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POLYMER SUPPORTED N,N′-BIS(SALICYLIDENE) HYDRAZINE Co(II) SCHIFF BASE COMPLEX AND ITS CATALYTIC ACTIVITY

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ABSTRACT

N,N′-bis(salicylidene)hydrazine cobalt (II) Schiff base complex immobilized on crosslinked polymer support has been prepared by suspension copolymerization of synthesized N,N′-bis(3-allylsalicylidene) hydrazine monomer along with styrene and divinyl benzene using azobisisobutyronitrile (AIBN) as initiator in the presence of poly(vinyl alcohol) and reacting prepared beads with cobalt (II) chloride solution in dimethyl formamide (DMF). The amount of divinyl benzene in suspension copolymerization has controlled the arrangement and the amount of the N,N′-bis(3-allylsalicylidene)hydrazine monomer in the crosslinked polymer beads. The network structure of the polymer beads has significantly controlled the efficiency of complexation of the N,N′-bis(salicylidene)hydrazine Schiff base with cobalt (II) ions. The swelling behavior has also been affected by the amount of crosslinking agent (DVB) used during copolymerization of functionalized monomer. The crosslinked polymer beads prepared with 1.75 mmol of divinyl benzene have shown highest efficiency of complexation (28.50%) and loading capacity (14.58%) for cobalt (II) ions from the solution of cobalt (II) chloride. The density and size of the beads have also varied on varying the concentration of the divinyl benzene in the reaction mixture. The structural information of the polymer supported cobalt (II) Schiff base

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complex obtained from IR, UV, and magnetic moment (μ) was compared with unsupported cobalt (II) Schiff base complex. The thermal studies have been carried out to determine the application of polymer supported cobalt (II) complex in catalyzing the reactions operating at high temperature. The kinetic investigations on decomposition of hydrogen peroxide recorded with unsupported and supported cobalt (II) Schiff base complex have been used to evaluate the catalytic activity of cobalt (II) complex anchored on polymer support and to estimate the order of reaction with respect to the concentration of hydrogen peroxide and cobalt (II) Schiff base complex. The energy of activation for decomposition of hydrogen peroxide with polymer anchored cobalt (II) complex has been found to be low (45.95 kJ mol^{-1}) in comparison to the unsupported cobalt (II) complex (66.38 kJ mol^{-1}). Reaction steps for the decomposition of hydrogen peroxide have been proposed and a suitable rate expression has been derived.

Key Words: Copolymerization; Catalytic activity; Polymer support; Schiff base complex

INTRODUCTION

The high efficiency and selectivity of polymer supported catalysts have renewed interest in developing environmentally benign recyclable metal catalysts with multidentate polymer anchored ligands which produce catalytic sites of high turn numbers[1] for organic synthesis. Although homogeneous catalysts are chemically efficient, but their catalytic activities[2,3] were frequently reduced to a minimum due to precipitation[4] aggregation, or formation of other products inhibiting the activity of the catalysts. However, polymer bound catalysts are able to overcome these limitations of homogeneous catalysts. The polymer bound catalysts enhance size and positional selectivity and carry out sequential catalytic reactions. They show long life and separated easily from the reactants and the products. They also show high thermal stability and recyclability. Polymer anchored multidentate ligands suppress catalyst deactivation due to stabilization of the complex in comparison to monodentate[5] and bidentate[6] ligands. To immobilize the catalysts, various polymer supports have been used.[7–9] Polymer support in the presence of the solvent provides preferential stereochemistry around the catalytic sites to enhance the catalytic activity of the immobilized catalyst. The linear insoluble polymers are most common supports[10] for immobilizing the catalysts in comparison to crosslinked chloromethylated polystyrene.[11] Many catalytic reactions involving polymer bound metal complexes have shown dependence on the structure of the polymer support[12] because the geometry of the polymer bound metal complex depends upon the structure, rigidity and flexibility of the polymer backbone.

The polymer bound cobalt (II) complexes have been used as oxygen carriers[13] and with square pyramidal geometry as oxidation catalysts.[14] The enantiomeric epoxidation of alkene has been carried out successfully using polymer bound catalysts.[15–18] The polymer bound metal complexes have shown excellent hydrogenation[19] in comparison to homogeneous catalysts.[20] The catalytic activity of the complex on polymer support also depends upon the distance of metal complex from the polymer backbone so that accessibility of the substrate to the metal ion is maximum.[21] These investigations have clearly suggested that the activity and selectivity of the catalyst are highly influenced by the polymer matrix and the geometry of the metal complex on polymer support, hence, synthesis of new polymer support using allyl chloride has been realized as an alternate to Merrifield resin commonly used as support for metal complexes. The cobalt (II) complexes using different ligands have been used as homogeneous and polymer supported catalysts but investigations on catalytic activity of homogeneous and polymer bound cobalt (II) salicylidene hydrazine Schiff base complex are not reported in the literature. Therefore, an effort has been made to synthesize polymer bound salicylidene hydrazine ligand by copolymerization of styrene, N,N′-bis(3-allyl salicylidene)hydrazine monomers in the presence of a suitable amount of divinyl benzene as crosslinking agent and the extent of complexation for cobalt (II) ions has been evaluated as a function of crosslinked density of the prepared beads. The catalytic activity of the polymer bound cobalt (II) Schiff base complex has been evaluated by recording the rate of decomposition of the hydrogen peroxide.

EXPERIMENTAL

Chemicals Used

Salicylaldehyde, hydrazine hydrate were reagent grade chemicals obtained from BDH UK. Styrene, allyl chloride and divinyl benzene (Aldrich Chemical Company USA) were vacuum distilled before using them in synthesis of crosslinked polymer beads.

FTIR-Spectra

The FTIR spectra of free N,N′-bis(salicylidene) hydrazine (SALHZ), N,N′-bis(3-allyl salicylidene) hydrazine, polymer supported N,N′-bis(salicylidene)hydrazine Schiff base and its complex with cobalt (II) ions were recorded on KBr pellets using a Perkin-Elmer 1600 Fourier Transform Infrared Spectrophotometer. The characteristic absorption bands were used to elucidate the structure of the ligand and its cobalt (II) complex.

Electronic Spectra

The electronic spectra of the unsupported ligand and its cobalt (II) complex were recorded in dimethyl formamide (DMF) using a UV-VIS 1601 PC Shimadzu Spectrophotometer. The electronic spectra of polymer anchored N,N′-bis(salicylidene) hydrazine and its cobalt(II) complex were recorded in paraffin oil.

Magnetic Measurements

The dipole moment (μ) and magnetic susceptibility (χ) of the unsupported N,N′-bis(salicylidene)hydrazine cobalt (II) complex and polymer supported N,N′-bis(salicylidene)hydrazine cobalt (II) complex were measured with a Gouy balance at 296K and diamagnetic corrections were made. The data were used to elucidate the structure of homogenized and heterogenized cobalt (II) complexes.

Estimation of Co (II) Ions Loading

The cobalt (II) ions loading capacity of N,N′-bis(salicylidene)hydrazine anchored polymer beads of different crosslinked densities was estimated by leaching cobalt (II) ions in solution and estimating the content of cobalt (II) ions with Perkin-Elmer 2100 Atomic Absorption Spectrophotometer at $\lambda_{max} = 240.7\,nm$.

Thermal Studies

Thermal stability of polymer anchored N,N′-bis(salicylidene)hydrazine Schiff base and its cobalt (II) complex has been evaluated by recording thermograms by Stanton Redcroft STA-780 Thermal Analyzer (UK) at a heating rate of 10°C/min under nitrogen atmosphere. The glass transition temperature (Tg) and melting point (m.p.) of polymer and Schiff base complex of cobalt (II) ion were recorded with Stanton Redcroft DSC-1500 Differential Scanning Calorimeter.

Elemental Analysis

The nitrogen content in unsupported and polymer supported N,N′-bis(salicylidene)hydrazine was estimated by using Perkin-Elmer-240C Elemental Analyzer.

Size Measurements of Polymer Beads

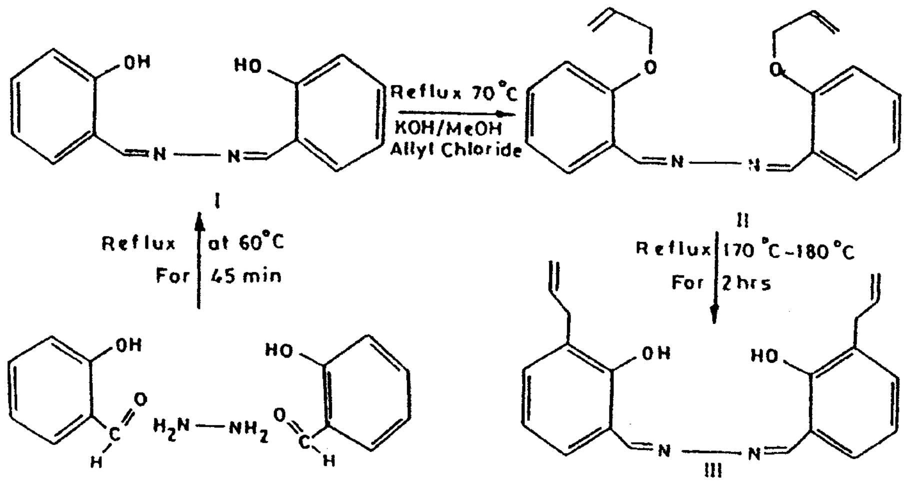
The size of polymer beads prepared with different amount of divinyl benzene was measured with Scanning Electron Microscope (Leo-435 UP England) by mounting beads on metal stubs and vacuum coating with gold.

Swelling Studies

The degree of swelling of the prepared beads with different crosslinked densities was determined by soaking beads for 24 h in dimethyl formamide (DMF) and recording variations in their size with Scanning Electron Microscope.

Synthesis of N,N′-bis(3-Allyl Salicylidene) Hydrazine Monomer

To prepare functionalized N,N′-bis(3-allyl salicylidene)hydrazine monomer (Structure III in Sch. 1), first of all N,N′-bis(salicylidene)hydrazine-(SALHZ) was synthesized by refluxing an ethanolic mixture of salicylaldehyde (20 mmol, 2.44 g) and hydrazine hydrate (10 mmol, 0.5 g) at 50°C for about 1 h, which produced yellow colored crystals on cooling the mixture. The crystals were separated by filtration and purified by washing repeatedly with ethanol and deionized water. Finally, the product was recrystallized from ethanol and dried in a vacuum desiccator on calcium chloride. The IR spectra of N,N′-bis(salicylidene)hydrazine (SALHZ) have shown



Scheme 1.

characteristic absorption bands at 1622 cm^{-1}ν (C=N), 1273 cm^{-1}, ν (C-O) phenolic, and 983 cm^{-1} for ν (N-N) of prepared quadridentate N,N′-bis-(salicylidene)hydrazine Schiff base ligand (Structure I in Sch. 1). The spectrum has shown a broad band between 3390 cm^{-1} to 2968 cm^{-1} due to hydrogen bonding which has covered the stretching vibration of phenolic OH which usually appeared[22] at 3400 cm^{-1}. The elemental analysis corresponded to $C_{14}H_{12}N_2O_2$ (Found in %; C, 70.14; H, 5.1; N, 11.81, Calcd. in %; C, 70.0; H, 5.0 and N, 11.67). To synthesize N,N′-bis(3-allylsalicylidene) hydrazine monomer (Structure III in Sch. 1), the potassium salt of N,N′-bis(salicylidene)hydrazine was prepared by mixing N,N′-bis(salicylidene) hydrazine (10 mmol, 2.4 g) and KOH (20 mmol, 1.14 g) in methanol (20 mL) and stirred vigorously for about 30 min at room temperature. The salt was obtained by removing the solvent with a vacuum evaporator. To obtain N,N′-bis(2-allyloxy salicylidene)hydrazine (Structure II in Sch. 1), 10 mmol (3.18 g) of potassium salt of N,N′-bis(salicylidene)hydrazine and 10 mmol (0.765 g) of allyl chloride in 20 mL of DMF was heated under reflux in the temperature range of 170°C–180°C for about 15 min on oil bath and cooled. The precipitated potassium chloride was removed and the solvent was evaporated to obtain the residue of N,N′-bis(2-allyloxy salicylidene)hydrazine (Structure II in Sch. 1) from the filtrate. After washing the residue repeatedly with cold water, brown colored crystals (Yield, 70%, m.p., 223°C) of N,N′-bis(2-allyloxy salicylidene)hydrazine (Structure II in Sch. 1) were obtained by recrystallization in ethylacetate. The IR spectrum of N,N′-bis(2-allyloxy-salicylidene)hydrazine (Structure II in Sch. 1) has shown characteristic absorption bands at 1624 cm^{-1} ν (C=N), 1150 cm^{-1} ν (C-O-C) ether and 982 cm^{-1} ν (N-N). The elemental analysis of N,N′-bis(2-allyloxy salicylidene) hydrazine (Structure II in Sch. 1) has shown 8.64% nitrogen content (Calcd, 8.76%) which corresponds to $C_{20}H_{20}N_2O_2$. Finally, 10 mmol (3.20 g) of N,N′-bis(2-allyloxy salicylidene)hydrazine (Structure II in Sch. 1) in 50 mL of DMF was heated on oil bath between 170°C–180°C for about two hrs. During this reflux, the N,N′-bis(2-allyloxy salicylidene)hydrazine (Structure II in Sch. I) was converted to N,N′-bis(3-allyl salicylidene)hydrazine (Structure III in Sch. 1) due to the shifting of allyl group to 3-position on salicylidene hydrazine as reported in the literature.[23] After cooling and evaporating the solvent, the brown colored residue was recrystallized twice from 2:1 mixture of toluene and petroleum ether (60–50) which produced 1.5 g brown crystals of N,N′-bis(3-allyl salicylidene)hydrazine (Structure III in Sch. 1) (Yield, 50%; m. p. 225°C–226°C). The IR spectrum of N,N′-bis(3-allyl salicylidene)hydrazine (Structure III in Sch. 1) has shown absorption bands at 1622 cm^{-1} ν (C=N), a broad band due to hydrogen bonding at 3472-2968, 1273 cm^{-1} ν (C-O) phenolic and 983 cm^{-1} ν (N-N) corresponding to the functional groups in the compound (Structure III in Sch. 1). The observed 8.62% of the nitrogen content (Calcd: 8.75%) corresponds to $C_{20}H_{20}N_2O_2$.

Preparation of Functionalized Crosslinked Polymer Beads

To obtain N,N′-bis(salicylidene)hydrazine Schiff base (SALHZ) immobilized on solid polymer support, the suspension polymerization of functionalized monomer (N,N′-bis(3-allyl salicylidene)hydrazine) was carried out using 50 mL degassed toluene containing styrene (48.97 mmol, 5.1 g), divinyl benzene (0.80 mmol, 0.1 g) and synthesized N,N′-bis(3-allyl salicylidene) hydrazine monomer (8.85 mmol, 2.83 g) and a 10 mL solution of azobisisobutyronitrile (0.15 g) in toluene. To initiate copolymerization, the solution of both monomers and initiator were added dropwise in a three-necked round bottom flask containing gelation (0.75 g), bentonite (2.0 g), boric acid (2.5 g), and poly(vinyl alcohol) (1.5 g) in 500 mL of water. The reaction flask was equipped with a mechanical stirrer and condenser to prevent the evaporation of monomers during copolymerization. The suspension was heated at 70°C, stirred vigorously to dissipate the heat generated during polymerization and crosslinking reactions taken placed between polymeric chains. The constant stirring also controlled the size of the beads. At the end of 2 h, the heating was stopped and suspension was allowed to cool to room temperature by stirring for another 30 min before transferring the suspension into a beaker. The yellow colored beads were allowed to settle and the supernatant liquid was removed. The resulting beads were washed with methanol (4 × 50 mL) and hot water to remove the impurities. The purified beads were finally dried in vacuum oven at 70°C for 24 h. (Yield, 78%, 6.264 g). The beads of different crosslinked densities were obtained by taking a different amount of divinyl benzene as shown in Table 1. The size of the beads were measured with a scanning electron microscope (Table 1). The IR spectrum of the beads was recorded on KBr pellets, which have shown absorption bands at 1619 cm^{-1} ν (C=N), 1270 cm^{-1} ν(C-O) and 980 cm^{-1} ν(N-N) corresponding to the functional groups of N,N′-bis(salicylidene)hydrazine ligand on polymer support. The amount of N,N′-bis(3-allylsalicylidene)hydrazine monomer in

Table 1. Composition and Characteristics of Cobalt (II) Complex Anchored Beads

Types of Beads	DVB mmol	Size (μm)	ρ (g cm^{-3})	S (%)	F. M. in Beads (mmol g^{-1})	EL (%)	EC (%)
I	0.80	146	0.44	6.20	1.80	7.56	21.00
II	1.15	133	0.47	4.82	2.15	9.88	23.00
III	1.50	124	0.49	3.62	2.35	12.68	27.00
IV	1.75	114	0.52	2.89	2.56	14.58	28.50
V	2.00	97	0.56	1.12	2.00	11.20	28.00

[Styrene] = 48.97 mmol, [F.M] = 8.85 mmol, Divinyl benzene (DVB), Functionalized monomer (F.M.), Swelling (S).

the polymer was estimated with the nitrogen content available in the known amount of the beads. The nitrogen content (4.04%) in the beads revealed that 1.0 g of beads (Type I) contains 1.8 mmol (0.428 g) of the ligand.

Complexation of Cobalt (II) Ions on Polymer Bound N,N′-bis(Salicylidene)Hydrazine Schiff Base

The complexation of cobalt (II) ions with polymer anchored N,N′-bis(salicylidene) hydrazine Schiff base has been carried out by keeping 1.0 g N,N′-bis(salicylidene) hydrazine anchored beads in a 40 mL solution of cobalt chloride (5.0 mmol, 1.1896 g) for about 8 hrs under reflux on oil bath at 90°C to 95°C. To enhance the extent of complexation of cobalt (II) ions, the beads were swollen in DMF for 1 h prior to the complexation with cobalt chloride. After refluxing the beads for 8 h in a solution of cobalt (II) chloride, the mixture was cooled and the separated beads were washed repeatedly with methanol and deionized water. Finally, the blue colored beads were dried in a vacuum desiccator over anhydrous calcium chloride (Yield, 70%). To prevent the oxidation of cobalt (II) to cobalt (III) state, the reaction was carried out under inert atmosphere. The IR spectra of the beads have shown absorption bands at 1603 cm^{-1}, ν (C=N), 1307 cm^{-1}, ν (C-O) phenolic, and 995 cm^{-1}, ν (N-N).

Measurements of Cobalt (II) Ions Loading

To determine the extent of complexation of cobalt (II) ions with polymer bound N,N′-bis(salicylidene)hydrazine ligand, 1.0 g of cobalt (II) ions loaded beads were placed in a conical flask containing 20 mL of 4 N acetic acid and refluxed for 2 h on heating mentle at 110°C. The amount of cobalt (II) ions released in the solution was estimated with a atomic absorption spectrometer at $\lambda_{\max} = 240.7$ nm. 1.0 g of beads (Type I) were found to contain 0.378 mmol of the cobalt (II) ions. The cobalt (II) ions loading of beads with different crosslinked density was estimated by applying a similar analysis procedure. The loading of cobalt (II) ions has been evaluated as: efficiency of complexation (% EC) and efficiency of loading (% EL) using the following equations and calculated values are recorded in Table 1.

$$\%\ \text{EC} = \frac{\text{Amount of Co(II) ions loaded g}^{-1}\text{ of beads}}{\text{Amount of ligand available for complexation g}^{-1}\text{ of beads}} \times 100$$

$$\%\ \text{EL} = \frac{\text{Amount of Co(II) ions loaded g}^{-1}\text{ of beads}}{\text{Amount of Co(II) ions taken initially}} \times 100$$

Decomposition Kinetics of Hydrogen Peroxide

To evaluate the catalytic activity of polymer supported cobalt (II) complex, the rate of decomposition of hydrogen peroxide has been evaluated by placing 100 mg of Co (II) ions loaded beads in a conical flask containing a 100 mL solution of hydrogen peroxide of known molarity prepared with hydrogen peroxide of two volume (0.6% w/w). The reaction flask was thermostatted to $25.0 \pm 0.1°C$ under constant stirring. The extent of hydrogen peroxide decomposed at different intervals of time was estimated by taking 5.0 mL aliquot of reaction mixture and titrating it with 0.01 M $KMnO_4$ in the presence of 0.01 M H_2SO_4. The procedure was repeated at different initial concentrations of hydrogen peroxide, reaction temperature, and taking beads of different loading capacity. The catalytic activity of polymer supported cobalt (II) complex for decomposition of hydrogen peroxide was compared with an unsupported cobalt (II) complex following a similar procedure as used for polymer supported cobalt (II) complex. The polymer anchored N,N′-bis(salicylidene)hydrazine without cobalt (II) ions has not shown any activity toward decomposition of the hydrogen peroxide.

RESULTS AND DISCUSSION

Polymer heterogenized homogeneous catalysts show high catalytic efficiency and activity provided the geometry of the metal complex is essentially unchanged and the anchored complex is easily accessible to the solvent and reactants. The heterogenized homogeneous catalyst on optimum crosslinked polymer support functions mechanistically as if the heterogenized catalyst is in solution, but operates as a separate immobilized phase. The homogeneous catalysts have been heterogenized on inorganic supports such as silica, alumina,[24] but due to lack of flexibility in these supports, the immobilized complex is unable to show the properties of homogeneous catalyst. The highly crosslinked polymer support show low catalytic activity as its metal ions loading capacity is low and the internal surface is not available to the reactants. As the crosslinked density increases, the mobility of the polymer segment or anchored complex is decreased. Similarly, the low crosslinked and linear polymer supports[25] are also not suitable due to the low internal surface needed to accommodate a high concentration of reactant molecules nearby to active sites onto polymer support. The immobilization of cobalt (II) complexes on polymer support by reacting the complex or ligand with functional group on polymer backbone is well reported,[26,27] but synthesis of polymer supported cobalt (II) complex using chelating polymer is not reported in the literature. The synthesis of chelating polymer by copolymerization of allylated ligand provides ample opportunities to prepare tailor-made polymer support with a high degree of chelating sites for the metal ions. The crosslinked beads, prepared by copolymerization of allylated ligand, have shown a high loading capacity as shown in Table 1. The degree of crosslinking has shown variations in the size and degree of swelling capacity, as is clear from the data. The degree of swelling (S%) has decreased on increasing the crosslinked density, whereas the metal ions loading capacity has continued to increased up to optimum crosslinked density (1.75 mmol of DVB) and has shown a significant decrease in the metal ions loading capacity. The beads with an optimum degree of crosslinking (1.75 mmol of DVB) have shown 2.89% degree of swelling as calculated using SEM photographs of the beads (Type IV) before and after swelling (Fig. 1a,b). The complexation of polymer supported N,N′-bis(salicylidene)hydrazine (Fig. 2a) with cobalt (II) ions (Fig. 2b) has shown a drastic increase in thermal stability which has clearly indicated that a polymer supported cobalt (II) complex could be used as a catalyst for high temperature reactions.

The structure and catalytic activity of the N,N′-bis(salicylidene)hydrazine cobalt (II) complex has not been reported in the literature. Therefore, the synthesis of cobalt (II) complex using N,N′-bis(salicylidene)hydrazine Schiff base and evaluation of its catalytic activity in comparison to homogeneous catalysts has been found useful to compare the effect of polymer support on the structure and catalytic activity of the complex. The N,N′-bis(salicylidene)hydrazine Schiff base has been prepared by reacting salicylaldehyde and hydrated hydrazine which has produced a sufficient amount of N,N′-bis(salicylidene) hydrazine (Yield: 71%). The IR spectra of N,N′-bis(salicylidene)hydrazine Schiff base have shown absorption bands at $1622\,cm^{-1}$ and $1273\,cm^{-1}$, which indicated the presence of azomethine group (C=N) and phenolic groups (C-O) in the ligand. The IR spectrum has also shown a band at $983\,cm^{-1}$ attributed to the presence of hydrazine group (N-N) in the compound. The formation of N,N′-bis(salicylidene)hydrazine Schiff base has also been confirmed by the elemental analysis of the prepared Schiff base. The hydrogen bonding in the ligand has shown a broad band for a frequency range of $3390\,cm^{-1}$ to $2968\,cm^{-1}$ which masked the absorption band of phenolic hydroxyl group available in the ligand.

Synthesis and Characterization of N,N′-bis(Salicylidene)Hydrazine Cobalt(II) Complex

The N,N′-bis(salicylidene)hydrazine cobalt (II) complex has been prepared by the reaction of N,N′-(salicylidene)hydrazine Schiff base and cobalt (II) chloride ($CoCl_2$, $6H_2O$), which has produced maroon colored crystalline N,N′-bis(salicylidene)hydrazine cobalt (II) complex (Yield: 70%). The IR spectra of the complex recorded on KBr pellet have shown absorption at $1607\,cm^{-1}$ for the presence of azomethine group (C=N). The shift in the position of absorption band from $1622\,cm^{-1}$ to $1607\,cm^{-1}$ in the prepared

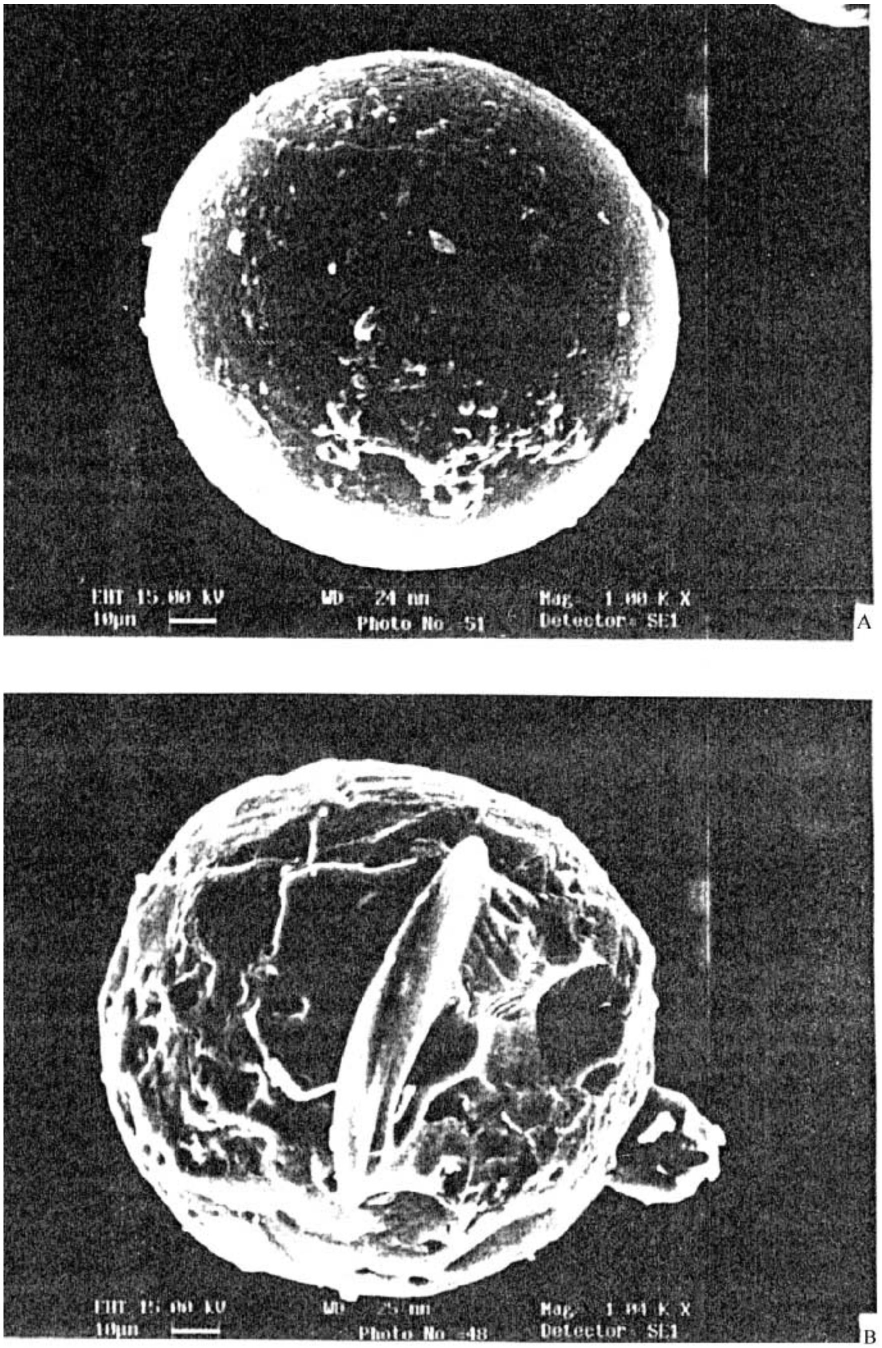


Figure 1. Scanning electron micrographs of crosslinked polymer beads before (A) and after swelling (B).

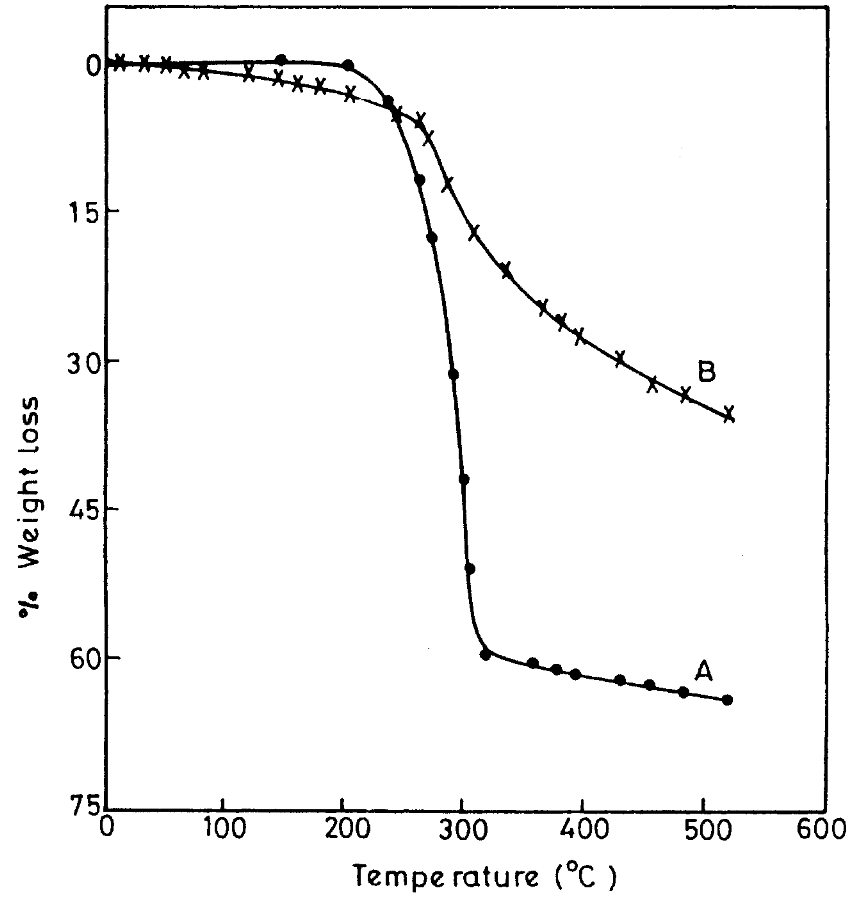


Figure 2. TG curves for polymer anchored Schiff base (A) and its cobalt (II) complex (B).

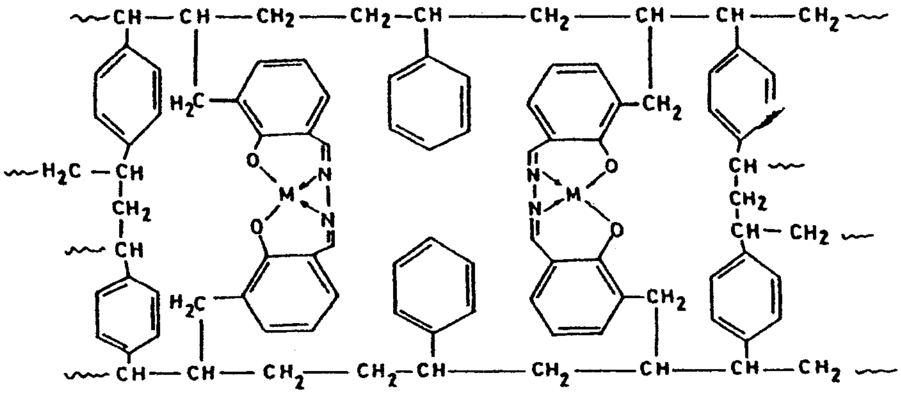
cobalt (II) complex has confirmed the coordination of azomethine with cobalt (II) ions through nitrogen atom. The absence of absorption band for OH group in the IR spectrum of the complex in the region 2968 cm^{-1}–3390 cm^{-1} has clearly indicated the complexation of cobalt (II) ions through the phenolic oxygen of the N,N′-bis(salicylidene)hydrazine Schiff base. The absorption band at 1273 cm^{-1} due to ν (C-O) phenolic and medium intensity band at 983 cm^{-1} due to ν (N-N) hydrazine in the spectrum of the free ligand (N,N′-bis(salicylidene)hydrazine) have undergone a shift to a high wave number at 1310 cm^{-1} and 998 cm^{-1}, respectively. These shifts in the absorption bands have clearly suggested the coordination of N,N′-bis(salicylidene) hydrazine Schiff base with cobalt (II) ions. The electronic spectra of the free Schiff base have shown bands at 246 nm and 299 nm, which on complexation with cobalt (II) ions shifted to 236 nm and 246 nm. The shift in these absorption bands has clearly indicated the coordination of ligand with the cobalt (II) ions. The electronic spectrum of the cobalt (II) Schiff base complex has shown two additional bands within the frequency range from 269 nm–455 nm The appearance of an absorption band at 269 nm has been attributed to charge transfer transitions (L-M) in the cobalt (II) complex. The low energy band at 455 nm in the complex is due to the presence of d-d transitions, which has been suggested for square planer structure of cobalt (II) complex with N_2O_2 chromophore. These observations are analogue to the previous investigations reported for low spin square planer complex of cobalt (II) ions with quadridentate chromophore.[28] The observed magnetic moment (μ) of cobalt (II) complex was 1.95 BM at 296K, which correspond to the presence of one unpaired electron. This has been attributed for the formation of low spin square planer structure in cobalt (II) complex.[29]

Synthesis and Characterization of Polymer Supported N,N′-bis(Salicylidene)Hydrazine Cobalt (II) Complex

In order to prepare polymer supported N,N′-bis(salicylidene)hydrazine cobalt (II) complex, first of all N,N′-bis(3-allyl salicylidene)hydrazine monomer (Structure III in Sch. 1) was prepared with allyl chloride and N,N′-bis(salicylidene)hydrazine as shown in Sch. 1. The appearance of characteristic absorption bands in the IR spectrum of the synthesized N,N′-bis(3-allyl salicylidene)hydrazine have confirmed the formation of this monomer. The copolymerization of this monomer with styrene and divinyl benzene has produced a crosslinked polymer with pendant N,N′-bis(salicylidene)hydrazine Schiff base for complexation with cobalt (II) ions. The amount of the N,N′-bis(salicylidene)hydrazine has been estimated by calculating the nitrogen content which has been found to be dependent on the degree of crosslinking in the synthesized polymer. The IR spectrum of N,N′-bis(salicylidene)hydrazine Schiff base anchored polymer beads has shown characteristic absorption bands for azomethine ν (C=N) at 1619 cm^{-1}, phenolic oxygen ν (C-O) at 1270 cm^{-1} and hydrazine ν (N-N) band at 980 cm^{-1} which have shown a slight variation in their values in comparison to unsupported N,N′-bis(salicylidene)hydrazine Schiff base. The spectra has also shown a broad band in the frequency region from 3377 cm^{-1}–2966 cm^{-1}, which has indicated the presence of hydrogen bonding as a part of the resonating ring system.[22] The electronic spectrum of the polymer supported N,N′-bis(salicylidene)hydrazine Schiff base complex has shown bands at 243 nm and 296 nm which correspond to π-π* and n-π* transitions in the ligand. The complexation of this polymer anchored ligand with cobalt (II) ions has given IR bands at 1603 cm^{-1} for the azomethine ν (C=N), which has indicated the coordination of cobalt (II) ions through nitrogen atom of the azomethine group. The phenolic ν (C-O) and hydrazine ν (N-N) bands were shifted to high wave number 1307 cm^{-1} and 995 cm^{-1}, respectively, which have clearly supported the coordination of cobalt (II) ions with polymer anchored ligand. The appearance of two new bands at 586 cm^{-1} and 454 cm^{-1} are the characteristics of M-O and M-N bonds, hence, these bands have further confirmed the coordination of cobalt (II) ions with polymer supported ligand. The UV spectra of polymer bound N,N′-bis(salicylidene)hydrazine cobalt (II) complex has shown absorption bands at 234 nm and 244 nm corresponding to π-π^* and n-π^* transitions. The variation in the peak position of the absorption bands has clearly indicated the coordination of the cobalt (II) ions with nitrogen of azomethine. Two new additional bands in the range of 267 nm−453 nm were also observed. The band at 453 nm has been attributed to d-d transitions which has confirmed the square planer structure of the N,N′-bis(salicylidene)hydrazine cobalt (II) complex anchored on polymer support. The band at 267 nm has been attributed to the coordination of ligand to cobalt (II) metal ions by charge transfer process (CT). The magnetic moment (μ) of the polymer supported cobalt (II) complex has been found to be 1.97 BM at 296K which has further supported the square planer geometry of the complex onto the polymer. The IR, UV and magnetic moment have clearly indicated that polymer supported cobalt (II) complex has similar geometry as found with unsupported cobalt (II) complex. However, the extent of complexation of cobalt (II) ions with supported ligand was different in composition to free ligand, which has been attributed to the variations in flexibility[30] and configurational hindrance[31] of the ligand at the polymer surface but the structure of the cobalt (II) complex was the same as supported by spectral and magnetic measurements.

Swelling and Complexation Behavior of Polymer Beads

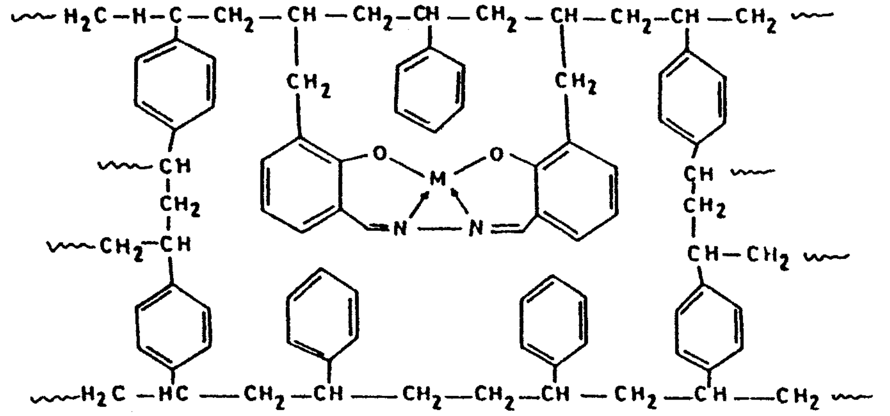
The polymer beads prepared with a different amount of divinyl benzene ranging from 0.8 mmol to 2.0 mmol at a constant concentration of styrene (48.97 mmol) and N,N′-bis(3-allyl salicylidene)hydrazine monomer (Structure III in Sch. 1) have shown a decreasing trend in the degree of swelling (%S) on increasing the amount of divinyl benzene (Table-1). This decreasing trend in degree of swelling on increasing the amount of divinyl benzene is due to the increase in crosslinking between polymer chains which has decreased the size of the pores in the beads, hence, limited the diffusion of swelling agent (DMF) inside the beads. The degree of crosslinking has also affected the size of the beads and extent of complexation of cobalt (II) ions with polymer anchored N,N′-bis(salicylidene)hydrazine. At low concentration of the divinyl benzene, the arrangement of the N,N′-bis(3-allyl salicylidene)-hydrazine in copolymer is attributed as a crosslinker as shown in polymer network structure (Structure IVA) which has created high flexible polymer matrix with high pore volume, hence the degree of swelling was high at low concentration of the divinyl benzene. On further increasing the amount of



Scheme 2. Structure IVA: the network structure of the beads at low concentraton of DVB.

divinyl benzene up to 1.75 mmol, the amount of functional monomer (N,N′-bis(3-allyl salicylidene)hydrazine) has continued to increase form 1.80 mmol to 2.56 mmol, but on further increasing the amount of divinyl benzene beyond 1.75 mmol, the amount of functional monomer in the polymer beads has decreased to 2.00 mmol (Table 1). At high concentration of divinyl benzene (>1.75 mmol), the functional monomer has consumed largely in the formation of polymer backbone and crosslinking between chains was exclusively by divinyl benzene. The polymer matrix obtained at high divinyl benzene was highly porous with small pore volume (Structure IVB). The network structure of the polymer beads obtained at a high amount of the divinyl benzene was different (Structure IVB) than obtained at a low amount of the divinyl benzene (Structure IVA).

The high degree of crosslinking has decreased the degree of swelling and also decreased the efficiency of complexation and efficiency of loading for



Scheme 3. Structure IVB: the network structure of the beads at high concentraton of DVB.

cobalt (II) ions. The beads prepared with 1.75 mmol of divinyl benzene have shown swelling of 2.89%, efficiency of loading of 14.58%, and complexation of 28.50% for cobalt (II) ions, hence, these beads were used for detailed investigations on kinetics of decomposition of hydrogen peroxide. The variation in density of the beads on increasing the amount of the divinyl benzene is due to the decrease in porosity due to a high degree of crosslinking between the chains as clear from the network structure of the beads (Structure IVB).

Catalytic Activity of Polymer Supported N,N′-bis(Salicylidene)Hydrazine Cobalt (II) Schiff Base Complex

To investigate the effect of heterogenization of cobalt (II) Schiff base complex on new polymer support, the rate of decomposition of hydrogen peroxide has been determined using both unsupported and supported cobalt (II) Schiff base complex under similar experimental conditions. The catalytic activity of the homogenized and heterogenized cobalt (II) complexes has been studied at different initial concentrations of hydrogen peroxide and as a function of a different amount of the catalyst (cobalt (II) complex). To vary the amount of the heterogenized catalyst in the reaction mixture, polymer beads of different cobalt (II) ions loading capacity were taken and a rate of decomposition of hydrogen peroxide has been used to compare the effect of heterogenization of cobalt (II) complex with respect to homogenized cobalt (II) complex. Polymer beads with an optimum degree of swelling and cobalt (II) ions loading (Type IV) were used for a concentration variation of hydrogen peroxide and a variation of reaction temperature. The rate of hydrogen peroxide decomposition has been evaluated by varying the concentration of hydrogen peroxide from $1.79 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ to $5.95 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$, at a constant concentration of the heterogenized cobalt (II) complex (Beads IV) at 25°C. The rate of decomposition of the hydrogen peroxide has been found to be high ($k = 5.4 \times 10^{-3}\,\mathrm{min^{-1}}$) in the presence of a heterogenized cobalt (II) complex in comparison to homogenized cobalt (II) complex ($k = 8.4 \times 10^{-5}\,\mathrm{min^{-1}}$) as clear from the plot (Fig. 3) drawn between log(a−x) vs. time using homogenized cobalt (II) complex ($8.0 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$) and heterogenized cobalt (II) complex ($7.29 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$) at a constant concentration of hydrogen peroxide ($3.57 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$). The linear decrease in log(a–x) as a function of reaction time (Fig. 3) has indicated that the rate of decomposition of hydrogen peroxide is first order with respect to the concentration of the hydrogen peroxide. The slope of log-log plot (Fig. 4a) drawn between the rate of decomposition (R_P) vs. concentration of hydrogen peroxide has been found to be in agreement, which has further confirmed first order with respect to the concentration of the hydrogen peroxide. A similar value was obtained with homogenized cobalt (II) complex (Fig. 4b). However, the rate of decomposition of

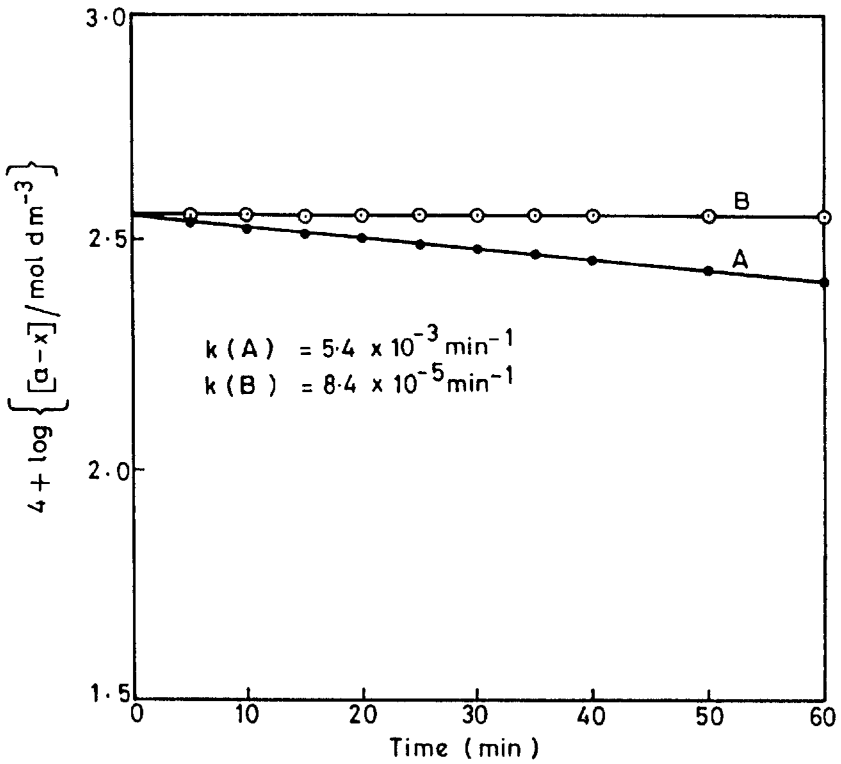


Figure 3. Effect of reaction time on decomposition of H_2O_2 with supported (A) and unsupported (B) cobalt (II) Schiff base complexes. $[H_2O_2] = 3.57 \times 10^{-2}$ mol dm^{-3}, [Co (II)] (A) = 7.29×10^{-4} mol dm^{-3}, (B) = 8.0×10^{-4} mol dm^{-3}, pH = 7.5, $\mu = 0.4$ mol dm^{-3}, Temp. = 25°C.

hydrogen peroxide in the presence of homogenized cobalt (II) complex was slow as clear from Fig. 4b. This has clearly indicated that the efficiency of the catalyst has increased on supporting at polymer due to the decrease in extent of deactivation of cobalt (II) ions due to segregation at polymer support and, the environment of ligand on polymer support has provided a sufficient chance for reacting molecules of hydrogen peroxide to interact with cobalt (II) ions for their decomposition. In order to determine the effect of concentration of cobalt (II) complex immobilized on polymer support, the rate of decomposition of hydrogen peroxide has been determined taking fixed amount of beads (100 mg dm^{-3}) of different cobalt (II) ion loading capacity ranging from 0.378 mmol g^{-1} to 0.56 mmol g^{-1} (Beads I–V) and taking fixed concentrations of hydrogen peroxide (3.57×10^{-2} mol dm^{-3}) at 25°C. The calculated rate of decomposition of hydrogen peroxide has been used to determine the order of reaction with respect to cobalt (II) ions by drawing log-log plot (Fig. 5a) between R_p Vs concentration of cobalt (II) ions present on polymer support. The slope of log R_p vs. log[cobalt (II) ions on polymer support] has been found to be in agreement (Fig. 5a), which has indicated

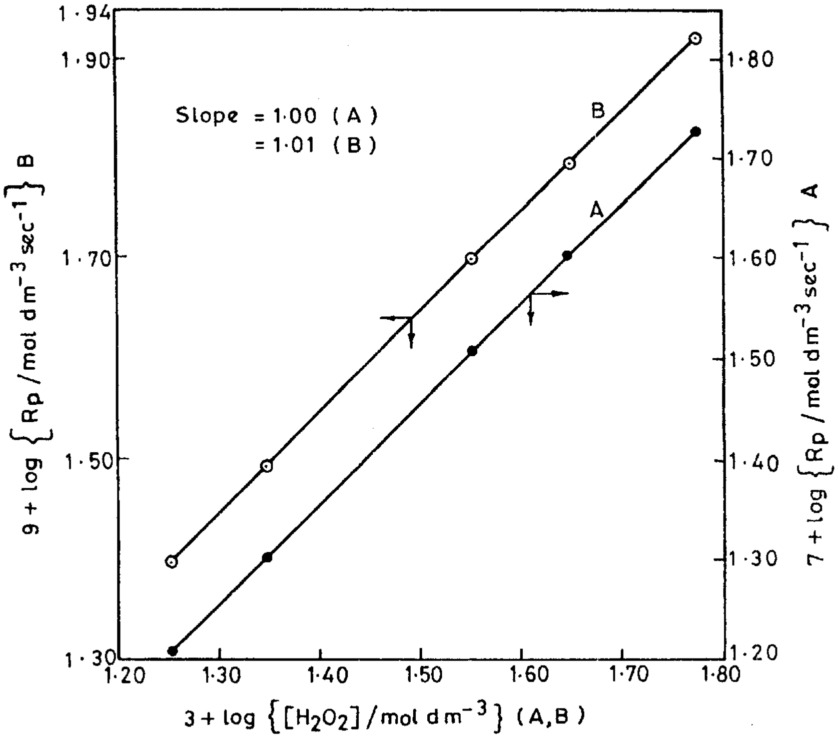


Figure 4. Log-log plot between Rp Vs [H_2O_2] with supported (A) and unsupported (B) cobalt (II) Schiff base complexes. [Co (II)] (A) = 7.29×10^{-4} mol dm^{-3}, (B) = 8.0×10^{-4} mol dm^{-3}, pH = 7.5, $\mu = 0.4$ mol dm^{-3}, Temp. = 25°C.

first order with respect to the concentration of cobalt (II) ions present in polymer supported cobalt (II) complex. To evaluate the effect of heterogenization of cobalt (II) ions on polymer support, the rate of decomposition of hydrogen peroxide has also been estimated by varying cobalt (II) ions concentration from 2.0×10^{-4} mol dm^{-3} to 10.0×10^{-4} mol dm^{-3} taking homogenized cobalt (II) complex and keeping a fixed concentration of the hydrogen peroxide (3.57×10^{-2} mol dm^{-3}) at 25°C. The order of decomposition reaction of hydrogen peroxide in the presence of homogenized cobalt (II) ions has been found to be in agreement as is clear from the plot (Fig. 5b) drawn between log R_p vs. log[cobalt (II) ions]. This has clearly indicated that the mechanism decomposition of hydrogen peroxide with unsupported catalyst is almost similar to the mechanism operating in the presence of a supported cobalt (II) complex. The temperature effect on decomposition of hydrogen peroxide in the presence of heterogenized and homogenized cobalt (II) ions has also been estimated by varying temperature from 25°C to 50°C at a constant concentration of the hydrogen peroxide (3.57×10^{-2} mol dm^{-3}). The rate of decomposition of hydrogen peroxide with heterogenized cobalt

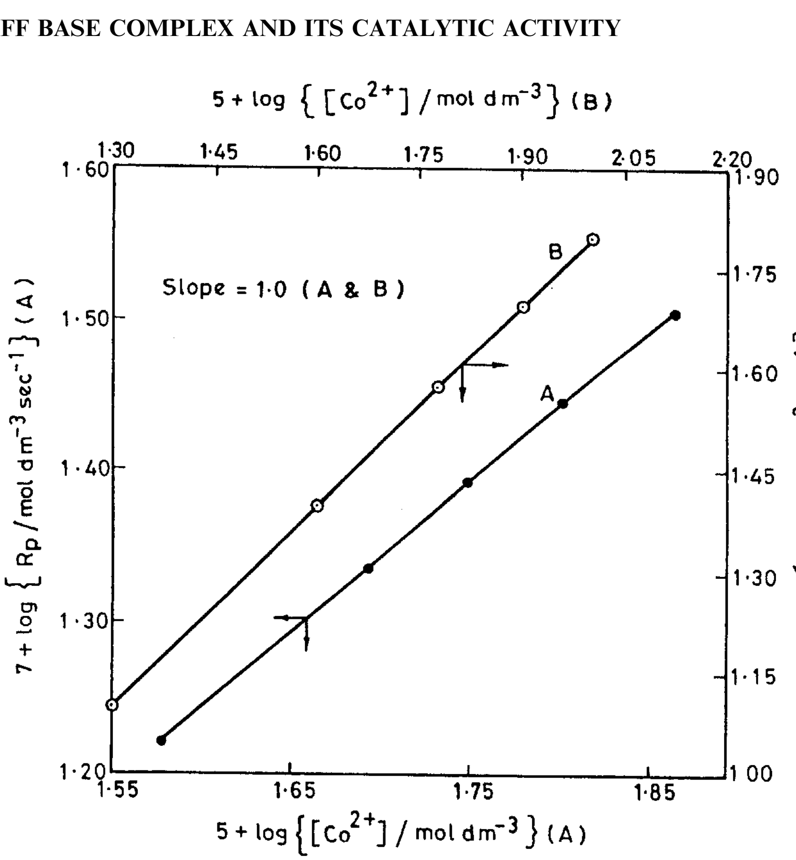


Figure 5. Log-log plot between Rp Vs [Co (II)] with supported (A) and unsupported (B) cobalt (II) Schiff base complexes. $[H_2O_2] = 3.57 \times 10^{-2}$ mol dm^{-3}, pH = 7.5, $\mu = 0.4$ mol dm^{-3}, Temp. = 25°C.

(II) ions has been found to be low ($E_a = 45.95$ kJ mol^{-1}) in comparison to homogenized cobalt (II) ions ($E_a = 66.38$ kJ mol^{-1}) as clear from the Arrhenius plot (Fig. 6). The low activation energy for the decomposition of hydrogen peroxide with heterogenized catalyst has clearly indicated that the immobilized ligand on polymer support has increased the catalytic activity of the cobalt (II) ions in comparison to the homogenized ligand. The rate of decomposition of hydrogen peroxide has shown inverse dependence to the concentration of the hydrogen ions during pH variation from 2.0 to 7.5 but has increased significantly on taking pH beyond 7.5 (Fig. 7). The rate of decomposition of hydrogen peroxide has shown variation with ionic strength (μ) of the medium, which has indicated the involvement of ions during the decomposition mechanism of hydrogen peroxide in the presence of the cobalt (II) complex. The reaction was inhibited in the presence of acetate ions due to its high affinity to coordinate with cobalt (II) ions in comparison to $^{-}$OOH ions produced as intermediate during decomposition of hydrogen peroxide. The rate of decomposition of hydrogen peroxide in the presence of Schiff

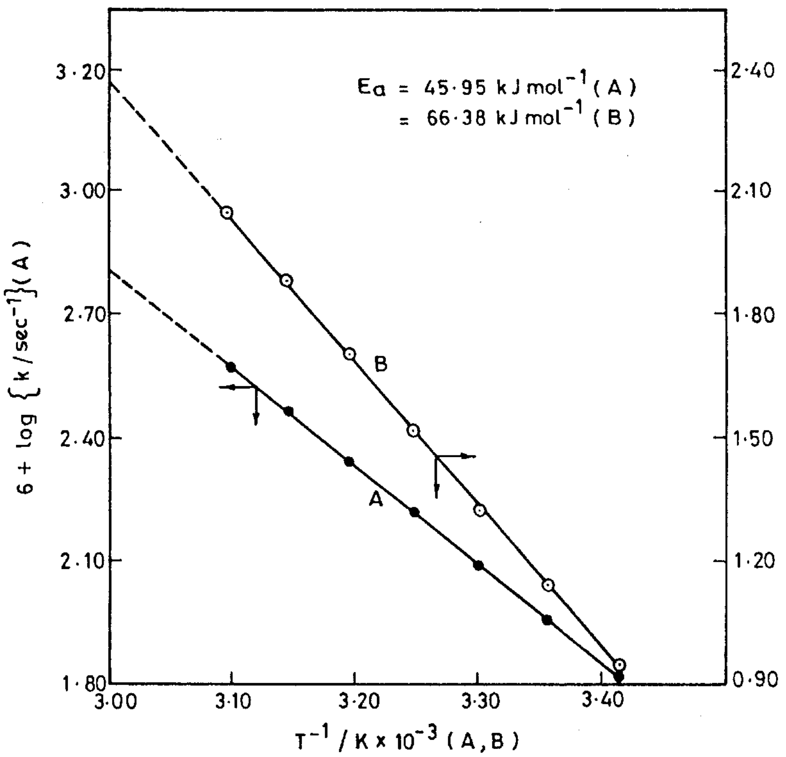


Figure 6. Arrhenius plot for decomposition of H_2O_2 using supported (A) and unsupported (B) and cobalt (II) Schiff base complexes. $[H_2O_2] = 3.59 \times 10^{-2}$ mol dm^{-3} [Co (II)] (A) = 7.29×10^{-4} mol dm^{-3}, (B) = 8.0×10^{-4} mol dm^{-3}, pH = 7.5, $\mu = 0.4$ mol dm^{-3}.

base complex of iron (III)[32] and cobalt (II)[33] on alumina and polymer support has shown second order dependence on the hydrogen peroxide concentration, which has indicated that the mechanism of decomposition of hydrogen peroxide also depends on the type of complex and the support used for immobilizing metal complex. The order of decomposition of hydrogen peroxide, both with supported and unsupported cobalt (II) complex, has been found to be the same, hence, similar reaction steps have been proposed for the decomposition of hydrogen peroxide in the presence of N,N′-bis(salicylidene) hydrazine cobalt (II) complex.

$$H_2O_2 \xrightarrow{k_d} \bar{O}OH + H^+ \tag{1}$$

$$(Co(II)(SALHZ)_2) + \bar{O}OH \xleftrightarrow{K} (Co(II)(SALHZ)_2OOH)^- \tag{2}$$

$$(Co(II)(SALHZ)_2OOH)^- \xrightarrow[SLOW]{k_1} (Co(II)(SALHZ)_2) + \frac{1}{2}O_2 + \bar{O}H \tag{3}$$

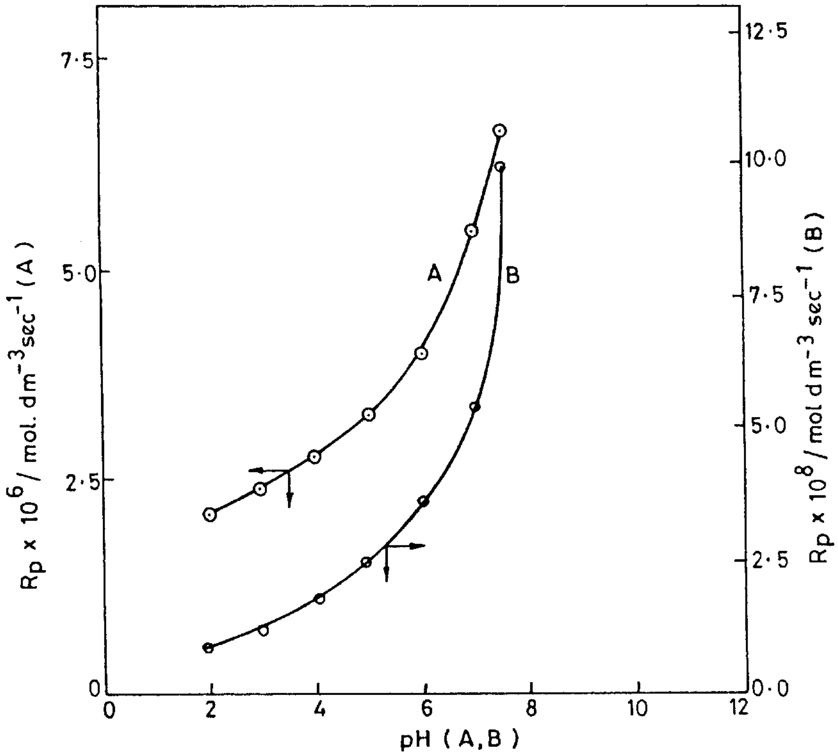


Figure 7. Effect of pH on rate of decomposition of H_2O_2 with supported (A) and unsupported (B) cobalt (II) Schiff base complexes. $[H_2O_2] = 3.57 \times 10^{-2}$ mol dm^{-3}, [Co (II)] (A) = 7.29×10^{-4} mol dm^{-3} (B) = 8.0×10^{-4} mol dm^{-3}, $\mu = 0.4$ mol dm^{-3}, Temp. = 25°C.

$$\bar{O}H + H^+ \xrightarrow{K_1} H_2O \tag{4}$$

The rate expression for decomposition of hydrogen peroxide has been derived using steps 1–4 considering reaction step 3 as a rate determining step.

$$\frac{-d[H_2O_2]}{dt} = \frac{k_d K k_1 [Co(II)(SALHZ)_2][H_2O_2]}{[H^+]} \tag{5}$$

Where k_d and k_1 are the rate constants for the dissociation of hydrogen peroxide and decomposition of the intermediate complex. The K is equilibrium constant for the formation of intermediate complex between ^{-}OOH ions and cobalt (II) Schiff base complex (Co (II) (SAlHZ)$_2$).

The rate expression as derived (Eq. 5) above is in agreement with the experimental observations for the order of reaction with respect to the concentration of hydrogen peroxide, cobalt (II) ions and concentration of hydrogen ions, hence, the proposed steps 1–4 have been considered reasonably correct to explain the decomposition of hydrogen peroxide using supported and unsupported cobalt (II) Schiff base complex.

CONCLUSION

The copolymerization of the allylated Schiff base monomer with styrene and divinyl benzene has produced polymer support with sufficient amount of pendant N,N′-bis(salicylidene)hydrazine ligand for complexation with cobalt (II) ions, hence, the prepared polymer beads have shown a high degree of complexation for cobalt (II) ions by the polymer anchored Schiff base. The catalytic activity has been found to be dependent on the degree of cross-linking and swelling of the polymer beads prepared taking a different amount of divinyl benzene. Rate expression has shown agreement with experimental observations.

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