

# Polymer anchored Schiff base complexes of transition metal ions and their catalytic activities in oxidation of phenol

K.C. Gupta\*, A.K. Sutar

*Polymer Research Laboratory, Department of Chemistry, Indian Institute of Technology, Roorkee 247667, India*

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## Abstract

The polymer anchored transition metal complexes of *N,N'*-bis(*o*-hydroxy acetophenone)ethylene diamine (HPED) Schiff base were prepared by reacting *N,N'*-bis(4-amino-*o*-hydroxy acetophenone)ethylene diamine (AHPED) Schiff base with cross-linked chloromethylated polystyrene beads and then loading of iron(III), cobalt(II) and nickel(II) ions in methanol. The *N,N'*-bis(4-amino-*o*-hydroxy acetophenone)ethylene diamine (AHPED) Schiff base was prepared by nitrosation and reduction of nitrosated HPED Schiff base in presence of Fe/HCl catalyst. The loading of AHPED Schiff base on chloromethylated polystyrene beads was 86% (2.58 mmol g<sup>-1</sup> of beads). The AHPED Schiff base anchored polymer beads have shown 85%, 86% and 89% complexation for iron(III), cobalt(II) and nickel(II) ions from solution of metal salts (2.6 mmol), whereas unsupported HPED Schiff base shown 80%, 88% and 77% complexation for iron(III), cobalt(II) and nickel(II) ions. The free and polymer supported metal complexes were analyzed for molecular weight (Mw) and composition by elemental analysis. The UV, IR and magnetic measurements of free and polymer supported metal complexes have confirmed the octahedral geometry for iron(III) and square planar geometry for cobalt(II) and nickel(II) ions complexes. The thermogravimetric analysis (TGA) of Schiff base has shown 55% weight loss at 500 °C but iron(III), cobalt(II) and nickel(II) ions complexes have shown 30%, 40% and 48% weight loss at same temperature. The iron(III), cobalt(II) and nickel(II) ions complexes have shown temperature of maximum decomposition rate ( $T_{max}$ ) as 325, 319 and 281 °C, respectively. The unsupported HPED Schiff base complexes of metal ions were found to be less stable although the trend in their thermal stability was almost same. The catalytic activity of free and polymer anchored HPED Schiff base complexes was evaluated by studying the oxidation of phenol at 70 °C. The percent conversion of phenol and turn over number (TON) was found to be optimum at 1:1:1 molar ratio of phenol, H<sub>2</sub>O<sub>2</sub> and metal ions in both free and polymer supported metal complexes. The activation energy for oxidation of phenol by polymer supported HPED Schiff base complex of iron(III) was found to be low (25 kJ mol<sup>-1</sup>) in comparison to HPED Schiff base complexes of cobalt(II) (57 kJ mol<sup>-1</sup>) and nickel(II) ions (31 kJ mol<sup>-1</sup>). On the basis of literature report, a mechanism for oxidation of phenol has been proposed.

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**Keywords:** Catalysis; Catechol; Schiff base complexes

## 1. Introduction

Various metal ions and their complexes have been used widely in homogeneous catalyzed reactions but inherent disadvantages associated with homogeneous catalysis were minimized by using supported metal complexes, which sometime have shown high catalytic activities in comparison to unsupported analogues [1–3]. The high chemoselectivity of supported catalysts was due to stereospecific control on interactions of active sites with reactants in comparison to free and unsupported complexes.

The supported catalysts are easily recovered without any substantial loss in their catalytic activity [3,4] but homogeneous catalysts are not recovered easily. The selective oxidation of phenol to catechol and hydroquinones is an industrially useful process and has been carried out using transition metals [5] and their complexes [6–9]. The Schiff base complexes of transition metals are efficient in loading of oxygen and in mimicking the enzyme activity [10], hence used successfully in oxidation of phenol [11,12]. The oxidation of phenol has also been reported using molecular sieves [13–15] and hydrotalcite [16]. The oxidation of phenol in presence of hydrogen peroxide is normally an activation process but accomplished in presence of transition metal catalysts [17]. The unsupported metal complexes proved to be more efficient catalyst in oxidation of

\* Corresponding author. Tel.: +91 1332 285325; fax: +91 1332 273560.  
E-mail address: [kcgptfcy@iitr.ernet.in](mailto:kcgptfcy@iitr.ernet.in) (K.C. Gupta).

phenols with a maximum yield of 40% [18,19] but silica gel supported manganese and cobalt(II) salts have shown a maximum yield of 64% for oxidation of phenol. Although metal complexes on various supports have been used in selective oxidation of phenols but oxidation of phenol using metal salen complexes on polymer supports found to be more efficient and selective in comparison to homogeneous systems [20]. In these investigations, the homogeneous cobalt salen complexes have shown poor catalytic activity in comparison to polymer bound cobalt(II) salen complexes. On doubling the concentration of polymer bound catalyst, the conversion of phenol was doubled, whereas in case of homogeneous conditions, the phenol conversion was increased to 1.7-fold. The activity of metal complexes on polymer supports has normally found to be more in comparison to metal complexes on inorganic supports [21–26]. Amongst the various polymer supports, the naturally occurring polymers such as chitosan have been used for anchoring the Schiff base complexes of palladium(II) to catalyze the Heck arylation of acrylic acid [27]. The polymer supported metal complexes found to be more catalytic in selective epoxidation of dienes [28], oligomerization of ethylene [29], decomposition of hydrogen peroxide [30], oxidation of alcohol [31,32] and selective oxidation of aliphatic and aromatic hydrocarbons [31,33] in comparison to homogeneous metal complexes. The length of Schiff base ligands and their types has influenced the loading of metal ions [34] as well as the catalytic activity of metal complexes on polymer supports [35]. The most commonly used ligands on polymer supports are aminomethylpyridine [3,36], phosphines [37,38], diketones [39], multidentate amines [20], salen [40] and hydrazine [41]. In order to develop new catalyst for selective oxidation of phenol, attempt has been made to synthesize polymer supported *N,N'*-bis(*o*-hydroxy acetophenone)ethylene diamine Schiff base complexes of iron(II), cobalt(II) and nickel(II) ions (P-HPED-M) and to characterize their catalytic activities in oxidation of phenol under different experimental conditions in comparison to unsupported metal complexes of HPED Schiff base.

## 2. Experimental

### 2.1. Materials

The cross-linked chloromethylated polystyrene beads were received from ion exchange India Ltd., Mumbai, India and used for supporting Schiff base complexes of metal ions. The anhydrous chloro salts of iron, cobalt and nickel were obtained from Ranbaxy, Mumbai, India. The phenol, hydrogen peroxide (30%), *o*-hydroxyacetophenone and ethylenediamine were procured from E. Merck, India and used without further purifications. All other chemicals and solvents were of analytical grade (>99%) and used after purification using standard methods [42].

### 2.2. Spectral, thermal, elemental and magnetic characterization

The IR spectra of Schiff base and its metal complexes were recorded on KBr pellet using Perkin-Elmer 1600 FTIR Spec-

trophotometer. The electronic spectra of Schiff base and their metal complexes were recorded with Shimadzu 1601 PC UV–vis Spectrophotometer by keeping sample mull in a cuvette. Thermogravimetric analysis (TGA) of Schiff base and its metal complexes was carried out using Perkin-Elmer Pyris, Diamond Thermal Analyzer under nitrogen atmosphere at a heating rate of 10 °C/min. The metal ions complexation on free and polymer supported Schiff base was determined by using the amount of metal ions loaded and the amount of Schiff base used for loading. The amount of metal ions loaded on Schiff base was estimated by analyzing the loading solution with Perkin-Elmer 3100 Atomic Absorption Spectrometer at  $\lambda_{\text{max}}$  of metal ions. The amount of Schiff base loaded on polymer beads and composition of Schiff base complexes was estimated using Haraeus Carlo Ebra 1108 Elemental Analyzer. <sup>1</sup>H NMR spectra of HPED Schiff base and its metal complexes were recorded on Bruker-300 MHz using tetramethylsilane as internal standard. The magnetic moment ( $\mu$ ) of metal complexes was measured using Vibrating Sample Magnetometer-155.

### 2.3. Synthesis of *N,N'*-bis(*o*-hydroxy acetophenone)ethylene diamine Schiff base and its metal complexes

*N,N'*-bis(*o*-hydroxy acetophenone)ethylene diamine Schiff base (HPED) was prepared by modifying the procedure reported in the literature [42]. The reaction mixture containing *o*-hydroxyacetophenone (20 mmol, 2.22 g) and ethylene diamine (10 mmol, 0.6 g) in methanol was refluxed at 60 °C for about 45 min. The reaction mixture after cooling at low temperature produced yellow colored crystals, which were filtered and recrystallized in methanol. To prepare the metal complexes of HPED Schiff base, the 100 mL methanolic mixture of Schiff base (10 mmol, 2.96 g) and metal salt containing 10 mmol of metal ions was refluxed at 70 °C. After 8 h, the solution was cooled, which produced crystallize metal complexes in mother liquor. Finally, the metal complexes were recrystallized in methanol and dried in vacuum desiccator.

### 2.4. Synthesis of polymer anchored *N,N'*-bis(*o*-hydroxyacetophenone)ethylene diamine Schiff base and its metal complexes

To prepare polymer anchored metal complexes of *N,N'*-bis(*o*-hydroxy acetophenone)ethylene diamine Schiff base (HPED), the *N,N'*-bis(4-amino-*o*-hydroxy acetophenone)ethylenediamine (AHPED) Schiff base was prepared by carrying out nitrosation and reduction reactions on HPED Schiff base and then reacting the prepared AHPED Schiff base with chloromethylated polystyrene beads. The nitrosation of HPED Schiff base was carried out using 10 mmol (2.96 g) of HPED Schiff base with sodium nitrite (10 mmol) in 1N hydrochloric acid (10 mL) at low temperature. The resultant *N,N'*-bis(4-nitroso-*o*-hydroxy acetophenone)ethylene diamine was filtered and washed with hot and cold water to remove reaction impurities. The reduction of *N,N'*-bis(4-nitroso-*o*-hydroxyacetophenone)ethylene diamine was carried out using

10 mmol of nitrosated HPED Schiff base in 1N hydrochloric acid (20 mL) in presence of metallic iron, which produced *N,N'*-bis(4-amino-*o*-hydroxy acetophenone)ethylene diamine (AHPED) Schiff base. To immobilize the prepared AHPED Schiff base on chloromethylated polystyrene, the methanol swollen polymer beads (5 g) were refluxed in 50 mL methanol containing 15 mmol (4.89 g) of AHPED Schiff base. After 8 h, the HPED Schiff base anchored polymer beads were separated and dried in vacuum desiccator. The HPED Schiff base anchored polymer beads were subsequently used for metal ions loading by keeping 5 g polymer beads in 50 mL aqueous solution of metal ions (13 mmol). To ensure the loading of metal ions, HPED Schiff base anchored polymer beads were kept for 10 h in solution of metal salt. Finally, the polymer beads were separated and washed with hot and cold water and dried at 70 °C in vacuum oven. The metal ions loading on free and polymer supported HPED Schiff base was calculated as efficiency of complexation (EC) of Schiff base using the amount of Schiff base taken for loading and amount of metal ions loaded on Schiff base

$$EC(\%) = \frac{\text{Metal ions loaded}}{\text{Schiff base taken}} \times 100$$

### 2.5. Evaluation of catalytic activity of metal complexes in oxidation of phenol

To evaluate the catalytic activity of free and polymer supported metal complexes of HPED Schiff base, the oxidation of phenol was carried out in presence of hydrogen peroxide as oxidant at pH 7 and fixed ionic strength (0.1 M). The oxidation of phenol was carried out by taking a calculated amount of metal anchored polymer beads in a two-necked round-bottomed flask containing 0.05 M phenol (4.7 g) along with 2 mL acetonitrile and then calculated volume of hydrogen peroxide (30%) was added to maintain 0.05 M (5.67 g) concentration of hydrogen peroxide in the reaction mixture. The acetonitrile in the reaction mixture was used as internal standard. Before starting, the stirring and heating of reaction mixture at 70 °C, the reaction flask was attached with water condenser and inlet for nitrogen. At fixed time intervals, the aliquots of reaction mixture were withdrawn and analyzed by gas chromatography for oxidation products of phenol. The oxidation of phenol was also studied taking different molar ratios of phenol to hydrogen peroxide and phenol to catalyst in reaction mixture at 70 °C. To determine the effect of temperature on oxidation of phenol, the reaction was studied by varying the reaction temperature from 60 to 80 °C taking constant molar ratio of phenol to H<sub>2</sub>O<sub>2</sub> and catalyst. To analyze the effect of catalyst on oxidation of phenol, the oxidation of phenol was studied without using catalyst in the reaction mixture. The retention time was used to identify the oxidation products of phenol by using the retention time of the standards. The peak areas in the chromatograms were used to determine the amount of reaction products and phenol oxidized in presence of hydrogen peroxide and catalyst.

## 3. Results and discussion

Investigations have revealed that polymer supported metal complexes are more efficient catalyst [20] in comparison to free and unsupported metal complexes and activity of supported catalysts found to be dependant on properties of polymer supports. The activity of the catalyst found to vary significantly with the amount of catalyst loaded on polymer supports [43,44] than the amount of unsupported catalysts. The activity of catalysts in temperature controlled reactions showed dependence on thermal stability of supported complexes and their interactions with reactants. The thermal analysis of polymer-supported complexes is useful to evaluate their applications in high temperature reactions and to provide a proof for the complexation of metal ions with Schiff base ligands. The thermogravimetric analysis (TGA) of pure Schiff base has shown a weight loss of 55% at 500 °C but its iron(III), cobalt(II) and nickel(II) ions complexes have shown a weight loss of 30%, 40% and 48% at same temperature, which clearly indicated that iron(III) complexes were more stable in comparison to cobalt(II) and nickel(II) ions complexes. The weight loss in metal complexes at 500 °C was due to the decomposition of HPED Schiff base of the complexes. The temperature of maximum rate of decomposition ( $T_{max}$ ) of polymer anchored Schiff base (P-HPED) has increased from 225 to 325 °C on complexation with iron(III) ions and increased to 319 and 281 °C on complexation with cobalt(II) and nickel(II) ions, respectively (Fig. 1) and after  $T_{max}$ , the rate of decomposition of metal complexes was slowed. In addition to thermal analysis, the free and polymer supported HPED Schiff base metal complexes were also characterized by IR and UV spectra to predict the complexation of metal ions as well as to predict the structures and geometry of metal complexes considering the observed magnetic moment of the metal complexes.

### 3.1. Characterization of *N,N'*-bis(*o*-hydroxy acetophenone)ethylene diamine Schiff base

The *N,N'*-bis(*o*-hydroxy acetophenone)ethylene diamine Schiff base (HPED) was obtained by refluxing ethylene diamine

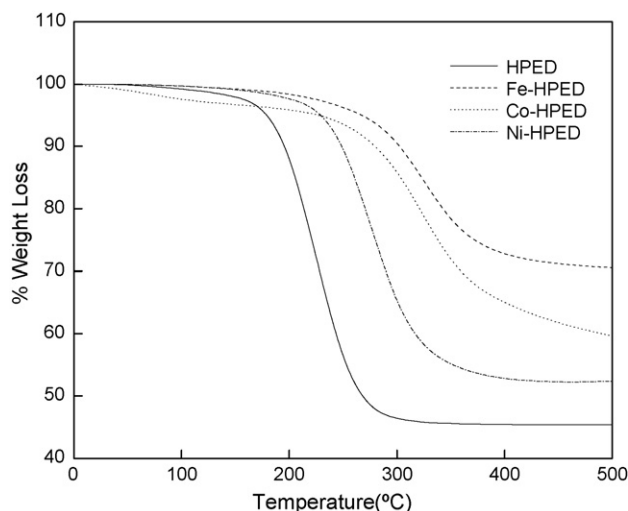
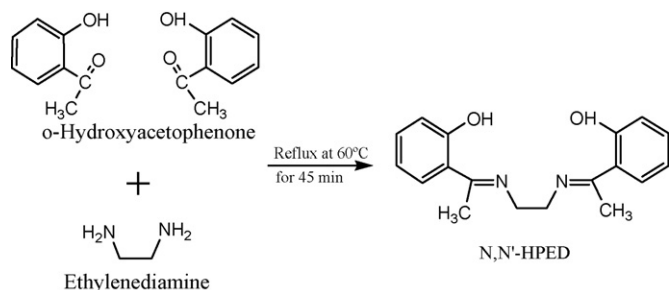


Fig. 1. Thermal stability of polymer supported complexes.



Scheme 1. Synthesis of *N,N'*-bis(*o*-hydroxy acetophenone)ethylene diamine Schiff base (HPED).

(ED) and *o*-hydroxy acetophenone (HP) for 45 min at 60 °C in methanol, which produced a substantial yield (77.67%) of HPED Schiff base (Scheme 1). The IR spectrum of HPED Schiff base has shown absorption at 1634 cm<sup>-1</sup> (>C=N), 1290 cm<sup>-1</sup> (>C–O) phenolic (Fig. 2A) and a broad band between 3300 and 2950 cm<sup>-1</sup> was also observed, which was assigned to phenolic OH. The elemental analysis of Schiff base has shown (%): C = 72.64, N = 8.99 and H = 6.07, Calcd. (%): C = 72.97, N = 9.46 and H = 6.76, which corresponds to C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> empirical formula of HPED Schiff base. The molecular weight of Schiff base was found to be 296.4 g mol<sup>-1</sup> (Calcd. 297 g mol<sup>-1</sup>). The electronic spectra of HPED Schiff base (Fig. 3) showed bands at 251 and 320 nm, which were assigned to π → π\* and n → π\* transitions. The <sup>1</sup>H NMR spectrum of HPED Schiff base has shown signals at δ (ppm) = 1.05 (3H), 4.08 (2H), 6.91 (1H), 7.0 (1H), 7.27 (1H) and 7.60 (1H), which correspond to structure of HPED Schiff base as shown in Scheme 1.

### 3.2. Synthesis and characterization of *N,N'*-bis(4-amino-*o*-hydroxy acetophenone)ethylene diamine Schiff base and its anchoring on polymer beads

The nitrosation of *N,N'*-bis(*o*-hydroxy acetophenone)ethylene diamine Schiff base was carried out in presence of NaNO<sub>2</sub>/HCl, which produced a significant yield (88.18%) of *N,N'*-bis(4-nitroso-*o*-hydroxyacetophenone)ethylene diamine Schiff base (Scheme 2). The elemental analysis of prepared *N,N'*-bis(4-nitroso-*o*-hydroxy acetophenone)ethylene diamine

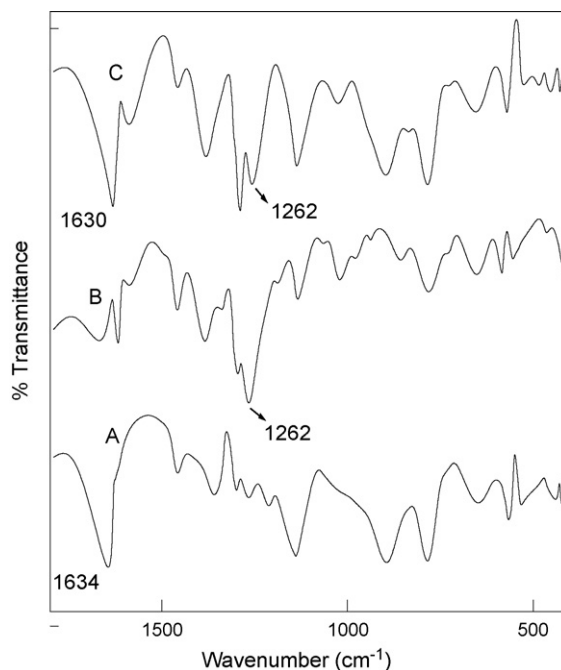
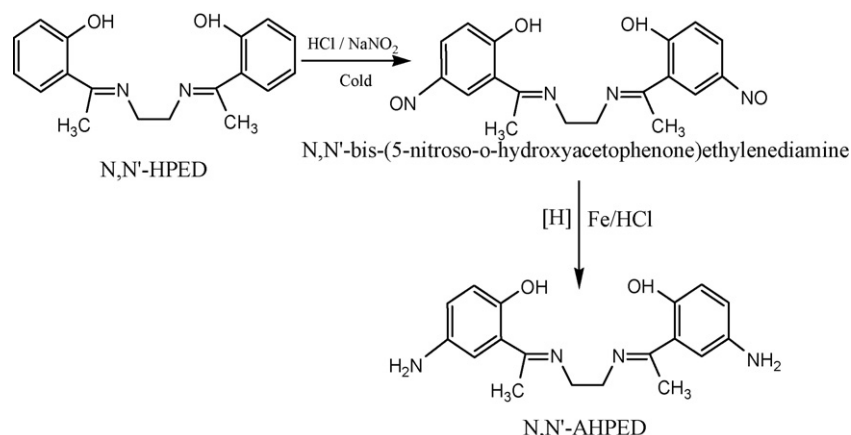


Fig. 2. FTIR spectra of free HPED Schiff base (A), polymer beads (B) and polymer anchored Schiff base (C).

Schiff base has revealed (%): C = 60.97, N = 15.6 and H = 5.60, Calcd. (%): C = 61.71, N = 16.0 and H = 5.71, which was correspond to C<sub>18</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub> empirical formula of nitrosated Schiff base. The molecular weight of *N,N'*-bis(4-nitroso-*o*-hydroxy acetophenone)ethylene diamine Schiff base was found to be 353.6 g mol<sup>-1</sup> (Calcd. 354 g mol<sup>-1</sup>). The IR spectrum of *N,N'*-bis(4-nitroso-*o*-hydroxy acetophenone)ethylene diamine Schiff base has revealed absorption bands at 1630 cm<sup>-1</sup> (>C=N), 1280 cm<sup>-1</sup> (>C–O) phenolic and 1550 and 1335 cm<sup>-1</sup> for N–O group. The nitrosation of HPED Schiff base has shown a shift in NMR signals in comparison to NMR signals observed in pure HPED Schiff base. The nitrosated HPED Schiff base has shown proton signals at δ (ppm) = 1.05 (3H), 4.07 (2H), 5.15 (1H), 7.20 (1H), 7.82 (1H) and 8.15 (1H), which were corresponding to the structure of nitrosated HPED Schiff base as shown in Scheme 2. The proton signals ortho to nitroso group



Scheme 2. Synthesis of *N,N'*-bis(4-amino-*o*-hydroxy acetophenone)ethylene diamine Schiff base (AHPED).

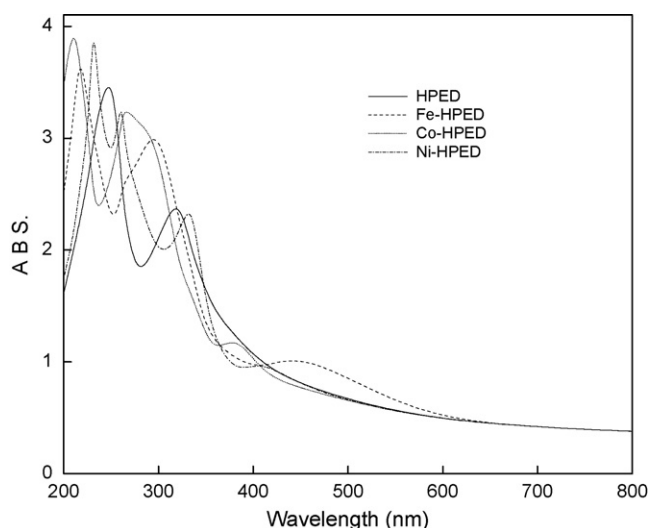
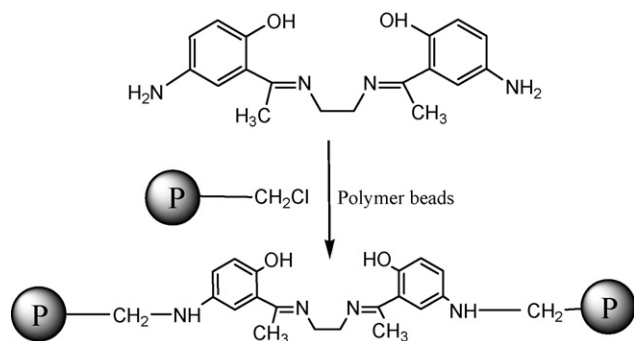


Fig. 3. Electronic spectra of Schiff base (HPED) and its metal complexes.



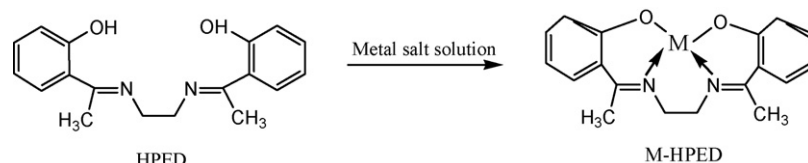
Scheme 3. Synthesis of polymer anchored Schiff base (P-HPED).

in HPED Schiff base were deshielded, hence appeared at 7.82 and at 8.15 ppm in place of 7.27 and 7.60 ppm of pure HPED Schiff base and proton signal at 7.0 ppm was missing due to nitroso substitution in the benzene. The *N,N'*-bis(4-nitroso-*o*-hydroxy acetophenone)ethylene diamine was subsequently reduced with iron metal in presence of hydrochloric acid, which produced 83.77% yield of *N,N'*-bis(4-amino-*o*-hydroxy acetophenone)ethylene diamine (AHPED) Schiff base as shown in Scheme 2. The m.p. of AHPED Schiff base was 186 °C and its elemental analysis (%): C = 86.08, N = 21.42 and H = 8.96, Calcd. (%): C = 87.09, N = 22.58 and H = 9.67 was corresponding to an empirical formula of  $C_{18}H_{22}N_4O_2$ . The molecular weight of AHPED Schiff base was found to be  $325.7 \text{ g mol}^{-1}$  (Calcd.  $326 \text{ g mol}^{-1}$ ). The IR spectrum of *N,N'*-bis(4-amino-*o*-hydroxy acetophenone)ethylene diamine Schiff base has shown absorption bands at  $1633 \text{ cm}^{-1}$  ( $>C=N$ ),

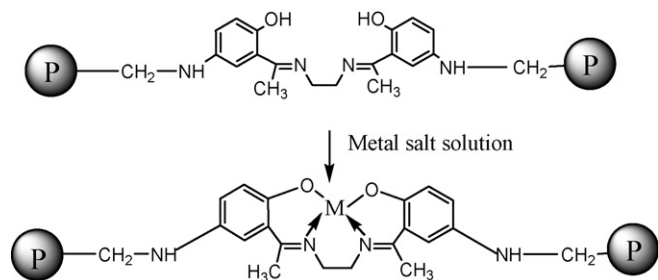
$1286 \text{ cm}^{-1}$  ( $>C-O$ ) phenolic and a band between 1633 and  $1650 \text{ cm}^{-1}$  corresponding to  $>C-N$  group. The NMR spectrum of AHPED has shown proton signals at  $\delta$  (ppm) = 1.05 (3H), 4.07 (2H), 5.15 (1H), 6.47 (1H), 6.66 (1H), 6.80 (1H), which correspond to AHPED Schiff base structure as shown in Scheme 2. The synthesized *N,N'*-bis(4-amino-*o*-hydroxy acetophenone)ethylene diamine Schiff base (AHPED) was anchored on chloromethylated divinyl benzene cross-linked polystyrene beads by refluxing AHPED Schiff base (15 mmol) with polymer beads (5 g) in DMF for 8 h at 60 °C. The AHPED Schiff base has shown 86% loading on polymer beads, which was corresponding to 2.58 mmol HPED Schiff base on 1 g of polymer beads (Scheme 3). The comparison of IR spectrum of HPED Schiff base anchored polymer beads (Fig. 2C) with IR spectrum (Fig. 2B) of pure polymer beads confirmed the loading of HPED Schiff base. The IR spectrum of polymer-anchored Schiff base (Fig. 2C) has shown new absorption bands at  $1628 \text{ cm}^{-1}$  ( $>C=N$ ),  $1281 \text{ cm}^{-1}$  ( $>C-O$ ) phenolic and a broad band between 1620 and  $1643 \text{ cm}^{-1}$  ( $>C-N$ ), which were absent in IR spectrum of pure polymer beads (Fig. 2B) but were present in unsupported HPED Schiff base (Fig. 2A). The IR spectrum of pure polymer beads has also shown absorption band at  $1262 \text{ cm}^{-1}$  (Fig. 2B), which was attributed for the presence of C-Cl bond of residual chloromethyl in polymer beads. The decrease in intensity of absorption band at  $1262 \text{ cm}^{-1}$  (C-Cl) in spectrum of polymer beads on reacting with AHPED Schiff base (Fig. 2C) has confirmed the attachment of HPED Schiff base on polymer beads. The appearance of new absorption bands and shift in other absorption bands of pure HPED Schiff base on anchoring with polymer beads has been used further as evidence for anchoring the HPED Schiff base on polymer beads.

### 3.3. Characterization of free and polymer anchored metal complexes of *N,N'*-bis(*o*-hydroxy acetophenone)ethylene diamine Schiff base

The loading of metal ions on free and polymer supported HPED Schiff base was carried out by keeping known amount of free HPED Schiff base and polymer anchored HPED Schiff base separately in aqueous solution of metal salt at 60 °C and after 10 h, the metal loaded free (Scheme 4) and supported Schiff base (Scheme 5) was separated. The complexation of metal ions on free and polymer anchored Schiff base was calculated by analyzing the solution with AAS after metal ions loading. The complexation of free HPED Schiff for iron(III), cobalt(II) and nickel(II) ions was 80%, 88% and 77% and polymer anchored HPED Schiff has shown 86%, 89% and 85% complexation for



Scheme 4. Loading of metal ions on unsupported Schiff base (HPED-M).



Scheme 5. Loading of metal ions on polymer supported Schiff base (P-HPED-M).

Table 1  
Complexation of metal ions (M) on free (HPED) and supported Schiff base (P-HPED)

Schiff base	Fe(III) ions (wt.%)	Ni(II) ions (wt.%)	Co(II) ions (wt.%)
HPED	80	88	77
P-HPED	86	89	85

iron(III), cobalt(II) and nickel(II) ions, respectively (Table 1), which clearly indicated that the complexation of metal ions was more on polymer supported HPED Schiff base than free HPED Schiff base. The nickel(II) ions have shown more affinity for complexation with HPED Schiff base in comparison to iron(III) ions cobalt(II) ions. The metal anchored Schiff base (HPED-M) and metal anchored polymer Schiff base (P-HPED-M) after separation and purification were characterized by various techniques to ascertain their structures and metal ions complexation. The IR spectra of metal ions loaded Schiff base have shown variations in absorption bands corresponding to  $>C=N$  and  $>C-O$  groups and shown new absorptions bands, which were attributed for the formation of  $M-O$  and  $M-N$  bonds in HPED Schiff base complexes of metal ions (Fig. 4). The disappearance of absorption band corresponding to  $(-C-OH)$  phenolic in HPED Schiff base on reacting with metal ions has also provided an evidence for the complexation of metal ions with HPED Schiff base. The polymer supported HPED Schiff base (Fig. 4A) has shown absorption bands at low frequency in comparison to unsupported Schiff base (Fig. 2A). On complexation with iron(III) ions, the  $>C=N$  bond frequency in free HPED Schiff base was decreased to  $1630\text{ cm}^{-1}$  from its original frequency of  $1634\text{ cm}^{-1}$ , whereas polymer supported HPED Schiff base has shown frequency variation from  $1630$  to  $1626\text{ cm}^{-1}$  for  $>C=N$  bond on complexation with iron(III) ions (Fig. 4A and B). The complexation of cobalt(II) ions with free and polymer supported HPED Schiff base has shown absorption bands at  $1617$  and  $1613\text{ cm}^{-1}$  (Fig. 4C), whereas nickel(II) ions has shown bands at  $1621$  and  $1617\text{ cm}^{-1}$  with free and supported HPED Schiff base (Fig. 4D). These variations in absorption band corresponding to  $>C=N$  group of HPED Schiff base on reaction with metal ions were considered as evidence for the interactions of metal ions with azomethyne nitrogen of HPED Schiff base. The interactions of iron(III) ions have shown new absorption band at  $435\text{ cm}^{-1}$  with free Schiff base and at  $430\text{ cm}^{-1}$  with polymer anchored Schiff base, which is due to the formation of  $M-N$  bond between iron(III) ions and Schiff base (Fig. 4B).

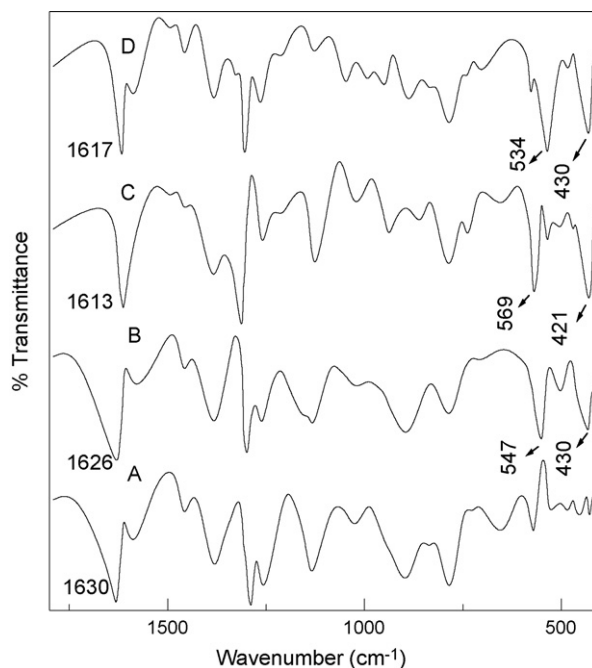
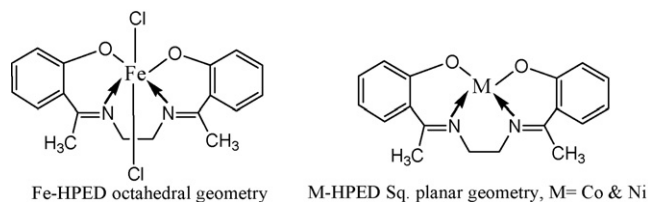


Fig. 4. FT-IR spectra of polymer supported Schiff base (A) and its metal complexes (B–D).

The complexation of cobalt(II) ions has shown absorption band at  $426$  and  $421\text{ cm}^{-1}$  for  $M-N$  bond with free and polymer supported Schiff base (Fig. 4C), whereas nickel(II) ions complexation with free and polymer supported Schiff base (Fig. 4D) has produced absorption bands at  $434$  and  $430\text{ cm}^{-1}$  for  $M-N$  bond. The appearance of these absorption bands has provided a clear indication that metal ions were involved in the formation of bond with nitrogen of Schiff base. The complexation of iron(III), cobalt(II) and nickel(II) ions has also produced absorption band due to the formation of metal bond with oxygen  $(-O-M)$  phenolic. The iron(III), cobalt(II) and nickel(II) ions on complexation with polymer supported Schiff base have produced absorption bands at  $547$ ,  $565$  and  $534\text{ cm}^{-1}$  as shown in Fig. 4. The further evidences for metal ions complexation with Schiff base were obtained from electronic spectra of pure Schiff base and its metal complexes (Fig. 2). The complexation of iron(III) ions with Schiff base has shown a shift in  $\pi \rightarrow \pi^*$  transition from  $251$  to  $221\text{ nm}$  and on complexation with cobalt(II) ions, the  $\pi \rightarrow \pi^*$  transition was observed at  $210\text{ nm}$  but in case of nickel(II) ions, the  $\pi \rightarrow \pi^*$  transition was observed at  $243\text{ nm}$ . On complexation with iron(III) ions, the  $n \rightarrow \pi^*$  transition of Schiff base was changed from  $320$  to  $284\text{ nm}$ , whereas it has been observed at  $273$  and  $268\text{ nm}$  with cobalt(II) and nickel(II) ions, respectively. The observed CT and  $d \rightarrow d$  transitions have also provided evidence for the complexation of metal ions with Schiff base. The complexation of cobalt(II) and nickel(II) ions with Schiff base has shown CT transitions at  $383$  and  $325\text{ nm}$ , respectively, whereas the complexation of iron(III) and nickel(II) ions with Schiff base has shown  $d \rightarrow d$  transitions at  $454$  and  $410\text{ nm}$ , respectively, which correspond to  $t_{2g}^5 e_g^0$ ,  $t_{2g}^6 e_g^1$  and  $t_{2g}^6 e_g^2$  electronic configurations for iron(III), cobalt(II) and nickel(II) ions in these complexes. The magnetic moment ( $\mu$ ) of Schiff base

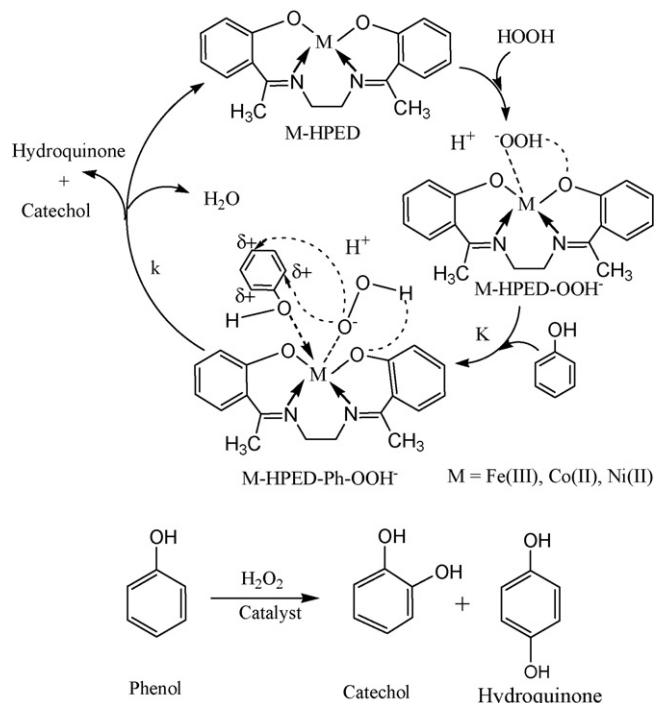


Scheme 6. Geometry and structures of Schiff base complexes of metal ions.

complexes of iron(III), cobalt(II) and nickel(II) ions was found to be 1.71, 1.74 and 0.01 BM, respectively, which has indicated that iron(III) and cobalt(II) complexes were paramagnetic in nature with one unpaired electron in each and nickel(II) complexes were diamagnetic in nature as all electrons were paired. The magnetic and electronic configurations of metal complexes have suggested for octahedral geometry with  $d^2sp^3$  hybridization for iron(III) complexes and  $dsp^2$  hybridization with square planar geometry for cobalt(II) and nickel(II) ions complexes (Scheme 6).

### 3.4. Oxidation of phenol

The catalytic activity of free and polymer supported metal complexes has been evaluated by studying the oxidation of phenol in presence of hydrogen peroxide. The oxidation products of phenol were determined by analyzing reaction mixture with gas chromatograph. The peaks in chromatograms were confirmed to catechol and hydroquinone by comparing the retention times with retention time of pure catechol and hydroquinone. The formation of these reaction products has been attributed to enzymatic behavior of metal complexes (Scheme 7). The free and polymer supported Schiff base complexes (HPED-M) produced active species (HPED-M-OOH<sup>-</sup>) through fast interactions of Schiff base complexes (HPED-M) with H<sub>2</sub>O<sub>2</sub> forming a temporary bond between dissociated species (OOH<sup>-</sup>) and central metal ions of the complex and hydrogen bonding with oxygen of Schiff base. The interactions of active species (HPED-M-OOH<sup>-</sup>) with phenol through rapid equilibrium (K) produced an intermediate species (HPED-M-Ph-OOH<sup>-</sup>) like metal porphyrins and metal thiocyanins systems [45], which facilitated the nucleophilic attack of OOH<sup>-</sup> species on ortho and para position on phenol to produce hydroxy substituted phenols. The



Scheme 7. Oxidation products of phenol.

intramolecular oxidation–reduction reaction between phenol (Ph) and active species (HPED-M-OOH<sup>-</sup>) in the intermediate (HPED-M-Ph-OOH<sup>-</sup>) and decomposition of intermediate through a rate-determining step (k) has ultimately produced catechol and hydroxy phenol (Scheme 7). The fast intramolecular electron transfer process might be responsible for high conversion of phenol by polymer supported Schiff base complexes than free metal complexes. The coordination sphere of intermediate (HPED-M-Ph-OOH<sup>-</sup>) was responsible for selective oxidation of phenol to catechol and hydroquinone. The oxidation of phenol by studied polymer supported metal complexes has varied from 55% to 70%, whereas with unsupported metal complexes, the oxidation of phenol was varied from 41.5% to 58.2% (Table 2). The high catalytic activity of polymer supported catalysts was attributed to the better control of catalyst interactions with phenol in comparison to homogeneous metal complexes in solution. The metal complexes in solution phase have likely formed dim-

Table 2  
Comparison of catalytic activity of supported (P-HPED-M) and unsupported metal complexes (HPED-M) in oxidation of phenol

Time (min)	% Conversion of phenol					
	P-HPED-Fe	HPED-Fe	P-HPED-Co	HPED-Co	P-HPED-Ni	HPED-Ni
0	0.0	0.0	0.0	0.0	0.0	0.0
15	21.5	18.3	6.5	4.4	13.5	5.6
30	40.4	28.6	25.4	19.5	32.4	18.7
45	52.0	38.0	37.0	24.9	44.0	29.0
60	57.2	45.6	42.2	30.0	49.2	37.1
90	63.2	50.8	49.0	33.6	56.0	43.3
240	68.8	57.0	53.8	39.9	60.8	49.6
720	69.4	58.0	54.4	41.1	61.4	50.0
1440	70.0	58.2	55.0	41.5	62.0	50.4

[H<sub>2</sub>O<sub>2</sub>]/[phenol]/[catalyst] = 0.05 M, temp. = 70 °C, CH<sub>3</sub>CN = 2.0 mL.

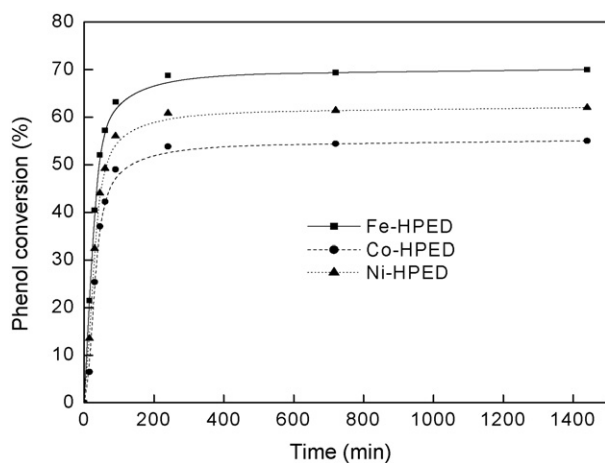


Fig. 5. Effect of reaction time on oxidation of phenol in presence of polymer supported metal complexes. [Phenol]:[catalyst]:[H<sub>2</sub>O<sub>2</sub>] = 1:1:1 at 0.5 M, temp.: 70 °C.

mers or multimers; hence, the activity of catalysts in solution phase was low than that on polymer support. The amount of phenol oxidized was almost equal to the sum of amount of catechol and hydroquinone produced, which discarded the formation of other reaction products including polymeric phenols. The oxidation of phenol was increased on increasing the reaction time but after 6 h, the oxidation of phenol was almost constant. The marginal increase in oxidation of phenol after 6 h was due to the decrease in active mass of phenol and hydrogen peroxide in the reaction mixture; hence, the increase in phenol oxidation after six hrs was insignificant (Fig. 5). The same trend in oxidation of phenol was also observed with unsupported catalysts on increasing the reaction time but the magnitude was low in comparison to supported catalysts (Table 2). The oxidation of phenol varied with type of catalyst and concentration of the reactants; hence, the oxidation of phenol was studied varying the molar ratio of phenol, metal complexes and hydrogen peroxide at constant pH and ionic strength of medium to identify the conditions for optimum activity of the catalysts. The energy of activation was determined by studying the oxidation of phenol at different temperatures.

#### 3.4.1. Effect of H<sub>2</sub>O<sub>2</sub> concentration on oxidation of phenol

The effect of H<sub>2</sub>O<sub>2</sub> concentration on oxidation of phenol was studied by varying the molar ratio of H<sub>2</sub>O<sub>2</sub> to phenol from 0.5 to 2.0 in acetonitrile (2 mL) at 70 °C keeping constant molarity (0.05 M) of phenol and metal complex in the reaction mixture. The oxidation of phenol was increased on increasing the molar

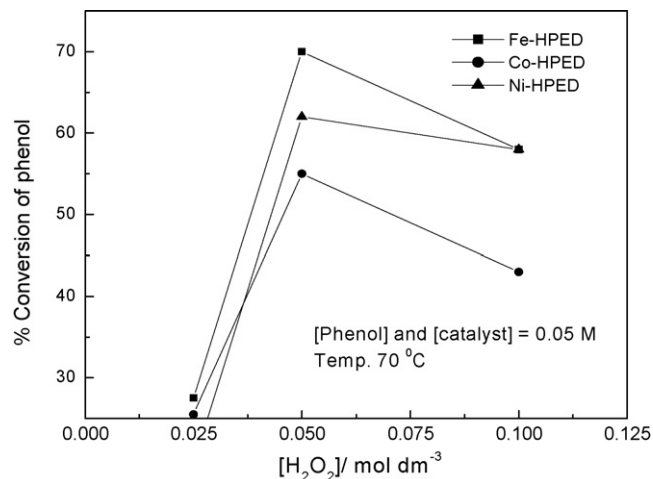


Fig. 6. Effect of H<sub>2</sub>O<sub>2</sub> concentration on phenol conversion. [Phenol]:[catalyst] = 1:1 at 0.05 M, temp.: 70 °C.

ratio of H<sub>2</sub>O<sub>2</sub> from 0.5 to 1.0 and was maximum at 1:1:1 molar ratio of H<sub>2</sub>O<sub>2</sub> to phenol and Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions (Fig. 6). But on further increasing the molar ratio of H<sub>2</sub>O<sub>2</sub> (>1) in the reaction mixture, the percent conversion of phenol was decreased with Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions, which was due to the decrease in molar ratio of phenol and catalyst with respect to molar ratio of H<sub>2</sub>O<sub>2</sub>. The oxidation of phenol at 1:1:1 molar ratios of H<sub>2</sub>O<sub>2</sub> to phenol and supported catalyst was found to be 70%, 55% and 62% within a reaction time of 24 h in presence of Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions, respectively (Table 3; Fig. 6), whereas unsupported Schiff base complexes of iron(III), cobalt(II) and nickel(II) shown 58.2%, 41.5% and 50.4% oxidation of phenol (Table 3). The selectivity for catechol and *o*-hydroquinone in oxidation of phenol was also influenced by molar ratio of hydrogen peroxide and selectivity for catechol was found to be maximum at 1:1:1 molar ratio H<sub>2</sub>O<sub>2</sub> to phenol and catalyst with both free and supported complexes of iron(III), cobalt(II) and nickel(II) ions (Table 3). The selectivity for catechol found to be high with supported catalysts than unsupported catalysts. The Schiff base complexes of iron(III) ions were more selective for catechol than cobalt(II) and nickel(II) ions. The rate of phenol conversion was found to be high ( $2.39 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ ) in presence of Schiff base complex of iron(III) ions in comparison to Schiff base complexes of nickel(II) and cobalt(II) ions, in which the rate of phenol oxidation was  $2.11 \times 10^{-6}$  and  $1.87 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ , respectively. The turn over number (TON) for the oxidation of

Table 3  
Oxidation of phenol and selectivity for catechol and hydroquinone

Metal complexes	Unsupported			Polymer supported		
	Phenol (wt.%)	Catechol (wt.%)	Hydroquinone (wt.%)	Phenol (wt.%)	Catechol (wt.%)	Hydroquinone (wt.%)
HPED-Fe	58.2	70.0	30.0	70.0	80.0	20.0
HPED-Ni	50.4	65.0	35.0	62.0	76.0	24.0
HPED-Co	41.5	60.0	40.0	55.0	70.0	30.0

[H<sub>2</sub>O<sub>2</sub>]/[phenol]/[catalyst] = 0.05 M, temp. = 70 °C, time = 24 h.



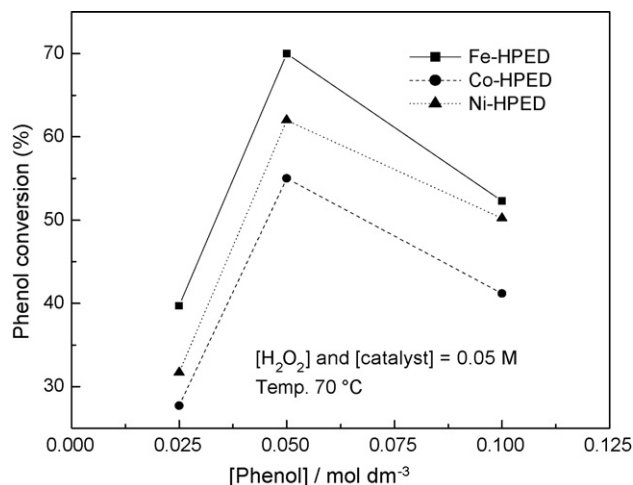


Fig. 7. Effect of concentration of phenol on its oxidation  $[H_2O_2]:[catalyst] = 1:1$  at 0.05 M, temp.: 70 °C.

phenol has been found to be high ( $16.17 \text{ g mol}^{-1} (\text{Fe}) \text{ h}^{-1}$ ) in presence of iron(III) complex in comparison to Schiff base complexes of nickel(II) ( $14.28 \text{ g mol}^{-1} (\text{Ni}) \text{ h}^{-1}$ ) and cobalt(II) ions ( $12.64 \text{ g mol}^{-1} (\text{Co}) \text{ h}^{-1}$ ).

#### 3.4.2. Effect of phenol concentration on oxidation of phenol

To determine the effect of phenol concentration on oxidation of phenol, the oxidation of phenol was also studied by varying its molar ratio from 0.5 to 2.0 with respect to molar ratio of  $H_2O_2$  and catalyst in the reaction mixture at 70 °C using 2 mL acetonitrile. During molar ratio variation of phenol, the molarity of  $H_2O_2$  and catalyst was kept constant (0.05 M). The oxidation of phenol was maximum at a molar ratio of 1:1:1 of phenol to  $H_2O_2$  and catalyst and a decreasing trend in oxidation of phenol was observed on further increasing the molar ratio of phenol (>1) in the reaction mixture (Fig. 7). The decreasing trend in oxidation of phenol at high molar ratio (2:1:1) of phenol to  $H_2O_2$  and catalyst was attributed to the decrease in concentration of hydrogen peroxide and catalyst in the reaction mixture. The oxidation of phenol was also low at a molar ratio 0.5:1:1 of phenol to  $H_2O_2$  and catalyst (Fig. 7), which was due to the low concentration of phenol (0.025 M) in comparison to  $H_2O_2$  and catalyst (0.05M). The oxidation of phenol at 1:1:1 molar ratio of phenol to hydrogen peroxide and catalyst was 70%, 55% and 62% in presence of Schiff base complex of iron(III), cobalt(II) and nickel(II) ions (Fig. 7). The variation in molar ratio of phenol did not influence the oxidation trend of phenol observed with metal complexes. The catalytic activity of Schiff base complexes of iron(III) ions in oxidation of phenol was more in comparison to Schiff base complexes of cobalt(II) and nickel(II) ions. The oxidation of phenol was also studied using unsupported Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions by varying the molar ratio of phenol from 0.5 to 2.0, which showed almost similar trends as observed with supported complexes except the oxidation of phenol was low. This confirmed that polymer supported catalysts were able to provide microenvironment to enhance the activity of catalyst in comparison to unsupported Schiff base complexes. The rate of phenol oxidation with supported iron(III) complexes

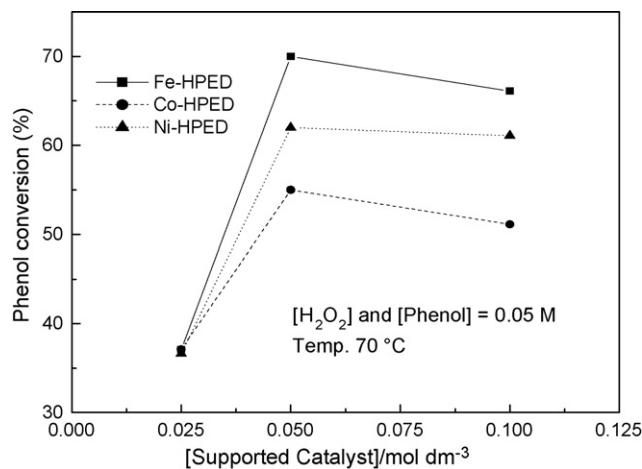


Fig. 8. Effect of supported catalyst concentration on oxidation of phenol.  $[Phenol]:[H_2O_2] = 1:1$  at 0.05 M, temp.: 70 °C.

varied from  $0.62 \times 10^{-6}$  to  $32 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$  and from  $0.41 \times 10^{-6}$  to  $2.65 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$  with supported complexes of cobalt(II) ions. The rate of oxidation of phenol with nickel(II) ions complexes was intermediate to rate of oxidation of phenol with Schiff base complexes of iron(III) and cobalt(II) ions. The turn over number (TON) for oxidation of phenol during phenol ratio variation in presence of cobalt(II) complexes was varied from 5.58 to 8.98  $\text{g mol}^{-1} (\text{Co}) \text{ h}^{-1}$  but in presence of Schiff base complexes of iron(III) ions, the TON varied from 12 to 63  $\text{g mol}^{-1} (\text{Fe}) \text{ h}^{-1}$ . The high activity of iron(III) complexes in oxidation of phenol may be attributed to octahedral geometry and high oxidation state of metal ions in the complex. The TON with Schiff base complexes of nickel(II) ions was intermediate to TON observed with Schiff base complexes of iron(III) and cobalt(II) ions.

#### 3.4.3. Effect of catalyst concentration on oxidation of phenol

The catalytic activity of polymer supported metal complexes in oxidation of phenol was also studied using different molar ratios of metal complexes at constant molarity (0.05 M) of phenol and hydrogen peroxide in acetonitrile at 70 °C. The molar ratio of catalyst to phenol was varied from 0.5 to 2.0 by adding a calculated amount of free and polymer supported metal complexes in reaction mixture. The oxidation of phenol was increased on increasing the molar ratio of catalyst from 0.5 to 1.0 in the reaction mixture and was maximum at a molar ratio of

Table 4  
Effect of reaction temperature on oxidation of phenol

Metal complexes	% Conversion of phenol					
	Unsupported			Polymer supported		
	60 °C	70 °C	80 °C	60 °C	70 °C	80 °C
HPED-Fe	28.0	58.2	56.0	35.0	70.0	61.0
HPED-Ni	19.6	50.4	42.0	29.5	62.0	50.5
HPED-Co	16.8	41.5	24.3	24.5	55.0	37.2

$[H_2O_2]/[phenol]/[catalyst] = 0.05 \text{ M}$ , temp. = 70 °C, time = 24 h.

Table 5

Phenol oxidation parameters at optimized molar ratio of phenol to hydrogen peroxide and catalyst at 70 °C

Parameters	P-HPED-M (supported)			HPED-M (unsupported)		
	Fe(III)	Ni(II)	Co(II)	Fe(III)	Ni(II)	Co(II)
Conversion (wt.%)	70.00	62.00	55.0	58.2	50.4	41.5
$R_p$ ( $10^{-6}$ mol dm $^{-3}$ s $^{-1}$ )	2.39	2.11	1.87	1.95	1.72	1.39
TON (g mol $^{-1}$ h $^{-1}$ )	16.17	14.28	12.64	13.20	11.65	9.38
$E_a$ (kJ mol $^{-1}$ )	25.00	31.00	57.00	29.00	37.00	82.00

[H<sub>2</sub>O<sub>2</sub>]/[CAT]/[phenol] = 0.05 M, temp. = 70 °C, time = 24 h, CH<sub>3</sub>CN = 2.0 mL.

1:1:1 of catalyst to H<sub>2</sub>O<sub>2</sub> and phenol (Fig. 8). On further increasing the molar ratio of catalyst (>1), the oxidation of phenol was decreased significantly. The catalytic activity of Schiff base complexes of iron(III) ions in oxidation of phenol was more in comparison to Schiff base complexes of cobalt(II) and nickel(II) ions (Fig. 8). The oxidation of phenol with supported complexes at a molar ratio of 1:1:1 of catalyst to phenol and H<sub>2</sub>O<sub>2</sub> was found to be 70%, 55% and 62% with Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions, respectively. These variations in molar ratio of catalyst to phenol and H<sub>2</sub>O<sub>2</sub> have clearly indicated that the activity of catalysts was optimum at 1:1:1 molar ratio of catalysts to phenol and H<sub>2</sub>O<sub>2</sub> in comparison to other molar ratio of catalysts in the reaction mixture. During molar ratio variation of catalyst, the selectivity of catechol has also shown variation and was maximum at a molar ratio of 1:1:1 of catalyst to H<sub>2</sub>O<sub>2</sub> and phenol (Table 3). The rate of oxidation ( $R_p$ ) of phenol at 1:1:1 molar ratio of catalyst to H<sub>2</sub>O<sub>2</sub> and phenol was  $2.39 \times 10^{-6}$ ,  $2.11 \times 10^{-6}$  and  $1.87 \times 10^{-6}$  mol dm $^{-3}$  s $^{-1}$  in presence of Schiff base complexes of iron(III), nickel(II) and cobalt(II) ions but at high molar ratio of catalyst (>1), the rate of oxidation ( $R_p$ ) of phenol was decreased to  $2.11 \times 10^{-6}$ ,  $1.93 \times 10^{-6}$  and  $1.57 \times 10^{-6}$  mol dm $^{-3}$  s $^{-1}$  in presence of Schiff base complexes of iron(III), nickel(II) and cobalt(II) ions. The rate of oxidation of phenol was  $1.84 \times 10^{-6}$ ,  $1.72 \times 10^{-6}$  and  $1.38 \times 10^{-6}$  mol dm $^{-3}$  s $^{-1}$ , respectively, in presence of unsupported Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions. The variation in rate of oxidation of phenol and selectivity for catechol with iron(III), cobalt(II) and nickel(II) ions was attributed to the difference in formation of active species (HPED-M-OOH $^{-}$ ) and difference in rate of intra molecular electron transfer [45] in intermediate species (HPED-M-Ph-OOH $^{-}$ ) formed with phenol and active species (Scheme 7).

#### 3.4.4. Effect of reaction temperature on oxidation of phenol

The oxidation of phenol was studied at different temperatures to determine the energy of activation for oxidation of phenol in presence of supported and unsupported catalysts. The energy of activation has shown dependence on type of catalysts and their interactions with reactants. To evaluate the energy of activation, the oxidation of phenol was studied on varying the reaction temperature from 60 to 80 °C using 1:1:1 molar ratio of phenol to H<sub>2</sub>O<sub>2</sub> and catalysts at constant molarity (0.05 M) in the reaction mixture. The oxidation of phenol was increased on increasing the reaction temperature from 60 to 70 °C but the increase in oxidation of phenol was more with Schiff base complexes of iron(III)

ions in comparison to Schiff base complexes of cobalt(II) and nickel(II) ions. On further increasing the reaction temperature (>70 °C), the oxidation of phenol was decreased, which was due the decomposition of hydrogen peroxide without oxidizing phenol into catechol and hydroquinone (Table 4). The selectivity for catechol in oxidation of phenol was also increased with the increase in reaction temperature from 60 to 70 °C but on further increasing the reaction temperature beyond 70 °C, the selectivity for catechol was decreased. The effect of temperature in oxidation of phenol by unsupported catalysts was also studied, which showed a similar trend for phenol oxidation and selectivity for catechol and hydroquinone as observed with supported catalysts (Table 3). However, the percent conversion of phenol with unsupported catalysts was low, which has clearly indicated that polymer support has played a significant role in electron transfer process in intermediate species; hence, decreased the energy of activation for oxidation of phenol. Although increase in reaction temperature has played a positive role in electron transfer process but at high temperature (>70 °C), the formation of active (HPED-M-OOH $^{-}$ ) and intermediate (HPED-M-Ph-OOH $^{-}$ ) species (Scheme 7) was disturbed, which decreased the oxidation of phenol and selectivity for catechol significantly (Table 4). The activation energy for oxidation of phenol in presence of polymer supported iron(III) ions complexes was low (25 kJ mol $^{-1}$ ) in comparison to cobalt(II) (57 kJ mol $^{-1}$ ) and nickel(II) ions complexes (31 kJ mol $^{-1}$ ); whereas, with unsupported Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions, the activation energy for oxidation of phenol was high (Table 5). The oxidation of phenol with hydrogen peroxide is an energy activated process but polymer support has contributed significantly in reducing the energy of activation of hydrogen peroxide in oxidation of phenol due to the fast electron transfer process during decomposition of intermediate (Scheme 7) to form oxidation product in comparison to unsupported catalyst. The microenvironment in polymer supported intermediate was more suitable in selective oxidation of phenol to catechol than unsupported catalysts; hence, the selectivity for catechol was more with supported catalyst than unsupported catalysts.

## 4. Conclusion

The *N,N'*-bis (4-amino-*o*-hydroxy acetophenone)ethylene diamine (AHPED) Schiff base was synthesized successfully to anchor on cross-linked chloromethylated polystyrene beads. The free and polymer supported HPED Schiff base was loaded with

iron(III), copper(II) and zinc(II) ions and characterized for their structures by different techniques. The iron(III) complexes were octahedral in geometry, whereas copper(II) and nickel(II) ions complexes were square planar. The catalytic activity of metal complexes was evaluated by studying the selective oxidation of phenol in presence of hydrogen peroxide in acetonitrile at 70 °C. The metal complexes on polymer support were more catalytic than unsupported catalysts. The activity of Schiff base complexes of iron(III) was highest in comparison to Schiff base complexes of cobalt(II) and nickel(II) ions. The oxidation of phenol was maximum at a molar ratio of 1:1:1 molar ratio of phenol to hydrogen peroxide and catalyst. The energy of activation for oxidation of phenol was low with polymer supported catalysts. The enzymatic action of catalysts found to be responsible for the activity of metal complexes in oxidation of phenol.

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