HYDROXYL-TERMINATED DENDRIMERS FOR REMEDIATION OF Cu^{+2}, Ni^{+2} AND Zn^{+2} METAL IONS FROM AQUEOUS SOLUTIONS

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Abstract
Heavy metal pollution is one of the most serious environmental issues. Heavy metal pose significant risks to human health due to high toxicity and aqueous solubility therefore metal containing water must be treated before being released in to the environment. Structral advantages and hydrophilic surface groups of dendrimers make them an excellent choice for the remediation of heavy metal ions. The main objective of this research was to evaluate the performance of hydroxyl-terminated triazine-based full generation generation one, two and three (HG1.0, HG2.0 HG3.0) in terms of their ability to remove Cu^{+2}, Ni^{+2}, and Zn^{+2} from metal ions aqueous solutions. The ability of these dendrimers to remove metal ions studied in terms of time interval, dendrimer generations and pH conditions. The presence of metals in the dendritic metal complexes was confirmed by spectrographic FT-IR and TGA studies. The results of these metal remediation indicate that the sorption of these metal ions has increased in relation to the number of dendrimer generations, the duration of time and the pH conditions.

Keywords: Dendrimers, Heavy metal, Remediation, Synthesis, TGA

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1. INTRODUCTION

Heavy metals are currently one of the most serious environmental hazards; due to their high toxicity and carcinogenic properties, they are toxic to humans, animals, and plants. Heavy metal ions such as Hg(II) As(II) Cd(II), Pb(II), and Cr(II) are among the dangerous pollutants that are routinely deposited in marine and tropospheric ecosystems. These harmful heavy metals should be removed from wastewater to protect humans and the environment [1-5]. Chemical precipitation, adsorption, ion exchange, reverse osmosis, electrochemical and other techniques are used to remove heavy metal contamination. Adsorption is one of the most used waste removal methods. Organic, polymeric carbon-based, and silica-based adsorbents have all been tried and shown to be effective in this application [5-10].

Dendrimers are unique hyperbranched macromolecules with different three-dimensional molecular topologies and terminal reactive functional groups. Dendrimers are more functionalized than linear polymers due to their substantial internal gaps and flexible molecular architecture. Dendrimers can also be used as effective adsorbents for the removal of a variety of pollutants. Dendrimers' potential applications include drug transport and solubility, cancer therapy, catalysis, nanoparticle creation, and pollution removal [11-13]

Through a set of different studies, the main objective of this research was to evaluate the performance of hydroxyl-terminated triazine-based full-generation dendrimers HG1.0, HG2.0 and HG3.0 in terms of their ability to remove Cu^{+2}, Ni^{+2} and Zn^{+2} metal ions from water. Dendrimer was synthesized by utilizing a divergent technique. Dendrimer development and production were studied using infrared spectroscopy and ^1H NMR. The skills of these dendrimers to remove these metal ions were investigated in terms of time interval, dendrimer

generations and pH conditions. FT-IR and thermal (TGA) analyses were performed to verify the existence of metals in the dendrimer of these dendritic metal complexes [14-16].

2. EXPERIMENTAL SECTION

2.1 Materials

Diethanolamine, Dichloromethane, Triazine trichloride, Homopiperazine, Copper (II) nitrate hexahydrate ($Cu(NO_3)_2{\cdot}6H_2O$), Zinc(II) nitrate hexahydrate $Zn(NO_3)_2{\cdot}6H_2O$, Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used for the synthesis of dendrimer and their application in metal sorption from aqueous solution.

2.2 Methods

2.2.1 Synthesis of hydroxyl-terminated triazine dendrimers

Cyanuric chloride (0.02 mmol) was dissolved in dichloromethane (DCM) and stirred on a hot plate stirrer for two hours. During stirring, the temperature was kept at 0-5°C followed by a mixture of homopiperazine (0.1 mmol) and sodium hydroxide (0.02 mmol) was added to the solution in a dropwise manner to produce 1,4-bis(4,6-dichloro-1,3,5-triazine-2-yl)-1,4-diazepine (HG0.5) as the core. HG0.5 was washed with methanol and acetone to remove the unreacted cyanuric chloride and dichloromethane. HG0.5 was mixed with diethanolamine and refluxed using a condenser equipped with a water-cooled jacket for two hours. After completion of the reaction, the reaction mass was allowed to cool down to room temperature, and finally, the desirable product HG1.0 was filtered and washed with acetone and DCM. HG1.0 dendrimer was again utilized and reacted with triazine trichloride, giving dendrimer generation HG1.5. Then all the steps were repeated until dendrimer generation three was synthesized [15, 17-21].

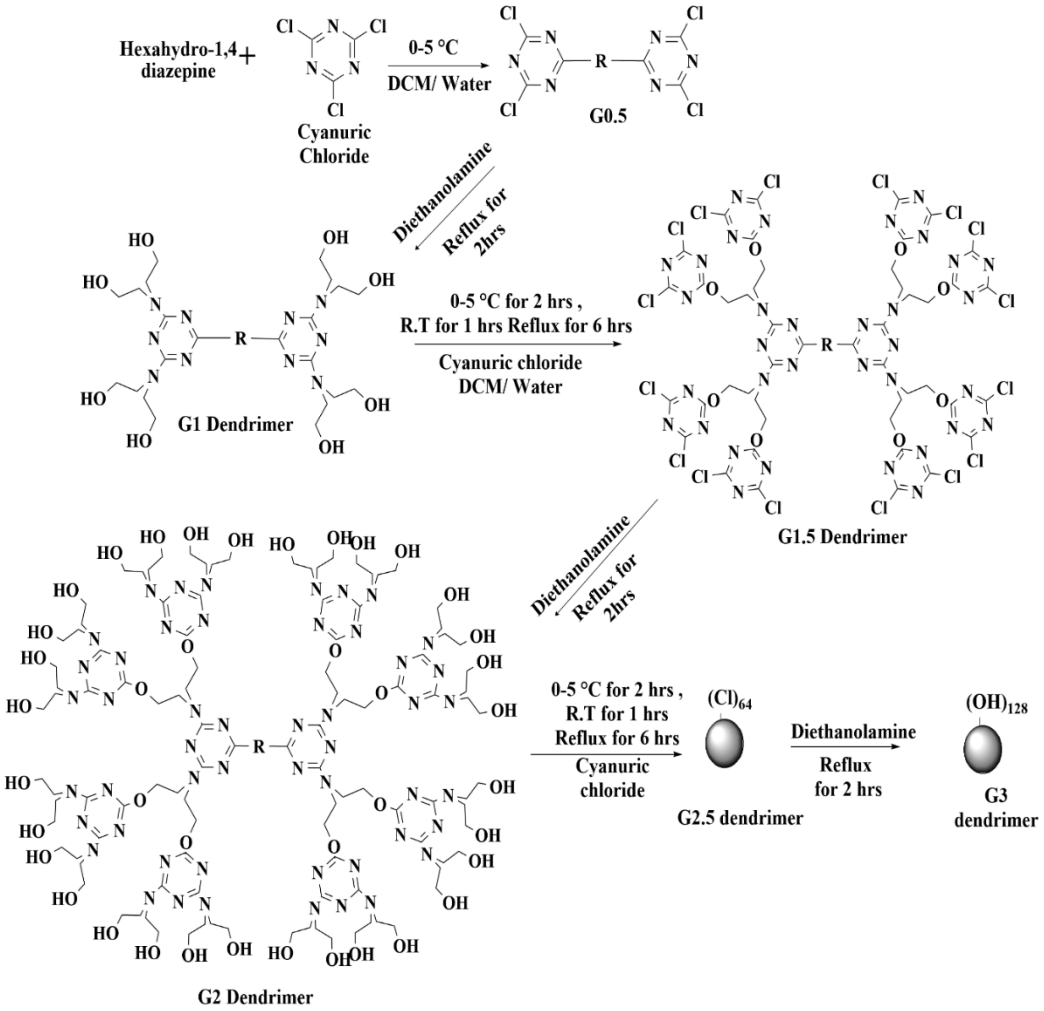
Yield: 83.52% FT-IR (Nujol, cm^{-1})v: 3441 (O-H stretching), 2984 (Aliphatic C-H stretching),1654 (Aromatic C=N stretching), 1053 (C-O stretching), 1305 (C-N stretching) [Fig.1 FT-IR spectrum of HG3 dendrimer].

^{1}H-NMR (500 MHz, D_2O, δ/ppm): 2.7780-2.7815 (t, 2H, -C<u>H$_2$</u>), 2.9649-2.9754 (t, 8H, -C<u>H$_2$</u>) as core, 3.6114- 3.6351 (m, 256H, N-C<u>H$_2$</u>-CH_2-OH), 3.6382-3.6608(m, 256H, N-CH_2-C<u>H$_2$</u>-OH) 3. 9884-4.0257 (t, 80H, N-C<u>H$_2$</u>-CH_2-O-triazine), 4.5249-4.6028 (m, 80 H, N-CH_2-C<u>H$_2$</u>-O-triazine). [Fig. 2 ^{1}H NMR spectrum of HG3 dendrimer] Molecular weight: 12081 Dalton

2.2.2 Experiment for heavy metals removal

The aqueous solution of three mmol metal salt [$Cu(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, $Zn(NO_3)_2$ $.6H_2O$) in 20mL water was added to 200 mg of dendrimer separately. The solution pH was set at 4, 7 and 9.2 using 1M HCI and 0.1N 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 EDTA disodium salt using the Murexide indicator[15, 22-25].

2.3 Reaction Scheme



Scheme 1. Reaction scheme of triazine dendrimers

3. RESULT AND DISCUSSION

3.1 Dendrimer Characterizations

Reaction scheme 1 outlines the synthetic technique that was employed in the synthesis of the hydroxyl-terminated triazine-based dendrimer. The dendrimers were produced by synthesis using the traditional divergent approach [18-21, 26-28].

The physicochemical characteristics of hydroxyl-terminated triazine-based dendrimers are laid forth in Table 1. Full-generation hydroxyl-terminated triazine-based dendrimers HG1.0, HG2.0, and HG3.0 were water-soluble light brown liquids. Chlorine-terminated core HG0.5 and half-generation dendrimers HG1.5 and HG2.5 were water-insoluble white solids.

Table 1 Description of the hydroxyl-terminated triazine-based dendrimers' physical characteristics

Dendrimer Generations	Chemical Formula	Physicality	Solvency in water	Speculative Surface Functional Groups (Numbers)
Core	$C_{11}H_{10}Cl_4N_8$	Solid white	Insoluble	$Cl_{(4)}$
HG1.0	$C_{26}H_{48}N_{12}O_8$	Brown liquid	Soluble	$OH_{(8)}$
HG1.5	$C_{51}H_{42}N_{36}Cl_{16}O_8$	Solid white	Insoluble	$Cl_{(16)}$
HG2.0	$C_{114}H_{200}N_{52}O_{40}$	Brown liquid	Soluble	$OH_{(32)}$
HG2.5	$C_{211}H_{170}Cl_{64}N_{148}O_{40}$	Solid white	Insoluble	$Cl_{(64)}$
HG3.0	$C_{466}H_{808}N_{212}O_{168}$	Brown liquid	Soluble	$OH_{(128)}$

The core, half-generation dendrimers HGI.5 and HG2.5 had chloride terminations, whereas the full-generation dendrimers HG10, HG2.0 and HG3.0 had hydroxyl terminations, according to FT-IR determinations of all dendrimer generations. The absorption bands for C-C1 stretching were observed in the core HG1.5 and HG2.5 in the IR spectrum, with absorption bands 771 cm^{-1},780 cm^{-1}, and 827 cm^{-1}, respectively. In contrast, the hands for O-H stretching were

absent, indicating that the regions of these structures contain C-Cl groups but no hydroxyl groups. The stretching of O-H resulted in hydroxy bands at 3457 cm^{-1}, 3448 cm^{-1}, and 3441 cm^{-1} in the IR spectra of HG1.0, HG2.0, and HG3.0, respectively. In contrast, the absorption bands for C-CI stretching were absent, indicating that their strictures contained only hydroxyl groups.

Fig.1. FT-IR spectrum of HG3.0 dendrimer

The progress of the reaction and the structure of the products were investigated using ^{1}H NMR spectroscopy. The peripheral and inner diethanolamine moiety of the HG3.0 dendrimer have two methylene groups at 3.6114-3.6608 ppm and 3.9884-4.6028 δ ppm, respectively, attached to nitrogen and oxygen.

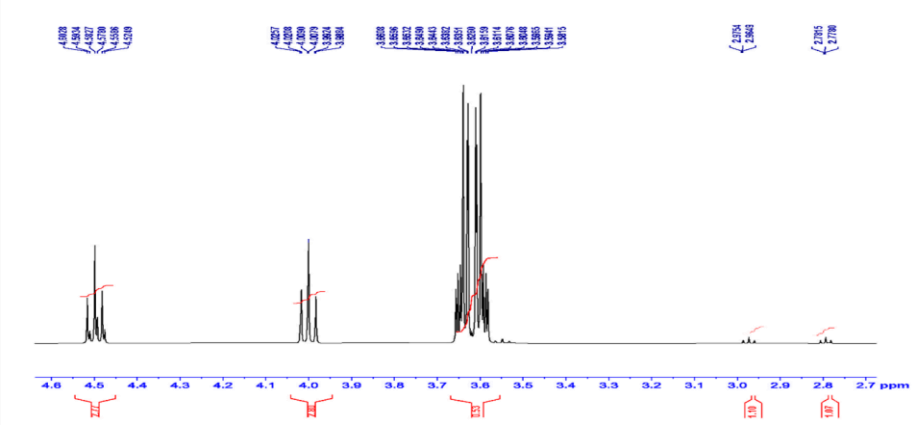


Fig.2. ^{1}H NMR spectrum of HG3.0 dendrimer

3.2 Metal-ion sorption Behaviour

Dendrimer sorption capacities have been observed to increase as generation numbers and time increase. The dendrimer of generation three had the highest sorption capacity [15, 29-31].

3.3 Behaviors of the dendrimers in dendrimer-metal solutions

Full-generation dendrimers were used to conduct the sorption investigation for heavy metals, as indicated in the experimental portions of this article [32,33].

3.3.1 Effect of contact time

Dendrimer was added to a metal ion solution and stirred continuously for 6, 12, 18, and 24 hours. After which, the solution was filtered, and the quantity of metal ion sorption was determined using the EDTA technique Cu^{+2}, Ni^{+2} and Zn^{+2} ion uptake increased with increasing time across all generations[15, 34,35].

Table 2 Effect of contact time on sorption of Cu^{+2}, Ni^{+2} and Zn^{+2} by HG1.0, HG2.0 and HG3.0 dendrimer.

Metal ions		Cu^{+2}	Ni^{+2}	Zn^{+2}
Dendritic Adsorbents	Contact time	pH	pH	pH

Generations	(Hours)	4	7	9.2	4	7	9.2	4	7	9.2
		mmol/g								
HG1.0	6	0.85	1.03	1.28	0.65	0.78	1.13	0.32	0.64	1.07
	12	1.37	2.1	2.49	1.44	1.64	2.39	0.85	1.45	2.18
	18	2.03	2.69	3.88	2.15	2.59	3.72	1.34	2.09	3.05
	24	2.03	2.69	3.88	2.15	2.59	3.72	1.34	2.12	3.05
HG2.0	6	1.0	1.26	1.55	0.81	1.08	1.45	0.59	0.93	1.20
	12	2.08	2.68	2.97	1.78	2.17	2.82	1.38	2.01	2.56
	18	2.84	3.28	4.40	2.61	3.27	4.36	1.74	2.58	3.76
	24	2.84	3.28	4.40	2.61	3.27	4.36	1.76	2.58	3.76
HG3.0	6	1.41	1.78	1.83	1.02	1.38	1.68	0.9	1.32	1.55
	12	2.56	2.81	3.55	2.35	2.41	3.17	2.08	2.73	3.31
	18	3.32	4.63	5.02	3.16	3.70	4.79	2.76	3.97	4.64
	24	3.32	4.63	5.02	3.16	3.70	4.79	2.76	3.97	4.64

3.3.2 Effect of pH

Metal ion uptake by different generations of synthesized dendrimer were studied at various pH. (Table 3) It was observed that metal ion uptake was increased for all generations with the increased pH as the protonation of ligands decreased, which led to higher metal uptake. The metals were removed successfully at low-high pH, but the results were outstanding at pH 9.2 [15, 36-38].

Table 3 Effect of pH on Cu^{+2}, Ni^{+2} and Zn^{+2} sorption by HG1.0, HG2.0 and HG3.0 dendrimer.

Generations of Dendrimers	pH	Metal Ion Uptake Capacity (mmol/g)		
		Cu^{+2}	Ni^{+2}	Zn^{+2}
HG1.0	4	2.03	2.15	1.34
	7	2.69	2.59	2.12
	9.2	3.88	3.72	3.05
HG2.0	4	2.84	2.61	1.73
	7	3.28	3.27	2.58
	9.2	4.40	4.36	3.76
HG3.0	4	3.32	3.16	2.85
	7	4.63	3.70	3.97
	9.2	5.02	4.79	4.64

3.3.3 Effect of generation

HG1.0, HG2.0, and HG3.0 dendrimer contains 8, 32 and 128 hydroxyl groups on the peripheries, respectively It was observed that with increase in generation number, metal ion uptake was increased as the number of terminal hydroxyl groups increased, it was shown that maximum adsorption was observed in HG3.0 dendrimer which effectively removed 5.02 mmol/g,4.79 mmol/g and 4.64 mmol/g of Cu^{+2}, Ni^{+2}, and Zn^{+2} respectively [39, 40].

Table 4 Effect of Generation on sorption of Cu^{+2}, Ni^{+2}, and Zn^{+2} by HG1.0 HG2.0 and HG3.0 dendrimer at 9.2 pH.

Generation of dendrimers	Metal Ion adsorbed (mmol/g)		
	Cu^{+2}	Ni^{+2}	Zn^{+2}
HG1.0	3.88	3.72	3.05
HG2.0	4.40	4.36	3.76
HG3.0	5.02	4.79	4.64

3.4 Characterization of metal-containing dendrimer

The FT-IR spectrum of metal-containing dendrimers was compared with that of pure parent HG3.0 dendrimer, which gave information about the binding site for metal sorption. IR absorption band at 3441 cm^{-1}, resembled the hydroxyl group in HG3.0 dendrimer. The absorption band shifts to 3399 cm^{-1}, 3394 cm^{-1} and 3388 cm^{-1} after Cu, Ni and Zn adsorption, respectively. So, it was observed that the surface hydroxyl group might be the active binding site for Cu, Ni and Zn metal ions. A very little shift was observed for C-O and C-N at cm^{-1} from the parent HG3.0 as follows 1064 cm^{-1}, 1063 cm^{-1} and 1068 cm^{-1} for C-O stretching after Cu, Ni and Zn, while for C-N

stretching after Cu, Ni and Zn adsorption the change observed as 1304 cm-^{1}, 1384 cm^{-1}, and 1384 cm^{-1}. Fig. 3 shows the FT-IR spectrum of metal-containing dendrimer (HG3-Cu^{+2}, HG3.0-Ni^{+2}, and HG3.0-Zn^{+2} and HG3.0 dendrimers.

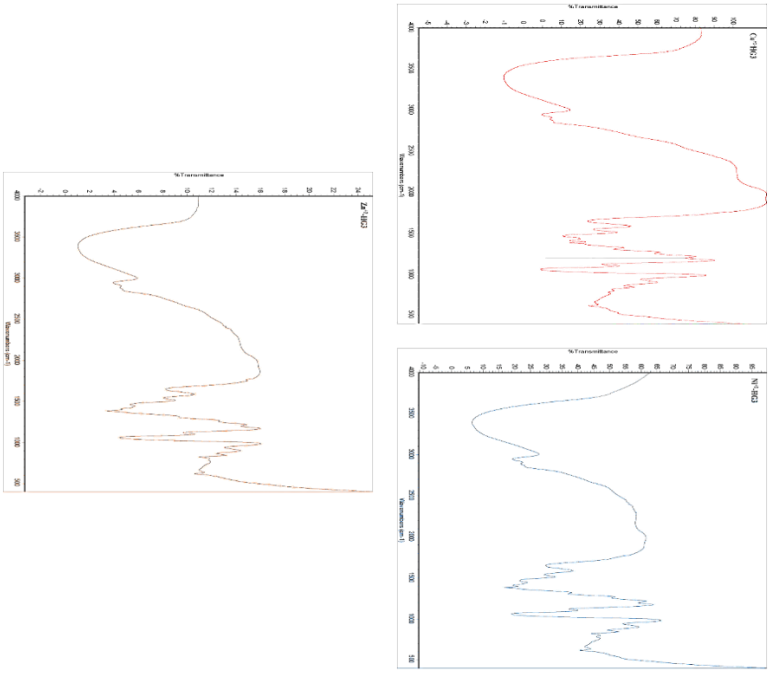


Fig 3. FT-IR of Cu^{+2}, Ni^{+2}, and Zn^{+2}

The thermal degradation analyses of the prepared pure and metal-containing dendrimer were performed by a TGA instrument with a heating rate of 30°C min in a nitrogen atmosphere TGA (Fig. 4) of pure dendrimer HG3.0 showed decomposed entirely up to 600°C leaving 1.84 % residual weight. Metal-containing dendrimers HG3.0-Cu^{+2}, HG3.0-$Ni^{+2,}$ and HG3.0-Zn^{+2} showed the same thermal decomposition behaviour, but final residual weights at 600°C were 8.42 %, 8.24 %, and 3.16 % respectively, due to the presence of metal oxides after complete decomposition (Fig 5). These confirmed the presence of metal ions in the final metal-containing dendrimer.

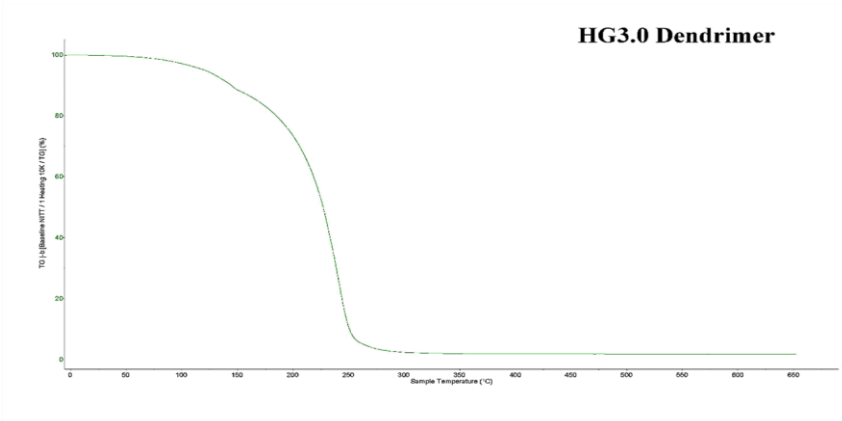


Fig.4. TGA of HG3.0

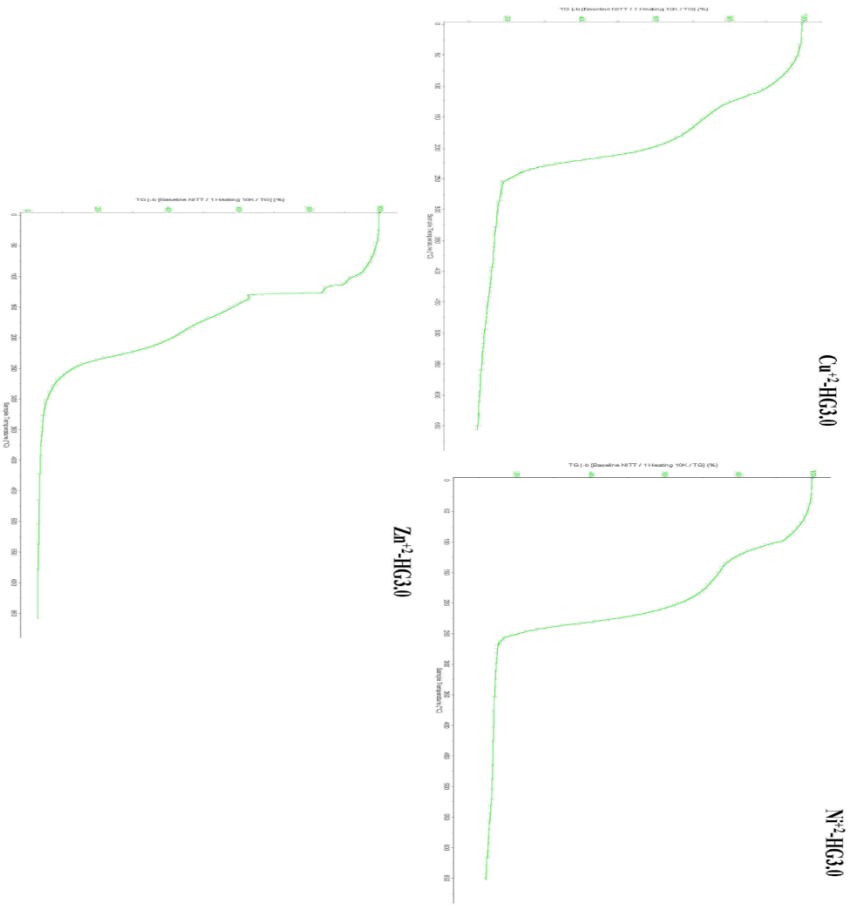


Fig 5. TGA of HG3.0-Cu^{+2}, HG3.0-Ni^{+2} and HG3.0-Zn^{+2}

4.0CONCLUSION

The hydroxyl-terminated triazine-based dendrimers were synthesized up to generation three, starting from the core hexahydro-1,4-diazepine. These dendrimers have 8, 32, and 128 hydroxyl groups, respectively and were characterized using FT-IR, ^{1}H NMR, and ESI-mass spectrometry. The sorption behaviour HG1.0, HG2.0 and HG3.0 of the full-generation dendrimer HG3.0 was the most effective. Thus, it isconcluded that the sorptive properties of dendrimer generations increased with increasing generation number, time, and pH. FT-IR and TGA studies of metal containing dendrimer (HG3.0-Cu^{+2}, HG3.0-Ni^{+2}, and HG3.0-Zn^{+2})) confirmed the presence of metal ions in final metal-containing dendrimers.

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Conflicts of interest

There are no conflicts to declare.

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Ethics Statement

Nil

Data Availability

The data that support the findings of this study are available from the author, upon reasonable request.

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