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Biological activities of microporous polymeric materials derived from 2,4dihydroxyacetophenone-p-phenylenediamine-formaldehyde

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ABSTRACT

A number of resins (2,4DHAPDF) were synthesized by condensation of 2,4 dihydroxyacetophenone (2,4-DHA) and p-phenylenediamine (p-PD)with formaldehyde (F) in the presence of 2 M HCl as a catalyst with three different molar ratios of reacting monomers (1:1:2, 2:1:3, 3:1:4) at 130^0C $\pm 2^0$C. Resins have been characterized by elemental analysis, infrared (IR) spectroscopy and nuclear magnetic resonance (^{1}HNMR) spectroscopy and the morphology of the resin was examined by SEM technique. The number average molecular weight of the resin was determined by non –aqueous conductometric titration. The antimicrobial activities of the terpolymer were screened on various bacteria and fungi. All the synthetic terpolymer showed excellent antimicrobial activities with increasing molar ratios of reacting monomers.

Keywords: Synthesis; Characterization; Molecular Weight; SEM; Antimicrobial activity.

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INTRODUCTION

The use of polymers in all spheres of life has been abundantly increased in recent years. Although various workers have pressing demand to synthesize eco-friendly polymers having some biological activities like antimicrobial. The invasion of polymers by fungi, bacteria and other organism is manifested by loss of mechanical properties, surface degradation, discoloration, staining and other deteriorations[1,2.] Phenolic resins have a large number of practical applications as electronic controls, insulating materials, protective adhesives and also in packing, adhesives and coating in electrical sensors. They have varied use in the aerospace industry and other applications have been reported in the field of activators, ion exchangers, catalyst and organometallic semiconductors etc. Moreover, they are useful as thermally stable materials because of their thermal stability, heat and chemical resistance and electrical insulation properties[3-5] Various researchers have studied the applications of terpolymer resins of substituted phenol and formaldehyde[6,7]. Terpolymers of salicylic acid-thiourea - trioxane and p-hydroxybenzoic acid- thiourea -trioxane have been reported in the literature [7-10].

The heavy metal ions toxicity has increased substantially because of the use of metal ions as catalyst in various industries. Many methods such as electrodeposition, co-precipitation and solid-liquid extraction have been developed for pre-concentration and removal of metal ions. However the metal ion removal by chelating ion-exchange resin using batch equilibrium method has gained rapid acceptance because of its wide variety of sorbent phases, high selectivity and high loading capacity and enhanced hydrophilicity [11-13].

Resorcinol-acetophenone copolymer was prepared by using trifluroacetic acid as catalyst having some antimicrobial activity[14]. Various hydroxybenzoic acid-formaldehyde copolymers have been reported as being used as ion-exchangers [15]. Similarly, 2,4-dihydroxybenzaldehyde oxime-formaldehyde polymers were synthesized in the presence of oxalic acid as a catalyst [16] The oximes carbazone and thiosemicarbazone derivativies of N (4-acetylphenyl) maleimide was radical homopolymerized and they show good antimicrobial activities.[17].

Chauhan et al. synthesized terpolymer based on p-chloroacetophenone oxime and also investigated their biological activities [18]

The present communication deals with synthesis, characterization and biological activities of a newly synthesized resins derived from 2, 4 dihydroxyacetophenone, p-phenylenediamine and formaldehyde with different molar ratios.

MATERIALS AND METHOD

Reagents and materials

All the Chemicals were AR grade or chemically pure grade. 2, 4 dihydroxy acetophenone, p-phenylenediamine purchased from Aldrich Chemical, formaldehyde from Merck while DMF and DMSO (HPLC grade) were used.

Apparatus

The terpolymer resins were subject to micro analysis for C, H, N on Elementar Vivio EL III, Scanning electron microscopy (SEM) using JEOL Model JSM- 6390 LV (Cochin).The molecular weight (Mn) of the resin measured by non-aqueous conductometric titration with the help of Elico CM 180 Conductivity Meter. Infrared was scanned on HAPP-GENZEL and NMR was scanned on BRUKER AVANCE II 400 NMR Spectrometer with dueterated dimethylsulphoxide (DMSO-$_{d6}$) as solvent at Sophisticated Analytical instrumentation Facility, Chandigarh.

Synthesis of 2,4DHAPDF resins

The new terpolymer resin 2,4DHAPDF, was synthesized (Figure. 1) by condensing 2,4-dihydroxy-acetophenone (2,4-DHA) and paraphenylenediamine (p-PD) with 37 % formaldehyde in a molar ratios of 1:1:2, 2:1:3, 3:1:4 in the presence of 2 M HCl as a catalyst at 130 ^{0}C ±2 ^{0}C for 5h in an oil bath with occasional shaking to ensure thorough mixing. The temperature of electrically heated oil bath was controlled with the help of dimmer stat. The solid resinous solid product obtained was immediately removed from the flask as soon as the reaction period was over and then purified.

The resinous product so obtained was repeatedly washed with cold distilled water dried in air and powdered with the help of agated mortar and pestle. The powdered was washed many times with hot water to remove unreacted monomers. The air- dried powder was extracted with chloroform and petroleum ether was used to remove 2,4 dihydroxyacetophenone-formaldehyde copolymer and other possible copolymers, which might be present along with 2,4DHAPDF terpolymer. It was further purified by dissolving in 8% sodium hydroxide solution, filtered and regenerated in 1:1 (V/V) HCl/water with constant and rapid stirring to avoid lump formation. The 2,4DHAPDF resin so obtained was filtered, washed several times with hot water and dried.

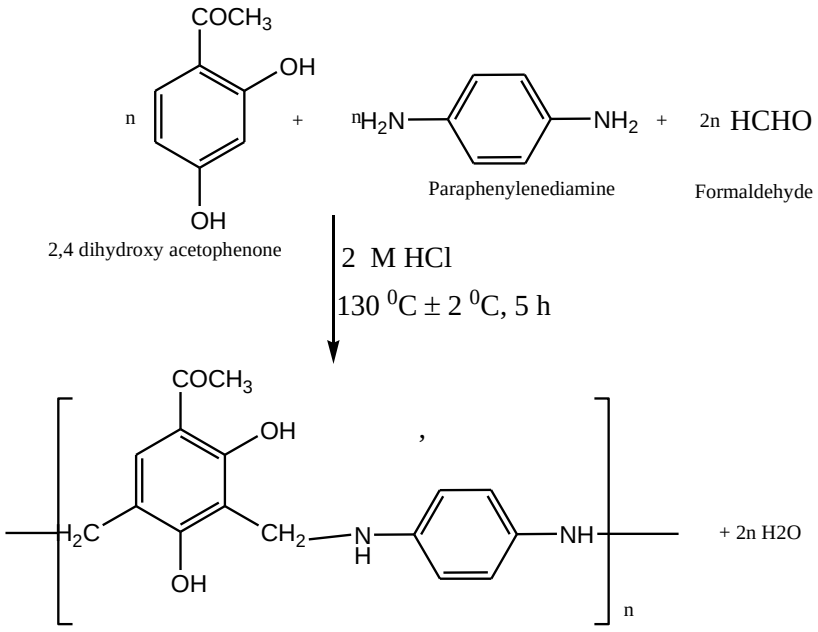

Figure. 1 Synthesis of 2,4DHAPDF – I resin.

RESULTS AND DISCUSSION

Resin samples were brown in colour, insoluble in commonly used organic solvents, but it was soluble in DMF and DMSO.

Characterization of synthesized resin

From the IR spectral studies it has been revealed that all the 2,4DHAPDF terpolymer resins give rise the nearly similar pattern of spectra. The assignment of Vibrational frequencies is based on the data available in the literature. A broad band appeared at 3334-3365 cm^{-1} is due to merging of two peaks (O-H, N-H). The medium band at 2923-2924 cm-1 is assigned to the stretching (C-H) of methylene group. The band obtained in the range of 1432-1625 is ascribed to aromatic ring. The band in the range of 1295-1331 is due to (C-N) stretching. The medium broad band in the range of 642-807 is attributed to substituted benzene ring.

The NMR spectra of all three (Resin-I, II, III) terpolymers were scanned in DMSO-d6. From the spectra, it is revealed that all 2,4DHAPDF terpolymers gave rise to different patterns of ^{1}HNMR spectra, since each of the 2,4DHAPDF terpolymer posse's sets of protons having different electronic environment. The NMR spectrum of the 2,4DHAPDF terpolymers exhibits signals in the region of 6.31-7.56δ (ppm), which may be due to the proton of aromatic ring (Ar-H), and signals in the region 13.10-13.16 δ (ppm) may be attributed to phenolic hydroxyl proton. This significant downfield chemical shift of the protons of the phenolic OH group clearly indicates intramolecular hydrogen bonding of -OH with the carbonyl group at the adjacent ortho position. A methylene proton Ar-CH_2-N moiety was inferred by the appearance of a weak singlet signal at

3.75-3.9 δ (ppm).The presence of a broad signal around 4.24-4.29 δ(ppm) revels the presence of –NH bridges. The methyl proton of the Ar-CO-CH_3 moiety may be identified by the intense peak at 2.23-2.52 δ ppm.

Determination of Molecular weight

The molecular weight (Mn) of the terpolymer was determined by non-aqueous conductometric titration in DMF against ethanolic KOH by using 50 mg of sample. The resistance of solution was measured and a plot of the specific conductance against the miliequivalents of potassium hydroxide required for neutralization of 100g of terpolymer was made (Figure.2). Inspection of such a plot revealed that there were many breaks in the plot. From this plot the first break through and the last break were noted. The calculation of (Mn) by this method is based on the following considerations [19-22].

1. The first break corresponds to neutralization by the more acidic phenolic hydroxyl group of all the repeating units;[2] the break in the plot beyond which a continuous increase is observed represents the stage at which phenolic hydroxyl group of all the repeating units are neutralized. The average degree of polymerization (DP), which is given by the following relation, is found to be the number average molecular weight (Mn) is 2982-4656 which is obtained by multiplying the DP by the formula weight of the repeating unit [23].

$$DP = \frac{\text{Total meq. of base required for complete neutralization}}{\text{meq. of base required for smaller intervals}}$$

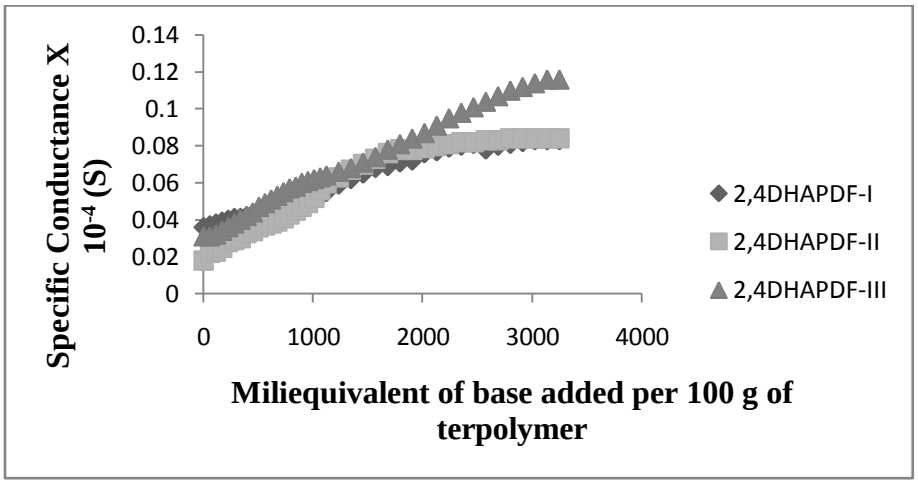

Figure 2. Plot of the specific conductance against miliequivalents potassium hydroxide

Scanning Electron Microscopy

The morphology of the 2,4DHAPDF-I resin was assessed by scanning electron microscopy, and the SEM patterns are shown in Figure.3. The SEM pattern shows micro sized particles.

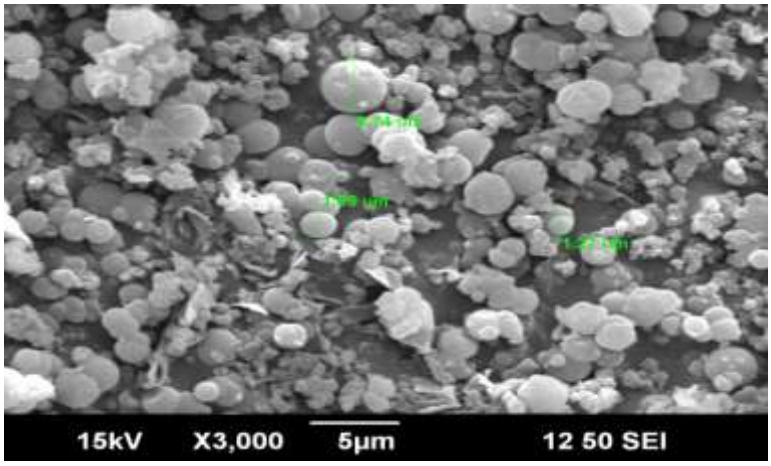

Figure 3. Scanning Electron Microscopy of 2,4DHAPDF-I

Antibacterial activities

Pure culture of pathogenic bacteria, viz., Escherichia coli, Staphylococcus aureus, and Pseudomonas aeruginosa were used for antibacterial activity. Agar diffusion method was used for antibacterial studies. Nutrient agar medium was used for culture of the bacteria. The composition was peptone (10.0 g), sodium chloride (10.0 g), yeast extract (5.0 g) and agar (20.0 g) in 1000 ml of distilled water. Initially, the stock cultures of bacteria were revived by inoculating in broth media and grow at 37 ^{0}C for 18 hrs. The agar plates of the above media were prepared and wells were made in the plate. Each plate was inoculated with 18 hrs. Old cultures (100 µl, 10^{-4} cfu) and spread evenly on the plate. After well were 20 min, the filled with of compound at different concentrations. The control wells with Gentamycin were also prepared. All the plates were incubated at 37^{0}C for 24 hrs and the diameter of inhibition zone was noted. Concentration of samples for antibacterial activity was taken as 800 µg/ml [24, 25].

In order to explore antibacterial activity against Escherichia coli, Staphylococcus aureus and Pseudomonas aeruginosa. Diameters of inhibition zone with respect to standard antibacterial drug (Gentamycin) were measured and results shown in table 1.

Table 1: Relative antibacterial activity of different resins (800 µg/ml)

Sr. No	Compound	Diameter of inhibition zone in mm		
		Escherichia Coli	Staphylococcus aureus	Pseudomonas aeruginosa
1	Resin-I	3	5	4
2	Resin-II	10	15	18
3	Resin-III	15	17	21
4	Gentamycin (Standard)	31	34	14

Comparative antibacterial activity of various resins and standard drug against bacteria viz. E. coli, P. aeruginosa and S. aureus was shown in figure 4.

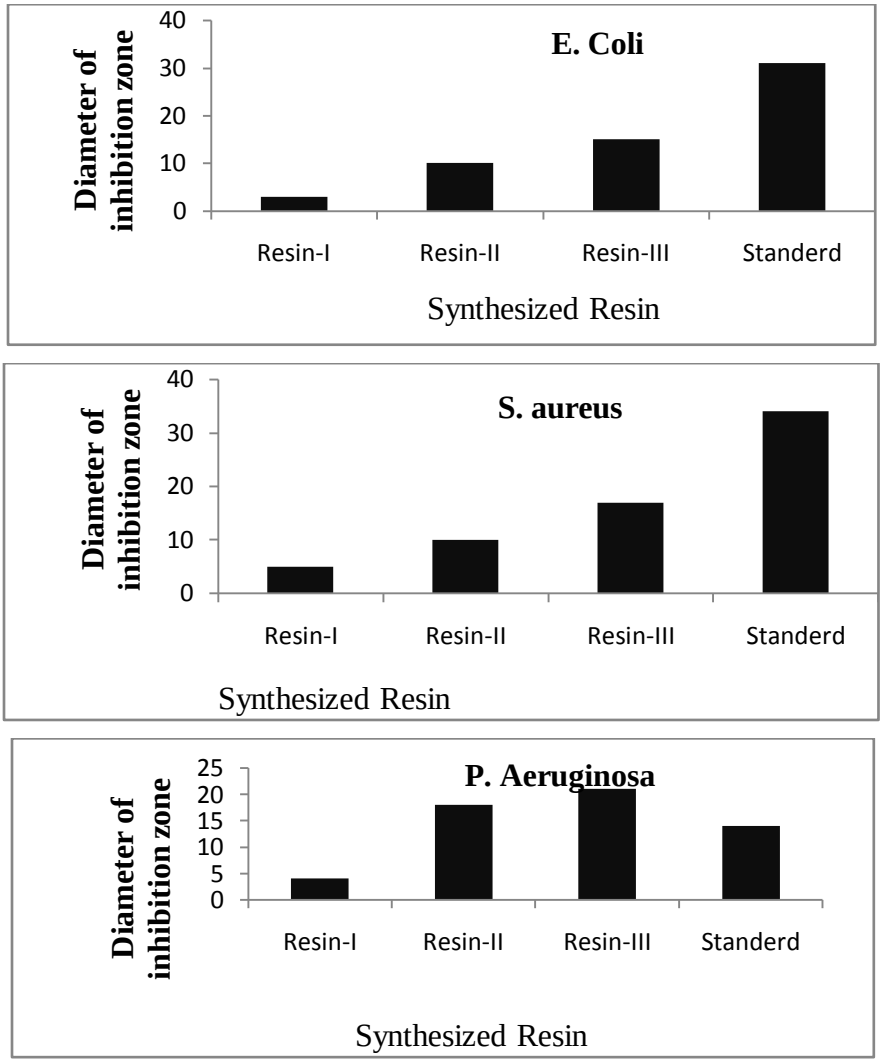

Figure 4. Comparative antibacterial activities of Resin-I, Resin-II, Resin-III

All the synthesized resins show activity against all bacteria. Resin II, Resin III shows better activity than standard against P. Aerugenosa. Among all the resins resin-III shows good activities. The order of toxicity of these resins.

Resin-III > Resin- II > Resin-I

It shows that from resins I to III as aromatic nucleus increases, antibacterial activity increases in the same order.

CONCLUSION

Resins were synthesized by condensing by 2,4 dihydroxyacetophenone (2,4-DHA) and p-phenylenediamine (p-PD)with formaldehyde (F) with three different molar ratios of reacting monomers (1:1:2, 2:1:3, 3:1:4). Resin II, Resin III shows better activity than standard against P. Aeruginosa. Among all, the resin-III shows good antibacterial activities. The order of toxicity of these resins: Resin-III > Resin- II > Resin-I

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