Scientific paper

Evaluation of Jeffamine® Core PAMAM Dendrimers for Simultaneous Removal of Divalent Heavy Metal Ions from Aqueous Solutions by Polymer Assisted Ultrafiltration

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Abstract

Different generations (G3-G4) of amine-terminated Jeffamine® T-403 core poly(amidoamine) PAMAM dendrimers (JCPDs) were used as new macromolecular heavy metal chelating agent templates in polymer assisted ultrafiltration (PAUF) for the investigation of their removal ability for some of the divalent metal ions: Cu, Co, Ni, Cd, and Zn from aqueous solutions under competitive conditions. The effects of pH and generation size of JCPDs were also investigated. Extent of binding (EOB) data can be appropriately expressed by a tetradentate coordination for JCPDs at pH 9 where the maximum removal of metal ions was observed. At pH 9.0, the affinity of both generations towards heavy metal ions was also observed in the decreasing order of Zn(II) > Co(II) > Ni(II) > Cu(II) > Cd(II). Results revealed that the highest total binding capacity was observed for G3-NH_2 (262.79 ± 1.62 mg/g) as a little bit higher than that of G4-NH_2 (257.27 ± 2.57 mg/g). EOB studies also proved the active contribution of amide groups to metal binding ability of PAMAMs. Both generations were selective towards Cu(II) ions at lower pH 5 and pH 7. From these results, it was concluded that studied JCPDs have the desired technical properties to be used for the removal of toxic metals from wastewaters.

Keywords: Poly(amidoamine) PAMAM dendrimers; Jeffamine® T-403; liquid phase retention (LPR); metal complexation; removal of heavy metals

1. Introduction

Toxic, particularly divalent heavy metal ions are the main contaminants of the surface, ground, and coastal water systems that lead to water contamination throughout the world.[1,2] These pollutants are not only found in wastewaters from various chemical manufacturing, mining, coating, extractive metallurgy but also nuclear and other industries, and greatly threaten the health of human populations and natural ecosystems.

Water free or decontaminated from toxic chemicals and pathogens is fundamental for human health and as raw material for many industries. There are particular cases that endanger the sustenance of this source like a rise in global demand due to population growth, prolonged droughts, and contamination by metals or organic and inorganic compounds.[3–5] Considering the water contamination, most of the available water remediation technologies are useful, but frequently are costly and time-consuming.[6]

The existence of heavy metal ions in water gives rise to numerous risks to human health. In the instance of industries, it leads to a rise in the overall cost of production due to purification processes. Several remedies, one of which is adsorbents such as ion exchange resins and activated charcoal, have been used extensively as an industrial research subject for the removal of heavy metal ions from wastewaters.[7] These materials have several drawbacks depending on their low selectivity, wide distribution and heterogeneity of pore size and structure for heavy metals. In this point, nanotechnology offers innovative solutions to prevent water contamination. Previous investigations have indicated that the treatment with nanomaterials as chelating agents to remove metal ions from water enhances its

quality and minimizes purification costs.[8] The potential of this approach to surmount limitations encountered in other removal strategies has been placed as an environmentally friendly method.[9–12]

Among available chelating agents, dendrimers have been described as the powerful macromolecules to encapsulate metal ions, and further recover and recycle to reuse.[13] Poly(amido amine) PAMAM dendrimers (PAMAMs) display an outstanding capacity to bind metal ions by forming stable coordination complexes.[14] These nanomaterials are three-dimensional, globular, repetitively branched, and synthetic organic molecules with hyper-branched and uniform structures that allow them numerous advantages as templates for binding of metal ions within their interior.[15] The high density of nitrogen ligands such as amino and amide functional groups that PAMAMs carry, allow them to behave like a container or a template by increasing their binding ability for various toxic and heavy metals.[14] Thus, PAMAMs may serve as potential polyfunctional ligand hosts for metal ions with coordination possibly occurring at the periphery, interior or both. In this sense, it was reported that loading of various metal ions with the implication of useful applications for metal ion sensor coatings on the electrode surface to commercially available amine-terminated PAMAMs are possible.[16,17]

One of the efficient methods to recover metal ions from contaminant waters is liquid phase polymer-based retention technique (LPR) or polymer assisted ultrafiltration (PAUF).[2,18–23] Former studies have shown that this method could be successfully used for the selective separation and recovery of heavy metals.[24–26] Many kinds of water-soluble polymers such as poly(acyrylic acid) (PAA) and poly(ethylene imine) (PEI) have been used as templates in LPR for the removal of corresponding various individual metal ions such as Cu(II), Cd(II), Ni(II), Pb(II), Cr(II), Cr(II), Co(II) and many others.[27] However, a limited number of studies has been conducted for the competitive or simultaneous removal of metal ion mixtures by polymers, especially for PAMAMs.[28] Polymers to be used in LPR studies can be assessed by many parameters but one of the most important parameters is the ligand density of the polymer. Low ligand density of the polymer to be used requires high volume of polymer and this could increase the viscosity of the solution that can lead to deteriorating effect on the permeate reflux.[29] Higher generation PAMAMs have a high number of amino groups, and so high ligand density. Furthermore, the chelating properties of PAMAMs can alter due to type of core, repeating branches and surface functional groups.[30]

Jeffamine® T-403 is a polymer, which has large and unsymmetrical chains having propylene oxide repeating units. These large repeating units can retard the steric hindrance but enhance the reactivity and water solubility.[31] In our former studies, we have demonstrated the microwave -assisted synthesis of Jeffamine® core PAMAMs (JCPDs) and their Cu(II) intradendrimer metal complexations.[31–33] Results of these studies revealed that JCPDs can show interesting chelating abilities towards metal ions as a new type polydentate chelating agent for LPR.

The aim of this study was to investigate the retention properties of different generations JCPDs through the LPR to study the selective and collective removal ability of some of the divalent heavy metal ions: Cu(II), Co(II), Ni(II), Cd(II), Zn(II) from aqueous solutions. Effects of pH and generation size on the complexation and selectivity of these metal ions were also considered.

2. Experimental

2. 1. Materials

All chemicals were of analytical grade and obtained from Merck and Fluka. Divalent nitrate salts of Cd, Co, Cu, Ni, Zn were used to prepare standard metal solutions. JCPDs, G3-NH_2 and G4-NH_2, were synthesized according to our recent study,[31] and detailed experimental procedures including potentiometric titrations are given in the Supplementary Information. The prepared dendrimers were stored in methanolic solution at ± 4 °C. Some selected properties and characterization data of dendrimers are presented in Table 1. The abbreviations G1-NH_2 to G4-NH_2 (first to fourth generation) were suggested for respective JCPDs with molecular weights ranging from 1124 to 10700 g/mol. 18.2 MΩ cm Milli-Q double distilled water was used for the preparation of all standard metal and dendrimer solutions. 0.1 and 0.01 M HNO_3 and NaOH were used to prepare initial pH adjustments. Amicon 8400

Table 1. Selected physico-chemical properties of JCPDs.[31]

Generation	Mw[a]	Mn[b] (SEC)	Mw (SEC)	PDI[c]	Number of tertiary amines (^{3}N)	Number of primary amines (^{1}N)	Number of amides (^{a}N)	Number of total nitrogen-containing groups (tN)
G1-NH2	1124	960	980	1.02	3	6	6	15
G2-NH2	2492	2300	2500	1.09	9	12	21	42
G3-NH2	5228	4300	4400	1.02	21	24	42	87
G4-NH2	10700	9200	9600	1.04	45	48	90	183

[a] Theoretical molecular weight (g/mol). [b] Nominal molecular weigth (g/mol). [c] Polydispersity Index: PDI = Mw/Mn

stirred ultrafiltration cell with MWCO of 1 kDa regenerated cellulose membranes supplied with Millipore were used in batch-complexation studies.

2. 2. Stock Metal Solutions

Individual stock metal solutions of 1000 mg/L were prepared by the addition of metal nitrate salts ($Cd(NO_3)_2$ $4H_2O$; $Co(NO_3)_2$ $6H_2O$; $Cu(NO_3)_2$ $3H_2O$; $Ni(NO_3)_2$ $6H_2O$; and $Zn(NO_3)_2$ $6H_2O$) to a desired volume of 18.2 MΩ cm Milli-Q water.

2. 3. Batch Complexation and PAUF Experiments

A systematic diagram of complexation can be seen in Fig. 1. PAMAMs used in PAUF experiments were JCPDs, G3-NH_2 and G4-NH_2, with the molecular weight of 5228 and 10700 g/mol, respectively. Before PAUF experiments, 250 mL of aqueous multi-metal PAMAM feeding solutions were produced by the addition of the correct amount of individual stock metal solutions of Cd(II), Co(II), Cu(II), Ni(II), and Zn(II). In complexation, the concentrations of G3-NH_2 and G4-NH_2 were 2.84 ° × 10^{-5} M and 8.12 × 10^{-6} M, and the molar ratios of each metal concentration to primary amine groups (^{1}N) of PAMAMs were kept constant at 0.2. The pH of feeding solutions was adjusted to the desired pH by the secure addition of 0.01 and 0.10 M HNO_3 and NaOH solutions. The feed solutions were stirred well with a magnetic stirrer for 45 min until equilibrium was reached at room temperature 25 ± 2 °C.

After complexation reaction, 150 mL of feed solution was transferred into Amicon 8400 UF cell, capacity of 400 mL. In the UF cell, an ultrafiltration disk membrane (YM-1) made from regenerated cellulose and supplied from Millipore (USA) was used. The commercial membrane had MWCO = 1000 g/mol (1 kDa); diameter of 76 mm and effective membrane area of 41.8 cm^2. The permeate flux of pure water in Amicon UF cell with regenerated cellulose membrane was equal to 10.95 L m^{-2} h^{-1}. The feed solution in UF cell was stirred gently at 250 rpm to reduce the concentration polarization on the membrane surface and provide homogeneity in the solution inside the cell. The filtration cell was pressurized by oxygen-free nitrogen gas. All experiments were conducted by applying a constant operating pressure of 400 kPa. A systematic diagram of PAUF can be seen in Fig.2.

2. 4. Measurement of the Retention and Metal Ion Binding to JCPDs in Aqueous Solutions

Feeding solutions were filtered and permeates were collected in equal time intervals (12 min). After two hours, 10 permeates were collected and the experiments were en-

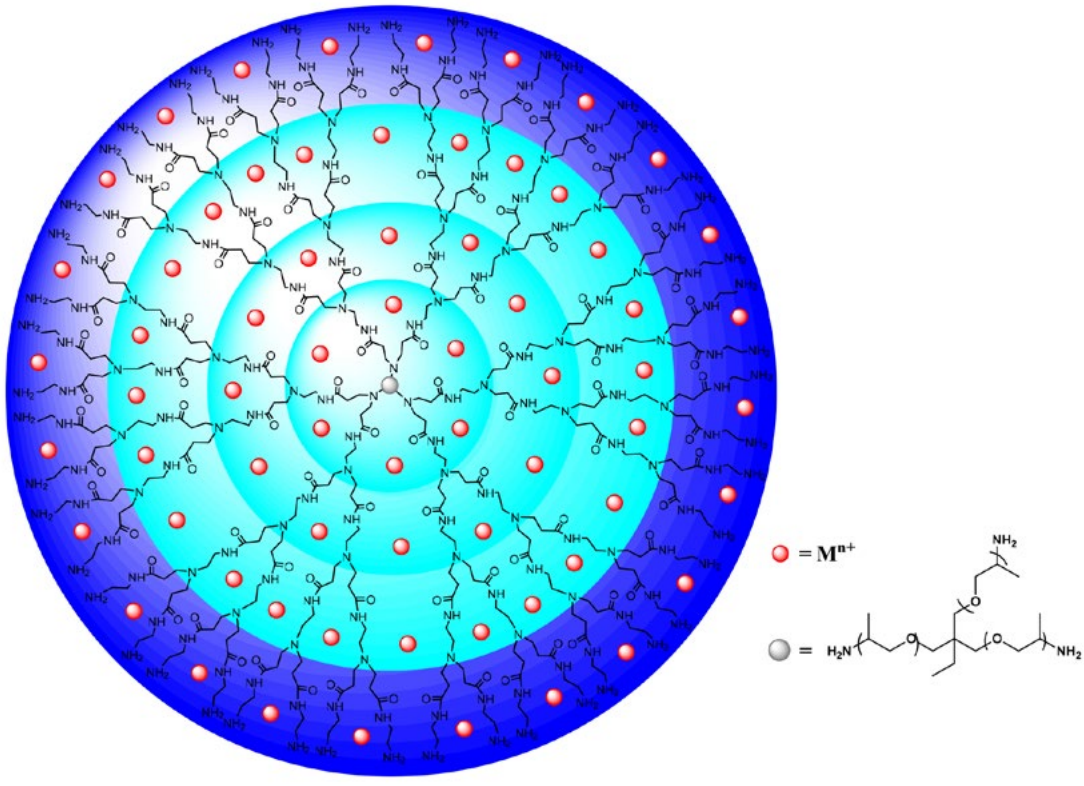

Figure 1. Representative chemical structure of G3-NH_2, Jeffamine,® and schematic representation of the metal complexation of G3-NH_2

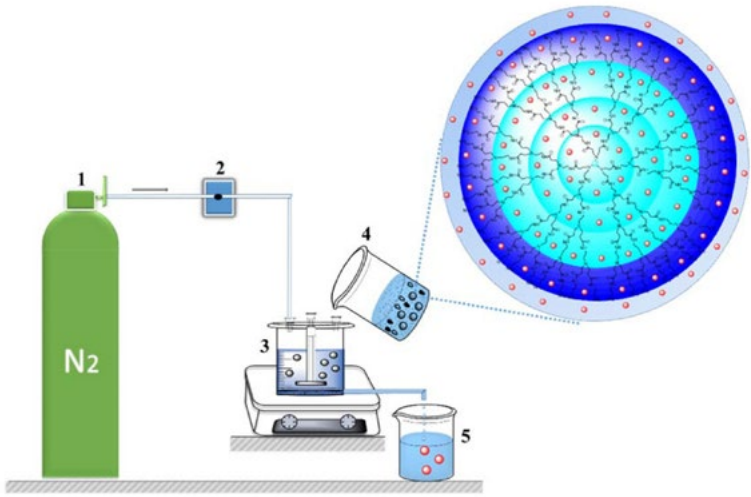

Figure 2. Schematic diagram of batch complexation and polymer assisted ultrafiltration (PAUF) assembly. 1- Cylinder with compressed air (pressure trap); 2- reducer with diaphragm valve and pressure gauge; 3- UF stirred cell; 4- batch stirred tank for complexation reaction (preparation of feed solution) and 5- permeate solution.

ded. Rates of filtrates were determined by continuously weighing the permeates on a digital electronic balance (Precisa), with an accuracy of 0.001 g. This was done to validate the functionality of used UF membrane by observing the initial and in time flux rate (L $m^{-2}h^{-1}$) consistency. Metal ion concentrations in each collected permeate were analyzed by atomic absorption spectroscopy (AAS). Percent retention value (R%) or fraction of binding (FB) of each metal ion was calculated by using equation 1.

$$R\% = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (1)$$

where, is the concentration of metal ion in initial feed solution (mol/L) and is the concentration of metal ion in permeate flux (mol/L).

The concentration of metal ions bound to dendrimer, C_m (mol/L) is expressed by equation

$$C_m = C_f - C_p \quad (2)$$

The extent of binding (EOB), the number of moles of a metal ion bound per mole of dendrimers was expressed as

$$EOB = \frac{C_m}{C_d} \quad (3)$$

where, is the total concentration of a dendrimer in the aqueous solution in mol/L.

2. 5. Analytical Methods

The concentration of the metal ions in feed and permeate solutions were measured by AAS following the procedure reported in the literature.[17, 19, 24] In order to determine Cd(II), Co(II), Cu(II), Ni(II), and Zn(II) concentrations, Shimadzu AA-6800 AAS instrument equipped with hollow cathode lamps (HCLS) was used. All of the chemicals used in experiments were of analytical grade. In all dilutions and standard preparations, 18.2 MΩ cm MilliQ water was used. AAS operating parameters used for the element of interest used throughout in all experiments can be seen in Table 2. Deuterium arc lamp background correction was applied for all the analytes.

3. Results and Discussion

The removal process of heavy metal ions by dendrimer can be affected by a number of parameters such as generation size, pH, formation and type of complexation, accessibility and reactivity of the functional groups available for binding with metal ion at the surface or inner stru-

Table 2. AAS parameters used in the determination of Cd, Co, Cu, Ni and Zn

Parameters	Cd	Co	Cu	Ni	Zn
Wavelength (nm)	228.8	240.7	324.8	232.0	213.9
HCL current (mA)	8.0	12.0	6.0	12.0	8.0
Acetylene flow rate (L/min)	1.8	1.6	1.8	1.6	2.0
Slit width (nm)	1.0	0.2	0.5	0.2	0.5
Background correction	D_2	D_2	D_2	D_2	D_2

cture. Tertiary amines, primary amines and amide functional groups are specific metal binding sites for various generations of PAMAMs. Table 1 compares the number of these functional groups for different generation JCPDs. It is clear that higher generations are expected to be more effective than lower generations due to higher number of amino groups (ligands) they possess on an equal equivalent base (Table 1). Thus, the highest two generations of JCPDs, G3-NH_2 and G4-NH_2, were used as the macromolecular templates for the selective and competitive binding of Cd(II), Co(II), Cu(II), Ni(II), and Zn(II) metal ions from aqueous solutions.

3. 1. Analytical Figures of Merit

Detailed calibration and analytical characteristics of the AAS method used for the determination of the feed and permeate Cd(II), Co(II), Cu(II), Ni(II), and Zn(II) can be seen in Table 3. These characteristics are limit of detection (LOD), limit of quantification (LOQ), linear range, regression coefficient and the best line equation. 3 s/m and 10 s/m where s is the standard deviation were used in the calculation of the LOD and LOQ values, respectively. It is clear from Table 3 that R^2 values for each analyte were found to be at least 0.99. Linear ranges for Cd, Co, Cu, Ni, and Zn elements were in the range of 0.2–2.5, 0.2–4.0, 0.3–4.0, 0.2–5.0, and 0.5–2.0 mg/L, respectively. Four repeated measurements were recorded for the preparation of regression lines and sample measurements, which are correlated with calibration by an appropriate enhancement factor (5–10). The reproducibility of the concentration measurement was within a maximum deviation of 5% in all cases studied.

3. 2. Effect of Generation Size and pH on the Selective and Competitive Binding of Divalent Heavy Metal Ions Cu(II), Co(II), Ni(II), Cd(II), and Zn(II) by PAUF with JCPDs

Selectivity of different generation JCPDs towards heavy metal ions were investigated at four different pH. In this way, low (pH 3.0, 5.0), neutral (pH 7.0), and high pH (pH 9.0) values were evaluated. Retention (%) profiles of the each metal were calculated by means of eqn. 1.

Table 4 summarizes the heavy metal retention (%) of JCPDs in aqueous solutions as a function of pH. No retention at low pH 3.0 indicates the release of all metal ions by both generations. At neutral pH 7.0 and low pH 5.0, both of the generations were selective towards Cu(II). 65.74 ± 1.18% and 70.96 ± 1.59% Cu(II) were retained at neutral pH 7.0 while 12.33 ± 1.13% and 12.13 ± 0.82% Cu(II) by G3-NH_2 and G4-NH_2 were retained at low pH 5, respectively. Taking into consideration the percent retention results obtained from pH 3.0, 5.0, and 7.0, it can be concluded that G3-NH_2 and G4-NH_2 started to be selective towards metal ions with an increase in pH from pH 3.0 to pH 5.0 and this selectivity was maintained up to pH 7.0.

At pH 7 it is interesting to note that JCPDs presented selectivity for Cu(II) ions with the maximum binding ca-

Table 3. Analytical figures of merit for Cd, Co, Cu, Ni, and Zn

Analytes	LOD (mg/L)	LOQ (mg/L)	Linear range (mg/L)	R^2	Equation (y = mx + n)
Cd	0.0159	0.0530	0.2–2.5	0.9948	0.2452x + 0.0277
Co	0.0228	0.0759	0.2–4.0	0.9960	0.0565x + 0.0041
Cu	0.0259	0.0864	0.3–4.0	0.9980	0.0752x – 0.0105
Ni	0.0205	0.0685	0.2–5.0	0.9966	0.0572x + 0.0224
Zn	0.0128	0.0425	0.5–2.0	0.9969	0.2940x – 0.0618

Table 4. Cd(II), Co(II), Cu(II), Ni(II), and Zn(II) retention% in aqueous solutions of JCPDs as a function of pH.

Generation	pH	Heavy metal ions Retention%[a]				
		Cd (II)	Co (II)	Cu (II)	Ni (II)	Zn (II)
G3-NH_2	3	–	–	–	–	–
	5	–	–	12.32 ± 1.13	–	–
	7	–	–	65.74 ± 1.18	–	–
	9	23.68 ± 2.13	93.53 ± 1.38	74.23 ± 1.26	85.00 ± 1.36	97.56 ± 1.95
G4-NH_2	3	–	–	–	–	–
	5	–	–	12.12 ± 0.82	–	–
	7	–	–	70.95 ± 1.59	–	–
	9	22.13 ± 2.89	94.99 ± 2.63	84.38 ± 1.85	86.5 ± 2.36	95.05 ± 3.15

[a]Retention% values are presented as mean ± confidence intervals for four repeated measurements

pacity for both generations in the presence of other divalent heavy metal ions. Our results are in good agreement with the previous computational study[34] conducted to determine active specific metal binding sites (amino groups) of PAMAMs. Results showed that Cu(II)-PAMAM complex exhibit higher stability due to stronger binding energy, shorter bond distances between the metal center and the ligand, and greater covalent degree because of the higher extent of orbital mixing. This result supports the selectivity towards Cu(II) metal ions at neutral pH but may also have implications for the use of JCPDs as effective ligands in sensing systems in future studies.

When the average metal ion retentions are considered, at higher pH 9.0, the metal binding affinity in generations of JCPDs had the same decreasing order of Zn(II) > Co(II) > Ni(II) > Cu(II) > Cd(II). When the average percent retentions of metal ions by G3-NH_2 in aqueous solutions were considered, it can be concluded that the selectivity follows the order of Zn(II) > Co(II) > Ni(II) > Cu(II) > Cd(II) with more than 74.23% except for Cd(II) 23.68%. In case of the average retention (%) profiles, the affinity of G4-NH_2 toward metal ions was observed in the same decreasing order with more than 84.38% for all metal ions except for Cd(II) 22.13%. However, if the confidence intervals are considered, the decreasing affinity order of G4-NH_2 towards metal ions was in the order of Zn(II) ≈ Co(II) > Ni(II) ≈ Cu(II) > Cd(II). Interestingly, Zn(II) and Co(II) were retained over 90% by both generations in the presence of other metals. This indicated that G3-NH_2 and G4-NH_2 were highly selective towards to Zn(II) and Co(II) at higher pH 9.0 and almost no generation effect can be observable towards metal ions at pH 9. In the case of Cu(II) the retention increased as the generation increased. Indeed, the results could be explained based on extent of protonation (α) of the amino groups of PAMAMs (Fig. S3), and the theory of hard-soft acid-base (HSAB).[35] In our experiments, we evaluated the removal of divalent ions of selected heavy transition metals from the first row: Zn, Cu, Ni, Co and second row: Cd by PAUF with JCPDs. According to theory, Cd(II) ion with lower ionic charge and greater ionic size is a kind of soft acid, which may bond to soft base strongly.[35] In accordance with the literature,[36] JCPDs may be taken as a type of hard base in our case with their good protonation abilities and extent of protonation profiles (Fig. S3). On the other hand, Zn(II), Cu(II), Ni(II), and Co(II) metal ions could be taken as borderline acids and they can bond to both hard and soft bases. When the metal ions and the dendrimers are in the same valence, the polarization of metal ions will take an important role in the interaction with dendrimers. The larger the metal ion radius is, the greater the polarization would be. Therefore, the bonding strength is expected in the decreasing order of Zn(II) (74 pm) > Co(II) (65 pm (low-spin)-74.5 pm (high -spin)) > Cu(II) (73 pm) > Ni(II) (69 pm) for hard acids. Cd(II) (95 pm) is expected to be in the last order as it is a soft acid to the contrary to other metal ions. These expectations almost validate our observation that the order of retention of metal ions for higher generation G4-NH_2 PAMAM dendrimer was in the order of Zn(II) ≈ Co(II) > Ni(II) ≈ Cu(II) > Cd(II) at pH 9, where almost all of the amino groups are available for binding for metal ions in competition (Fig. S3). Higher or almost equal retention of Ni(II) ions compared to Cu(II) ions could be attributed to Jeffamine® core even if PAMAMs could bind Cu(II) over Ni(II) in waste water.[25] It was noteworthy that the position of the metal ions changes dynamically as they interact with the amine-terminated PAMAMs depending on the pH.[37] Metal ions proceed to localize to the interior of the dendrimers first contacting the surface amine groups of dendrimers and finally reaching to the core of the dendrimer as the pH increased and dendrimer is fully deprotonated.[37] It could be also inferred that metal laden JCPDs could be regenerated by decreasing the pH of the aqueous polymer solutions from pH 9 to pH 3. In other words, it can be possible to remove heavy metals from mixtures at high pH 9.0 and purify or regenerate them at lower pH 3.0 by using both generations of JCPDs as the polymer support for the collective removal of metal ions by PAUF.

3. 3. Selective and Collective Removal of Cu(II), Co(II), Ni(II), Cd(II), and Zn(II)

Fig. 3 shows the EOB and FB of total metal ions in aqueous solutions of JCPDs, G3-NH_2 and G4-NH_2. G3-

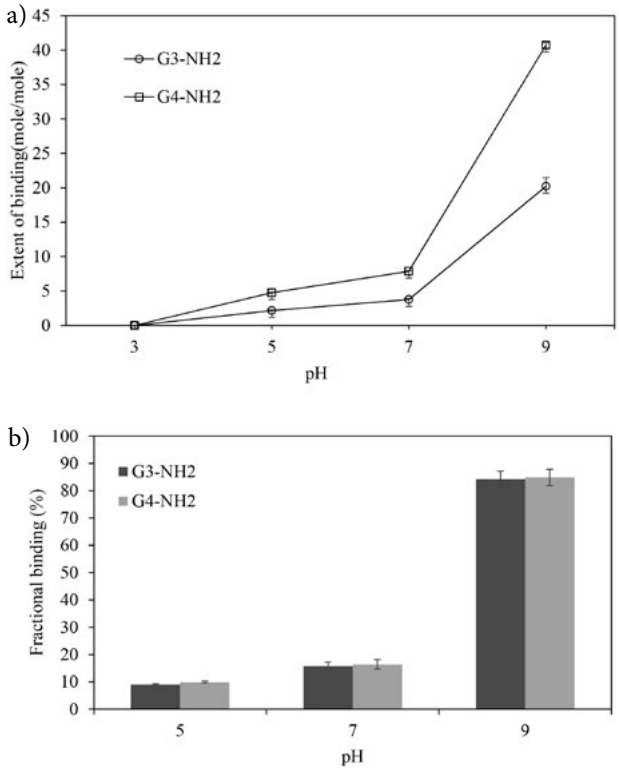

Figure 3. (a) EOB and (b) FB of total metal ions in aqueous solutions of JCPDs at room temperature as a function of pH.

NH_2 has 21 tertiary amine, 42 amide groups and 24 terminal primary amine groups while G4-NH_2 has 45 tertiary amine, 90 amide groups and 48 terminal primary amine groups (Table 1). Both of the G3-NH_2 and G4-NH_2 JCPDs retain selectively Cu(II) ions at pH 5 and neutral pH 7 whereas they bind all metal ions at higher pH 9 (Table 3). Thus, there exist a competition between the metal ions at pH 9. For G3-NH_2 PAMAM dendrimer, EOB of 2.16 ± 0.05, 3.77 ± 0.06, 20.22 ± 0.39 ions per dendrimer molecule were observed whilst 4.75 ± 0.08, 7.87 ± 0.15, 40.73 ± 1.24 were measured for G4-NH_2 at pH 5, 7 and 9, respectively. It can be concluded that EOB of total metal ions in aqueous solutions of JCPDs goes through a maximum as pH increases. From pH 3 to pH 7, EOB increases linearly for both generations. However, a remarkable increase in EOB for both generations was observed with a pH increase from pH 7 to pH 9. EOB increased from pH 7 to 9 was significantly higher for G4-NH_2 in comparison with G3-NH_2. This could be attributed to the large number of present metal binding sites (amino groups), which increase exponentially with the generation number increase (Table S1). Meanwhile, it could be clearly seen from FB profiles that there is no explicit generation effect on metal binding for JCPDs.

Similar trends in the competition of Cd(II), Co(II), Cu(II), Ni(II), and Zn(II) ions in the presence JCPDs in aqueous solutions with different pH values ranging from pH 3.0 to 9.0 suggest that these metal ions should have the similar binding mechanism for G3-NH_2 and G4-NH_2 or they bind to the similar sites. These sites are in general the internal tertiary amine sites of PAMAMs and they have the limited and alternating number of tertiary amine groups avalable for binding with metal ions as the generation changed (Table 1). Hence, PAMAMs could have bonded a limited number of metal ions. In the presence of an excess amount of metal ions for binding, there occurs a binding competition between the metal ions towards to JCPDS (Table S1).

To enlighten the mechanism of binding and assess the respective role of amino groups on the uptake of metal ions by different generations of JCPDs at different pH values, the relationship between EOB for metal ions (M(II)) and generation size was illustrated in Fig. 4. The symbols stand for measured EOB values assuming two commonly observed coordination models for M(II) ions: bidentate [i.e, 1M(II)/2N i.e each M(II) ion coordinates with two amino groups] and tetradentate coordination [i.e, 1M(II)/4N]. Fig. 4 suggests that EOB data can be adequately described by a tetradentate coordination model for amine -terminated JCPDS. This result is a promising evidence that at pH 9, all of the available amino groups of dendrimers could take a role in binding by forming tetradentate coordination model. Investigation of the Fig. 4 reveals also that all of the amide groups of JCPDs take an active role in complexation with divalent heavy metal ions only at higher pH 9. In a former study, Ottavani et al.[38] characterized that deprotonation of the amide groups of PAMAMs starts at pH 6 and continues towards the higher pH 12. This result is also consistent with our findings, and with the result reported by Diallo et al.[39] that "hard" Lewis acids (metal ions) form strong complexes with "hard" Lewis bases including organic ligands with O and N donors (e.g amide and amines). In summary, due to high contribution of deprotonated amino groups, maximum bindings were observed at pH 9.

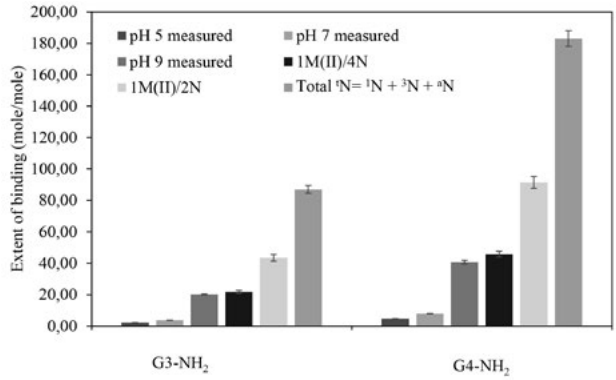

Figure 4. Maximum EOB for M(II) ions in solutions of JCPDs as a function of total number of nitrogen-containing groups (^{1}N: primary amines; ^{3}N: tertiary amines; ^{a}N: amides; total ^{t}N = ^{1}N + ^{3}N + ^{a}N).

The structure of the amine-terminated PAMAMs is expected to come in densely closed packed-in conformation as the pH increases.[40] Therefore, the complexation ability of PAMAMs increases with the contribution of compact structure of them with activated amide groups in addition to tertiary and terminal amine groups at the values, especially above pH 7 (Fig. S3). The retention of metal ions inside of PAMAMs can be performed by covalent bonding, hydrogen bonding or entrapping.[41] One of the possible reasons why Cu(II) retention was observed at pH 5, where almost all of the amino groups of PAMAMs are protonated, can be the entrapping of hydrated Cu(II) ion complexes inside the dendrimer due to PAMAMs encapsulation abilities at lower pH.[42]

Fig. 5 shows the EOB and selectivity features of different generations of amine-terminated JCPDs for metal ion mixture of Cu(II), Co(II), Ni(II), Cd(II), and Zn(II) at higher pH 9, where all of the amino groups of dendrimers are neutral (Fig S3). In Fig. 5, individual EOB values of metal ions while they are in competition with each other in the aqueous solutions of different generations of JCPDs are ranged between 2.51 and 4.73 for G3-NH_2 while 4.76 and 9.29 for G4-NH_2. EOB values for all heavy metals ions increase as the generation number increases due to an increase in the number of specific binding sites with generation size increase. That is, higher binding capacities were observed for G4-NH_2 than those of G3-NH_2. When the average EOB values are considered, it is clear from Fig. 5 that the selectivity follows the order: Zn(II) > Co(II)

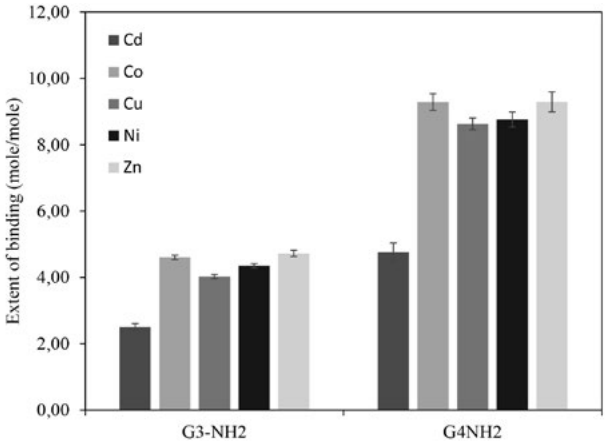

Figure 5. EOB and selectivity properties of different generation JCPDs towards heavy metals Cd(II), Co(II), Cu(II), Ni(II), and Zn(II) at pH 9.

> Ni(II) > Cu(II) for both generations. These results present extra proof that the dendrimer-metal ion interactions depend not only the nature of the media but also the specific binding sites (number of amine groups) of the generation of PAMAMs, electronegativity, and ionic radious of the heavy metals according to Pearson's hard-soft principles.[35]

3. 4. Effect of Initial Free Metal Ion Concentration on Dendrimer-metal Complexation

Complexation studies of JCPDS, G3-NH_2 and G4-NH_2, with the mixture of heavy metal solutions were evaluated to assess their metal ions removal ability from aqueous solutions. At this point, free metal ion concentration [M^{2+}] has a critical importance. If the solubility of metal is not adequate for complexation at the studied pH, then sudden metal hydroxide formation is expected, and this will form a mass deposition on the membrane surface.[43] Therefore, it would not be possible to mention a successful membrane dialysis process even if it was reported in a recent study[43] that the presence of PAMAM dendrimers in aqueous solutions does not prevent hydrolysis of metal ions. In dendrimer-multi metal batch complexation process, taking into consideration this factor, we conducted experiments in the pH range of 3.0–9.0, where it was not observed any precipitation of metal hydroxides. A clear precipitation was observed above the pH 9.20. For this reason, batch complexation experiments were conducted between the pH ranges of pH 3.0-9.0 in alignement with the literature.[24]

3. 5. Metal Ion Uptake

In order to compare the effect of generation on the metal ion uptake of JCPDs, their binding capacities either for Cd(II), Co(II), Cu(II), Ni(II), and Zn(II) ions under competitive conditions (aqueous metal mixture solutions) were determined, and the results were presented in Table 5. As shown in Table 5, the metal ion uptake is ranged between ~48 and ~60 mg metal ion per gram polymer. Binding capacity order of G3-NH_2 is Zn(II) > Cd(II) > Co(II) > Cu(II) > Ni(II) whereas that of G4-NH_2 is Zn(II) > Cu(II) > Co(II) > Cd(II) > Ni(II). It was found that Zn(II), Cd(II), and Co(II) metal ions bonded at over 50 mg/g for both generations at pH 9.

Normally, the total binding capacity of G4-NH_2 is expected to be higher than that of G3-NH_2 when the number of metal binding sites of JCPDs are considered (Table 1). However, we observed the total binding capacity of G3-NH_2 (262.79 ± 1.62 mg/g) as a little bit higher than that of G4-NH_2 (257.27 ± 2.57 mg/g). This result reveals an important point that the binding capacities of dendrimers not only depend on the pH of the media, EOP and type of the dendrimer but also on the structural conformation that the generation has.

It was reported that a portion of metal hydrates resides in the water pools in the open structure of the earlier generation dendrimers (G<4). This finding reveals that generation-3 PAMAM, with more open structure, can entrap more water molecules that can complex the metal ions in comparison with generation-4 PAMAMs.[37] Our finding is in good agreement with these results and could be used to explain why G3-NH_2 has a binding capacity higher than G4-NH_2.

Table 5. Metal ion uptake and binding properties of different generation (G3-G4) JCPDS under competitive conditions at pH 9.

Metal ion (M(II))	G3-NH_2 (mg/g)[a]	G4-NH_2 (mg/g)[a]
Cd	53.98 ± 0.21	50.02 ± 0.29
Co	51.92 ± 0.20	51.16 ± 0.32
Cu	48.95 ± 0.14	51.25 ± 0.24
Ni	48.83 ± 0.14	48.06 ± 0.26
Zn	59.11 ± 0.13	56.78 ± 0.18
Total	262.79 ± 1.62	257.27 ± 2.57

[a]Average binding capacity (mg/g) for four repeated measurements.

4. Conclusions

The performance of different generations of JCPDs in removing some of the divalent heavy metal ions from aqueous solutions was investigated in this paper. The highest heavy metal ion removal or binding capacity was observed for G3-NH_2. JCPDs were detected to be selective at pH 5.0 and at neutral pH 7.0 under competitive conditions with other heavy metals. At high pH 9.0, both generations could remove all of the metal ions present in the media. The affinity of both generations towards metal ions was also observed in the same decreasing order of Zn(II) > Co(II) > Ni(II) > Cu(II) > Cd(II) when the average retention percentages were considered. Only the Cu(II) retention increased with increasing generation and pH. Zn(II) and Co(II) were retained over 90% retention for both generations at pH 9.0. Regeneration of metal laden PAMAMs could be achieved by decreasing the pH of aqueous solution to lower than 5. These results indicate that amine-terminated JCPDs are expected to be new promising macromolecular chelating agent templates for the removal of toxic heavy metals from wastewaters. Results also imply that generation-3 and 4 amine-terminated JCPDs effectively interact with metal ions, and thus might provide a convenient competitor in nanosensing for future studies.

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Povzetek

Različni generaciji (G3-G4) Jeffamine® T-403 dendrimerov (JCPD) z osnovno strukturo poli(amidoamin) PAMAM dendrimerov in s terminalnimi aminskimi skupinami smo uporabili kot novo makromolekularno osnovo za kompleksiranje težkih kovin v procesu ultrafiltracije s pomočjo polimerov (PAUF). Raziskali smo njihovo zmožnost za odstranjevanje nekaterih divalentnih kovinskih ionov: Cu, Co, Ni, Cd in Zn iz vodnih raztopin pod kompetitivnimi pogoji. Raziskali smo tudi učinek pH in generacije JCPD. Rezultate za obseg vezave (EOB) lahko ustrezno razložimo s tetradentatno koordinacijo z JCPD pri pH 9, pri katerem smo opazili največji delež odstranjenih kovinskih ionov. Pri pH 9,0 smo za obe generaciji opazili naslednjo selektivnost nasproti ionom težkih kovin: Zn(II) > Co(II) > Ni(II) > Cu(II) > Cd(II). Največjo skupno vezavno kapaciteto smo opazili za G3-NH_2 (262,79 ± 1,62 mg/g) in je bila nekoliko višja kot za G4-NH_2 (257,27 ± 2,57 mg/g). EOB študija je tudi dokazala aktiven prispevek amidnih skupin na PAMAM k zmožnosti vezave kovin. Obe generaciji sta bili selektivni za Cu(II) ione pri nižjem pH 5 in pH 7. Iz teh rezultatov lahko sklepamo, da imajo obravnavani JCPD želene tehnične lastnosti za uporabo pri odstranjevanju strupenih kovin iz odpadnih vod.