

Designing of Triazine Based Dendrimer and its Application in Removal of Heavy Metal Ions from Water

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Abstract: A hydroxyl terminated triazine based dendrimer was synthesized up to generation 3 from *N,N'*-bis(4,6-dichloro-1,3,5-triazin-2-yl)propane-1,3-diamine as core using divergent method. Synthesized dendrimer and its generations were characterized by FT-IR, ¹H NMR, ¹³C NMR and elemental analysis. Adsorption behavior of full generation dendrimer G1, G2 and G3 were evaluated for metal ions such as Cu, Ni and Zn from aqueous solutions by ETDA method. Sorption capacities of these generations were evaluated in relation to pH and generation number. Dendrimer-metal complexes were further characterized by FT-IR and TGA to confirm presence of metal in final metal containing dendrimer.

Keywords: Dendrimer, Metal ion adsorption, Thermo gravimetric analysis, FT-IR

Introduction

Dendrimers are nanosized, void spaced, monodispersed macromolecules blessed with high degree of terminal functionality and branching¹⁻². Because of these unique properties, dendrimers have already displayed their potential in field of drug delivery³, cancer therapy⁴, catalysis⁵, dendrimer encapsulated nanoparticles⁶.

Triazine trichloride is one of the most important derivatives⁷ known from a long period time. In nucleophilic substitution of triazine trichloride, three chlorine atoms of triazine trichloride can be substituted in temperature controlled manner⁸. Triazine trichloride also shows good selectivity towards aliphatic amino to hydroxyl moiety in attacking nucleophile. Using triazine trichloride a dendrimer can be synthesized without involving functional group interconversion or protection/ deprotection step. Therefore, triazine trichloride was found to be valuable monomer in many dendrimer synthesis⁹⁻¹².

Most of the heavy metals are either toxic or carcinogenic. Discharge of these metals in water sources possesses a great threat to humans and environment¹³⁻¹⁴. Adsorption is one of the methods used for removal of heavy metal ions from water. It has a benefit that it removes metal ions with relatively low concentrations from water. Common adsorbents used for removal of heavy metal ion are activated carbon¹⁵, oxide minerals¹⁶, zeolites¹⁷, polymer fibers¹⁸, resins¹⁹, bio adsorbents²⁰ etc.

Due to void spaced structures with high terminal functionality, dendrimers are perfect adsorbents for removal of heavy metal ions such as copper, zinc, nickel cadmium, mercury *etc*²¹. Diallo *et al.*,²² reported the first dendrimer for removal of Cu²⁺ from water. Polyamidoamine dendrimers were to bind Cu(II) ions from water and recovered Cu(II) ions from water using dendrimer mediated ultrafiltration²³⁻²⁴. Recently many groups have described extensive studies on the removal of heavy metal ions from water using dendrimer²⁵⁻²⁷.

In present work, we have synthesized *N,N'*-bis(4,6-dichloro-1,3,5-triazin-2-yl)propane-1,3-diamine as core for dendrimer synthesis²⁸. Dendrimer was then developed up to generation 3 using divergent method²⁹⁻³⁰. The synthesized dendrimer and generations were characterized by FT-IR, ¹H NMR, ¹³C NMR and elemental analysis. The dendrimer generations were used as adsorbents to remove heavy metal ions such as Cu²⁺, Ni²⁺ and Zn²⁺ from water. Adsorption behavior of the dendrimer generations were estimated by EDTA method¹⁹ in relation to pH and generation number. Dendrimer metal complexes were further characterized by FT-IR and Thermogravimetric analysis (TGA) to confirm presence of metal in dendrimer metal complexes.

Experimental

Cyanuric chloride (Triazine trichloride), propane-1,3-diamine, acetone, dichloromethane and methanol were purchased from Sigma-Aldrich (India) Ltd. Nickel nitrate (Ni(NO₃)₂·6H₂O), copper nitrate (Cu(NO₃)₂·6H₂O), zinc nitrate (Zn(NO₃)₂·6H₂O), sodium hydroxide and hydrochloric acid were purchased from Merck (India) Ltd. All the reagents and solvents for the synthesis and analysis were used as received. FTIR studies were carried out in the range of 250-4000 cm⁻¹ using Perkin Elmer-Spectrum RX-FTIR spectrometer instrument through KBr disc and pellet method or nujol mull method. ¹H NMR and ¹³C NMR spectra were recorded at 400 MHz in Bruker Avance II 400 (Germany) using TMS as internal standard. Thermogravimetric analysis was performed on Perkin Elmer Pyris-1 TGA instrument with heating rate of 10 °C/min and in nitrogen atmosphere.

Synthesis of N,N'-bis(4,6-dichloro-1,3,5-triazin-2-yl)propane-1,3-diamine (Core)

Cyanuric chloride (0.02 mmol) was dissolved in dichloromethane and kept in an ice bath. A solution of propane-1,3-diamine (0.01 mmol) containing sodium hydroxide (0.02 mmol) in water was added drop wise in the solution of cyanuric chloride at 0-5 °C with stirring. The solution was stirred at 0-5 °C for 2 h. Then the solution was filtered, washed with methanol and acetone and dried under vacuum: A white colored solid was formed.

Yield 83%; FT-IR(KBr, cm⁻¹): 3291(NH), 2872, 2780(Aliphatic C-H), 1722, 1625 (C=N of triazine), 841,792 (C-Cl); ¹H NMR (400MHz, DMSO-*d*₆) δ ppm: 1.8031-1.8649 (m, 2H, N-CH₂-CH₂-CH₂-N), 3.4304-3.4660 (m, 4H, N-CH₂-CH₂-CH₂-N); ¹³C-NMR (75MHz, DMSO-*d*₆) δ ppm: 28.70 (N-CH₂-CH₂-CH₂-N), 38.18 (N-CH₂-CH₂-CH₂-N), 166.01, 171.66 (Triazine part); Anal. Calcd. for C₉H₈Cl₄N₈: C, 29.21; H, 2.18; N, 30.28 found: C, 29.30; H, 2.20; N, 30.30.

Synthesis of generation 1 dendrimer (G1)

N,N'-bis(4,6-dichloro-1,3,5-triazin-2-yl)propane-1,3-diamine

(0.01 mmol) of *N,N'*-bis(4,6-dichloro-1,3,5-triazin-2-yl)propane-1,3-diamine was dissolved in an excess of diethanolamine (0.04 mmol) which was used as both solvent and reactant. The resulting mixture was refluxed for 2 h. After cooling, it was dispersed and washed by acetone repeatedly to give generation 1 dendrimer which was light brown colored.

Yield 75%; FT-IR (KBr, cm^{-1}) ν : 3373(O-H), 2949, 2881(aliphatic C-H), 1664(C=N of triazine), 1056 (C-O) ; ^1H NMR (400MHz, D_2O) δ ppm: 1.9091-1.9403(m, 2H, N-CH₂-CH₂-CH₂-N), 3.3211-3.3460 (m, 2H, N-CH₂-CH₂-CH₂-N), 3.5980-3.6485 (m, 16H, N-CH₂-CH₂-OH), 3.9480-3.9856 (m, 16H, N-CH₂-CH₂-OH); ^{13}C -NMR (75MHz, D_2O) δ ppm: 28.72 (CH₂), 38.22 (N-CH₂), 50.66 (N-CH₂-CH₂-OH), 60.18 (N-CH₂-CH₂-OH), 166.61, 171.16 (triazine part); Anal. Calcd. for $\text{C}_{25}\text{H}_{48}\text{N}_{12}\text{O}_8$: C, 46.57; H, 7.50; N, 26.07; Found: C, 46.75; H, 7.55; N, 26.10.

Synthesis of generation 1.5 dendrimer (G1.5)

Cyanuric chloride (0.08 mmol) was dissolved in dichloromethane and kept in an ice bath. A solution of G1 dendrimer (0.01 mmol) containing sodium hydroxide (0.08 mmol) in water was added drop wise in the solution of cyanuric chloride at 0-5 °C with stirring. The solution was stirred at 0-5 °C for 2 h and refluxed for 6 h. Then the solution was filtered, washed with methanol and acetone and dried under vacuum: A white colored solid was formed.

Yield 84%; FT-IR (KBr, cm^{-1}) ν : 3217(N-H), 2833, 2780(Aliphatic C-H), 1777, 1752, 1721 (C=N of triazine), 1053(C-O), 775(C-Cl); ^1H NMR (400MHz, DMSO-*d*6) δ ppm: 1.9201-1.9549 (m, 2H, N-CH₂-CH₂-CH₂-N), 3.3425-3.3759 (m, 4H, CH₂-NH), 4.0175-4.0759 (m, 16H, N-CH₂-CH₂-O-Tri), 4.1641-4.2015 (m, 16H, N-CH₂-CH₂-O-Tri); ^{13}C -NMR (75MHz, DMSO-*d*6) δ ppm: 28.70 (CH₂), 38.10 (N-CH₂), 51.01 (N-CH₂-CH₂-O-tria), 60.58 (N-CH₂-CH₂-O-tri), 163.01, 168.66, 170.18, 172.28 (Triazine part); Anal. Calcd. For $\text{C}_{49}\text{H}_{40}\text{Cl}_{16}\text{N}_{36}\text{O}_8$: C, 32.19; H, 2.21; N, 27.58; Found: C, 32.25; H, 2.27; N, 27.60.

Synthesis of generation 2 dendrimer (G2)

Generation 1.5 dendrimer (0.01 mmol) was dissolved in an excess of diethanolamine (0.16 mmol) which was used as both solvent and reactant. The resulting mixture was refluxed for 2 h. After cooling, it was dispersed and washed by acetone repeatedly to give generation 2 dendrimer which was light brown colored.

Yield 75%; FT-IR (KBr) ν : 3356(O-H), 2942, 2881, 2840 (aliphatic C-H), 1676, 1619(C=N of triazine), 1065(C-O); ^1H NMR (400MHz, D_2O) δ ppm: 1.9331-1.9694 (m, 2H, N-CH₂-CH₂-CH₂-N), 3.3225-3.3519 (m, 4H, CH₂-NH), 3.6813-3.7303 (m, 64H, N-CH₂-CH₂-OH), 3.8631-3.9182 (m, 64H, N-CH₂-CH₂-OH), 4.0175-4.0759 (m, 16H, N-CH₂-CH₂-O-tri), 4.1641-4.2015 (m, 16H, N-CH₂-CH₂-O-tri); ^{13}C -NMR (75MHz, D_2O) δ ppm: 28.50 (CH₂), 38.08 (N-CH₂), 60.81(N-CH₂-CH₂-O-tri), 61.28 (N-CH₂-CH₂-OH), 63.88(N-CH₂-CH₂-Otri), 65.70 (N-CH₂-CH₂-OH), 163.01, 168.66, 170.78, 172.28 (Triazine portion); Anal. Calcd. For $\text{C}_{113}\text{H}_{200}\text{N}_{52}\text{O}_{40}$: C, 46.37; H, 6.89; N, 24.88; Found: C, 46.40; H, 6.95; N, 24.90.

Synthesis of generation 2.5 dendrimer (G2.5)

Cyanuric chloride (0.32 mmol) was dissolved in dichloromethane and kept in an ice bath. A solution of G2 dendrimer (0.01 mmol) containing sodium hydroxide (0.32 mmol) in water was added drop wise in the solution of cyanuric chloride at 0-5 °C with stirring. The solution was stirred at 0-5 °C for 2 h and refluxed for 6 h. Then the solution was filtered, washed with methanol and acetone and dried under vacuum: A white colored solid was formed.

Yield: 70%; FT-IR (KBr, cm^{-1}) ν : 3215(NH), 2881, 2833(aliphatic C-H), 1778, 1752, 1722(C=N of triazine), 1054 (C-O), 776 (C-Cl); ^1H NMR (400MHz, DMSO-*d*6) δ ppm: 3.3382-3.3728(t, 4H, CH₂-N), 3.9662-4.0226(m, 80H, N-CH₂-CH₂-O-Tri), 4.0777-4.1440(m, 80H, N-CH₂-CH₂-O-Tri); ^{13}C -NMR (75MHz, DMSO-*d*6) δ ppm: 28.8 (N-CH₂-CH₂-CH₂-N), 38.2(N-CH₂-CH₂-CH₂-N), 60.0(N-CH₂-CH₂-OH), 61.2(N-CH₂-CH₂-O-tri),

63.3(N-CH₂-CH₂-OH), 65.5(N-CH₂-CH₂-O-Tri), 164.1, 166.4, 168.8, 171.7, 172.5, 174.0 (Triazine Portion); Anal Calcd. for C₂₀₉H₁₆₈Cl₆₄N₁₄₈O₄₀: C, 32.74; H, 2.19; N, 27.04; Found: C, 32.80; H, 2.25; N, 27.17.

Synthesis of generation 3 dendrimer (G3)

Generation 2.5 dendrimer (0.01 mmol) was dissolved in an excess of diethanolamine (0.64 mmol) which was used as both solvent and reactant. The resulting mixture was refluxed for 2 h. After cooling, it was dispersed and washed by acetone repeatedly to give generation 1 dendrimer which was light brown colored.

Yield: 71% FT-IR (KBr, cm⁻¹) ν : 3371(OH), 2948, 2839(Aliphatic C-H), 1733(C=N of triazine), 1063(C-O); ¹H NMR (400MHz, D₂O) δ ppm: 3.3211-3.3440 (t, 4H, CH₂-N), 3.6438-3.7243(m, 264H, N-CH₂-CH₂-OH), 3.7929-3.8586(m, 264H, N-CH₂-CH₂-OH), 3.9107-3.9520 (m, 80H, N-CH₂-CH₂-O-Tri), 4.0197-4.0315(m, 80H, N-CH₂-CH₂-O-Tri); ¹³C-NMR (75MHz, D₂O): 28.00(N-CH₂-CH₂-CH₂-N), 38.14(N-CH₂-CH₂-CH₂-N), 59.90(N-CH₂-CH₂-OH), 60.62 (N-CH₂-CH₂-O-Tri), 63.31(N-CH₂-CH₂-OH), 66.69(N-CH₂-CH₂-O-tri), 168.16, 169.91, 171.51, 175.57, 177.20, 179.11(Triazine portion); Anal Calcd. For C₄₆₅H₈₀₈N₂₁₂O₁₆₈: C, 46.33; H, 6.70; N, 22.31; Found C, 46.40; H, 6.77; N, 22.40.

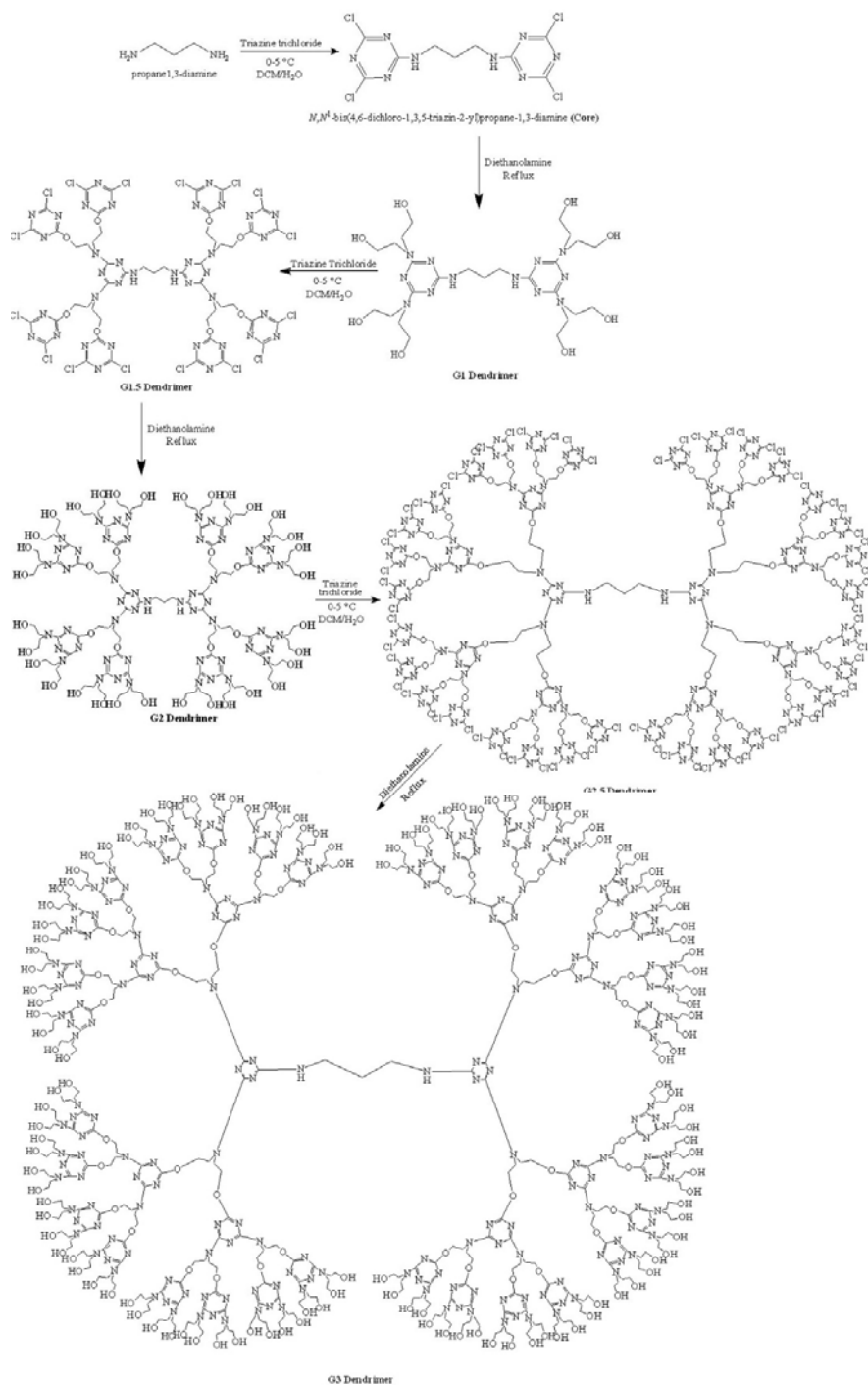
Batch adsorption experiments

Aqueous solution of 3 mmol metal salt [Ni(NO₃)₂.6H₂O, Cu(NO₃)₂.6H₂O, Zn(NO₃)₂.6H₂O] in 20 mL water was added to 200 mg of dendrimer(G1, G2 and G3) separately. The solution pH was set at 7, 9 and 10 by using 0.1 N NaOH. 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 non-complexed metal ions and dried in vacuum oven. The filtrate and washings were collected to 50 mL volumetric flask and titrated against ethylenediaminetetraacetic acid disodium (EDTA-2Na) salt using Murexide indicator to determine amount of metal adsorbed by dendrimer¹⁹.

Results and Discussion

Synthetic route used to synthesize triazine based dendrimer is outlined in Scheme 1. Temperature controlled nucleophilic substitution chlorine atom of triazine trichloride was exploited throughout the synthesis.

N,N'-Bis(4,6-dichloro-1,3,5-triazin-2-yl)propane-1,3-diamine was synthesized in first step as core for dendrimer synthesis as per literature method²⁸ with modification. Synthesis was carried out at low temperature to ensure that only one chlorine atom of two moles triazine trichloride was replaced by one mole of propane-1,3-diamine. Excess of reactants were removed by washing with acetone and methanol as core compound was insoluble in both of these solvents. Core was then reacted with diethanolamine in second step, which was used as both solvent and reactant²⁹ at refluxing temperature to give generation 1 (G1) dendrimer. Generation 1 dendrimer (G1) was dispersed in dichloromethane and decanted to remove excess of diethanolamine. G1 dendrimer was again reacted with cyanuric chloride to give 1.5 generation (G1.5) dendrimer. G1.5 was again reacted with diethanolamine to give generation 2 (G2) dendrimer. The steps were iterated to obtain generation 2.5 (G2.5) and 3 (G3) dendrimer by divergent method. The products were washed and dispersed in solvents to remove excess of reactant from final product. The synthetic route was easy and free from tedious protection/ deprotection or interconversion of functional groups.



Scheme 1. Synthesis of Triazine based Dendrimer

Characterization

Dendrimer generations can be physically confirmed by their solubility and appearance (Table 1). Full generation hydroxyl terminated dendrimers G1, G2 and G3 were freely soluble in water and were light brown liquids. Whereas chlorine terminated core compound and half generation dendrimer G1.5 and G2.5 were insoluble in water and were white solids.

Table 1. Physical description of dendrimer generations

Compound	Molecular formula	Appearance	Solubility in water	Surface groups (number)
Core	C ₉ H ₈ C ₁₄ N ₈	White solid	Insoluble	Cl (4)
G1	C ₂₅ H ₄₈ N ₁₂ O ₈	Brown liquid	Soluble	OH (8)
G1.5	C ₄₉ H ₄₀ Cl ₁₆ N ₃₆ O ₈	White solid	Insoluble	Cl(16)
G 2	C ₁₁₃ H ₂₀₀ N ₅₂ O ₄₀	Brown liquid	Soluble	OH(32)
G2.5	C ₂₀₉ H ₁₆₈ Cl ₆₄ N ₁₄₈ O ₄₀	White solid	Insoluble	Cl(64)
G3	C ₄₆₅ H ₈₀₈ N ₂₁₂ O ₁₆₈	Brown liquid	Soluble	OH (128)

All the dendrimer generations were investigated by FT-IR (Table 2), it was evident that core, half generation dendrimers G1.5 and G2.5 were all chlorine terminated whereas full generation G1, G2 and G3 were all hydroxyl terminated compounds. IR Spectrum of core, G1.5 and G2.5 showed absorption bands at 792, 775 and 776 cm⁻¹ respectively for C-Cl stretching whereas bands for O-H stretching was absent which confirmed presence of C-Cl groups in their structures an absence of hydroxyl groups. IR spectrum of G1, G2 and G3 showed absorption bands at 3373, 3356 and 3371 cm⁻¹ for O-H stretching and showed no absorption band for C-Cl which confirmed presence of hydroxyl groups in their structures. Both full and half generation dendrimer showed absorption bands for C=N stretching between 1700-1680 cm⁻¹ which confirms presence of triazine ring. It was also noted that all dendrimer generations showed C-O stretching frequency for either alcohol linkage in case of full generation dendrimer or ether linkage for half generation dendrimers only exception was core compound. Since core does not contain either alcohol or ether functional group. Progress of reaction and structure of products were investigated by ¹H NMR spectroscopy. ¹H NMR spectrum of core compound shows two triplets, one at 1.8031-1.8649 and second 3.4304-3.4660 which corresponds to propyl moiety in core.

Table 2. IR absorption bands for different generations.

Compound	IR absorption band (cm ⁻¹) for functional group			
	O-H	C=N	C-O	C-Cl
Core	-	1722	-	792
G1	3373	1664	1056	-
G1.5	-	1777	1053	775
G2	3356	1676	1065	-
G2.5	-	1778	1054	776
G3	3371	1733	1063	-

¹H NMR spectrum of G1 dendrimer shows two triplets at 1.9091-1.9403 and 3.3211-3.3460 value corresponds to propyl group in core and two multiplets 3.5980-3.6485 and 3.9480-3.9856 which corresponds to two methylene protons of diethanolamine which confirms nucleophilic substitution of chlorine atom in core compound by diethanolamine. Similarly, G1.5 dendrimer showed these triplets at 1.9201-1.9549 and 3.3425-3.3759 for propyl moiety in core but, two multiplets for methylene protons of diethanolamine appeared

down field at 4.0175-4.0759 and 4.1641-4.2015 due to substitution of hydroxyl proton by triazine trichloride changed environment of methylene protons. ^1H NMR spectrum of G2 shows triplets at 1.9331-1.9694 and 3.3237-3.3519 for core moiety and four multiplets, 3.6873-3.7303, 3.8631-3.9182 for two methylene groups of peripheral diethanolamine and 4.0171-4.0719, 4.1641-4.2014 for two methylene protons of inner diethanolamine since four methylene groups were in four different environments. In ^1H NMR spectrum of G2.5 methylene groups of both inner and peripheral diethanolamine moiety appeared as two multiplets at 3.9662-4.0226 and 4.0777-4.1140 because the dendrimer is terminated by triazinetri chloride there fore shifts of these methylene groups were under two different environments. In case of G3 dendrimer, ^1H NMR again showed four multiplets for methylene groups at 3.6438-3.724, 3.7929-3.8586 for peripheral diethanolamine moiety, 3.9107-3.9520 and 4.0197-4.0315 for inner diethanolamine groups.

All the products were also investigated by ^{13}C NMR spectroscopy. ^{13}C NMR spectrum of core showed peaks at 28.70 and 38.18 for propyl core and 166.01, 171.66 for triazine part of structure. ^{13}C NMR of G1 showed peaks at 28.72, 38.22 for core part, peaks at 166.61, 171.16 for triazine part and 50.66, 60.18 for diethanolamine. ^{13}C NMR of G1.5 shows peaks at 28.7 and 38.18 for propyl core, peaks at 163.01, 168.66 for inner triazine part 170.18, 172.28 outer triazine part and 51.07, 60.58 for diethanolamine part of structure. ^{13}C NMR spectrum of G2, showed peaks at 28.50, 38.08 for core part, 163.01, 168.66 for inner triazine part and 170.18, 172.28 for outer triazine part along with peaks at 61.28, 65.70 for inner methylene groups and 60.81, 63.88 for outer methylene groups of diethanolamine part. As dendrimer grows no of peaks for triazine part increased which was evident from ^{13}C NMR spectrum of G2.5 which showed peaks at 28.8, 38.2 for core part, 61.2, 65.5 for inner diethanolamine part and 60.063.3 for outer diethanolamine part and 164.1, 166.4, 168.8, 171.7, 172.5, 174.0 for triazine part of G2.5 dendrimer. ^{13}C NMR of G3 dendrimer showed, 28.00, 38.14 for core part, 59.90, 63.31 for outer diethanolamine part, 60.62 66.69 for inner diethanolamine part and 168.16, 169.91, 171.51, 175.57, 177.20, 179.11 for triazine part. Elemental data of products are given in Table 3. All the calculated percentage matches theoretical percentages which confirm their structures.

Table 3. Elemental data of synthesized dendrimers

Compound	Percentage of elements					
	Theoretical			Practical		
	C	H	N	C	H	N
Core	29.21	2.18	30.28	29.30	2.20	30.30
G1	46.57	7.50	26.07	46.75	7.55	26.10
G1.5	32.19	2.21	27.58	32.25	2.27	27.60
G 2	46.37	6.89	24.88	46.40	6.95	24.90
G2.5	32.74	2.19	27.04	32.80	2.25	27.17
G3	46.33	6.70	22.31	46.40	6.77	22.40

Metal ion adsorption

All the hydroxyl terminated full generation dendrimer G1, G2 and G3 were used to adsorb heavy metal ions. Capacities of dendrimers to adsorb Cu^{2+} , Ni^{2+} and Zn^{2+} ions in relation pH and generation by EDTA method.

The sorption capacities of dendrimer generation in relation to pH illustrated in Table 4. For all the dendrimer generations, metal ion adsorption increased with increase in pH. At higher pH values protonation of ligands decreases which leads to higher metal adsorption²⁶. For all metals adsorption was maximum at 10 pH.

Table 4. Sorption capacities of dendrimer generation in relation to pH

Dendrimer	Metal ion	Metal ion uptake, mmol/g		
		pH=7	pH=9	pH=10
G1(OH) ₈	Cu ²⁺	1.20	2.10	2.30
	Ni ²⁺	1.07	1.97	2.10
	Zn ²⁺	0.95	1.91	2.06
G2(OH) ₃₂	Cu ²⁺	2.10	3.55	3.61
	Ni ²⁺	2.04	3.43	3.46
	Zn ²⁺	2.04	3.30	3.34
G3(OH) ₁₂₈	Cu ²⁺	4.08	5.03	5.20
	Ni ²⁺	3.90	4.44	4.97
	Zn ²⁺	3.83	4.35	4.71

Table 5 shows sorption capacities of dendrimer generation at pH 10. It was revealed that sorption capacities of the dendrimer generation increases with increase in generation number. Generation 3 dendrimer had highest sorption capacity. As generation number increased, no of terminal hydroxyl groups also increased which led to more closed structure and high metal ion adsorption. It was also revealed that dendrimers showed highest adsorption for Cu²⁺ ions and lowest adsorption for Zn²⁺ ions.

Table 5. Sorption capacities of dendrimer generation at pH 10

Dendrimer	Metal ions adsorbed mmol/g		
	Cu ²⁺	Ni ²⁺	Zn ²⁺
G1	2.30	2.10	2.06
G2	3.61	3.46	3.33
G3	5.20	4.97	4.71

Characterization of dendrimer metal complexes

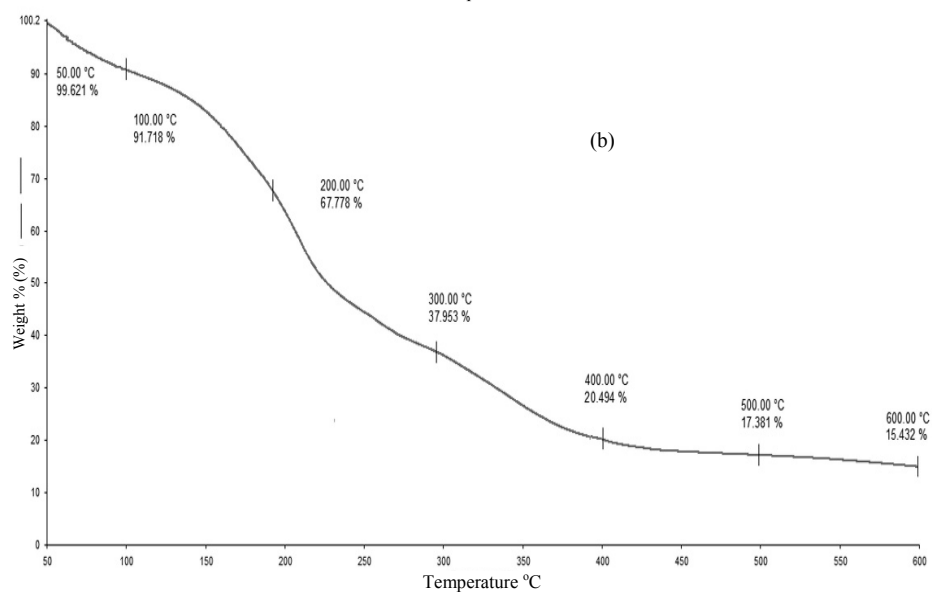
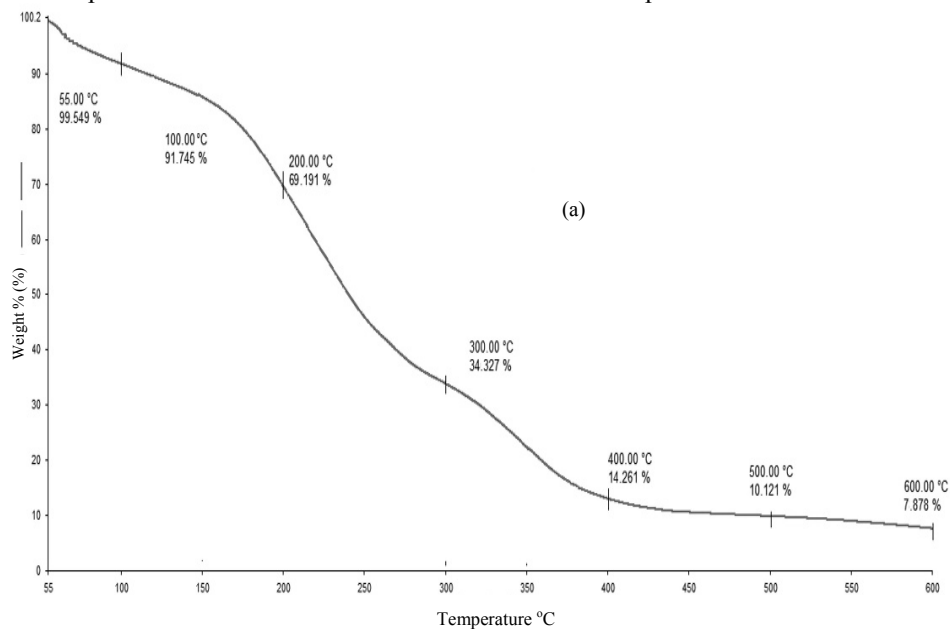
G3 dendrimer showed highest metal ion adsorption capacity. G3 dendrimer containing Cu, Ni and Zn was further characterized by FT-IR and Thermo gravimetric analysis and compared with pure G3 dendrimer to confirm presence of these metals in final metal containing dendrimer.

FTIR results are furnished in Table 6. FT-IR spectrum of metal containing dendrimer were compared with FT-IR spectrum of parent pure dendrimers which gives information about binding site in G3 dendrimer. IR absorption band at 3371 cm⁻¹ resembles to hydroxyl group in pure generation 3 dendrimer. This absorption band shifts to 3411 cm⁻¹, 3484 cm⁻¹ and 3441 cm⁻¹ after adsorption of Cu, Ni and Zn respectively. A very little shift is observed for C-O at 1064 cm⁻¹ and C-H at 2848 cm⁻¹ from the parent G3 dendrimer. So it was revealed that surface hydroxyl group may be the active binding site for metal ions adsorption²⁶.

Table 6. FT-IR absorption bands for dendrimer and metal containing dendrimer

Pure dendrimer and metal containing dendrimer	FTIR absorption bands cm ⁻¹		
	O-H	C-H	C-O
G3	3371	2848	1063
G3-Cu	3411	2848	1063
G3-Ni	3484	2848	1063
G3-Zn	3441	2848	1063

The thermal degradation analyses of the prepared pure and metal containing dendrimer were performed by TGA instrument with heating rate of $10^{\circ}\text{C min}^{-1}$ in an N_2 atmosphere. TGA (Figure 1) of pure G3 dendrimer shows two stage thermal decomposition, dendrimer losses 18% of wt. up to 150°C due to bound moisture, then decomposes completely up to 600°C leaving final residual weight of 7%. Dendrimer metal complexes G3-Cu, G3-Ni and G3-Zn showed same thermal decomposition but final residual weights at 600°C were 15.43%, 14.17% and 12.77% respectively for due to presence of metal oxides. These confirm presence of metal ions in final dendrimer metal complexes²⁶.



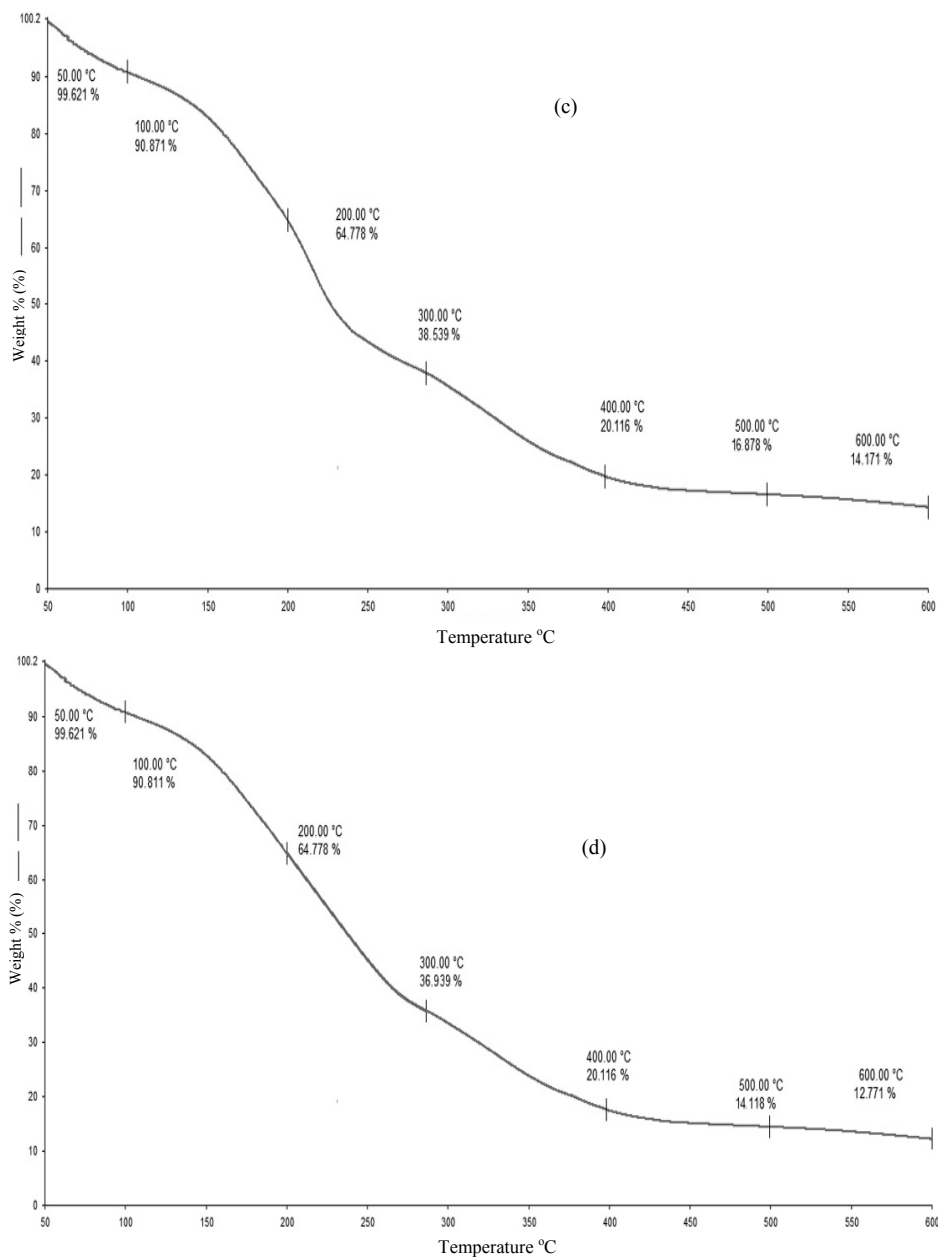


Figure 1. TGA Graphs of a) G3-Dendrimer; b) G3-dendrimer containing Cu metal; c) G3 dendrimer containing Ni metal; d) G3 dendrimer containing Zn metal

Conclusion

Hydroxyl terminated triazine based dendrimer was synthesized up to generation 3 using divergent method without involving protection/deprotection or interconversion of functional group. All the dendrimer generations were fully characterized by spectral techniques.

Sorption capacities of dendrimer generations increase with increase in generation number and pH. All dendrimer generations showed maximum metal adsorption at pH 10. G3 dendrimer showed highest sorption capacity for all metal ions. FT-IR spectrum and TGA analysis of G3 dendrimer and its metal complexes further confirmed presence of metals in final metal containing dendrimer.

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