophilic species. Certain active sites show a preference for specific ions, utilizing the concept of cationic binding to nucleophilic centers during adsorption [65]. Cationic preference for these active sites is determined by the HSAB (hard soft acid–base) theory. The proportion between the covalent and ionic index of an ion determines its uptake efficiency at the binding centers; the higher the proportion, the greater the soft character and the tendency to bind through S > N > O

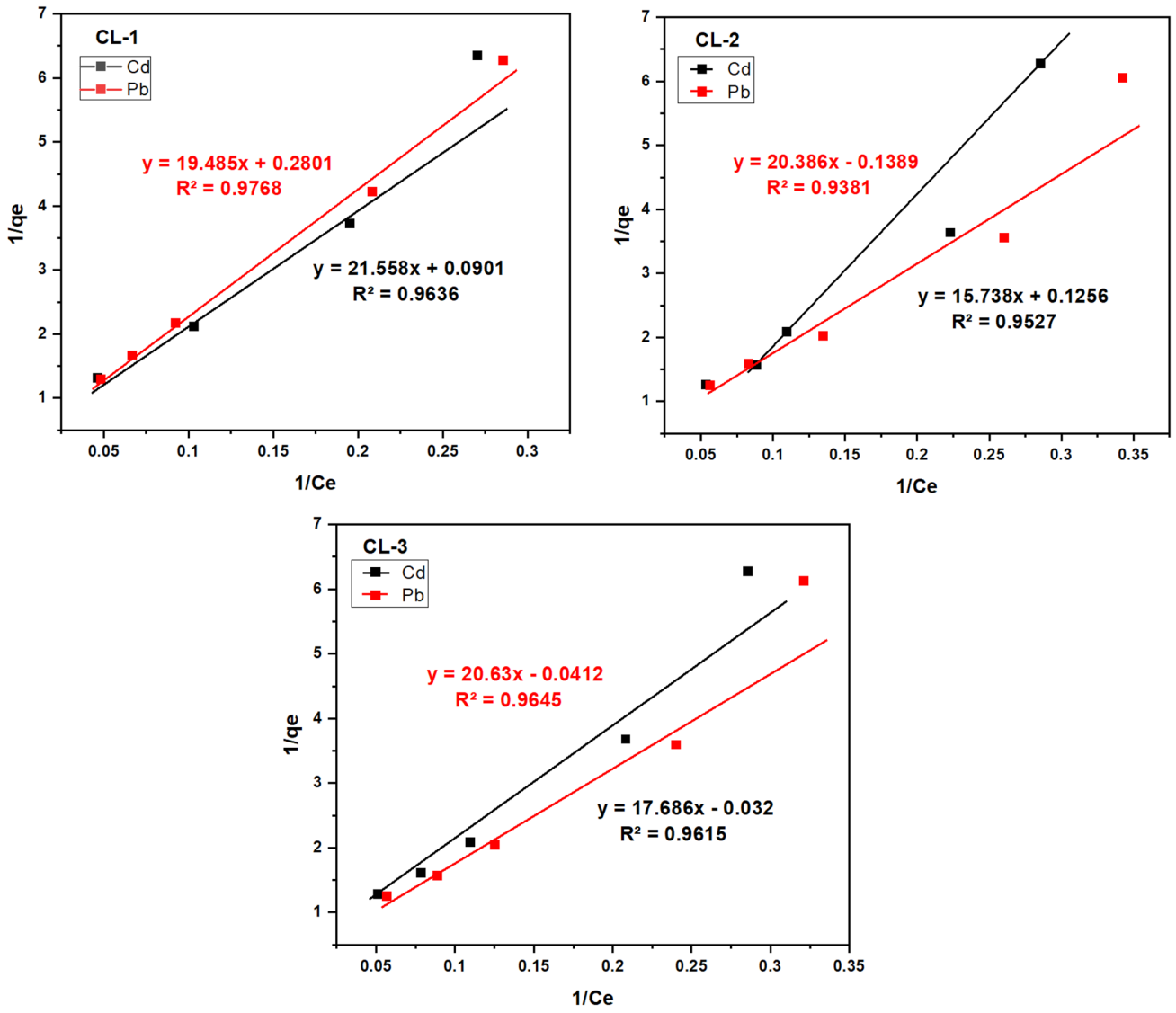


Fig. 14 Langmuir adsorption isotherms for various cross-linked polyamidoximes (CL-1, CL-2 and CL-3)

Table 1 Freundlich and Langmuir isotherm parameters for the adsorption of Cd(II) and Pb (II) ions by cross-linked polyamidoximes

Polymer	Cations	Freundlich Parameters			Langmuir Parameters			
		R^2	K_f	n	R^2	Q_o	b	R_L
CL-1	**Cd**	0.96	16.88	1.16	0.96	11.09	0.004	0.92
	Pb	0.96	15.79	1.19	0.97	3.57	0.01	0.77
CL-2	**Cd**	0.93	16.96	1.07	0.95	7.19	0.006	0.88
	Pb	0.94	12.30	1.20	0.93	7.96	0.007	0.86
CL-3	**Cd**	0.96	16.94	1.10	0.96	24.27	0.001	0.96
	Pb	0.95	14.43	1.11	0.96	31.25	0.001	0.96

sites [66]. A study was conducted to evaluate the competitive adsorption of various cations (Fig. 16) by preparing a 40 mg/L aqueous solution for each of the following ions: Fe(II), Cd(II), Pb(II), and Cu(II). These solutions were then introduced to the adsorbent under optimal conditions, which included a 3 h contact period, pH of 6 and 0.1 g of adsorbent. The results showed that iron ions were adsorbed the most, followed by lead, cadmium, and copper ions.

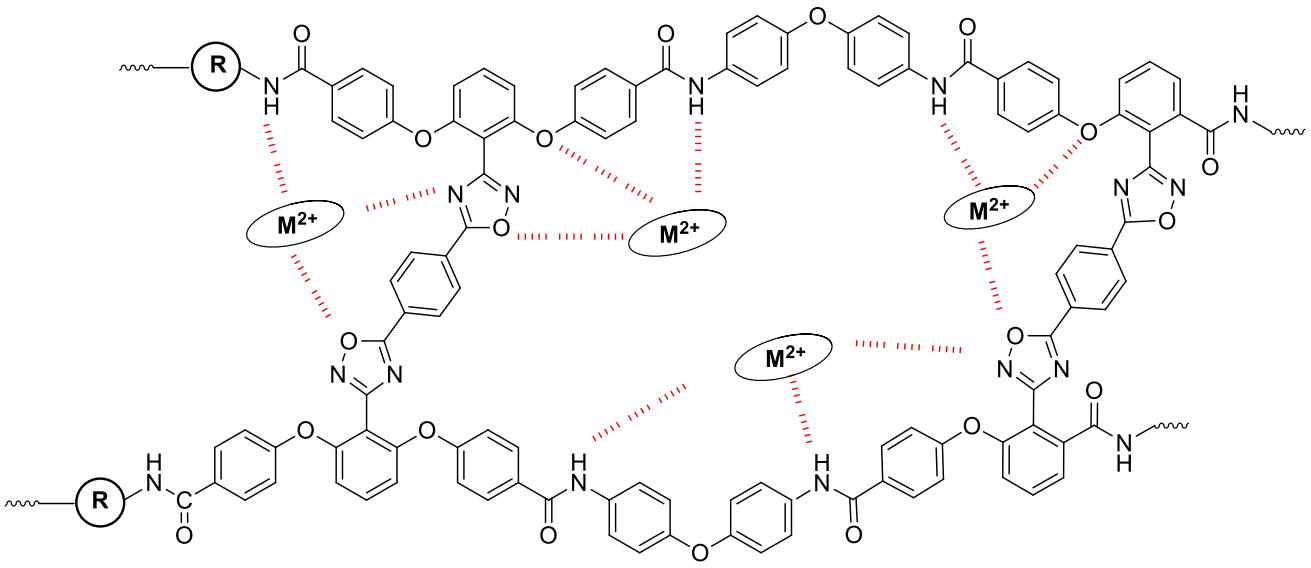


Fig. 15 A representative mechanism for cationic binding with CL-1

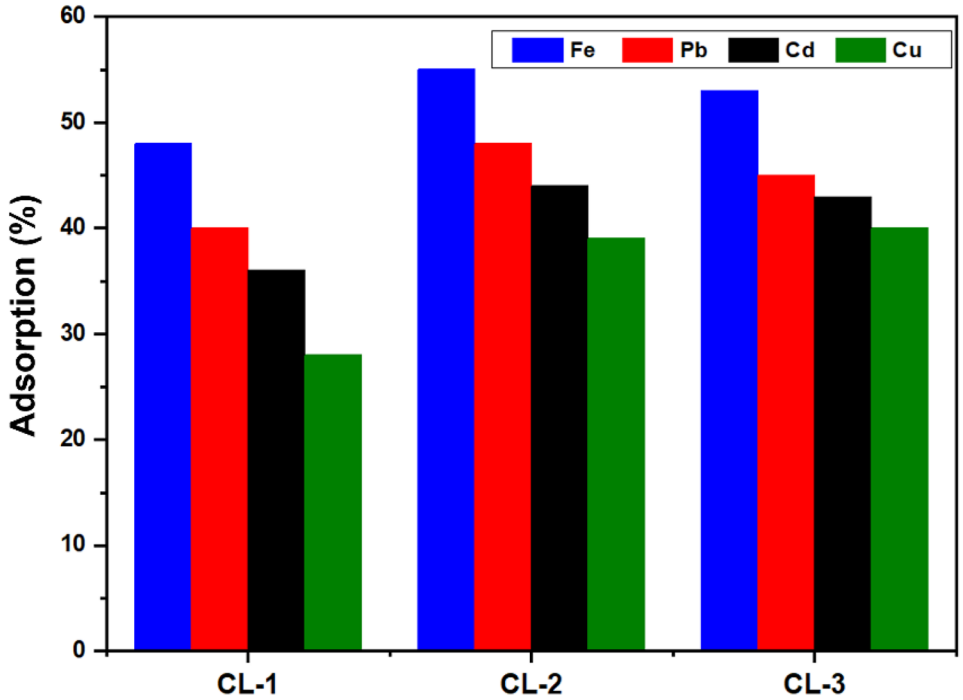


Fig. 16 Relative uptake of divalent metal ions by cross-linked polyamidoximes (CL-1, CL-2 and CL-3)

The reason for this could be that Fe ions, with the highest ionic strength in the set, are more likely to connect with the nucleophilic sites than the other cations in the solution. The amount of cations adsorbed by the cross-linked PAOs lies in the range of 28–55%, which may be attributed to the competition of ions to be coordinated through the active sites. Therefore, the developed adsorbent system can effectively be applied to remove the heavy metal ions, provided that the competitive cations are lesser in concentration.

Conclusions

Polyamidoxime polymers PAO (1–3) were cross-linked using terephthaloyl chloride to create heat-resistant architectures CL (1–3) with enhanced chain rigidity and alignment. Their ability to adsorb metals was thoroughly investigated, leading to the fine-tuning of various conditions for optimum metal uptake. The best adsorption performance was recorded as 86% for Cd ions and 88% for Pb ions

with CL-2 polymer, influenced by factors like the pH, exposure time, initial concentration, and the amount of polymer used. The Langmuir isotherm model fits the data well, indicating uniform monolayer adsorption of positively charged ions at the polymer's reactive sites. Consequently, these crosslinked polyamidoximes show promise as a material for extracting heavy metals like Cadmium (II) and Lead (II) from aqueous media. In mixed cationic environments, all the synthesized cross-linked polymers demonstrated the highest selectivity for Iron (II), followed by Lead (II), Cadmium (II), and Copper (II) ions.

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Data availability Data will be made available on request.

Declarations

Competing interests The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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