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Synthesis of the ketimine of chitosan and 4,6-diacetylresorcinol, and study of the catalase-like activity of its copper chelate

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ABSTRACT

In this study, a new chitosan derivative (ketimine) was synthesized by condensation of chitosan with 4,6-diacetylresorcinol (DAR) at heterogeneous medium. The ketimine derivative of chitosan (DAR-chitosan) was characterized by elemental (C, H, N), spectral (DR-UV–vis and FT-IR spectroscopy), structural (powder XRD), and morphological (SEM) analyses. The degree of substitution (DS) of DAR-chitosan was evaluated by elemental analysis and ^{13}C CP-MAS NMR spectroscopy and found to be around 12%. The copper (II) metal complex of DAR-chitosan was prepared and characterized by FT-IR, DR-UV–vis and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Thermal behaviors of the synthesized compounds were investigated by DSC and TG-DTG-DTA analysis. The catalytic activity of copper (II) complex of chitosan derivative (DAR-chitosan-Cu) was investigated on hydrogen peroxide decomposition. The copper chelate showed high efficiency (over 80%) towards the decomposition of hydrogen peroxide as heterogeneous catalyst.

1. Introduction

Chitosan is a natural, cationic amino polysaccharide co-polymer of glucosamine and *N*-acetylglucasamine, obtained by the alkaline, partial *N*-deacetylation of chitin (Muzzarelli, 1977). Chitosan has been considered as a non-toxic, biodegradable, biocompatible and environmentally friendly material with many superior properties (Jigar & Sinha, 2007; Muzzarelli & Ilari, 1994). This biopolymer has applications ranging from artificial skin, photography, cosmetics, food and nutrition, ophthalmology and wastewater treatment (Ravi Kumar, Muzzarelli, Muzzarelli, Sashiwa, & Domb, 2004). In addition, chitosan has received significant interest for removal of heavy metal ions due to its good metal-binding capacities and easy reuse, as well as its relatively low cost compared with activated carbon and its possible biodegradability after usage (Muzzarelli, 2011; No & Meyers, 2000).

In the last years there have been many studies interested in chemical modification of chitosan and its derivatives to enhance their properties and consequently expand their potential applications (Heras, Rodriguez, Ramos, & Agullo, 2001; Terada et al., 1999; Yalçınkaya, Demetgül, Timur, & Çolak, 2010). Hence, functionalization of chitosan provided catalysts for oxidation of alkyl benzene (Chang, Wang, & Su, 2002), cyclopropanation of olefins (Sun, Xia, & Wang, 2002), Suzuki and Heck reactions (Hardy, Hubert, Macquarrie, & Wilson, 2004).

The presence of primary amine in the polymeric chain of chitosan leads to the possibility of a several chemical modifications, including the preparation of Schiff bases (Moore & Roberts, 1981; Muzzarelli et al., 1988). It is well known that, the diketone; 4,6-diacetylresorcinol (DAR) serves as a starting material for the generation of multidentate symmetrical Schiff bases (Shebl, 2009). In this sense the modification of chitosan with aldehydes and ketones to produce Schiff bases may result in a potentially complexing material for metallic species with potential analytical and environmental applications (Hardy et al., 2004; Wang, Sun, & Xia, 2003).

It is well known that, chitosan can be chemically modified at very high degrees of substitution by homogenous reactions but at low levels by heterogeneous reactions (typically up to $DS > 0.3$). Although very high DS can be achieved when chitosan is dissolved in acidic solutions, many studies show that functionalization, even under mild conditions, dramatically reduces the molecular weight of the chitosan (Macquarrie & Hardy, 2005).

It has been known for about a century that the decomposition of H_2O_2 to H_2O and O_2 is considerably accelerated by many metal ions (Haber & Weiss, 1934; Kremer, 1985). The decomposition of hydrogen peroxide has been used as a model reaction for the investigation of the catalytic activity of various metal complexes and has also been studied as a catalase model. The catalase like properties of copper (II) complexes has also been investigated, but reports on this activity of copper (II)-containing systems reported are relatively

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scarce (Gao, Martell, & Reibenspies, 2003). The difference in reactivity of Cu(II) complexes towards H_2O_2 is due to the change in the redox potential of Cu(II) ions as a result of ligation with different ligands (Ozawa, Hanaki, Onodera, Kasai, & Matsushima, 1991).

The development of heterogeneous catalysts has become a major area of research recently, as the potential advantages like easy of separation, recovery, and reuse of catalysts, and the clean separation of product from the reaction mixture (Macquarrie & Hardy, 2005).

This study is aimed to synthesize of ketimine derivative of chitosan by condensation with 4,6-diacetylresorcinol (DAR) under heterogeneous reaction medium. Also, is aimed to prepare the metal complex (Cu^{2+}) of chitosan derivative and to investigate the catalytic activity of the chelate towards to hydrogen peroxide decomposition reaction.

2. Materials and methods

2.1. Instrumentation

Infrared (IR) spectra were recorded on a Perkin Elmer RX-1 FT-IR spectrophotometer using KBr pellets (4400–400 cm^{-1}). Room temperature diffuse reflectance spectra in the ultra- violet and visible region (DR-UV–vis) were recorded on a Varian Cary 100 model UV-Vis spectrophotometer. Elemental analyses were carried out with LECO-CHNS-932. The surface morphology of chitosan and derivatives were examined by scanning electron microscope (SEM). The samples observed by using a JEOL JSM 5500LV Scanning Electron Microscope with double sided carbon tape at an accelerating voltage of 5 kV. Metal analysis was carried out by ICP-AES (Varian model-Liberty Series II) in a solution prepared by decomposition of the complex with HNO_3 followed by dilution with bidistilled water. Differential scanning calorimetry (DSC) analyses were carried out by Perkin Elmer Pyris. The samples were heated from 40 °C to 350 °C at a heating rate of 10 °C min^{-1}. Thermogravimetric analyses (TG-DTA) of the samples were performed with DuPont 951 thermal analyzer under air atmosphere at a heating rate of 10 °C min^{-1}. X-ray diffraction spectrometry (XRD-powder) was obtained using a Rigaku System RadB X-Ray Diffractometer, using monochromated Cu Kα radiation in the range 2–40° (2θ), at 25 °C.

2.2. Materials

Chitosan with high molecular weight was purchased from Aldrich (Cat. number 41941-9, >75% deacetylated, Brookfield viscosity 800 cps). 4,6-Diacetylresorcinol (DAR) was used as crosslinking agent and was prepared by following literature procedure (Abou-Hussein, 2010). Cu^{2+} ion was used as its acetate salt for Cu(II) complex of crosslinked chitosan derivative. Working solutions of hydrogen peroxide were prepared weekly by volumetric dilution of 30% H_2O_2 (Merck) and were standardized daily by titration with potassium permanganate. All other chemicals were analytically pure and used without further purification.

2.3. Synthesis of ketimine derivative of chitosan (DAR-chitosan)

Ketimine derivative of chitosan (DAR-chitosan) ligand was prepared in two steps. The first step was the formation of 4,6-diacetylresorcinol (DAR) by acetylation of resorcinol (Emara, Tawab, El-ghamry, & Elsabee, 2011). The second step was the condensation of 4,6-diacetylresorciol (DAR) with chitosan. The crosslinking agent DAR (4.4 mmol) dissolved in methanol (50 dm^3) was added dropwise to the suspension of swollen 2.0 g of chitosan powder (8.8 mmol of glucosamine residue) in methanol with magnetic stirring. The mixture was refluxed for 24 h, which resulted in a yellow-colored compound. It was then decanted and thoroughly washed with methanol to remove any unreacted crosslinking agent and then dried in vacuum at 60 °C to give DAR-chitosan as a powder in yellow color (Scheme 1).

2.4. Synthesis of Cu(II) complex of DAR-chitosan (DAR-chitosan-Cu)

1.05 g of DAR-chitosan was suspended in methanol and stirred at 60 °C and then a hot solution of 0.50 g of $Cu(CH_3COO)_2{\cdot}H_2O$ in methanol (20 ml) was added drop wise. The mixture was stirred and refluxed for 24 h. The complex was filtered through a Gooch-3 filter and washed with methanol, water, dimethylsulfoxide (DMSO) and dimethylformamide (DMF) to remove the adsorbed metal ions, then dried in the vacuum oven (Scheme 2).

Yield: 1.10 g (78%); analytical data for DAR-chitosan-Cu: 6% Cu; color: green.

2.5. Catalase-like activity studies

The decomposition of H_2O_2 catalyzed by DAR-chitosan-Cu(II) complex can be monitored by titrating the undecomposed H_2O_2 with standard $KMnO_4$ solution (0.01 M). The chosen concentration of H_2O_2 was 3.5×10^{-2} M. In addition, the chosen amount range of catalyst was from 0.01 mmol to 0.1 mmol Cu(II) at a constant concentration of H_2O_2, pH and temperature.

The procedure for a study as follows; 50 mg of DAR-chitosan-Cu(II) complex (0.1 mmol Cu) loaded in a flask containing a 10 ml of 3.5×10^{-2} M hydrogen peroxide solution in aqueous phosphate buffer pH 6.86. Then, the reaction flask was thermostatted to 25 °C under constant stirring. Finally, the extent of hydrogen peroxide decomposed at different intervals of time (each 10 min; from 0 to 60 min,) was estimated by taking 2.5 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 amount of DAR-chitosan-Cu(II). The reusability of the catalyst was also evaluated. After each experiment, the catalyst was separated from the reaction mixture by simple filtration. And also, the catalyst was washed with water and dried carefully before using in the subsequent run.

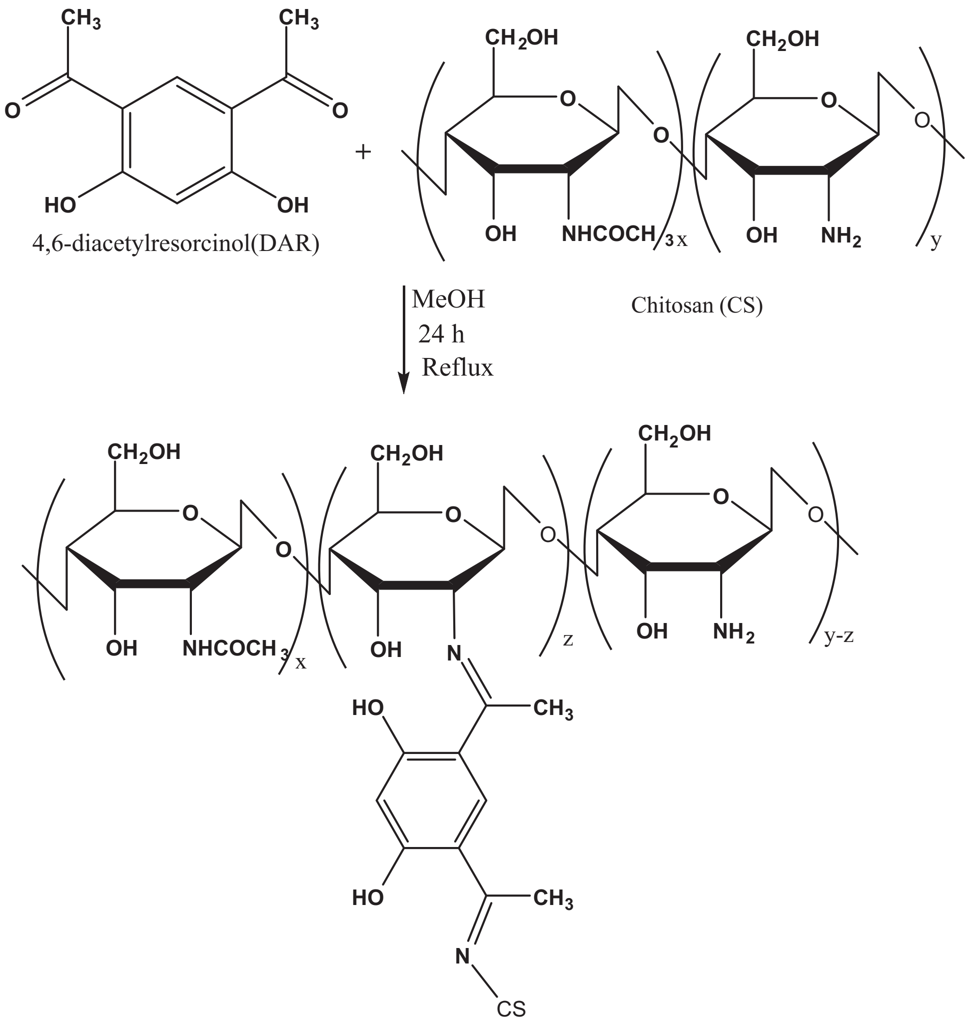
On the other hand, the reference experiments were operated by using CS and DAR-chitosan as catalysts.

3. Results and discussion

3.1. Solubility

Solubility of chitosan is related to the ionic concentration, pH, the distribution of acetyl groups along the chain, the intra-chain H bonds involving the hydroxyl groups and the molecular weight. It is well known that, solubilization of chitosan occurs by protonation of the $-NH_2$ group on the C-2 position of the D-glucosamine repeat unit, whereby the polysaccharide is converted to a polyelectrolyte in acidic media (Rinaudo, 2006).

The synthesized crosslinked-chitosan derivative (DAR-chitosan) was insoluble in aqueous solutions of organic acids and common solvents like acetone, ethanol, toluene, dichloromethane and DMF. This case can be explained by the decrease in number of $-NH_2$ groups of chitosan due to the condensation of carbonyl groups of DAR with these primary amino groups (Scheme 1). Also, the DAR-chitosan-Cu complex was insoluble in aqueous solutions of organic acids and other dilute acid solutions. Hence, this property of the complexes is important for easy separation from the reaction mixture while used as catalyst in the H_2O_2 decomposition reactions.



Scheme 1. Synthesis pathway of ketimine derivative of chitosan with DAR.

3.2. Elemental analysis

Carbon, hydrogen and nitrogen elements analyses results of chitosan powder and chitosan derivative are given in Table 1. The results show that, carbon content was increased after the chemical modification of chitosan because of the absence of nitrogen in DAR. Therefore, it can be easily understood the reason of the increase in the ratio C/N from 5.15 to 6.28 for DAR-chitosan. Therefore, the degree of substitution (DS) of DAR-chitosan was found to be around 12%.

The result of ICP-AES with respect to percent of metal by weight for DAR-chitosan is also given in Table 1. The result suggests that, the value of metal content of metal complex can be in a satisfaction range (6% Cu).

Table 1
Elemental analysis results of the compounds.

Compound	Element (%)				
	Cu	C	H	N	C/N
Chitosan	–	42.35	7.06	8.23	5.15
DAR-chitosan	–	45.86	6.68	7.30	6.28
DAR-chitosan-Cu	6				

3.3. Spectral (FT-IR and DR-UV–vis) analysis

The FTIR spectrum of chitosan shows a broad-OH stretching absorption band between 3450 and 3100 $\mathrm{cm^{-1}}$ and the aliphatic C—H stretching at 2880 $\mathrm{cm^{-1}}$ (Fig. 1a). The absorption band between 1220 and 1020 $\mathrm{cm^{-1}}$ attributed to the free primary amino group (NH_2) at C2 position. In addition, the peak at 1655 $\mathrm{cm^{-1}}$ represented the acetylated amino group of chitin, which indicated that the sample is not fully deacetylated. The peak at 1376 $\mathrm{cm^{-1}}$ is due to the symmetrical angular deformation of CH_3, the peak at 1320 $\mathrm{cm^{-1}}$ due to C—N stretching of the amino groups and the peak at 1030 $\mathrm{cm^{-1}}$ due to C—O—C stretching vibration (Mansouri et al., 2004; Tian, Liu, Hu, & Zhao, 2004). Fig. 1b shows the FT-IR spectrum of the DAR-chitosan. The main absorption bands were observed as 3100–3500 $\mathrm{cm^{-1}}$ (broad, O—H), 2937–2820 $\mathrm{cm^{-1}}$ (C—H), 1570 $\mathrm{cm^{-1}}$ (aromatic, —C=C—) and 850–700 $\mathrm{cm^{-1}}$ (substituents of aromatic ring). The broad peak at 1639–1668 $\mathrm{cm^{-1}}$ range is assigned to the mixed mode of vibration arising from azomethine moiety, ν(C=N) and ν(C=O) of chitosan amide group vibration.

The broadening at the range of 3100–3500 $\mathrm{cm^{-1}}$ due to the O—H absorption of the DAR and the differences at 2800–2950 $\mathrm{cm^{-1}}$, 1350–1450 $\mathrm{cm^{-1}}$ and 700–900 $\mathrm{cm^{-1}}$ region at FT-IR spectrum of CS, might be attributed to the condensation of DAR with chitosan.

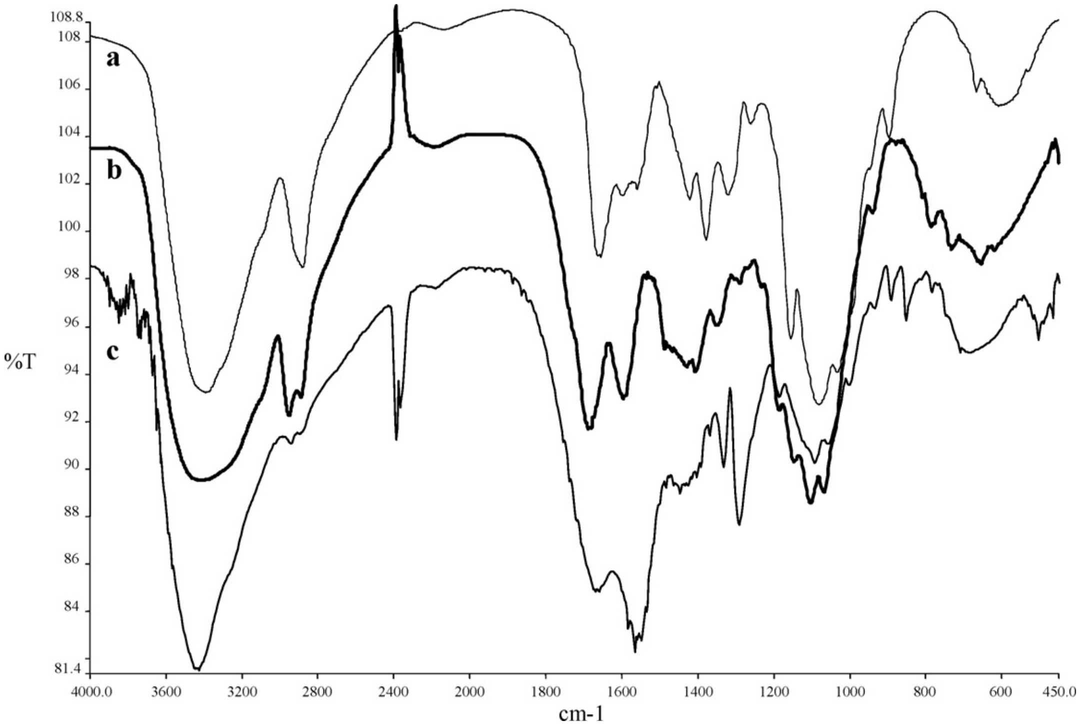
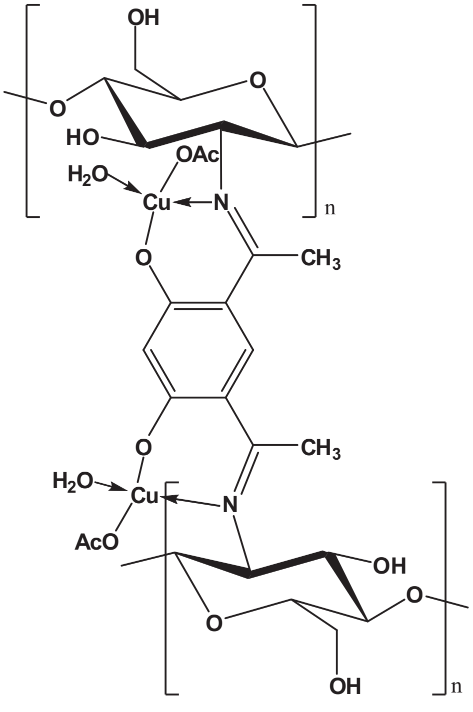


Fig. 1. The FT-IR spectra of CS (a), DAR-chitosan (b) and DAR-chitosan-Cu (c).

On the other hand, the FT-IR spectrum of DAR-chitosan-Cu(II) is given in Fig. 1c. The broad band at 3100–3500 cm^{-1} region of DAR-chitosan spectrum become sharper in the spectrum of DAR-chitosan-Cu might be due to the deprotonation of OH groups of DAR moiety to coordinate to Cu(II) ions. The new weak peaks observed at 420–500 cm^{-1} region might be explained by the metal–N and metal–O coordination (Demetgül, Karakaplan, Serin, & Dığrak, 2009). In addition, the C=N bands of DAR-chitosan were shifted from 1639 to 1631 after complex formation with Cu(II) ion because of the involvement of nitrogen atoms in the coordination (Demetgül, Karakaplan, & Serin, 2008).

The DR-UV–vis spectra of DAR-chitosan and DAR-chitosan-Cu are given in Fig. 2 and Fig. 3, respectively. It is known from the literature that there is not any peak observed in the spectrum of chitosan at the range of 300–800 nm (Kumar et al., 2010). In contrast, there are two peaks (286 and 370 nm) observed in the spectrum of DAR-chitosan at that range attributed to the benzene π–π* and imine (C=N) n–π* transitions, respectively (Demetgül et al., 2010).

In the spectrum of the DAR-chitosan-Cu, the bands of the azomethine n–π* transition are shifted to lower frequencies indicating



Scheme 2. The proposed structure of DAR-chitosan-Cu(II).

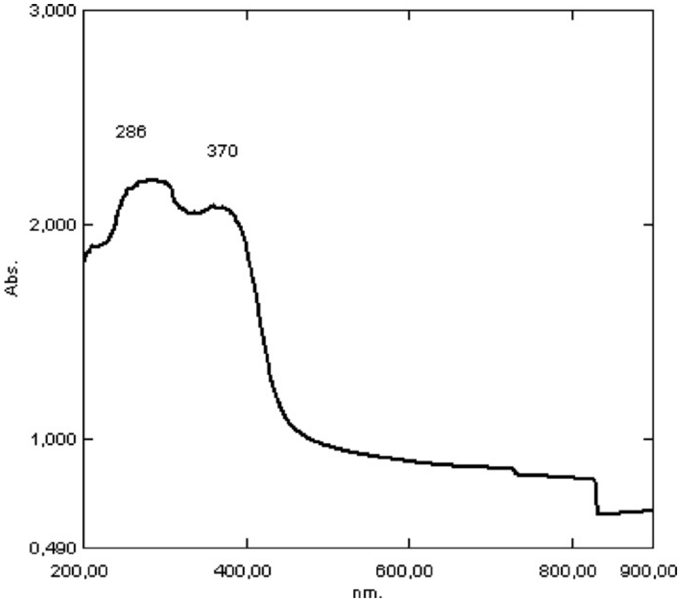


Fig. 2. UV–vis spectrum of DAR-chitosan.

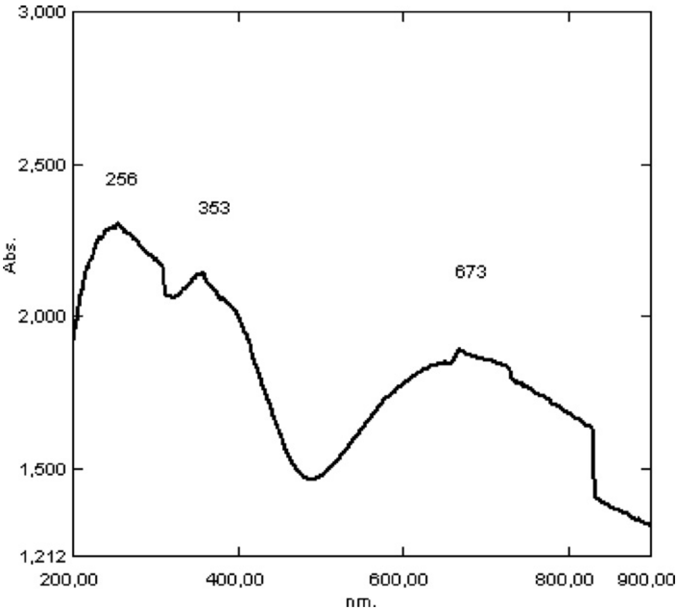


Fig. 3. UV–vis spectrum of DAR-chitosan-Cu.

that the imine nitrogen atom is involved in coordination to the metal ion (Demetgül et al., 2010). In addition, the band observed at around 670 nm might be assigned to d–d transition of the metal ion (Tümer, Ekinci, Tümer, & Bulut, 2007).

3.4. CP–MAS ^{13}C NMR analysis

It was studied with solid state ^{13}C NMR to characterize the structure and to identify degree of substitution (DS) of DAR-chitosan because of the insoluble property. The analysis of CP–MAS ^{13}C NMR spectrum of DAR-chitosan shows that peaks at 103, 80, 71, 56 and 51 ppm are attributed to the glucose amine ring carbons of the chitosan skeleton (Fig. 4). Also it shows that the peaks attributed to acetyl carbons at 170 ppm (C=O) and 19 ppm ($-CH_3$). In addition, new peaks as weaker than others were observed at 161–165, 131, 108, 32 and 27 ppm as different from CP–MAS ^{13}C NMR spectrum of chitosan which have acetyl groups (Capitani, Crescenzi, De Angelis, & Segre, 2001). These new peaks are attributed to imine (C=N) carbons, aromatic carbons and methyl carbons of DAR moiety, respectively.

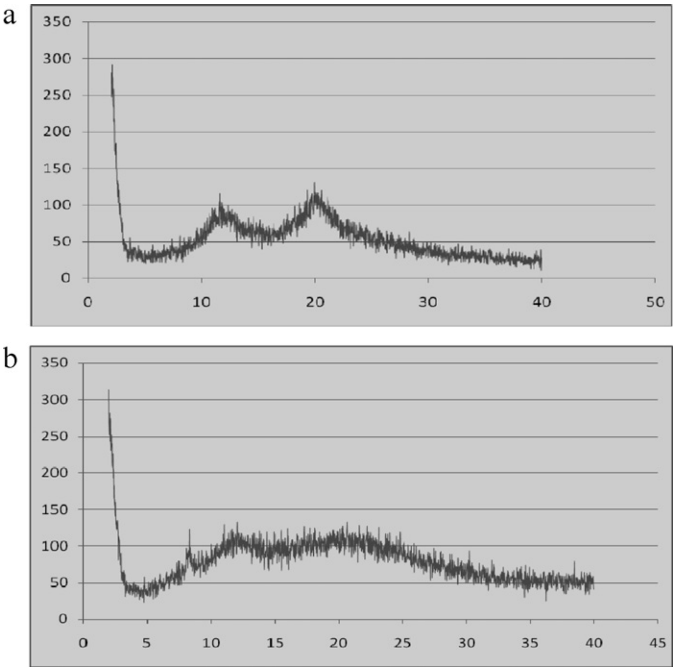


Fig. 5. XRD diffractograms of DAR-chitosan (a) and DAR-chitosan-Cu(II) (b).

The degree of substitution (DS) of DAR-chitosan was calculated from the relative integral of methyl carbons of DAR compared to the methyl carbons integral of the acetyl group of polysaccharidic backbone as almost 12%. This result seems to be significant due to the synthesis conditions (heterogeneous) (Demetgül & Serin, 2008). On the other hand, it is estimated that the polymer backbone was not distorted and the chemical modification occurred without any degradation because of the case reported in the literature (Macquarrie & Hardy, 2005).

3.5. XRD

The XRD spectra of DAR-chitosan and DAR-chitosan-Cu are given in Fig. 5a and b, respectively. It was reported that chitosan shows two characteristic sharp peaks of crystalline nature at 2θ of 10° and 20° (Jayakumar, Reis, & Mano, 2007; Muzzarelli, Tanfani, Emanuelli, Muzzarelli, & Celia, 1981). The results indicate that the intensity of peaks of DAR-chitosan decreases also with the

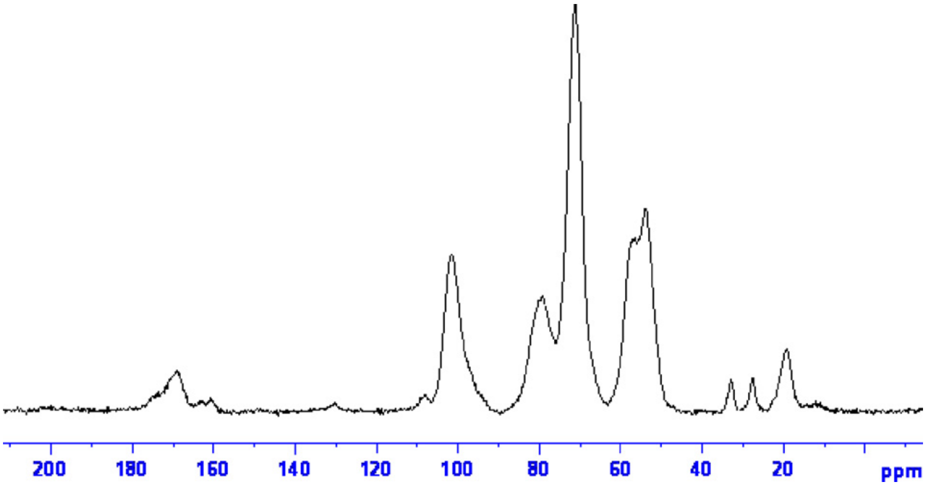


Fig. 4. ^{13}C CP-MAS NMR spectrum of DAR-chitosan.

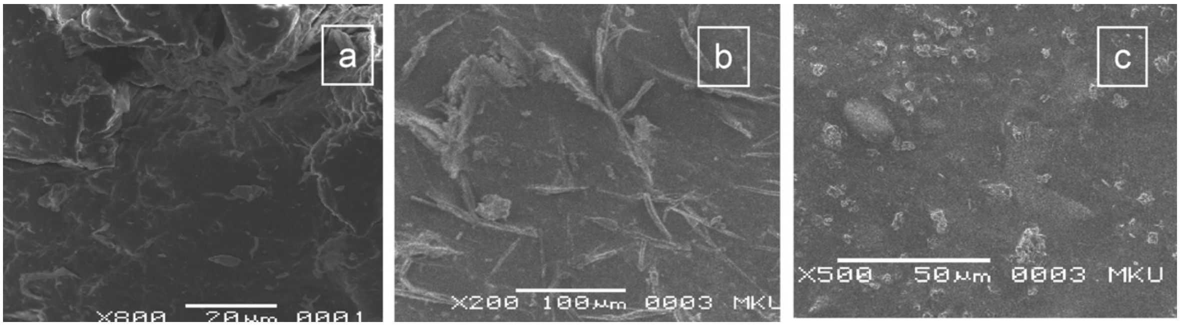


Fig. 6. SEM images of CS (a), DAR-chitosan (b) and DAR-chitosan-Cu (c).

broadening of peaks when compared to free chitosan. This feature may be attributed to the deformation of strong hydrogen bonds in the free chitosan unit and the bulky aromatic unit of DAR condensed on it. This indicates that DAR-chitosan is less crystalline and more amorphous than free chitosan (Ou et al., 2010). The XRD spectra of Cu(II) complex of DAR-chitosan shows a weak sharp peak at about 8° might be due to the chelation on the polymer.

3.6. SEM

The SEM images of the surface morphology of CS, DAR-chitosan and DAR-chitosan-Cu are shown in Fig. 6. The difference in structural morphology between chitosan and DAR-chitosan is further supported by the difference in their SEM images. The film form of crosslinked chitosan derivative displayed a more regular smooth surface compared to surface of chitosan. This is attributed to the condensation of crosslinking agent (DAR) on chitosan (Krishnapriya & Kandaswamy, 2010).

On the other hand, the surface of DAR-chitosan-Cu does not exhibit the same structure as DAR-chitosan may be due to the metal sites coordinated to chitosan derivative.

3.7. Thermal properties (DSC and TG-DTG-DTA)

It is well known that for chitosan and its derivatives; the endothermic peaks observe for water vapor elimination and the exothermic peaks observe for depolymerization and decomposition of the polymer (Demetgül et al., 2008).

The DSC curve of DAR-chitosan is given in Fig. S1. The main thermal degradation process of the DAR-chitosan takes place at temperature (275 °C) lower than the degradation stage of chitosan, indicating that the DAR-chitosan polymer is less stable than chitosan. It seems that the instability of the DAR-chitosan polymer compared with chitosan might be due to the decrease in the number of primary amino groups after the chemical modification process which is lowered crystallinity of chitosan (Demetgül et al., 2008).

The TG-DTG-DTA curves of DAR-chitosan-Cu are given in Fig. 7. The main thermal degradation process of the DAR-chitosan-Cu takes place at around 421 °C as an exothermic peak. This can be assigned to the complex formation by the coordination of C=N and OH groups of ketimine moieties to the metal ion. These results show that DAR-chitosan-Cu has a higher thermal stability than DAR-chitosan. On the other hand, the residue value of DAR-chitosan-Cu is more than value of DAR-chitosan might be due to the formation of metal oxide (CuO).

3.8. Catalase-like activity studies

Variables such as the time and amount of the catalyst were found to have important roles in the decomposition of H_2O_2. The Cu(II) complex of DAR-chitosan was used for these investigations into the catalytic decomposition of H_2O_2. The conditions of catalytic reactions for hydrogen peroxide decomposition were chosen according to the similar studies in the literature (Gupta & Abdulkadir, 2008). The extent of decomposition increased with the time and amount of the catalyst. The plots of hydrogen peroxide decomposition over DAR-chitosan-Cu as a function of reaction time is given in Fig. 8. It was observed that 60 min is an adequate reaction time for this catalytic reaction. The effect of amount of catalyst also studied for this catalytic reaction and the plot of this investigation is given in Fig. S2. It is seen that, the increase in amount of catalyst also increases the efficiency in decomposition of H_2O_2. In contrast, the

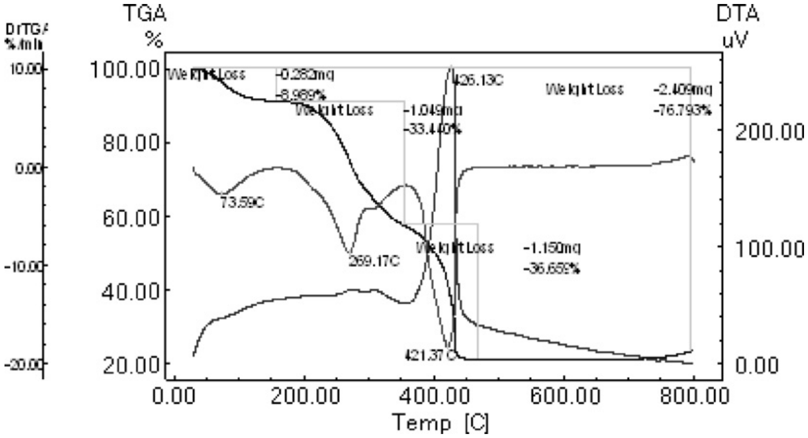


Fig. 7. TG-DTG-DTA curves of DAR-chitosan and DAR-chitosan-Cu.

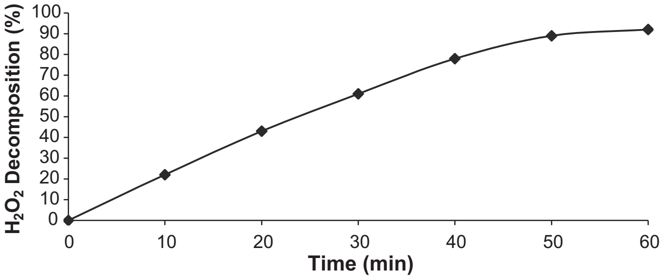


Fig. 8. H_2O_2 decomposition over DAR-chitosan-Cu(II) as a function of reaction time. The reaction conditions; catalyst 0.1 mmol Cu(II), 25 °C, 10 ml 3.5×10^{-2} M H_2O_2 and pH 6.86.

amount of more than 0.09 mmol of Cu(II) have not increased the efficiency any more.

The reusability property of DAR-chitosan-Cu also studied and the plot of the results is given in Fig. S3. The catalytic activity of catalyst in terms of efficiency (%) slightly decreased with increasing number of cycles of the reaction. The capacity of the catalyst drops about 10% during the consecutive ten recycling. It was seen that the catalyst displayed very good reusability (Darabi et al., 2009). The results showed that DAR-chitosan-Cu(II) can be used as a heterogeneous catalyst in H_2O_2 decomposition reactions.

The mechanism of the catalytic reaction has been proposed in the literature is given in formulas (1)–(3) (Jose, John, Gigimol, & Mathew, 2003).

Chitosan and chitosan derivative powders were used as catalysts for reference experiment. As a result of the reference experiments it can be easily stated that chitosan and chitosan derivative do not have catalytic activity on the decomposition of hydrogen peroxide.

$$H_2O_2 \rightarrow {}^{-}OOH + H^{+} \tag{1}$$

$$\text{L-Cu} + {}^{-}OOH \rightarrow \text{L-Cu}({}^{-}OOH) \tag{2}$$

$$\text{L-Cu}({}^{-}OOH) + H_2O_2 \rightarrow \text{L-Cu} + H_2O + {}^{-}OH + O_2 \tag{3}$$

4. Conclusions

The new chitosan derivative (DAR-chitosan) was prepared by condensation of chitosan (CS) with 4,6-diacetylresorcinol (DAR) as crosslinking agent at heterogeneous medium. The result suggests that, the value of metal content of metal complex can be in a satisfaction range (6% Cu). In addition, the results of the thermal studies are shown that DAR-chitosan-Cu has a higher thermal stability than DAR-chitosan. Furthermore, the synthesized Cu(II) complex displayed a good catalytic activity towards the decomposition of hydrogen peroxide as a heterogeneous catalyst.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbpol.2012.03.013.

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