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Thermal degradation and antibacterial study of transition metal complexes derived from novel terpolymer ligand

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1. Introduction

In the recent past synthesis of coordination polymers attracted great enthusiasm owing to their fascinating characteristics such as ability to bind toxic metal ions, thermal stability, act as a catalyst, photoluminescence properties [1–4]. Due to its features as high thermal stability and antimicrobial behavior, the synthesis of polymer-metal complexes attracted researchers [5]. Saeed and co-workers synthesized new thermally stable epoxy polymers containing copper and nickel ions using diglycidal bisphenol A ether with metal complexes in aminothiourea [6]. Azarudeen et al. synthesized new terpolymer ligand and metal chelates derived from anthranilic acid aminopyridine, formaldehyde anthranilic acid, phenyl hydrazine and the complex were studied for thermal stability and antibacterial screening. The results reveals that all the complexes are highly thermally stable and more potent antibacterial agents than their corresponding ligands [7,8]. Some divalent transition metal complexes of 8-hydroxquinoline were prepared and described for their warm air stability and antibacterial activities [9].

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ABSTRACT

Metal complexes are prepared by the buildup of 8-hydroxyquinoline-5-sulphonic acid, formaldehyde and guanidine with 2 M HCl acid is required as a catalyst for polymerization with different feed ratio (3:1:5) of monomers. The structure of metal complexes and ligand were elucidated by NMR, FTIR and elemental analysis. Thermogravimetric analysis was used for the investigation of thermal stability of the terpolymer ligand metal complexes. Additionally, Freeman-Carroll method was utilized for the calculation of activation energy with the help of TGA data. The surface morphology of terpolymer ligand was examined by scanning electron microscopy. The antimicrobial activities of metal complexes and its ligand were tested against *S. aureus*, *E. coli*, and *K. Pneumoniae Klebseilla* bacteria.

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> The organic copolymer resin and their metal complexes were prepared from hexametylenediammine, formaldehyde and 8hydroxyquinoline-5-sulfonic acid [10]. Nanosized 8hydroxyquino-late complexes were synthesized by utilizing simple and layer-by-layer chemical deposition method and contemplated [11]. Terpolymeric ligands and its metal complexes were synthesized involving salisaldehyde, phenylthiourea with glutaraldehyde and investigated for thermal stability and antibacterial properties [12]. Chelation properties of new chelating polymer were investigated and X-ray diffraction data indicates that the incorporation of the metal ions significantly improved the degree of crystallinity [13]. R. Chitra et al synthesized 7-Acryloyloxy-4-methylcoumarin monomer with N-cyclohexyl-Acrylamide in different feed ratio using Azobis isobutyl nitrite as initiator in DMF. The synthesized copolymer were tested for their antibacterial activity and was carried out by using Escherichia coli, Salmonella typhi and bacillus cereus [14].

> Recently, however, 2-(N-phthalimido) ethyl methyacrylate and p-chlorophenyl methacrylate homo and copolymers have been prepared in DMF solution at 70 °C using 2,2 azobisisobutyronitrile as initiator, the synthesized copolymer has been evaluated on different microorganisms and these polymers enable bacteria, fungi and yeast to grow by 10–52, 20–58, and 18–56 percent respec-

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tively [15]. Sharma et al synthesized acetylthiophene polymer were assessed the antimicrobial activity of copolymer films against bacteria by calculating minimum inhibitory concentrations [16]. The acrylate monomer, 7-acryloyloxy-4-methyl coumarin was synthesized by reacting 7-hydroxy-4-methyl coumarin with acryloyl chloride at 0-5 °C in the presence of NaOH. Synthesized copolymers were tested for their antimicrobial properties by using Staphylococcus citreus, Escherichia coli and Bacillus subtilis [17]. A novel comparative thermodynamic investigation of a terpolymer and its composite was carried out by Velmurugan et al. [18].

The present research article reports investigation of synthesis of new terpolymer metal complexes and ligand. Further, Structure of the terpolymer ligand and its metal complexes were confirmed by different spectroscopic and physical methods. The thermal stability and antimicrobial screening for the metal complexes and their ligand were performed and reported.

2. Materials and methods

Entire starting materials utilized were of AR grade. The 8hydroxyquinoline-5-sulphonic acid (Fisher India), Guanidine (S.D. Fine Chemicals) and formaldehyde (Sigma Aldrich) were procured from the market.

2.1. Synthesis of 8-hydroxyquinoline-5-sulphonic acid terpolymer

New 8-HQ-5SAGF was prepared by gathering 8hydroxyquinoline-5-sulphonic acid, formaldehyde and Guanidine with 2 M HCl as a catalyst in molar ratio 3:1:5, with intermittent shaking in an oil bath. Then the reaction mixtures were refluxed about 124 °C \pm 2 °C temp up to 5 h. The yellow color solid product was acquired and washed sometimes with warm water. After specified time, the product obtained was extracted with ethoxyethane to unreacted starting materials and corrosive monomers which can be available alongside 8-HQ-5SAGF terpolymer. It was completely filtered and isolated by dissolving in 8% NaOH. The copolymers were then reprecipitated to 1:1 (v/v) by drop savvy expansion with conc. HCl and water to avoid lump formation. The substance which was filtered, powdered and dried. The terpolymer yield was found to be 81%. The reaction is shown in Fig. 1.

2.2. Preparation of metal complexes

The complexes was prepared by polycondensation system employing the integrated terpolymers with Ni²⁺, Zn²⁺ and Cu²⁺ ions. In the reaction vessel a weighted quantity of polymer sample (2 mol) 2 g of 8-HQ-5-SAGF was taken and covered ethanol declare allowed for swelling up to 2 h. In the reaction mixture 1 g of copper nitrate dissolved in ethanol was then added. Reaction mixture was subsequently refluxed for 3 h at about 60 °C temperature in an oil bath with intermittent shaking. The brown color solid product obtained was immediately separated. The obtained product was washed and recrystallized with ether and ethanol respectively to get rid of the polluting influences. The unadulterated product of terpolymer metal complexes were air dried. The same procedure was additionally utilised for the preparation of 8-HO-5-SAGF complexes with Zn²⁺ and Ni²⁺ metal ions. The reaction route of the 8-HQ-5-SGAF complex with Zn²⁺, Ni²⁺ and Cu²⁺metal ion is displayed in Fig. 2.

2.3. Physicochemical analysis

Elemental examination is performed using the instrument Perkin Elmer 789N QP-2010. The spectrum of FTIR in KBr pellets was tested within the range of 4000–500 cm⁻¹. At SAIF Chandigarh University Panjab the ¹H NMR spectrum was reported using DMSO d_6 solvent in a 400 MHz Bruker.

2.4. Thermal analysis

Perkin Elmer TGA/DTA analyser was used to evaluate the thermal analysis of the terpolymer ligand and its metal complexes in air with a heating rate of 20 °C min⁻¹ between temperatures ranges 40–700 °C. The thermogram was recorded at Cochin University Sophisticated Analytical Instruments Facility (SAIF), STIC, and Cochin.

2.5. Anti-bacterial activity

Cell wall and membrane are the significant defensive obstacles to bacterial resistance in the environment. The bacterial cell wall performs a significant role in keeping the natural form of the bacteria. Cell membrane elements generate distinct adsorption mechanism for complexes and gram-positive and gram-negative bacteria. Lipopolysaccharides are the distinctive components of the gram-negative bacterial cell wall that offer highly loaded



Fig. 1. Reaction and structure for 8-HQ-5-SAGF terpolymer.



Fig. 2. Synthesis route of 8-HQ-5-SAGF terpolymer metal complexes.

region and attract complexes. Teichoic acid (a compound present in the walls of gram 7 positive bacteria) on the other hand reflected only in the cell wall of gram-positive bacteria, so that complex is spread along the molecular chain of phosphate, stopping their aggregation. Many studies have shown that complex is more active against gram-positive bacteria rather than gram-negative bacteria because the gram-negative bacterial cell wall consists of lipopolysaccharides, lipoproteins and phospholipids. These compounds create obstacle for macromolecules to enter into the bacterial cell wall. By comparison, the gram-positive bacteria's cell wall involves a slender layer of peptidoglycan as well as teichoic acid and abundant pores that enable foreign molecules to enter leading in cell membrane damage and cell death. In fact, as opposed to gram-negative bacteria, gram-positive fungi have elevated adverse stress on the cell wall surface that can hold complexes. The newly synthesized compounds were investigated against K. Pneumoniae Klebseilla, S. aureus and E. coli, for evaluating their antibacterial study by employing disc diffusion method. The dimethyl sulphoxide sterile solvent were used for the preparation of test solutions of 8-HQ-5-SAGF metal complexes and ligand. Then the bacterial were grown in a brain heart infusion agar. A hollow tube were used to dig wells in the media and then with the help of micropipette add 0.1 mL sample solution in each well. The petridishes were incubated for 24 h at a temperature of 37 °C. The inhibition zone of for the standard, test samples and control was determined.

3. Results and discussion

3.1. Elemental analysis

The synthesized 8-HQ-5-SAGF terpolymer was analysed for carbon, hydrogen, nitrogen and sulphur at Indian Institute of Technology, Mumbai. The results are presented in Table 1. The elemental analysis data are in good agreement with the theoretical (calculated) data. The elemental analysis data were used to assign empirical formula and empirical weight to terpolymer ligand (Table 2).

3.2. Fourier transform infrared spectra

The terpolymer ligand FTIR spectrum is portrayed in the Fig. 3. In the spectrum of ligand an expansive band displayed up in the locale 3505 cm⁻¹ can be allocated to the phenolic hydroxy (–OH) group stretching frequency showing intermolecular hydrogen bonding [19]. Stretching vibrations of the –NH linkage (imide) might be accounted by the peak at 3102–3080 cm⁻¹ and the sharp band 819 cm⁻¹ indicates bending vibrations of the –NH (imide) group [20]. A Sharp band doled out at 2789 cm⁻¹ might be because of aromatic -CH stretching. The band appearing within the range of 1602–1413 cm⁻¹ may be attributed to guinoline ring stretching frequency of -C=C. The band at 1413–1503 cm⁻¹ shows the methylene bridges present in the polymeric chain. The tetra substitution moiety 1,5,6,8 in quinoline ring are shown at 724, 1044, 1136 and 1191 cm⁻¹. Fig. 4 shows that bands are broadened in FTIR spectra of 8-HQ-5-SAGF metal complexes when compared with the ligand spectrum, the band belonging to the bending vibration for -N-H found in range of 1555 cm⁻¹ is moved to the lesser frequencies (1501) which indicate the attachment of nitrogen atom of the imide (-NH) group to the central metal ion. It is additionally confirmed by the presence of N \rightarrow M stretching vibration at (448–558).

3.3. ¹H NMR analysis

The ¹H NMR study of 8-HQ-5-SAGF terpolymer was recorded in DMSO d_6 and the spectrum is depicted in Fig. 5. The unsymmetrical multiplet signal in the region 8.16(δ) ppm allotted to the protons in quinoline ring. A sharp and solid peak at 9.1 ppm is credited to phenolic hydroxyl group shows intramolecular hydrogen bonding. A medium single crests obtained at δ 4.9 ppm might be allotted to – NH bridging and at 7.3 ppm allotted to the –C=NH proton (imine). Triplet signal in the area 9.8 (δ) ppm allotted to the –SO₃H group [21].

The spectrum of the Zn^{2+} complex show multiplets at the locale 7.7 ppm might be assigned to the aromatic protons as shown in Fig. 6. The methylenic proton might be appeared as doublet at 2.5 (δ) ppm. The signal obtained at δ 4.9 ppm in ligand is fully vanished in the metal complex spectrum provides clear indication for the complexation of the metal ions and ligand with the help of lone pair of nitrogen [22].

3.4. SEM analysis

Morphology of the 8-HQ-5-SAGF terpolymer ligand was examined by scanning electron microscopy as shown in Fig. 7. From the

Table	1						
Micro	analysis	and	empirical	formula	of	terpolymer	

Terpolymer	% of C observed (Cal.)	% of H observed (Cal.)	% of N observed (Cal.)	% of S observed (Cal.)	Empirical formula of repeating unit	Empirical formula Weight
8-HQ-5- SAGF	47.81 (48.97)	3.41 (3.5)	10.91 (10.71)	11.07 (12.24)	$C_{32}H_{28}N_6O_{12}S_3\\$	784.79

Table 2

Thermogravimetric data of 8-HQ-5-SAGF and its metal complexes.

Compound	Percentage (%) weight loss at various temperature							T ₅₀ **	Activation energy (Ea) kJ/mol
	200	300	400	500	600	700			
Ligand (8-HQ-5-SAGF)	14.32	18.30	48.93	67.32	87.5	99.01	730	530	23.31
8-HQ-5-SAGF-Cu	10.87	16.47	61.83	81.47	83.57	-	560	475	21.77
8-HQ-5-SAGF-Zn	10.40	16.22	53.5	82.85	84.14	-	510	460	19.54
8-HQ-5-SAGF-Ni	9.57	13.49	55.94	66.34	73.27	-	420	400	16.31

* Maximum decomposition temperature.

** Half decomposition temperature.



Fig. 3. FTIR Spectrum of 8-HQ-5-SAGF terpolymer.

images, the resin was found be more amorphous in nature than crystalline. Further, the resin was found to be less close packed with high porous and deep pits over the surface which is responsible for the adsorption of metal ions. The deep pits present in the resin are liable for the swelling and the reactivity of the active sites are covered in the polymer [23].

3.5. Thermal analysis

Thermal analysis of the 8-HQ-5-SAGF metal and terpolymer were analysed using Thermogravimetric analysis. Thermogram of the terpolymer and its metal complexes are displayed in Fig. 8 and their percentages of mass loss at different temperatures are incorporated in Table-2. The thermogram of the 8-HQ-5-SAGF terpolymer ligand displays three phase of disintegration. On the preliminary step decay was mild and originates from 40 °C to 140 °C pertains to the weight loss of 5.12% discovered and 5.30% estimated due to the removal of one crystalline water. The second stage of degradation initiates from the 140 °C to 320 °C corresponds to weight reduction 37.37% and 37.45% calculated might be loss of three -SO₃H and three -OH group. In the third phase deterioration starts from 320 °C to 400 °C evaluating the quick mass loss of 60% discovered and 60.70% calculated due to the elimination of quinoline ring and methylene gathering. The final step of debasement takes place from the temperature range 400–600 °C comparing to the evacuation of guanidine moiety.

Thermogravimetric curves of all the metal complexes exhibits two debasement stages. In case of 8-HQ-5-SAGF-Cu²⁺, Ni²⁺ and Zn²⁺ primary mass reduction is because of exclusion of crystal or lattice water molecules. The first degradation stage is fast and starts from 150 to 400 °C may be due to the evacuation of noncoordinated portion of the ligand. The second step of decomposition is slow ranges from 400 to 600 °C and decomposes coordinated portion. Finally, it may form the representative metal oxide.



Fig. 4. FTIR Spectrum of 8-HQ-5-SAGF-Zn terpolymer metal complexes.



Fig. 5. ¹H NMR spectrum of 8-HQ-5SAGF terpolymer.



Fig. 6. ¹H NMR spectrum of 8-HQ-5SAGF-Zn metal complexes.

On the basis of thermal degradation values and the energy activation determined by Fremann-Caroll technique for both the metal complexes and their ligand, the thermal stability of the terpolymer ligand is higher than its metal complexes. The order of thermal stability is as follows 8-HQ-5-SAGF-ligand > 8-HQ-5-SAGF-Cu²⁺ > 8-HO-5-SAGF-Zn²⁺ > 8-HO-5-SAGF-Ni²⁺.

3.6. Antibacterial studies

In order to explore antimicrobial properties both the complexes and terpolymer ligand were tested for antibacterial activity versus K. Pneumoniae Klebsiella and E. coli as a Gram-negative bacterium and S. aureus as Gram-positive bacteria and the results presented in Table 3 as zone inhibition values. The metal complexes and terpolymer ligand show reasonable activity versus K. Pneumoniae Klebsiella, E. coli and S. aureus. The ligand 8-HQ-5-SAGF shows inhibition zone of 12, 11, and 12 mm versus Klebsiella, E. coli, and S. aureus. The Ni²⁺ complex shows superior antibacterial activity as compared to Zn²⁺ and Cu²⁺ compounds against all the bacterial strains of S. aureus E. coli, and K. Pneumoniae Klebsiella. The maximum antibacterial actions (20 mm) has been observed for 8-HQ-5-SAGF-Ni²⁺ against K. Pneumoniae Klebsiella. The complex HQ-5-SAGF-Cu²⁺ and 8-HQ-5-SAGF-Zn²⁺ shows similar inhibition zone against *E. coli, Klebsiella* microbe. The metal complexes shows excellent activity than the terpolymer ligand this may be because of the metal ions binds with donor atoms of the terpolymer and the delocalization of π -electron over the whole quinoline ring. Due to this effect lipophilic properties of metal ions rises. The



Fig. 7. SEM photograph of 8-HQ-5-SAGF terpolymer.



Fig. 8. TGA thermograms of (a) 8-HQ-5-SAGF ligand (b) 8-HQ-5-SAGF-Cu(II) (c) 8-HQ-5-SAGF-Zn(II) (d) 8-HQ-5-SAGF-Ni(II).

Table 3 Antibacterial analysis of 8-HQ-5SAGF ligand and its metal complexes.

Compound	Zone of Inhibition (mm)					
	E. coli	K. Pneumoniae Klebsiella	S.aureus			
8-HQ-5-SAGF-ligand	12	11	12			
8-HQ-5-SAGF-Cu ²⁺	08	10	13			
8-HQ-5-SAGF-Zn ²⁺	08	16	11			
8-HQ-5-SAGF-Ni ²⁺	16	20	15			
Standard (Ciprofloxacin)	32	30	26			
Control (DMSO)	-	-	-			

presence of -OH and the aromatic ring enhances the antibacterial activities of metal complexes [24].

4. Conclusions

The metal complexes were prepared by gathering 8hydroxyquinoline-5-sulphonic acid, formaldehyde and Guanidine in the presence of 2 M HCl as a catalyst. The structure of both the metal complexes and its ligand was confirmed on the basis of spectral and physico-chemical investigation. The thermal stability of the metal complexes is less compared to its terpolymer ligand. The metal complexes possess greater activity versus certain bacterial strains such as K. Pneumoniae Klebsiella, Staphylococcus aureus, and Escherichia coli. The antibacterial studies shows that the metal complexes and its terpolymer ligand were capable antibacterial agents.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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