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Synthesis of Schiff Base through the Condensation Reaction Between Cellulose Dialdehyde with Ethylenediamine and Aniline as Well as Antibacterial Activity Test

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ABSTRACT
Schiff base was created using a condensation reaction involving Ethylene diamine or Aniline and dialdehyde cellulose (DAC), which was obtained by oxidizing α-cellulose with sodium periodate as the oxidizing agent. The cellulose dialdehyde was identified through qualitative analysis, which involved observing the formation of a brick red sediment during the Fehling test and a rise in solubility in water. Additionally, the presence of an aldehyde group was confirmed by analyzing the FT-IR spectrophotometer data, which showed a peak at a wave number of 1635.64 cm^{-1}. The synthesized dialdehyde cellulose has an oxidation degree of 80.9% and a carbonyl level of 10.36%. The Schiff base was analyzed using an FT-IR spectrophotometer, which revealed peaks at wave numbers 1635.64 cm-1 and 1604.77 cm^{-1}. These peaks suggest the creation of a Schiff base bond (C=N) resulting from the condensation of the amine group from Ethylene diamine and Aniline with the aldehyde group from DAC. The antibacterial activity of Schiff bases was evaluated using the disc plate diffusion method. The Schiff base resulting from the condensation of DAC with Ethylenediamine at concentrations of 0.15%, 0.30%, and 0.45% was tested against *S.aureus* and *E.coli*. Clear zones of inhibition were seen, indicating the antibacterial effect. The Schiff base resulting from the condensation of DAC with Aniline at concentrations of 0.15%, 0.30%, and 0.45% showed clear zone diameters of 6.9 mm, 9 mm, and 12.5 mm against *S.aureus* and 7 mm, 12.5 mm, and 13 mm against *E.coli*. The clear zone diameters in a row were 10 mm, 10.8 mm, and 20.1 mm against *S.aureus* and 10.5 mm, 14.6 mm, and 17.1 mm against *E.coli.* The condensation of dialdehyde cellulose with ethylene diamine and Aniline leads to Schiff base formation. This Schiff base has antibacterial characteristics that are effective against *S.aureus* and *E.coli.*

Keywords: Antibacterial, Aniline, Cellulose, Ethylenediamine, Schiff Base

ABSTRAK
Basa Schiff dibuat menggunakan reaksi kondensasi yang melibatkan Etilen diamina atau Anilin dan dialdehida selulosa (DAC), yang diperoleh dengan mengoksidasi α-selulosa dengan natrium periodat sebagai zat pengoksidasi. Selulosa dialdehida diidentifikasi melalui analisis kualitatif, yang melibatkan pengamatan pembentukan sedimen merah bata selama uji Fehling dan peningkatan kelarutan dalam air. Selain itu, keberadaan gugus aldehida juga dikonfirmasi melalui analisis data spektrofotometer FT-IR yang menunjukkan puncak pada bilangan gelombang 1635,64 cm-1. Selulosa dialdehida hasil sintesis mempunyai bilangan oksidasi 80,9% dan kadar karbonil 10,36%. Basa Schiff dianalisis menggunakan spektrofotometer FT-IR yang menunjukkan puncak pada bilangan gelombang 1635,64 cm-1 dan 1604,77 cm-1. Puncak ini menunjukkan terciptanya ikatan basa Schiff (C=N) yang dihasilkan dari kondensasi gugus amina dari Etilen diamina dan Anilin dengan gugus aldehida dari DAC. Aktivitas antibakteri basa Schiff dievaluasi menggunakan metode difusi pelat cakram. Basa Schiff hasil kondensasi DAC dengan Ethylenediamine pada konsentrasi 0,15%, 0,30%, dan 0,45% diuji terhadap S.aureus dan E.coli. Terlihat adanya zona hambat yang jelas, menunjukkan adanya efek antibakteri. Basa Schiff hasil

kondensasi DAC dengan Anilin pada konsentrasi 0,15%, 0,30%, dan 0,45% menunjukkan diameter zona bening sebesar 6,9 mm, 9 mm, dan 12,5 mm terhadap S.aureus serta 7 mm, 12,5 mm, dan 13 mm terhadap E. .coli. Diameter zona bening berturut-turut adalah 10mm, 10.8mm, dan 20.1mm terhadap S.aureus dan 10.5mm, 14.6mm, dan 17.1mm terhadap E.coli. Kondensasi selulosa dialdehida dengan etilen diamina dan anilin menyebabkan pembentukan basa Schiff. Basis Schiff ini memiliki sifat antibakteri yang efektif melawan S.aureus dan E.coli.

Kata Kunci: Antibakteri, Anilin, Basa Schiff, Etilendiamin, Selulosa

1. Introduction

Cellulose is the predominant polymer of organic chemicals found in abundance on the planet. The annual production of cellulose from plants is projected to reach 1012 tons. It is widely thought that each plant includes a minimum of 33% cellulose. Conversely, wood contains approximately 50% cellulose, whereas cotton contains around 90% cellulose. The cellulose produced is mainly processed into paper pulp staples; some are used for sustainable chemical processes. The chemical processes performed on cellulose include cellulose esterification, cellulose oxidation, and cellulose etherification [1].

Cellulose, composed of recurring glucose monomer units, has sparked a worldwide revival of interdisciplinary cellulose study owing to its distinctive properties. In recent decades, cellulose has gained interest as a polysaccharide with potential for Schiff base synthesis. This synthesis can be extensively adjusted to customize its properties for various uses, such as antibacterial purposes [2].

These oxidation methods frequently entail modifying polymers by adding surface hydroxyl groups. These polymers are typically produced using coupling agents or in situ polymerization of immobilized initiators on the substrate surface [3]. The periodic oxidation method provides a practical and significant technique for modifying hydroxyl groups in cellulose. It is recognized for its precise oxidative breakdown of the C-2 and C-3 glycol bonds in the glucose ring, forming C-2/C-3 dialdehyde products. These products serve as reactive intermediates for subsequent modification. The process of oxidizing α-cellulose using Sodium Periodate will produce cellulose dialdehyde [4].

Bacteria are a crucial category of microorganisms due to their significant positive and negative impact. Bacteria are ubiquitous microorganisms in various environments, such as the air, water, and soil. They are also commonly present in the intestines of animals, the moist layers of the mouth, nose, and throat, and on the surfaces of both the human body and plants [5]. Bacteria are the tiniest unicellular organisms, with some measuring about 0.4 µm (micrometer) in diameter. A cell comprises cytoplasm and core material enclosed by a cell wall. This cell wall is further enveloped in certain bacteria by a capsule or mucilage layer [6].

Schiff bases are chemical compounds that include an imine functional group characterized by a carbon-nitrogen double bond (C=N). This derivative can be synthesized by condensing primary amines with carbonyl molecules, such as aldehydes and ketones. The discovery of Schiff's base dates back to 1864 and is credited to Hugo Schiff. Schiff bases possess imine groups (-RC=N-) inside their structure [7].

The antibacterial characteristics of cellulose fibers containing active amine groups have been acknowledged, and covalent attachment is a highly efficient and favoured way for chemically modifying cellulose surfaces to integrate amines [8].

From previous studies, aldehydes from ozonolysis of palm oil fatty acid metal esters with Aniline and phenylhydrazine to observe antibacterial activity. The antibacterial activity of Schiff bases was tested using the agar diffusion method in DMSO (Dimethyl Sulfoxide) solvent against *Staphylococcus aureus* and *Escherichia coli* bacteria. The results showed that the two Schiff bases effectively inhibited *Escherichia coli* bacteria, with antimicrobial indices of 0.75 and 1.22, respectively. Against *Staphylococcus aureus* bacteria, the antimicrobial index was 0.12 and 0.42, respectively [9].

A series of oxazepine-derived Schiff bases were also synthesized through condensation with aromatic aldehydes in ethanol solvent and acetic acid as catalysts. The antibacterial properties were then tested against *Staphylococcus aureus*, *Escherichia coli*, *Salmonella typhii* and *Klebsiella pneumoniae*, which gave the results that the Schiff bases obtained showed good antibacterial activity against *Salmonella typhii* and *Klebsiella* *pneumoniae* and moderate against *Staphylococcus aureus* and *Escherichia coli*. It has also been tested for its ability to inhibit the corrosion of soft steel in 1N H_2SO_4 media, resulting in a Schiff base corrosion efficiency value reaching 89.58% [10].

From the background described above, researchers are interested in researching the condensation of cellulose dialdehyde with ethylenediamine or Aniline into Schiff bases, followed by the antibacterial activity test of the two Schiff bases.

2. Materials and Methods

2.1. Equipment

In this study, the tools used were reflux apparatus, hotplate and FTIR Spectrophotometer.

2.2. Materials

Materials used in this study were α-Cellulose commercial, sodium hydroxide, hydrochloric acid, Ethylenediamine, Aniline, Ethanol 96%, and sodium periodate were purchased from E-Merck.

2.3. Research Procedure

2.3.1 Synthesis of Cellulose Dialdehyde

A total of 8.7 g of sodium periodate was dissolved with 200 mL of distilled water in a 500 mL Erlenmeyer glass at room temperature and conditions without light, then 4 g of α-cellulose was added and stirred vigorously at 35^{o}C for 24 h. After the reaction, ethanol was added gradually until a solid was formed and filtered using Whatmann filter paper No. 42. The residue was then rinsed and dried in a desiccator. Then, the results obtained were tested qualitatively using Fehling reagent. Then, the results were analyzed with FT-IR spectroscopy, the degree of oxidation was calculated, and the carbonyl content was determined [11].

2.3.2 Synthesis of Schiff Bases from Cellulose Dialdehyde with Ethylenediamine

0.676 g of SDA was put into a 3-neck flask measuring 250 mL. Then, the SDA was dissolved using 20 mL of absolute ethanol. A reflux device is assembled with a magnetic bar, thermometer, and $CaCl_2$ tube. Then 0.24 g (0.004 mol) of ethylene diamine was added slowly through the penates funnel and refluxed for 5 h. After the reaction, it was filtered using Whatman no. 42 filter paper and rinsed intensively with distilled water. Then, the precipitate was washed with 5 mL of distilled water and 5 mL of hot ethanol. The results obtained were dried in a desiccator and weighed. The structure was analyzed using an FT-IR spectrophotometer, and nitrogen content was tested using the Kjeldahl method and tested for antibacterial activity [12].

2.3.3 Synthesis of Schiff Base from Cellulose Dialdehyde with Aniline

0.676 g of SDA was put into a 3-neck flask measuring 250 mL. After that, the SDA was dissolved using 20 mL of absolute ethanol. A reflux device is assembled with a magnetic bar, thermometer, and $CaCl_2$ tube. Then 0.372 g (0.004 mol) of ethylene diamine was added slowly through the penates funnel and refluxed for 5 h. After the reaction, it was filtered using Whatman no. 42 filter paper and rinsed intensively with distilled water. The precipitate was then washed with 5 mL of distilled water and 5 mL of hot ethanol. The results obtained were dried in a desiccator and weighed. The structure was analyzed using an FT-IR spectrophotometer, and nitrogen content was tested using the Kjeldahl method and tested for antibacterial activity [12].

3. Results and Discussion

3. 1 Synthesis of Cellulose Dialdehyde

The results of determining the degree of oxidation through neutralization titration were 80.9%, and the carbonyl content was 10.36%. The formation of dialdehyde cellulose was also supported qualitatively by forming a brick-red precipitate with Fehling's reagent and increasing solubility in aquadest (water). The FT-IR spectrum shows the formation of cellulose dialdehyde, characterized by the appearance of the C=O aldehyde group in the wave number area of 1635.64 cm^{-1}. Still, at this wave number, it shows that the vibration peak is sharper than that of cellulose before oxidation, whereas in the wave number area of 3471.87 cm^{-1} indicates –OH group; 2939.52 cm^{-1} indicates the C-H sp^3 stretching group; at a wave number of 1033.85 cm^{-1} shows a symmetric C-O group and 879.54 cm^{-1} shows a C-H sp^3 bending group (Figure 1).

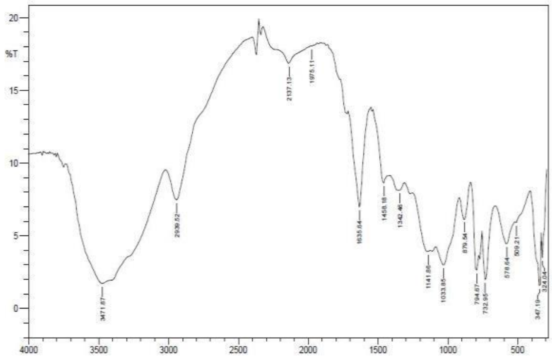
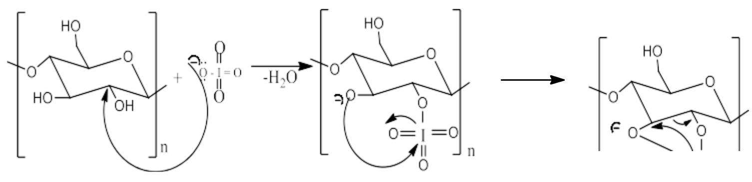


Figure 1. FT-IR Spectrum of cellulose dialdehyde

The reaction between cellulose and sodium periodate begins with the attack of the C atom on C2 of cellulose by the nucleophile, namely the O atom of sodium periodate, and the release of OH- occurs. OH- attacks the H proton in the –OH group of the C3 atom. O- on C3 binds I on periodate to form cyclic, and this is unstable, so the ring opening occurs on the C2 and C3 atoms to form cellulose dialdehyde and sodium iodate. Hypothetical reaction mechanism for the formation of cellulose dialdehyde.

$NaIO_4 \longrightarrow Na^+ + IO_4^-$



Cellulose

Figure 2. Reaction mechanism formation of cellulose dialdehyde

3. 2 Synthesis of Schiff Base from Cellulose Dialdehyde with Ethylenediamine

The results obtained from the condensation reaction of 0.676 g of cellulose dialdehyde with 0.24 g of ethylenediamine were 0.208 g in the form of a yellowish-brown powder. Nitrogen test data using the Kjeldahl method on Schiff base shows that the nitrogen content resulting from the condensation reaction of cellulose dialdehyde with ethylenediamine is 2.82%.

FT-IR spectrophotometry data shows the groups contained in the Schiff base, which gives a spectrum with vibration peaks in the wave number area of 3441.01 cm^{-1} indicating N-H vibrations in $-NH_2$ and –OH groups which overlap in the number area wave 3500- 3300 cm^{-1}; 2924.09 cm^{-1} shows the C-H vibration at $-CH_2$; 1635.64 cm^{-1} indicates the C=N group; 1118.71 cm^{-1} indicates a symmetric C-O group (Figure 3).

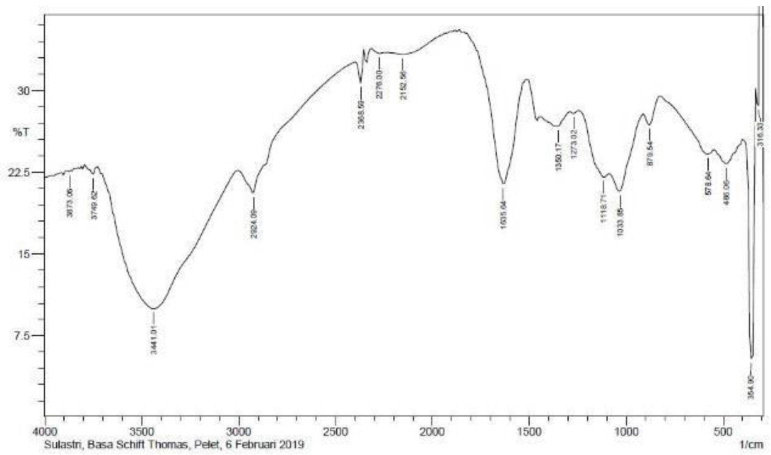


Figure 3. FT-IR Spectrum of Schiff base result of condensation of cellulose dialdehyde with ethylenediamine

The reaction mechanism for the formation of Schiff bases is hypothetically as shown in Figure 4

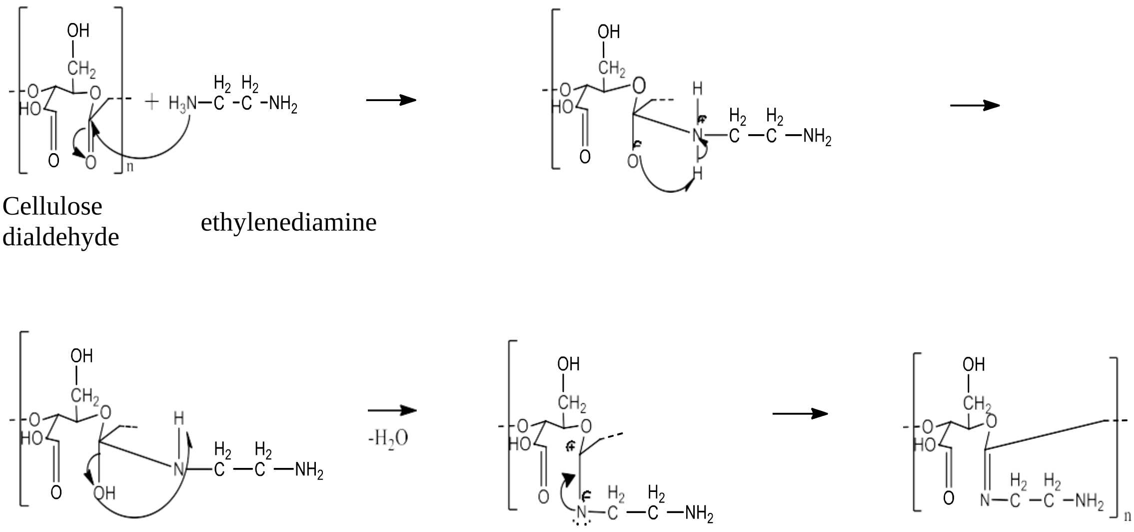


Figure 4. Reaction mechanism of Schiff base formation resulting from the condensation of cellulose dialdehyde with ethylene diamine

3. 3 Synthesis of Schiff Base from Cellulose Dialdehyde with Aniline

The results obtained from the condensation reaction of 0.676 g of cellulose dialdehyde with 0.372 g of Aniline were 0.253 g in the form of a yellowish-brown powder. Nitrogen test data using the Kjeldahl method on Schiff base shows that the nitrogen content resulting from the condensation reaction of cellulose dialdehyde with Aniline is 1.42%

FT-IR spectrophotometry data shows the groups contained in the Schiff base, which gives a spectrum with vibration peaks in the wave number area of 3410.15 $cm^{-1,}$ indicating N-H vibrations in $-NH_2$ and $–OH$ groups which overlap in the number area wave 3500- 3300 cm^{-1}; 2931.80 cm^{-1} shows the C-H vibration at $–CH_2$; 1604.77 cm^{-1} shows the C=N group which also overlaps with the C=C vibration in benzene; 1056.99 cm^{-1} indicates a symmetric C-O group (Figure 5).

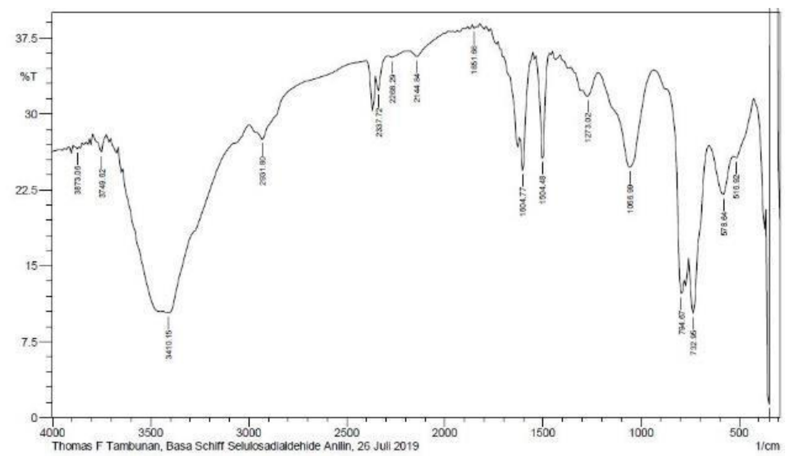


Figure 5. FT-IR spectrum of Schiff base result of condensation of cellulose dialdehyde with Aniline.

Hypothetical Schiff base formation reaction mechanism (Figure 6)

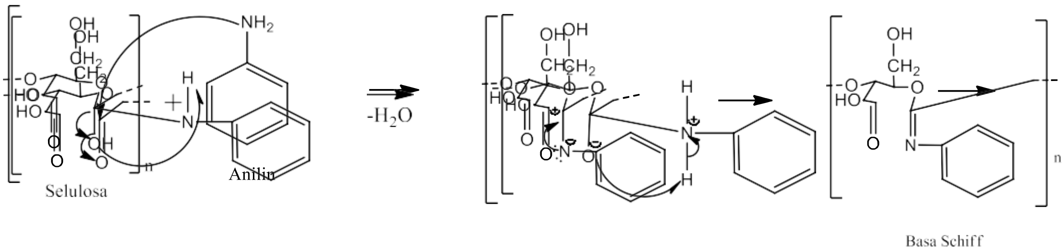


Figure 6. Reaction mechanism of Schiff base formation resulting from the condensation of cellulose dialdehyde with Aniline

Table 1. Synthesis results antibacterial test

Bacteria	Treatment	Concentration (%)	Paper Disk Diameter (mm)	Inhibition Zone Diameter (mm)
Escherichia Coli	Shiff Base I	0.15	6	7
		0.30	6	12.5
		0.45	6	13
	Shiff Base II	0.15	6	10.5
		0.30	6	14.6
		0.45	6	17.1
Staphylococcus aureus	Shiff Base I	0.15	6	6.9
		0.30	6	9.0
		0.45	6	12.5
	Shiff Base II	0.15	6	10.0
		0.30	6	10.8
		0.45	6	20.1

4. Conclusion

1. Schiff base can be synthesized through a condensation reaction between the amine group from ethylenediamine and Aniline with the carbonyl group from dialdehyde cellulose resulting from the oxidation of commercial cellulose with sodium periodate. The formation of Schiff base in the reaction of Cellulose dialdehyde with ethylene diamine and Aniline is supported by the appearance of vibration peaks in the wave number area of 1635.64 cm^{-1} and 1604.77 $cm\text{-}^{1,}$ respectively, which indicates the C=N group.

2. The Schiff base compound can act as an antibacterial, where the Schiff base compound (1) shows the most excellent antibacterial activity on *E.Coli* bacteria with a large inhibition zone at a concentration of 0.45%, equal to 13 mm and on *S.Aureus* bacteria at a concentration of 0.45%, amounting to 12.5 mm. Basa Schiff (2) showed the greatest antibacterial activity on *E. Coli* bacteria with a large inhibition zone at a concentration of 0.45%, amounting to 17.1 mm and on *S. Aureus* bacteria at 0.45%, amounting to 20.1 mm. Based on the level of strength, the antibacterial activity of Schiff base compounds 1 and 2 is classified as moderate.

5. Acknowledgements

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6. Conflict of Interest

Authors declare no conflicts of interest

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