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Removal of heavy metal ions from water by Hydroxyl terminated Triazine-based Dendrimer

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ABSTRACT

Waste water containing heavy metal ions is being discharged from numerous industries and can cause several problems due to high toxicity and water solubility. It is crucial to treat metal containing water before discharging into the environment. Dendrimers are a new class of macromolecules. Due to their dense terminal functionality and internal cavities, they are perfect for water remediation by adsorption. In this paper, we have synthesized hydroxyl terminated triazine-based dendrimer generations by divergent method using piperazine, triazine trichloride and diethanolamine as starting materials. Full generation dendrimers G1(OH)$_8$, G2(OH)$_{32}$ and G3(OH)$_{128}$ were terminated by 8, 32 and 128 hydroxyl groups, respectively. Structures of dendrimer generations were characterized by infrared spectroscopy (FT-IR), ^{1}H NMR, ^{13}C NMR, and electrospray ionization mass spectrometry. Hydroxyl terminated full dendrimers G1(OH)$_8$, G2(OH)$_{32}$ and G3(OH)$_{128}$ were used as adsorbents in a series of experiments to study the adsorption behavior in the removal of Cu^{2+}, Ni^{2+} and Zn^{2+} ions from water. Sorption behaviors of synthesized dendrimer generations were investigated in relation to pH and generation number. Results revealed that generation 3 dendrimer G3(OH)$_{128}$ had the highest sorption capacity. Sorption capacity of dendrimers was increased with increase in generation number and pH. Metal-containing dendrimer was further studied by FT-IR and thermo gravimetric analysis. Both analytical methods have confirmed the presence of metal in the final metal containing dendrimer.

Keywords: Triazine trichloride; Diethanolamine; Metal ion adsorption; Water remediation

1. Introduction

Currently, large quantities of waste water containing heavy metals such as mercury, lead, copper, nickel, zinc, cadmium, and chromium are being discharged from numerous industries such as metal plating, smelting, battery manufacturing, petroleum refineries, paint manufacturing, pesticides, pigment manufacturing, printing, and photographic industries [1]. Because of their high solubility in marine conditions, metal ions could be absorbed by living organisms through which they can enter food chains; which may cause accumulation of these heavy metals in the human body beyond the permitted concentration, causing serious health disorders [2] as most of these metals are either carcinogenic or toxic [3].

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Therefore, it is crucial to treat metal-containing water before discharging into the environment.

A number of physico-chemical methods are used to remove heavy metal ions from water, such as chemical precipitation [4], electro dialysis [5], membrane filtration [6], and photo dialysis [7,8]. These methods have significant drawbacks, which are, for instance, incomplete removal, high-energy requirements, high-cost and production of toxic sludge [9]. Metal ion adsorption is one of the common methods used for the removal of metal ions from water. It has an advantage that it removes metal ions with relatively low concentration in aqueous solutions. Common adsorbents used for the removal of heavy metal ions are activated carbon [10], oxide minerals [11], zeolites [12], polymer fibers [13], resins [14], bio adsorbents [15], etc.

Dendrimers are a new class of macromolecules with distinctive properties such as monodisperse molecular weight distribution, nano-scale size, and high degree of branching, internal cavities, and large no. of modifiable surface functional groups [16]. Due to their void spaced structures with dense modifiable surface functional groups, dendrimers can efficiently adsorb metal ions such as copper, zinc, nickel cadmium, mercury, etc. and are perfect for water remediation [17,18]. Diallo et al. [19] reported the first dendrimer for the removal of metal ion from water. Diallo et al. used polyamidoamine dendrimers which were able to bind Cu(II) ions [20] and recovered Cu ions from water using dendrimer mediated ultrafiltration [21]. Recently, many groups exploited dendrimers for the removal of heavy metal ions from water [22–25].

In this paper, we have synthesized 1,4-biz(4,6-trichloro-1,3,5-triazin-2-yl)piperazine as a core for dendrimer synthesis. Dendrimer was synthesized up to generation three by divergent method using diethanolamine and cyanuric chloride as linkers. Full generation dendrimers $G1(OH)_8$, $G2(OH)_{32,}$ and $G3(OH)_{128}$ were terminated by 8, 32, and 128 hydroxyl groups respectively. Dendrimer growth and generations were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, and electrospray ionization mass spectrometry. Hydroxyl terminated full dendrimers $G1(OH)_8$, $G2(OH)_{32}$ and $G3(OH)_{128}$ were used as adsorbents in a series of experiments to study the adsorption behavior in removal of Cu^{2+}, Ni^{2+} and Zn^{2+} ions from water. Sorption behaviors of synthesized dendrimer generations were investigated in relation to pH and generation number by complexometric titration. Metal-containing dendrimer was further studied by FT-IR and thermo gravimetric analysis (TGA) to determine the presence of metal in metal-containing dendrimer.

2. Materials and methods

Triazine trichloride (cyanuric chloride), piperazine, acetone, dichloromethane, and methanol were purchased from Sigma-Aldrich (India) Ltd. Nickel nitrate ($Ni(NO_3)_2{\bullet}6H_2O$), copper nitrate ($Cu(NO_3)_2{\bullet}6H_2O$), zinc nitrate $Zn(NO_3)_2{\bullet}6H_2O$, 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. FT-IR studies were carried out in the range of 250–4,000 cm^{-1} using Perkin Elmer-Spectrum RX-FT-IR spectrometer instrument through KBr disc and pellet method and Nujol mull method. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz in Brucker Avance II 400 (Germany) using TMS as an internal standard. Mass spectra were recorded on Waters Micromass Q-ToF Micro (USA) instrument equipped with electrospray ionization. TGA was performed on Perkin Elmer Pyris-1 TGA instrument with a heating rate of 10 ˚C min^{-1} in nitrogen atmosphere.

2.1. *Synthesis of 1,4-biz(4,6-trichloro-1,3,5-triazin-2-yl) piperazine (Core)*

Cyanuric chloride (0.02 mmol) was dissolved in dichloromethane and kept in an ice bath. A solution of piperazine (0.01 mmol) containing sodium hydroxide (0.02 mmol) in water was added dropwise 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: 75%.

FT-IR (KBr, cm^{-1}): 2,780($\nu_{C–H}$), 1,690 ($\nu_{C=N}$), 768 ($\nu_{C–Cl}$). ^{1}H NMR (400 MHz, DMSO-d_6, δ): 3.2049(b, 8H, piperazine). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 49.10 (piperazine carbon) 166.01, 169.71(Triazine carbon).

2.2. *Synthesis of generation 1 dendrimer ($G1(OH)_8$)*

1,4-biz(4,6-trichloro-1,3,5-triazin-2-yl) piperazine (0.01 mmol) 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 with honey-like consistency. Yeild: 78%.

FT-IR (Nujol, cm^{-1}): 3,312 ($\nu_{O–H}$), 2,937, 2,876 ($\nu_{C–H}$), 1,665 ($\nu_{C=N}$), 1,038 cm^{-1} ($\nu_{C–O}$). ^{1}H NMR (400 MHz, D_2O, δ): 3.2805 (b, 8H, piperazine CH_2), 3.5205–3.5425 (t, 16 H, N–CH_2), 3.8942–3.9204 (t, 16H, CH_2–OH). ^{13}C NMR (75 MHz, D_2O, δ): 49.55 (piperazine part), 59.55 (N–CH_2) 62.40 (CH_2–OH), 167.17, 169.55 (triazine part).

2.3. Synthesis of generation 1.5 dendrimer (G 1.5)

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 dropwise 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: 75%.

FT-IR (KBr, cm^{-1}): 2,971, 2,922, 2,881($\upsilon_{C–H}$), 1,690 ($\upsilon_{C=N}$) 1,065 ($\upsilon_{C–O}$), 768 ($\upsilon_{C–Cl}$). ^{1}H NMR (400 MHz, DMSO-d$_6$, δ): 3.2805 (b, 8H, piperazine CH$_2$), 3.9405–3.9825 (t, 16 H, N–CH$_2$), 4.0742–4.1104 (t, 16H, CH$_2$–O–). ^{13}C NMR (75 MHz, DMSO-d$_6$, δ): 49.70 (piperazine carbon), 58.20 (N–CH$_2$), 64.10 (–CH$_2$–O–), 167.10, 176.10 (Inner triazine part), 169.70, 179.10 (peripheral triazine part).

2.4. Synthesis of generation 2 dendrimer ($G2(OH)_{32}$)

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 with honey like consistency. Yield: 78%.

FT-IR (Nujol, cm^{-1}): 3,349 cm^{-1} ($\upsilon_{O–H}$), 2,941 cm^{-1}, 2,881 cm^{-1}($\upsilon_{C–H}$), 1,050 cm^{-1} ($\upsilon_{C–O}$). ^{1}H NMR (400 MHz, D$_2$O, δ): 3.2754 (b, 8H, piperazine CH$_2$), 3.7066-3.7333(m, 64H, outer N–CH$_2$ part), 3.9237- 3.9544 (m, 64H, outer CH$_2$–OH part), 4.0194–4.0394 (m, 16H, inner N–CH$_2$ part), 4.0877–4.1049 (m, 16H, inner N–CH$_2$ part). ^{13}C NMR (75 MHz, D$_2$O, δ): 49.70 (piperazine carbon), 58.20 (peripheral N–CH$_2$), 59.22 (inner N–CH$_2$), 61.10 (peripheral –CH$_2$–OH), δ 67.10 (inner –CH$_2$–O–), 167.10, 176.10 (inner triazine part), 169.10, 179.10 (outer triazine part).

2.5. 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 dropwise 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: 75%.

FT-IR (KBr, cm^{-1}): 2,951, 2,879, 2,779 ($\upsilon_{C–H}$), 1,614 ($\upsilon_{C=N}$) 1,027 ($\upsilon_{C–O}$), 793 ($\upsilon_{C–Cl}$). ^{1}H NMR (400 MHz, DMSO-d$_6$, δ): 3.2308 (b, 8H, piperazine CH$_2$), 3.9636–3.9824 (t, 80 H, N–CH$_2$), 4.0480–4.0818 (t, 80H, CH$_2$–O–). ^{13}C NMR (75 MHz, DMSO-d$_6$, δ): 49.84 (piperazine carbon), 59.52 (peripheral N-CH$_2$ carbon), 61.46 (inner N–CH$_2$ carbon), 64.16 (peripheral N–CH$_2$–O carbon), 66.16 (inner –CH$_2$–O–), 167.50, 169.92, 170.12, 177.50, 179.60, 182.84 (triazine carbon).

2.6. Synthesis of generation 3 dendrimer ($G3(OH)_{128}$)

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 3 dendrimer which was light brown colored with honey like consistency. Yield: 78%.

FT-IR (Nujol, cm^{-1}): 3,356 cm^{-1} ($\upsilon_{O–H}$), 2,947 cm^{-1}, 2,839 cm^{-1}($\upsilon_{C–H}$), 1,064 cm^{-1} ($\upsilon_{C–O}$) ^{1}H NMR (400 MHz, D$_2$O, δ): 3.2145 (b, 8H, piperazine CH$_2$), 3.6645- 3.7008 (m, 264H, outer N–CH$_2$ part), 3.9237–3.9544 (m, 264H, outer CH$_2$–OH part), 4.0399–4.0611 (m, 80H, inner N–CH$_2$ part), 4.1499–4.1911 (m,80H, inner N–CH$_2$ part). ^{13}C NMR (75 MHz, D$_2$O, δ): 49.30 (piperazine carbon), 58.10 (peripheral N–CH$_2$), 59.23 (inner N–CH$_2$), 61.05 (peripheral –CH$_2$–OH), δ 67.20 (inner –CH$_2$–O–), 167.10, 176.70, 169.10, 179.15, 170.70, 183.70 (Triazine portion) ESI-MS: Calculated molecular weight: 12059.72 Found: 12056.4 [M], 12057.4 [M + H], 12058.4 [M + 2].

2.7. Adsorption experiments

Aqueous solution of 3 mmol metal salt [Ni (NO$_3$)$_2$•6H$_2$O, Cu(NO$_3$)$_2$•6H$_2$O, Zn (NO$_3$)$_2$•6H$_2$O] in 20 mL water was added to 200 mg of dendrimer 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 an aqueous solution of the same pH to remove non-complexed metal ions and dried in a vacuum oven. The filtrate and washings were collected in 50 mL volumetric flask and titrated against ethyelediamine tetracetic acid disodium salt using Murexide indicator.

3. Results and discussion

3.1. Synthesis and characterization

Temperature-controlled nucleophilic aromatic substitution of chlorine atom of triazine trichloride was used throughout dendrimer synthesis. In the first step, 1,4-biz(4,6-trichloro-1,3,5-triazin-2-yl)piperazine was synthesized as a core for dendrimer synthesis as per method [26] using piperazine and cyanuric chloride as starting materials. Unreacted compounds were removed by washing with acetone and methanol. In the second step, chlorine-terminated core was further reacted with diethanolamine at refluxing temperature to give hydroxyl-terminated full generation dendrimer G1(OH)$_8$ [27,28]. G1(OH)$_8$ was dispersed

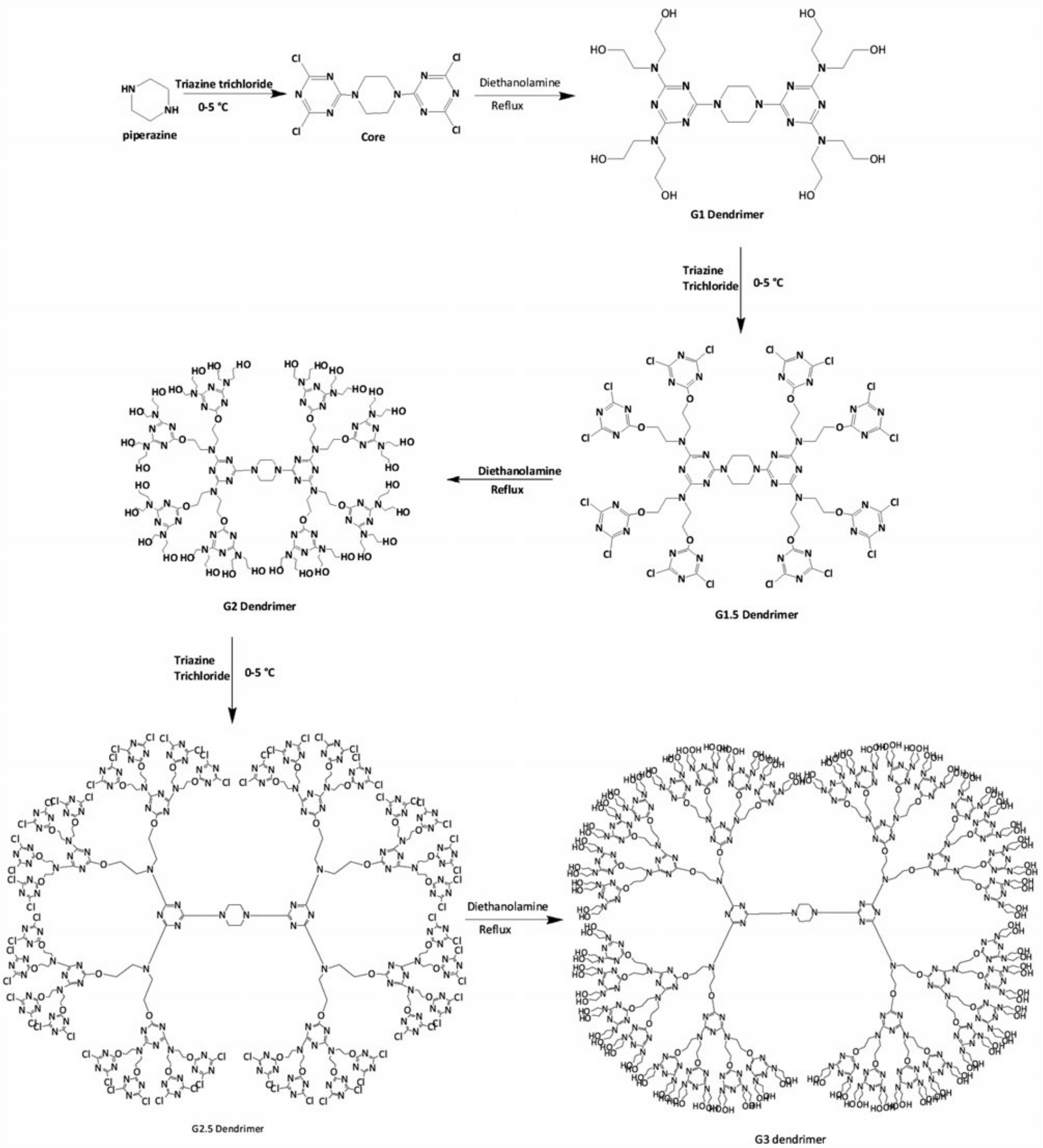


Fig. 1. Synthesis of triazine-based dendrimer.

Table 1
FT-IR Absorption Bands (cm^{-1}) for core and different generation of dendrimers

	IR absorption band(cm^{-1}) for functional group		
Compound	O–H	C–Cl	C–O
Core	–	768	–
$G1(OH)_8$	3,312	–	1,038
G1.5	–	753	1,060
$G2(OH)_{32}$	3,349	–	1,050
G2.5	–	753	1,060
$G3(OH)_{128}$	3,356	–	1,064

in dichloromethane and acetone to remove unreacted diethanolamine. $G1(OH)_8$ was reacted with 8 mol cyanuric chloride to give chlorine-terminated half generation dendrimer (G1.5). G1.5 was further reacted with diethanolamine to give generation 2 dendrimer $G2(OH)_{32}$. The above two steps were repeated to give G2.5 and $G3(OH)_{128}$ dendrimer in fifth and sixth step, respectively (Fig. 1). All the products were completely purified by either by washing or by dispersing in solvents.

Dendrimer growth and structure of both full and half generation dendrimers were characterized by FT-IR, ^1H NMR, ^{13}C NMR, and ESI-mass spectrometry. These techniques proved precious to monitor progress

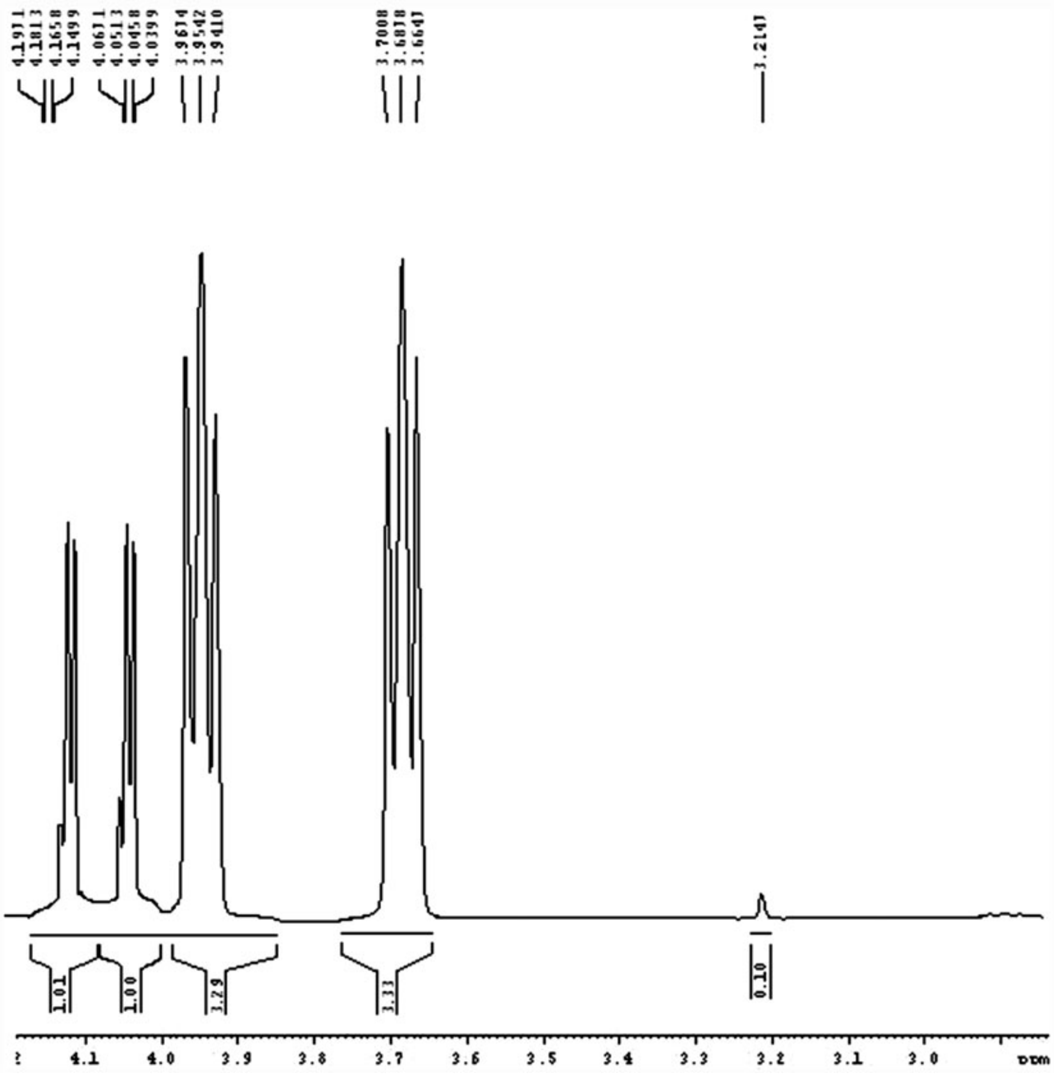


Fig. 2. ^1H NMR spectrum of $G3(OH)_{128}$.

of the reaction as well as characterization of dendrimer generations. The full generation dendrimers G1 $(OH)_8$, $G2(OH)_{32}$ and $G3(OH)_{128}$ were terminated by hydroxyl groups on the periphery whereas core, G1.5 and G2.5 half generation dendrimer were terminated by chlorine groups on the periphery. As shown in Table 1. Infrared spectrum showed the O–H stretching frequency at 3,312, 3,349 and 3,356 cm^{-1} for G1, G2 and G3 dendrimers, respectively, whereas C–Cl stretching frequency was not detected as an evident of hydroxyl groups on their periphery and absence of chlorine atoms. Infrared spectrum showed C–Cl stretching frequency at 768, 753 and 793 $cm^{-1,}$ respectively, for core, G1.5 dendrimers and G2.5 dendrimer, whereas O–H stretching remained undetected which was an evidence of chlorine groups on their periphery and absence of the hydroxyl group. Also C–O stretching frequency was present in G1, G 1.5, G2, G 2.5, and G3 at 1,038, 1,060, 1,050, 1,027, and 1,064 cm^{-1} due to the presence of either ether linkage or hydroxyl group whereas C–O stretching frequency remained absent in the core.

^1H NMR proved as an invaluable tool to investigate the progress of the chemical reaction. ^1H NMR spectrum of core compound showed only one peak δ 3.2049 for piperazine protons whereas $G1(OH)_8$, G1.5 and G2.5 showed additional two triplets for methylene groups for diethanolamine unit as two methylene groups of diethanolamine were in two different environments. ^1H NMR spectrum of $G1(OH)_8$ showed two triplets at δ 3.5205–3.5425 and δ 3.8942–3.9204 for diethanolamine, which was evidence of substitution of chlorine atom of core by diethanolamine. In ^1H NMR spectrum of G1.5 and G2.5 these triplets appeared in downfield region, at δ 3.9405–3.9825 and at δ 4.0742–4.1104 for G1.5 and δ 3.9636- 3.9824 and δ4. 0,480–4.0818 for G2.5, respectively, as evidence of substitution of hydroxyl group by triazine moiety. ^1H NMR spectrum of $G2(OH)_{32}$ and $G3(OH)_{128}$ (Fig. 2) showed four triplets for methylene groups as inner and

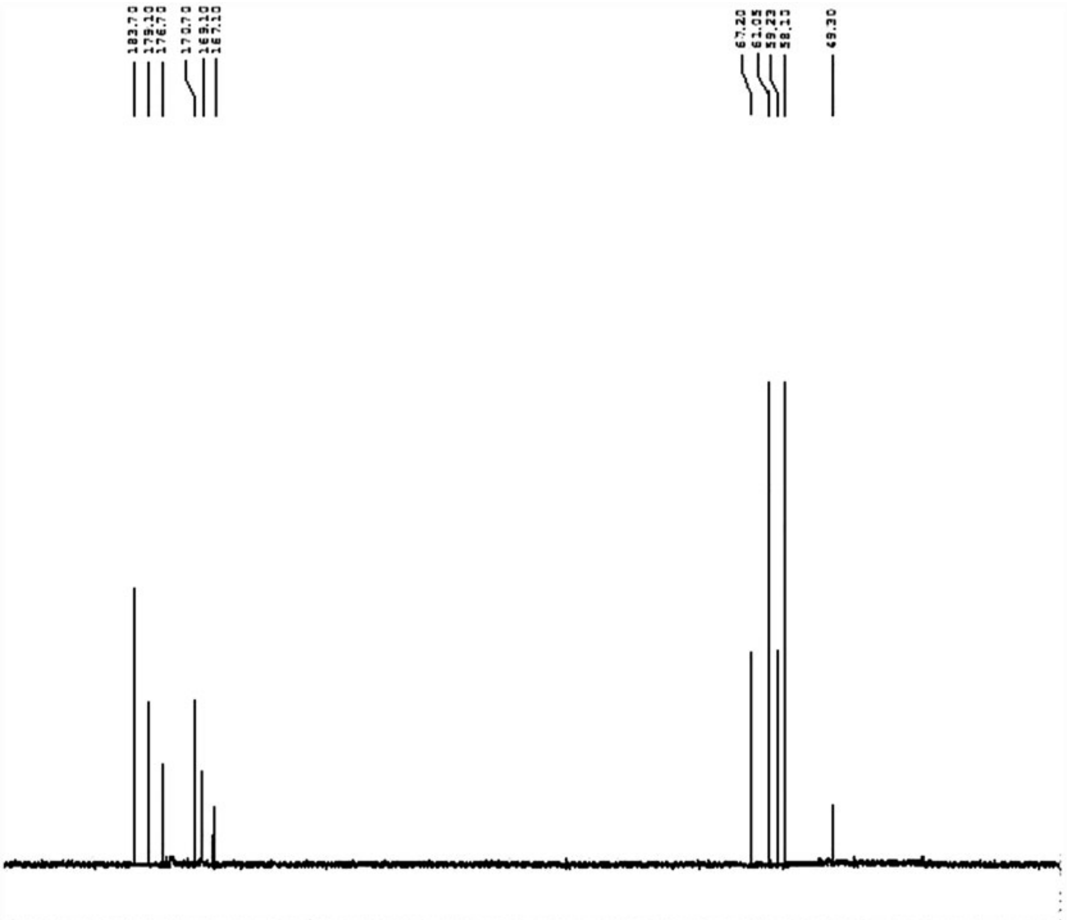


Fig. 3. ^{13}C NMR spectrum of $G3(OH)_{128.}$

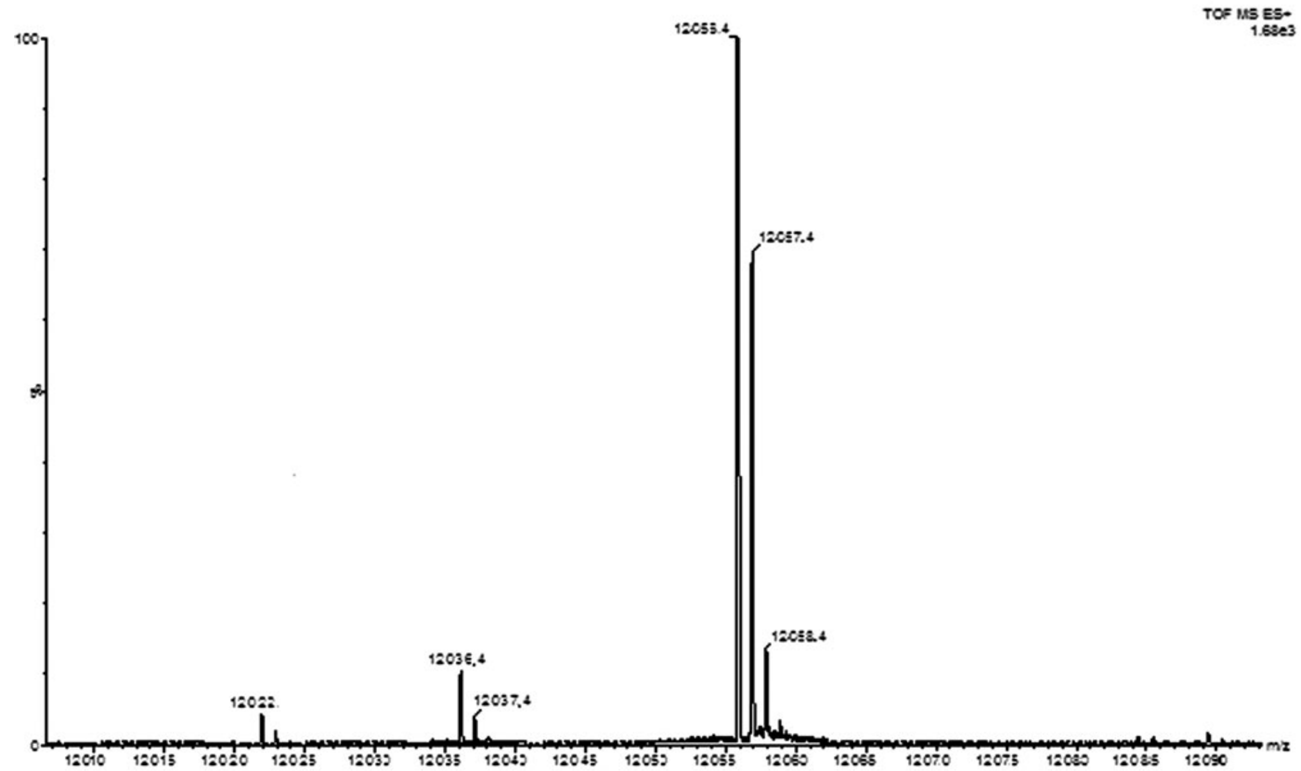


Fig. 4. ESI-Mass spectrum of $G3(OH)_{128}$.

Table 2
Sorption capacities of dendrimer generations at various pH

Dendrimer	Metal ion	Metal ion uptake (mmol g^{-1})		
		pH 7	pH 9	pH 10
$G1(OH)_8$	Cu^{2+}	1.15	2.05	2.26
	Ni^{2+}	1.05	1.95	2.09
	Zn^{2+}	0.99	1.89	2.06
$G2(OH)_{32}$	Cu^{2+}	2.05	3.40	3.51
	Ni^{2+}	2.10	3.50	3.66
	Zn^{2+}	2.12	3.30	3.36
$G3(OH)_{128}$	Cu^{2+}	4.10	5.00	5.19
	Ni^{2+}	3.98	4.90	4.95
	Zn^{2+}	3.85	4.65	4.75

Table 3
Metal sorption capacities of different dendrimer generations at pH 10

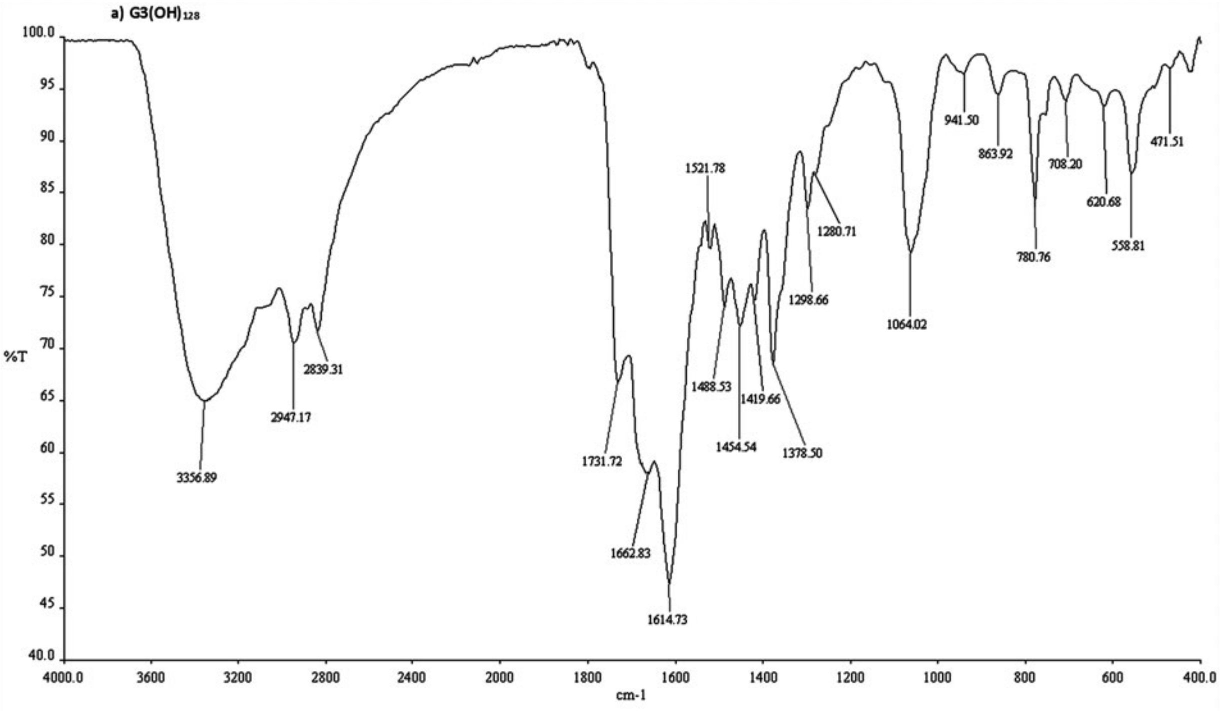
Dendrimer	Metal ions adsorbed (mmol g^{-1})		
	Cu^{2+}	Ni^{2+}	Zn^{2+}
$G1(OH)_8$	2.25	2.09	2.06
$G2(OH)_{32}$	3.51	3.66	3.36
$G3(OH)_{128}$	5.19	4.95	4.75

Table 4
FT-IR absorption bands in $G3(OH)_{128}$ dendrimer and metal-containing dendrimer

G3 dendrimer and metal-containing dendrimer	FT-IR absorption bands (cm^{-1})			
	O–H	C–H	C–O	C–N
$G3(OH)_{128}$	3,356	2,839	1,064	1,454
$G3(OH)_{128}$–Cu	3,447	2,839	1,064	1,450
$G3(OH)_{128}$–Ni	3,457	2,839	1,064	1,450
$G3(OH)_{128}$–Zn	3,410	2,840	1,065	1,455

peripheral methylene groups were in four different environments.

Progress of the reaction was also monitored by ^{13}C NMR. ^{13}C NMR spectrum of core showed peaks at δ 49.10 for piperazine carbon and δ 166.01, δ 169.71 for triazine carbon as secondary amine protons of piperazine was substituted by cyanuric chloride. ^{13}C NMR spectrum of G1 dendrimer, apart from peaks at δ 49.55, 167.17, and 169.55 values, showed two additional peaks at δ 59.55 and δ 62.40 for methylene groups as evidence of nucleophilic substitution of chlorine atoms of core by secondary amines of diethanolamine. ^{13}C NMR spectrum of G1.5 dendrimer showed further two additional peaks for triazine carbons at periphery δ 176.10 and δ 179.10 as a result of substitution of the hydroxyl group by triazine trichloride. ^{13}C NMR spectrum of G2 dendrimer showed further two additional peaks at δ 59.22 and δ 67.10 for methylene carbons of diethanolamine at the periphery. ^{13}C NMR spectrum of G2.5 showed δ 49.84 for piperazine carbon, δ 59.52 and 64.16 for methylene protons


a) G3(OH)$_{128}$

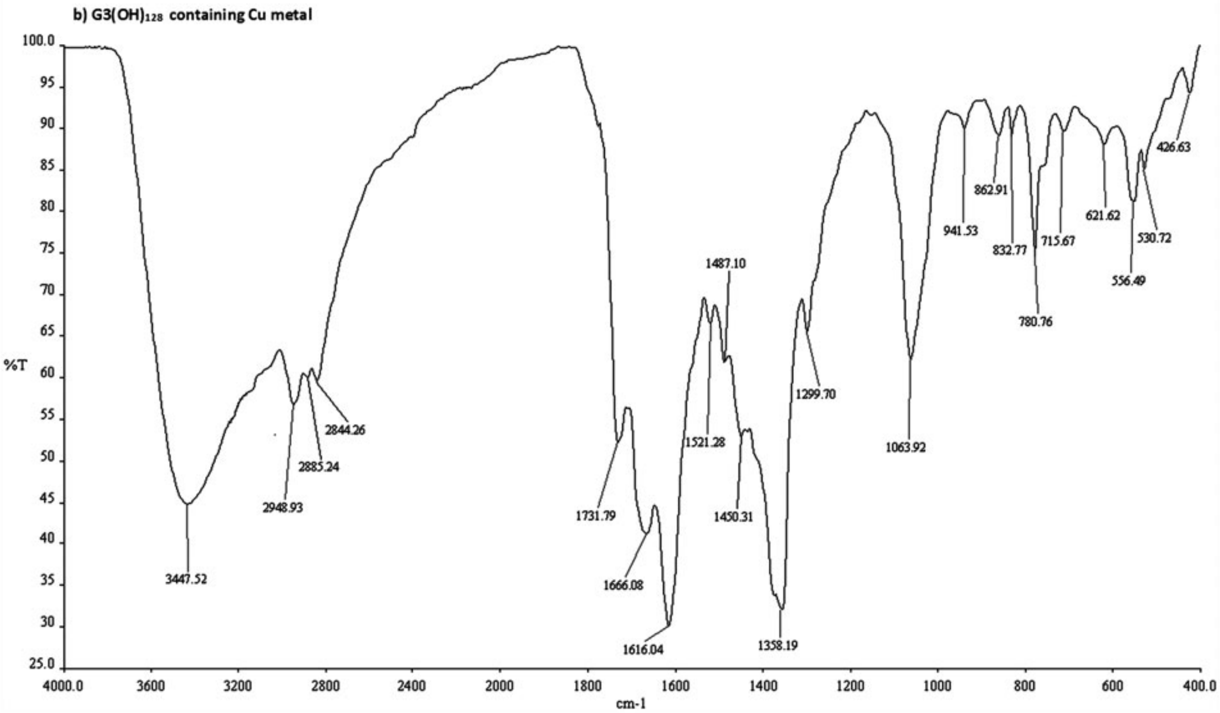

b) G3(OH)$_{128}$ containing Cu metal

Fig. 5. FT-IR spectrum of (a) G3(OH)$_{128}$ (b) G3(OH)$_{128}$ containing Cu metal.

and δ 167.50, 169.92, 170.12, 177.50, 179.60, and 182.84 for triazine portion. ^{13}C NMR spectrum of G3 (Fig. 3) showed 49.30 for piperazine carbon, 58.10 and 61.05 for peripheral methylene groups, 59.23, and 67.20 for inner methylene groups and 167.10, 176.70, 169.10, 179.15, 170.70, and 183.70 for triazine portion.

ESI-Mass spectrum showed that the molecular weight of $G3(OH)_{128}$ dendrimer was 12056.4 m/z value which was equal to its theoretical molecular weight (Fig. 4).

3.2. Ion adsorption behavior

Metal adsorption capacities of dendrimers were measured in relation to pH and generations as shown in Table 2. For all the generations, metal ion adsorption was increased with an increase in pH. At higher pH values, a significant binding of metal ion was observed as all ligands in dendrimer becomes unprotonated [20,21]. At pH 10, adsorption of metal ions by all dendrimer generations were maximum.

Metal adsorption capacities of the dendrimer generations were also studied in relation to generation number. Table 3 showed metal sorption capacities of $G1(OH)_8$, $G2(OH)_{32}$ and $G3(OH)_{128}$ for Cu^{2+}, Ni^{2+} and Zn^{2+} ions respectively. Third generation dendrimer showed the highest capacity for metal ion adsorption. As the generation number increased metal adsorption also increased because with an increase in the generation, number of the terminal hydroxyl group increased. It was also evident from the data that Cu^{2+} ions was adsorbed in higher quantities by all dendrimer

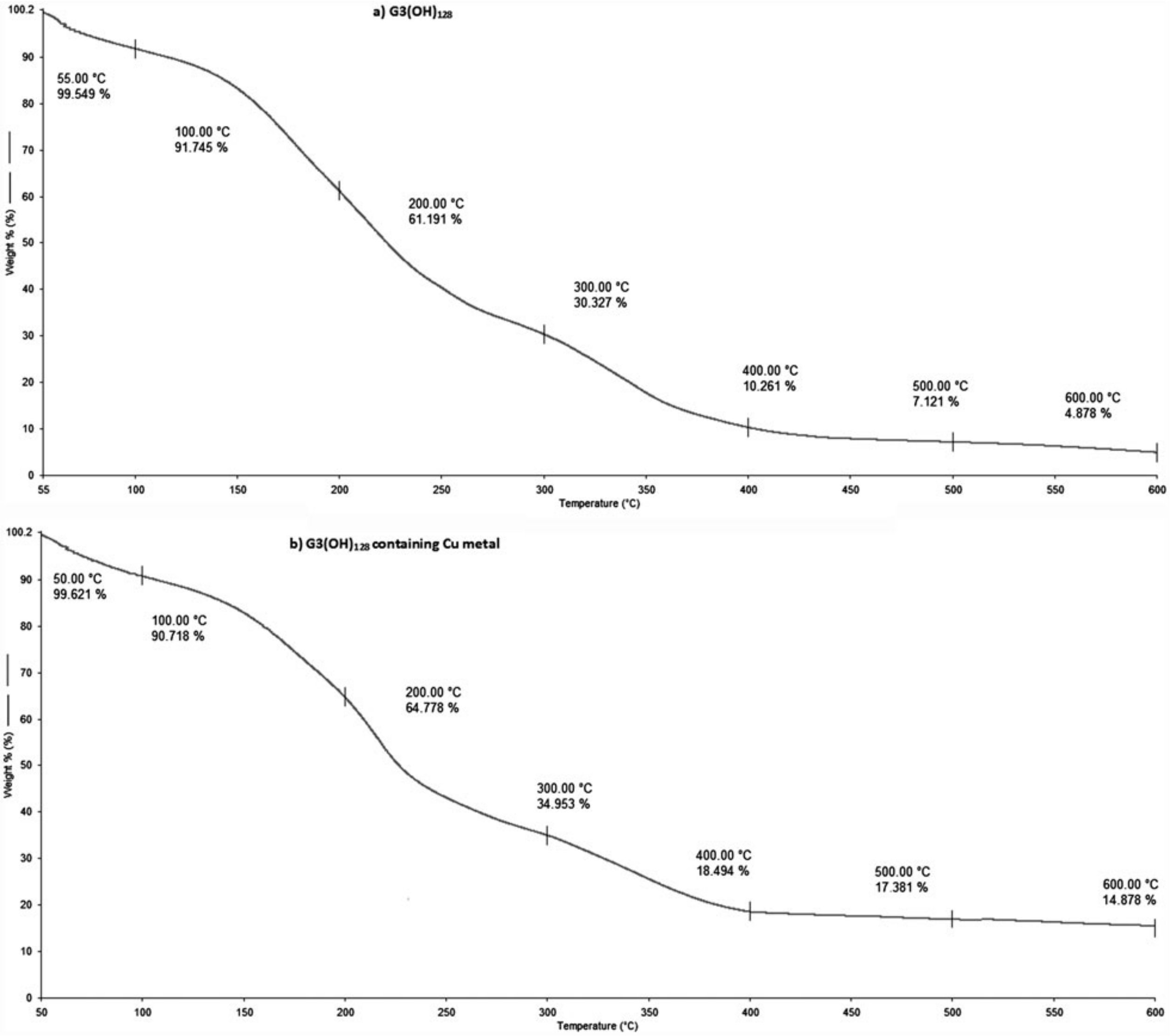


Fig. 6. TGA graphs: (a) $G3(OH)_{128}$ (b) $G3(OH)_{128}$ containing Cu metal.

Table 5
%wt. loss at different temperatures for $G3(OH)_{128}$ and $G3(OH)_{128}$ containing metals

Products	%wt. reduced for dendrimer generations at diff. temperature (˚C)										
	100	150	200	250	300	350	400	450	500	550	600
$G3(OH)_{128}$	8	18	39	61	70	85	90	92	93	95	95
$G3(OH)_{128}$–Cu	10	16	36	60	66	74	82	82	83	85	86
$G3(OH)_{128}$–Ni	11	16	37	63	67	77	83	84	85	86	87
$G3(OH)_{128}$–Zn	11	17	38	63	67	77	83	85	86	87	88

generations, whereas Zn^{2+} ions were adsorbed in relatively lesser quantities.

3.3. Characterization of metal containing dendrimers

Metal containing $G3(OH)_{128}$ dendrimer was further characterized by FT-IR and TGA to confirm the presence of metal in metal-containing dendrimers.

FT-IR results are furnished in Table 4. FT-IR spectrum of metal containing dendrimers was compared with FT-IR spectrum of parent pure G3 dendrimer which gave information about binding site for metal adsorption. IR absorption band at 3,356 cm^{-1} resembled to the hydroxyl group in generation 3 dendrimer. The absorption band shifts to 3,447, 3,457 and 3,410 cm^{-1} after the adsorption of Cu, Ni and Zn, respectively. A very little shift was observed for C–O at 1,064 cm^{-1} and C–N at 1,454 cm^{-1} from the parent $G3(OH)_{128}$. So, it was observed that the surface hydroxyl group may be the active binding site for metal ions. Fig. 5 showed FT-IR spectrum of $G3(OH)_{128}$ dendrimer and $G3(OH)_{128}$ containing Cu ions.

The thermal degradation analyses of the prepared pure and metal-containing dendrimer were performed by a TGA instrument with heating rate of 10˚C min^{-1} in an N_2 atmosphere. TGA (Fig. 6) of pure dendrimer $G3(OH)_{128}$ showed two stage thermal decomposition, dendrimer loses 18% of wt. up to 150˚C due to bound moisture, then decomposed completely up to 600˚C leaving 5 % residual wt. at 600˚C. Metal-containing dendrimers $G3(OH)_{128}$–Cu, $G3(OH)_{128}$–Ni and $G3(OH)_{128}$–Zn showed same thermal decomposition behavior but, final residual weights at 600˚C were 14, 13 and 12 %, respectively, due to the presence of metal oxides after complete decomposition(Table 5). These confirmed the presence of metal ions in final metal-containing dendrimer [24].

4. Conclusion

Hydroxyl-terminated dendrimer generations based on triazine containing 8, 64 and 128 hydroxyl groups were prepared from 1,4-biz(4,6-trichloro-1,3,5-triazin-2-yl)piperazine. Dendrimer generations were fully characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, and ESI-mass spectrometry. Sorption behaviors of full generations dendrimer showed that generation 3 dendrimer $G3(OH)_{128}$ had the highest sorption capacity. Sorption capacities of dendrimer generations increased with an increase in generation number and pH. FT-IR and TGA studies of metal-containing dendrimer confirmed the presence of metal ions in final metal-containing dendrimer.

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