

Synthesis and Characterization of Triazine-Based Dendrimers and Their Application in Metal Ion Adsorption

Ahmad Nozad Golikand, Khadijeh Didehban, Leila Irannejad

Department of Metallurgy, Material Research School, NSTRI, Tehran, Iran

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ABSTRACT: This article described the synthesis of triazine-based dendrimers with poly(ethylene glycol) core by convergent method. Compound **1** was prepared by coupling of amino group of diethanolamine with cyanuric chloride in dry THF (tetrahydrofuran). Reaction of compound **1** with *p*-aminobenzylamine resulted in compound **2**. Compound **4** was synthesized using coupling reaction of amino group of compound **2** with cyanuric chloride, then coupling of amine groups of *p*-aminobenzylamine with compound **3** in the hybrid solvents. The final dendrimer (*den-OH*) were synthesized using reaction of dendron **4** with compound **5**. Ethylene diaminetetraacetic acid

modified final dendrimer were successfully prepared via coupling ethylene diaminetetraacetic acid dianhydride and *den-OH*. The growth of dendrons and their structures were investigated by using usual spectroscopy methods and elemental analysis. The chelating behavior and sorption capacities of triazine dendrimers were determined in relation to pH dependency for some metal ions such as Cu^{+2} , Ni^{+2} , and Zn^{+2} using atomic absorption methods. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1245–1251, 2012

Key words: triazine; dendrimer; metal sorption

INTRODUCTION

Dendrimers are highly branched, monodispersed, and terminated with multiple functional groups. Their perfect and well-defined structure leads to a number of interesting characteristics and features, including low viscosity, good solubility, and compatibility.^{1,2} Numerous dendritic architectures have been reported including polyamines,³ polyphenylethers,⁴ triazine-containing dendrimers,^{5,6} polyamidoamines,⁷ carbosilanes,⁸ and polynuclear metal complex,⁹ to name just a few.

Triazines—especially melamine—can recognize other molecules by the donation and acceptance of hydrogen bond, metal chelating, π - π interaction, and the ability of dendrimers to perform as catalysts, filters, or sorbents. The properties are mainly dependent on the structural characteristics of repeating units and facile functionalization of their terminal groups. In contrast, control over the macromolecular configuration is a key goal in dendrimer chemistry. The high level of control over macromolecular configuration gives researchers the ability to control and fine-tune functionality of a dendrimer, a powerful

tool that has potentiality for application in the field of environmental remediation.¹⁰

The first dendrimer family which is based on melamine was prepared by Simanek and coworker.¹¹ Development of dendrimers which are based on triazine is interesting due to their easy synthesis, the ability to control diversity in their composition, and their intrinsic potential for molecular recognition.¹² Dendritic resins with the triazine unit which are tethered to an alcohol functionalized waxy resin have been prepared for the explicit purpose of capitalizing on the ability of melamine dendrimers to scavenge protons. Nowadays, triazine-based dendrimers are used as a potential material for preparation of dendritic ligands and metal complexes.¹³ Most heavy metal ions are toxic or carcinogenic and hence present a threat to human health and the environment when they exist in or are discharged into various water resources.¹⁴

Adsorption is one of the methods commonly used to remove metal ions from various aqueous solutions with relatively low metal ion concentrations. The efficiency of adsorption depends on the capability of the adsorbent to concentrate or adsorb metal ions from the solution onto its surfaces so that metal ions can be separated or removed from the solution. There are many type adsorbents, including activated carbon, oxide minerals, polymer fibers, resins, and biosorbents, that have been used to adsorb metal ions or enrich trace amounts of metals from various

Correspondence to: A. N. Golikand (anozad@gmail.com).

aqueous solutions.^{15–17} Density of ligand groups, type of hetroatom of ligand groups and their affinities in different dendrimers including factors that strongly affect the adsorption phenomenon. Adsorption of metal ions from a solution to an adsorbent can be controlled by the surface functional groups of the adsorbent. In the adsorption process, metal ions in the aqueous solution may be transported to the surfaces through diffusion or convection. This is due to various physical or chemical interactions between the metal ions and the surface functional groups of the adsorbent. The surface complex formation, ion exchange, and chelating have often been considered as the important adsorption mechanisms for heavy metal ions on various adsorbents. It has been reported that adsorbents with carboxyl, sulfonic, and phosphonic groups on the surface favor metal ion adsorption through the ion exchange mechanism, while those containing nitrogen on the surface (with amino, hydrazine, thioamide, and imidazoline groups) facilitate metal ions adsorption through the chelating mechanism.^{18–21}

In particular, the amino group on an adsorbent has been found to be one of the most effective chelating groups for adsorption or removal of heavy metal ions from aqueous solutions.²² This is because of the step-by-step synthesis, precise control of size, shape, and possibility of attaching end functional groups, such as primary amines, carboxylates, and hydroxymates, which can result in a substantial increase of bonding capacity for a variety of toxic metal ions. Free surface functional groups can form complexes or conjugates with drug molecules or ligands. The first dendrimer was reported on the employ to removal of metal ions in water in 1999 by Diallo et al.²³ Recently, several groups have carried out extensive studies on the removing of metal ions in aqueous solution.^{24–26} Because of poly(ethylene glycol), increase water solubility of resulting dendrimers, have variety of potential applications in the fields of cell mimic systems, coatings, chemical sensors, hydrogel, and drug delivery.^{27–29}

From this point of view, we have initiated a program to clear the structure and properties of the synthesis of barbell-like dendritic triazine and functionalized with EDTA. The prepared functionalized dendrimers were used as a sorbent in series of adsorption experiments to investigate the behaviors of the synthetic dendrimers in removing metal ions from aqueous solutions.

EXPERIMENTAL

Materials

poly(ethylene glycol) 1000, cyanuric chloride, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$,

diethanolamine, *p*-aminobenzylamine, ethylene diaminetetraacetic acid, and *N,N*-diisopropylethyamine were purchased from Merck.

Instrumental measurements

FT-IR spectra were measured on a Shimadzu model FT-IR-8101M spectrometer. The NMR spectra were recorded on 400 MHz Bruker SP-400 AVANC in DMSO-d_6 . The elemental analysis instrument in this study Vario EL III was used to characterization of synthetic compounds. The thermogravimetric analysis (TGA) was performed using a Dupont 651US. The scan rate of TGA was $10^\circ\text{C}/\text{min}$ in air atmosphere. The metal absorption capacities of polymer nanocomposites were measured by atomic absorption spectrophotometer AA-3600A shimadzu spectrophotometer at room temperatures in aqueous solution.

Synthesis of compound 2

A solution of diethanolamine (0.42 g, 4 mmol) in 10 mL THF was added to cyanuric chloride (0.37 g, 2 mmol) dissolved in 10 mL THF at 0°C and the reaction mixture was stirred at room temperature for 4 h, then *p*-aminobenzylamine (0.24 g, 2 mmol) dissolved in 10 mL THF was added at 70°C to above mixture. The mixture was stirred overnight. THF was removed by distillation under reduced pressure and the crude product was recrystallized in EtOAc. Yield = 76%. $^1\text{H-NMR}$ (400 MHz, DMSO-d_6 , ppm): δ 6.94 (d, 2H aromatic, ortho to N), 6.78 (d, 2H aromatic, meta to N), 4.59 (t, 2H, OH), 3.88(t, 2H, $\text{CH}_2\text{-Ph}$), 3.69 (b, *N*-H), 3.58–3.63 (m, 16H, CH_2). $^{13}\text{C-NMR}$ (DMSO-d_6 , δ): 174.7, 171.5 (triazine part), 147.7, 134.6, 128.6, 122.1 (aromatic part), 61.5, 59.6, 48.3 (CH_2). FT-IR (KBr, cm^{-1}): 3291(ν_{OH}), 2890 ($\nu_{\text{C-H}}$), 1570, 1523 ($\nu_{\text{C=N}}$), 1630 ($\nu_{\text{C=C}}$), 1108 ($\nu_{\text{C-O}}$). Elem. Anal. Calcd for $\text{C}_{18}\text{N}_7\text{O}_4\text{H}_{29}$: C, 53.1%, N, 24.1%, H, 7.12% Found: C, 53.52%, N, 24.39%, H, 7.49%.

Synthesis of compound 3s and 4

A solution of dendron 2 (1.63 g, 4 mmol), *N,N*-diisopropylethyamine (0.8 g, 6 mmol), and cyanuric chloride (0.42 g, 4 mmol) was mixed in 60 mL of MeOH/THF (1 : 1, v/v) at 0°C and the reaction mixture was stirred at room temperature for 5 h until compound 3 was obtained by recrystallization in EtOAc/Aceton (5 : 1). A solution of *p*-aminobenzylamine (0.24 g, 2 mmol) in 10 mL THF/MeOH was added slowly to the above mixture at 70°C and the resulting mixture was stirred overnight. The excess of the solvents was removed by distillation under reduced pressure the crude product was obtained by

chromatography on silica gel. Rf = 0.73, (SiO₂, chloroform/methanol v/v, 2 : 3). ¹H-NMR (400 MHz, DMSO-d₆, ppm): δ 6.91 (d, aromatic protons, ortho to N), 6.77 (d, aromatic protons, meta to N), 4.57 (t, OH), 3.85 (m, CH₂-Ph), 3.61 (b, N-H), 3.52–3.59 (m, CH₂). ¹³C-NMR (DMSO-d₆, δ): 174.1, 170.2 (triazine part), 148.2, 136.7, 129.5, 124.7 (aromatic part), 62.3, 58.4, 49.3, 41.4 (CH₂). FT-IR (KBr, cm⁻¹): 3287(ν_{O-H}), 2895 (ν_{C-H}), 1573, 1526 (ν_{C=N}), 1637 (ν_{C=C}), 1123 (ν_{C-O}). Elem. Anal. Calcd for C₄₆N₁₉O₈H₆₅: C, 54.6%, N, 26.3%, H, 6.4% Found: C, 54.9%, N, 25.9%, H, 6.6%.

Synthesis of compound 5

Compound 5 synthesized and through divergent method with similar route reported in literature.⁶

Synthesis of den-OH

A solution of compound 5 (1 g, 0.75 mmol), compound 4 (6.1 g, 6 mmol), and *N,N*-diisopropylethyamine (0.8 g, 6 mmol) in 40 mL THF/dioxane were placed in a round-bottomed flask. The mixture was refluxed for 4 h. The excess of solution was removed by distillation under reduced pressure; the crude product was dissolved in MeOH and precipitated in diethylether at 0°C several times and washed with THF. FT-IR: ν cm⁻¹ 3361(ν_{O-H}), 2865(ν_{C-H}), 1567, 1524 (ν_{C=N}), 1156 (ν_{C-O}). ¹H-NMR (400 MHz, DMSO-d₆, ppm): δ 6.90 (d, aromatic protons, ortho to N), 6.74 (d, aromatic protons, meta to N), 4.56 (b, OH), 3.81 (m, CH₂-Ph), 3.63–3.66 (m, CH₂), 3.56–3.61 (PEG). ¹³C-NMR (DMSO-d₆, δ): 175.8, 173.2 (triazine part), 151.4, 137.7, 131.7, 126.8 (aromatic part), 64.9, 57.6, 46.9, 43.8 (CH₂). Elem. Anal. Calcd for C₂₃₄N₈₂O₅₄H₃₃₂: C, 54.2%, N, 22.2%, H, 6.7% Found: C, 54.4%, N, 22.9%, H, 6.6%.

Synthesis of den-COOH

Ethylene diaminetetraacetic acid dianhydride (An-EDTA) was used to prepare EDTA functionalized dendrimer according to literature method.³⁰

A solution of dendrimer-OH (1.15 g, 0.5 mmol) and An-EDTA (9 g, 35 mmol) in dry DMF (20 mL) was placed in a round-bottomed flask. The mixture was stirred at 80°C in a heating bath under argon atmosphere for 24h. The reaction mixture was cooled at room temperature and poured into 200 mL water, the precipitate was filtered, then washed with water and after that with methanol and finally dried in vacuum. FT-IR: ν cm⁻¹ 3631–2652(ν_{O-H}), 2865(ν_{C-H}), 1567, 1524(ν_{C=N}), 1688(ν_{C=O}), 1148(ν_{C-O}). ¹H-NMR (400 MHz, DMSO-d₆, ppm): δ 6.93 (d, aromatic protons, ortho to N), 6.76 (d, aromatic protons, meta to N), 4.36 (t, CH₂-CO₂), 3.80 (m, CH₂-Ph), 3.64–3.66 (m,

CH₂), 3.57–3.61 (PEG), 2.83–2.85 (N-CH₂CH₂-N). ¹³C-NMR (DMSO-d₆, δ): 174.7, 173.6 (triazine part), 170.5, 169.1 (CO), 152.5, 138.5, 133.6, 126.9 (aromatic part), 65.1, 58.8, 47.5, 45.4, 39.4 (CH₂). Elem. Anal. Calcd: C, 50.1%, N, 15.8%, H, 5.6% Found: C, 50.4%, N, 15.5%, H, 5.8%.

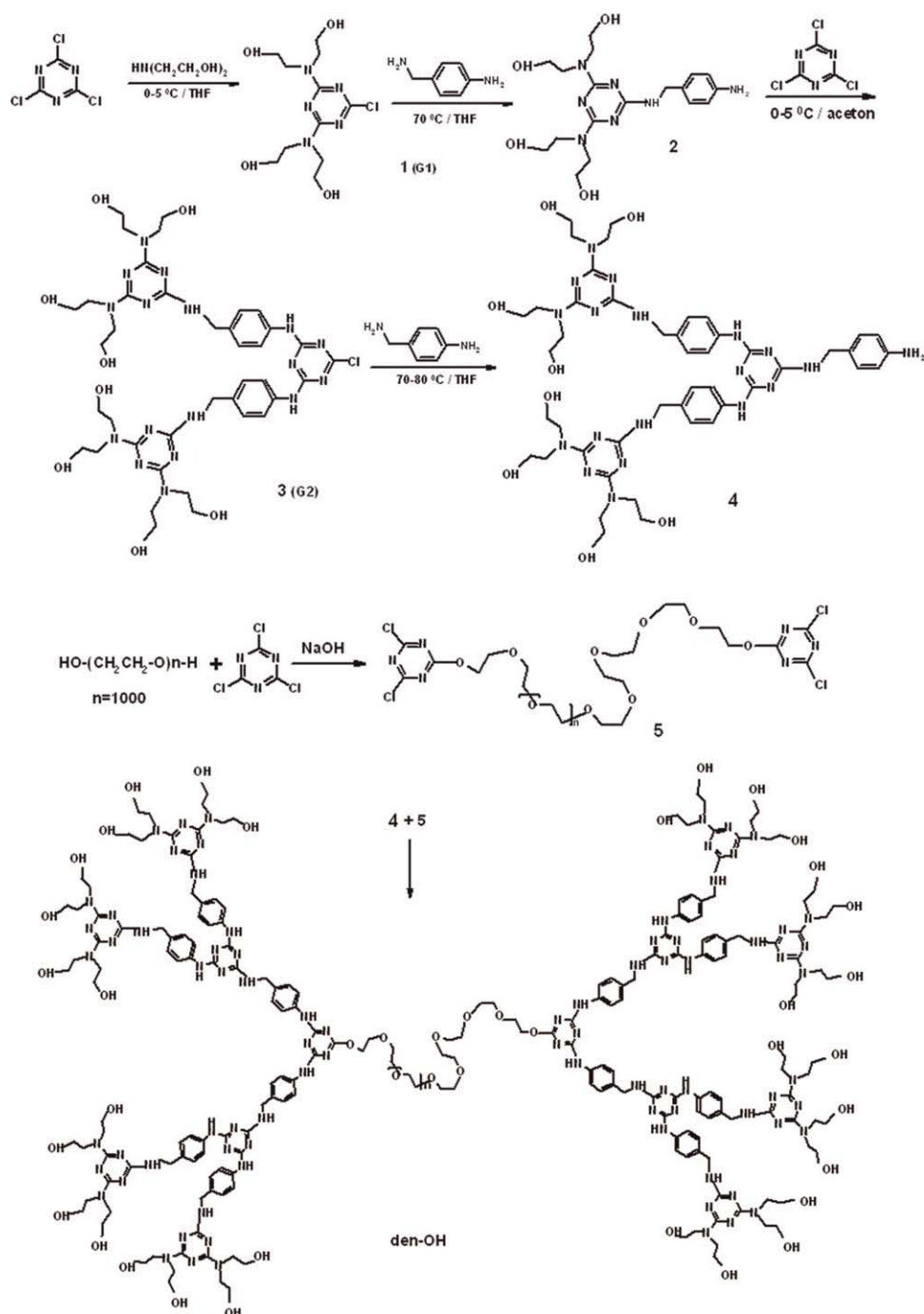
Adsorption experiments

A solution of 3 mmol metal salt [Ni (NO₃)₂·6H₂O, Cu (NO₃)₂·6H₂O, Zn (NO₃)₂·6H₂O] in 10 mL water was added to 200 mg of dendrimer separately. The solution pH was set at 1, 3, and 5. The mixture was shaken in a thermostatic water-bath shaker which operated at 25°C for 24 h. The metal-dendrimer complexes were collected by filtration, washed with aqueous solution of the same pH to remove noncomplexed metal ions. The residue concentration of metal ions was measured by atomic absorption spectrometry.

RESULTS AND DISCUSSION

Structure characterization of dendrimer

Dendritic fragments were characterized using a combination of ¹H-NMR and ¹³C-NMR spectroscopy and elemental analysis. These methods proved to be invaluable in detecting impurities and defects. The reactions of cyanuric chloride with aromatic amines were reported a stepwise and selective reaction of three symmetric chlorides in the triazine ring. These amine substitutions were carried out at different reaction temperatures and solvents for three individual chlorides in the triazine ring. Triazine-based dendrimer was synthesized through convergent method. After that *den-OH* functionalized with EDTA similar routes was reported in literatures.³¹ By means, compound 1 and 2 were synthesized using 1 equivalent cyanuric chloride and 2 equivalent ethanolamine in tetrahydrofuran as a solvent at low temperature. The results indicate that the reaction temperature is the important parameter in controlling the amine substitution. Under the reaction temperature of 0 to 5°C and by using THF as the solvent, the first chloride in the triazine ring was selectively substituted by 1 equivalent of ethanolamine. The substitution of 2nd equivalent amines on the second chloride occurred at 25 to 30°C. The third chloride in the triazine ring was reactive for the third equivalent of *p*-aminobenzylamine at high temperature (Scheme 1). The ¹H-NMR spectrum of compound 2 show a doublet signal at 6.94 ppm for the aromatic protons ortho, to *N*-Ph and a doublet signal at 6.78 ppm for the aromatic protons, meta to *N*-Ph group. OH, methylene, and CH₂-Ph groups appeared at 3.58, 4.59, and 3.88, respectively. In ¹³C-NMR pectrum of compound 2 signals at 171–174 ppm related to triazine part, signals at 122–147



Scheme 1 Synthetic route of triazine-based dendrimer.

show aromatic part and signals at 48–61 ppm show methylene groups.

Compound 3 was synthesized by reaction between compound 2 and cyanuric chloride in mixture of solvents at low temperature. Then, in presence of *p*-aminobenzylamine at high temperature, compound 4 was resulted. The $^1\text{H-NMR}$ spectrum of compound 4, the chemical shift at 6.77–6.91 ppm CH protons of aromatic parts, protons of $\text{CH}_2\text{-Ph}$ groups and methylene groups appeared at 3.85 and 3.52 ppm, respectively. The integral ratio of aromatic protons to ali-

phatic protons of diethanolamine parts is 0.74 (in comparison to 0.75 as a theoretical calculation) show that the reaction was completed and the growth of dendritic part was confirmed. The growth of dendritic parts, confirmed through the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ data and CHN analysis, therefore, this method could be applied for the determination of growth of dendritic parts. For the preparation of final dendrimer (*den-OH*) containing hydroxyl groups at the periphery, first compound 5 was synthesized using reaction of poly(ethylene glycol) as a core with

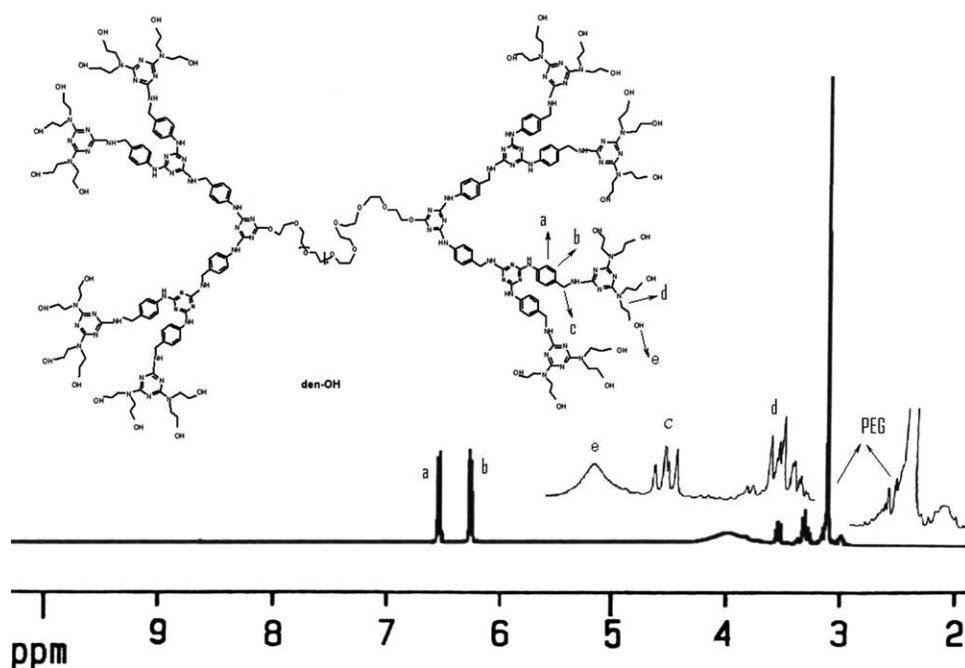


Figure 1 $^1\text{H-NMR}$ spectra of den-OH in DMSO.

triazine (Scheme 1) according to literature.⁶ Final compound *den-OH* was prepared by reaction between compound 5 and dendron 4 and the obtained product was purified as explained in the experimental section. The purity of the compounds was confirmed using TLC, NMR, and CHN. The degree of substitution of dendron 4 in *den-OH* was calculated from $^1\text{H-NMR}$ signals in region 6.90–6.73 and 3.5–3.6 corresponds to protons of aromatic rings and PEG.

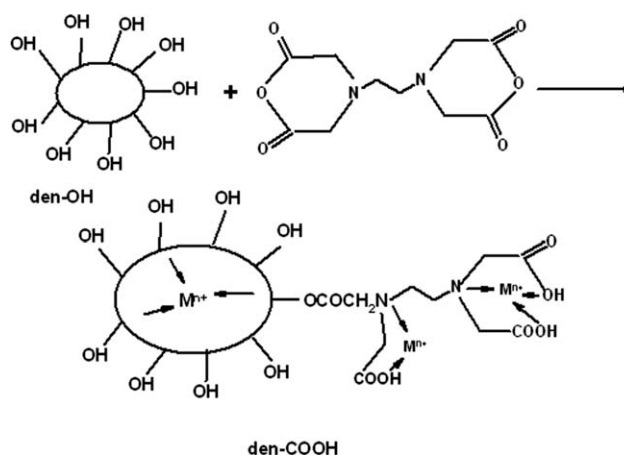
In Figure 1, Signals at 6.90–6.73 and 3.56–3.61 ppm corresponded to the aromatic rings of *p*-aminobenzylamine and PEG as a core. The ratio of $^1\text{H-NMR}$ signals in regions 6.74–90 (corresponds to C-H aromatic) to 3.56–3.61 (corresponds to PEG protons) gives degree of substitution. The integral ratio of CH protons of *p*-aminobenzylamine to PEG part of molecules is 0.51 (in comparison to 0.54 as theoretical calculation). This shows that the reaction was completed and compound *den-OH* was confirmed. Synthetic triazine-based dendrimer (*den-OH*) is a unique chelating agent, because of its nitrogen and oxygen ligands, and the possibility of attaching functional groups, such as carboxylates, which can result in a substantial increase of bonding capacity for variety of toxic metal ions. Therefore, in the next step, EDTA-functionalized dendrimer was synthesized via coupling of hydroxyl end group of *den-OH* with ethylene diaminetetraacetic acid dianhydride (Scheme 2).

The degree of substitution was calculated from $^1\text{H-NMR}$ signals in region 3.63–76 and 4.36 ppm corresponding to aromatic ring of *den-OH* and $\text{CH}_2\text{-CO}_2$ group. In $^1\text{H-NMR}$ spectrum of *den-COOH*, the

$\text{CH}_2\text{-CO}_2$ protons at 4.36 ppm and aliphatic protons of $\text{-N-CH}_2\text{-CH}_2\text{-N-}$ group at 2.83–85 ppm can be recognized. All of them can be applied for calculation of degree of substitution. For example, the integral ratio of C-H aromatic protons at 6.93–76 ppm to $\text{CH}_2\text{-CO}_2$ protons at 4.36 ppm shows that the degree of substitution was 82%. In $^{13}\text{C-NMR}$ spectrum of *den-COOH* signals at 169–171 ppm related to carbonyl part and in FT-IR spectrum signals at 1688 cm^{-1} is related to the formation of -COO- groups.

Ion absorption behaviors

The absorption capacity of dendrimers determined the relation of pH dependency on Cu^{+2} , Ni^{+2} , and Zn^{+2} using atomic absorption methods.



Scheme 2 Synthetic route of *den-COOH*.

TABLE I
Sorption Capacity and Sorption Molar Ratio
of Triazine-Based Dendrimer

Metal sorption capacity (mmol/g)	pH	Metal sorption capacity (mg/g)	Dendrimer
3.73	5	237	Den-OH-Cu
2.13	5	125	Den-OH-Ni
2.98	5	195	Den-OH-Zn
3.64	5	251	Den-COOH-Cu
3.99	5	214	Den-COOH-Ni
2.72	5	178	Den-COOH-Zn

The findings are shown in Table I. In all cases, by increasing of the pH values, the metal sorption capacities of the dendrimers increased. In higher pH values, the protonation of ligands of the dendrimer especially, in the amino and oxygen (the hydroxyl and carboxyl groups) decreased which led to a higher metal absorption.

The maximum metal sorption in *den-OH* was observed for Cu^{+2} while the lowest metal content was observed for Ni^{+2} . On the other hands, the maximum metal sorption in the modified dendrimer, *den-COOH*, was observed for Cu^{+2} while the lowest metal content was observed for Zn^{+2} . Furthermore, the metal sorption capacities in *den-COOH* higher than *den-OH* are stable complexes with metal ions, due to modified dendrimer bearing EDTA in surface. Synthetic dendrimers were mixed with aqueous solutions of metal ions such as Cu^{+2} , Ni^{+2} , and Zn^{+2} in pH values of 1, 3, and 5. The metal sorption capacities of dendrimers were measured by atomic absorption techniques. Table II shows the pH-dependent behavior of the *den-COOH* for sorption of various metal ions. The FT-IR spectra data of the metal-complexed dendrimers in comparison with those of noncomplexed gave some information about the bonding site of the dendrimer-metal ions. The wavenumber shifts for absorption bands of $\text{C}=\text{O}$, $\text{C}-\text{O}$, $\text{C}-\text{N}$, and $\text{O}-\text{H}$ corresponding to dendrimer-metal complex formation were summarized in

TABLE II
Metal Sorption Capacity of Den-OH in Various pHs

Metal sorption capacity (mmol/g)	pH	Dendrimer
1.15	1	Den-OH-Cu
1.01	1	Den-OH-Ni
0.74	1	Den-OH-Zn
2.75	3	Den-OH-Cu
2.12	3	Den-OH-Ni
1.49	3	Den-OH-Zn
4.05	5	Den-OH-Cu
3.23	5	Den-OH-Ni
2.14	5	Den-OH-Zn

TABLE III
FT-IR Absorption Bonds (cm^{-1}) for Den-OH,
Den-COOH, and Its Metal Complexes

Assignment	O—H, N—sH	C—H	C=O	C—O	C—N
Den-OH	3351	2871	—	1124	1429
Den-OH-Cu	3491	2869	1669	1130	1426
Den-OH-Ni	3487	2868	1671	1118	1423
Den-OH-Zn	3411	2866	1679	1120	1423
Den-COOH	3457	2932	1682	1168	1347
Den-COOH-Cu	3473	2944	1697	1112	1418
Den-COOH-Ni	3451	2911	1690	1131	1407
Den-COOH-Zn	3489	2938	1693	1143	1407

Table III. Absorption band in 3351 cm^{-1} for *den-OH* corresponds to hydroxyl or amine groups and after complex formation shifts to 3491 cm^{-1} , 3487 cm^{-1} , and 3411 cm^{-1} for Cu^{+2} , Ni^{+2} , and Zn^{+2} , respectively. A small shift was observed for $\text{C}-\text{O}$ and $\text{C}-\text{N}$ stretching band from 1124 cm^{-1} and 1429 cm^{-1} in parent *den-OH*. The absorption band in 3457 cm^{-1} for *den-COOH* corresponds to hydroxyl or amine groups, after complex formation shifts to 3473 cm^{-1} , 3451 cm^{-1} , and 3489 cm^{-1} for Cu^{+2} , Ni^{+2} , and Zn^{+2} , respectively.

The absorption band of $\text{C}-\text{O}$ stretching for *den-COOH* was decreased when metal ions were complexes formation. However, the peaks at a wavenumber of 1577 cm^{-1} were not changed with the complexation of the metal ions. This suggests that the $\text{C}=\text{N}$ groups in the triazine rings were not involved in the complexation of the metal ions. The thermal degradation of *den-OH* and *den-COOH* were performed with a heating rate of $10^\circ\text{C}/\text{min}$ in an N_2 atmosphere. The TGA curves are presented in Figure 2.

The main weight loss of *den-OH* and modified dendrimer, *den-COOH*, occurs between the range of $280\text{--}420^\circ\text{C}$ and $340\text{--}530^\circ\text{C}$, respectively. The *den-OH* is slightly less stable than *den-COOH* up to a temperature of 600°C . At the final stage about 28% weight remains in *den-OH* was observed until 600°C , where as weight remains in *den-COOH* was 34%. The

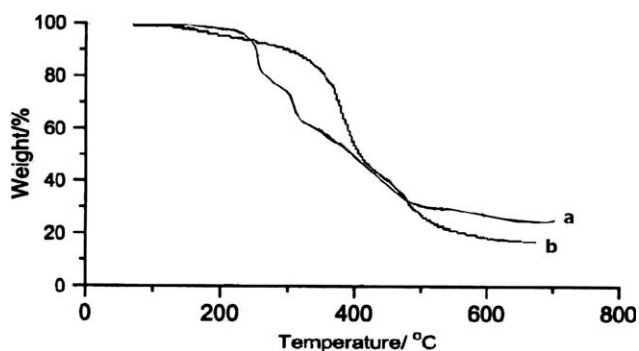


Figure 2 TGA diagrams of pure dendrimer (not chelated ions) (a) *den-OH* (b) *den-COOH*.

TABLE IV
Percentage Weight Residual for Den-OH, Den-COOH, and Its Metal Complexes

Products	Reduced mass (wt %) of products at different temperatures (°C)										
	100	150	200	250	300	350	400	450	500	550	600
Den-OH	3	4	7	8	12	21	48	61	75	80	82
Den-OH-Cu	4	5	20	32	37	51	52	53	55	57	58
Den-OH-Ni	3	9	12	21	45	51	61	64	67	69	72
Den-OH-Zn	5	7	8	13	30	41	52	54	58	59	61
Den-COOH	–	2	4	18	29	42	51	63	71	72	76
Den-COOH-Cu	5	7	9	11	15	52	61	61	62	63	65
Den-COOH-Ni	4	5	8	9	13	46	62	65	67	67	68
Den-COOH-Zn	6	8	9	22	23	29	68	71	73	79	80

thermal stability of *den-COOH* due to strong hydrogen bonding increased. Thermal gravimetry analysis data of *den-OH*, *den-COOH*, and their metal complexes are summarized in Table IV.

According to this table, thermal stability of metal-dendrimer complex increased with increasing of metal content.

The Table IV shows that with an increase in metal content in dendrimer, the final decomposed residue increased. On the other hands, thermal behavior of *den-COOH-Cu* and *den-COOH-Ni* complexes are similar to the parent dendrimer until about 350–400°C, but between 350°C and 600°C metal-dendrimer complex decomposed more strongly than the noncomplex dendrimer.

CONCLUSIONS

The triazine-based dendrimers with polymeric core and hydroxyl groups in peripherally were synthesized and modified with EDTA. Functionalized dendrimer by EDTA formed complexes with Cu^{+2} , Ni^{+2} , and Zn^{+2} . FT-IR and TGA conformed the presence of metals in final dendrimer-metal complexes. All complexes showed a change of the chemical shift in FT-IR spectra due to the metal ion complexation of the EDTA-containing dendrimer. The highest metal content was obtained for *den-COOH-Cu* complex. EDTA containing dendrimer showed excellent sorption for various metal ions.

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