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Study of Boron Complexation with Pyridoxine: Effect of Interaction Time, Temperature, and Amount of Pyridoxine

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Abstract

Borax is one of the compounds of boron (B), which is widely used as an anti-fungal, wood preservative, and antiseptic in cosmetics. Boron can form complexes with biomolecules such as pyridoxine, so it is interesting to know the interaction between borax and pyridoxine. This study seeks to investigate the complexation of boron, which is obtained from borax, with pyridoxine under various conditions of time, temperature, and the amount of pyridoxine. The resulting complex was characterized by UV-Vis spectrophotometry, Fourier Transform Infrared (FT-IR), and X-Ray diffraction (XRD). The study was initiated by optimizing the complexation of boron and pyridoxine. The maximum wavelengths of pyridoxine were found in the 205 nm and 292 nm regions, while the boron-pyridoxine complex was found in the 237 nm region. The obtained contact time, temperature, and amount of pyridoxine are 40 minutes, 60 °C, and 2 mL respectively. The results of the Fourier transform infrared (FT-IR) analysis of the boron-pyridoxine complex showed that there were OH groups, aromatic C=C groups, aliphatic C-C groups, B-H groups, and B-O groups. The results of the XRD analysis of the boron-pyridoxine complex obtained a diffraction angle of 30.93°.

Keywords: Boron-pyridoxine complex, borax, pyridoxine, complexation

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Abstrak

Boraks merupakan salah satu senyawa dari boron (B), yang banyak digunakan sebagai bahan anti jamur, pengawet kayu, dan antiseptik pada kosmetik. Boron dapat membentuk kompleks dengan biomolekul seperti piridoksin, sehingga menarik untuk mengetahui interaksi antara borax dengan piridoksin. Penelitian ini bertujuan untuk mempelajari kompleksasi antara boron yang berasal dari borax dengan piridoksin. Untuk mempelajari reaksi kompleksasi dilakukan dengan memvariasi lamanya waktu interaksi, suhu dan pengaruh jumlah piridoksin. Karakterisasi kompleks yang terbentuk dipelajari dengan dengan spektrofotometri UV-Vis, spektrofotometri Fourier Transform Infra Red (FT-IR) dan X-Ray Diffraction (XRD). Penelitian diawali dengan penentuan panjang gelombang serapan maksimum antara boron dan piridoksin. Panjang gelombang serapan maksimum untuk piridoksin diperoleh pada daerah 205, nm dan 292 nm, sedangkan kompleks boron-piridoksin didapatkan pada daerah 237 nm. Hasil yang didapatkan dari pengaruh waktu yaitu sebesar 40 menit, pada pengaruh suhu yaitu sebesar 60 ˚C dan pada jumlah piridoksin yaitu sebesar 2 mL. Hasil analisis Fourier Transform Infra Red (FT-IR) kompleks boron-piridoksin menunjukkan bahwa adanya gugus gugus OH, gugus C=C aromatik dan gugus C-C alifatik, gugus B-H, dan gugus B-O. Hasil analisis XRD kompleks boron-piridoksin ditunjukkan adanya puncak pada sudut difraksi 30,93°.

Kata Kunci: Kompleks boron-piridoksin, boraks, piridoksin, kompleksasi

INTRODUCTION

Boron is an essential element for humans, animals, and plants. Boron is required for plant growth at low concentrations. Its functions include the growth and repair of cell walls, cell division, fruit and seed development, sugar transport, and hormone development [1]. Numerous products and industries, including semiconductors, pharmaceuticals, fertilizers, insecticides, and optical materials, use boron compounds [2]. By forming complexes with biomolecules like riboflavin, adenosine monophosphate, pyridoxine, pyrimidine nucleotides, ascorbic acid, and steroid structure as well as sugar molecules like ribose, glycoprotein, glycolipid, and

polysaccharides that contain adjacent cis-hydroxyl groups, boron compounds differ primarily in their chemical properties but also in their biological activity [3]. Borax or sodium tetraborate (NaB_4O_7 $10H_2O$), is a chemical compound derived from boron (B). It is a white, odorless crystal, and stable at room temperature. Borax is widely used in cosmetics as an antifungal, wood preservative, and antiseptic [4]. In addition, it is also used in the glass, porcelain, cleaning equipment, and pesticide industries.

The methods for boron determination include inductively coupled plasma mass spectrometry (ICP-MS), inductive optical emission spectrometry (ICP-OES), approximation, and electrical conductivity methods. The ICP-MS or ICP-OES have limitations and are not suitable for analysis. Due to its time-consuming and complex operation, the electrical conductivity method can only measure samples with low salt content due to interference from the salt conductivity [2]. Ionometric approximation methods are prone to high error rates when the boron concentration in the sample is low due to decreased electrode sensitivity [1]. Due to the limitations of the currently available methods for measuring boron, the method used in this study was UV-Vis spectrophotometry to develop a simple method that can be applied to environmental-relevant sample analysis. One of the new, fast, and non-toxic spectrophotometric methods for the determination of boron in borax samples is based on the absorption of pyridoxine and boron-pyridoxine complexes.

Pyridoxine is an amphoteric compound that is a bipolar molecule with constant values (pKa) of 5.6 and 9.4. Under acidic, neutral, and basic conditions, pyridoxine can manifest in three different forms. Pyridoxine has two significant peaks in its absorption spectra and is neither strongly ionized nor weakly ionized in neutral circumstances (pH 5.72-8.12). The pyridoxine will gradually protonate and display a net positive charge as the pH value decreases. It is recognized for being an effective Lewis acid complexing agent due to the phenolic oxygen and pyridinic nitrogen atoms in it, as well as in rare circumstances due to the hydroxymethyl groups. [2,5]. This study examined the complexation of boron with Vitamin B6 (pyridoxine) reagents, which have lone pairs of electrons on the N (nitrogen) and O (oxygen) atoms so that they are easily excited and easily readable by UV-Vis Spectrophotometers [6]. Based on the optical absorption characteristics of the boron-pyridoxine complex, this approach is a non-toxic spectrophotometric for the detection of boron in aqueous samples. This study uses variations in the effects of time, temperature, and the amount of pyridoxine. The resulting complexes were also characterized by Fourier transform infrared (FT-IR) and X-ray diffraction (XRD) spectrometry.

MATERIALS AND METHODS

Materials

The materials used are pyridoxine ($C_8H_{11}NO_3$), hydrochloric acid (HCl) 6N, methanol (CH_3OH), borax ($Na_2[B_4O_5(OH)_4]8H_2O$), and distilled water (H_2O).

Determination of Maximum Wavelength

10 mg of borax were dissolved in 100 mL of distilled water to obtain a 100 mg/L borax solution. A total of 1 mL of a 100 mg/L borax solution was pipetted and heated in a furnace at 600 °C for 3 hours, then cooled to room temperature. A total of 3 mL of 6N HCl was added and shaken for 1 minute; then, 1.1 mL of vitamin B6 (pyridoxine) at 100 mg/L was added and stirred at room temperature for 15 minutes. After that, 5 mL of methanol was added, and the absorption of boron-pyridoxine derivatives was measured at wavelengths of 200–400 nm using UV-Vis spectrophotometer Orion Aqua Mate 8000 type to determine the maximum wavelength of boron-pyridoxine derivative absorption.

Optimization of Pyridoxine-Boron Complexation

In this study, there were 3 variations of the conditions used, including the effect of time, the effect of temperature, and the effect of the amount of pyridoxine on the formation of the boron-pyridoxine complex. Boron-pyridoxine complexation was measured using a UV-Vis spectrophotometer Orion Aqua Mate 8000 type at a wavelength of 237 nm.

Effect of Interaction Time

A total of 10 mg of borax in 100 mL of distilled water to obtain a solution of 100 mg/L borax. In addition, 1 mL of 100 mg/L borax solution was put into the furnace, heated at 600 ˚C for ± 3 hours, and then cooled to room temperature. A total of 3 mL of 6 N HCl was added to the mixture and shaken for 1 minute, then added 1.1 mL of 100 mg/L vitamin B6 (pyridoxine) solution, then stirred at 25 °C for 20, 30, 40, 50, and 60 minutes. The mixture was added to 5 mL of methanol and measured the absorption of the boron-pyridoxine derivative was at a wavelength of 237 nm.

Effect of Temperature

A total of 10 mg of borax in 100 mL of distilled water will yield a solution of 100 mg/L borax. In addition, 1 mL of a 100 mg/L borax solution was put into the furnace, heated at 600 °C for 3 hours, and then

cooled to room temperature. A total of 3 mL of 6 N HCl was added to the mixture and shaken for 1 minute. Then, 1.1 mL of a 100 mg/L vitamin B6 (pyridoxine) solution was added, and the mixture was stirred with temperature changes of 30, 40, 50, 60, and 70 °C for 40 minutes. The mixture was added to 5 mL of methanol and measured the absorption of the boron-pyridoxine derivative was at a wavelength of 237 nm.

Effect of Amount of Pyridoxine

A total of 10 mg of borax was dissolved in 100 mL of distilled water to obtain a solution of 100 mg/L of borax. In addition, 1 mL of 100 mg/L borax solution was put into the furnace, heated at 600 °C for 3 hours, and then cooled to room temperature. A total of 3 ml of 6 N HCl was added to the mixture and shaken for 1 minute, then 1.1 ml of vitamin B6 (pyridoxine) 100 mg/L with changes of 1, 2, 3, 4, and 5 mL, stirred at 60 °C for 40 minutes. The mixture added as much as 5 mL of methanol and measured the absorption of the boron-pyridoxine derivative at a wavelength of 237 nm.

Characterization of Complex Compound with FT-IR

The samples were measured by FT-IR type Shimadzu Prestige-21 using pellet KBr. Pellets were made by mixing 2 mg of the sample with 100 mg of KBr which was then scanned by FT-IR with a range of wave numbers in the range of 4500-500 cm^{-1}.

Characterization of Complex Compounds with XRD

The samples were measured by X-Ray Diffraction type Rigaku mini flex-600. The boron-pyridoxine complex of 0.01 g was placed on an aluminum plate. The diffraction data retrieval was carried out with a diffraction range of 2θ = 20° to 80° with the reading speed set to 0.08 per second and a wavelength of 1.5406.

RESULTS AND DISCUSSION

Determination of Maximum Wavelength for Analysis

The maximum wavelength is the electronic transition's value, resulting in the greatest absorbance. Measurements were performed at the maximum wavelength because the change in absorbance for each concentration unit was greatest at that wavelength, resulting in maximum analytical sensitivity. The maximum wavelength in the 200–400 nm range was determined using UV-Vis spectrophotometry. **Figure** 1 depicts the UV-Vis spectrum of the pyridoxine (A) and boron-pyridoxine complex (B). The UV-Vis spectrum of pyridoxine shows two peaks at 205 nm and 292 nm, while the wavelength of the boron-pyridoxine complex is at a wavelength of 237 nm.

The reaction between pyridoxine with borax forms a boron-pyridoxine complex by combining two pyridoxine molecules and one boron [2]. Electronic transitions can occur from bonding electrons, both sigma (σ) and pi (π) bonds as well as non-bonding electrons (n) present in organic molecules. There are only two types of excited states of electrons in organic molecules, namely pi star (π*) and sigma star (σ*). The n to π* electron transition requires less energy than the π to π * transition, but because the non-bonding orbital is spaced apart from the π * antibonding orbital, the number of n electrons that transition to π* is less than the number of transition electrons from π to π *.

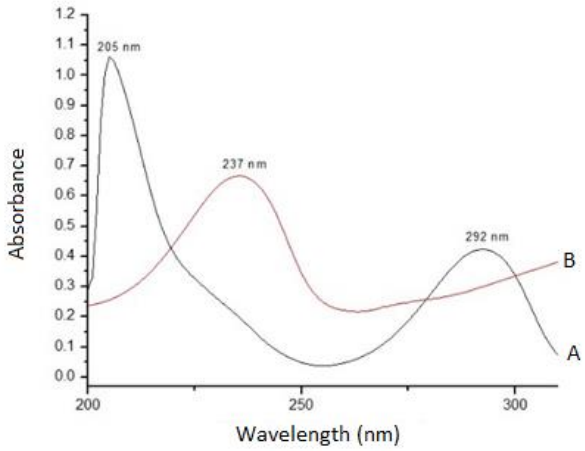

Figure 1. UV Vis Spectrum of Pyridoxine (A) and Boron-Pyridoxine Complexes (B)

The electronic transition of pyridoxine at 205 nm is the transition from π to π* while the electronic transition at 292 nm is the transition from n to π*. The unshared electron pair on the hetero atom excited to the antibonding orbital thus involves the least amount of energy, and therefore the n to π* transition has the longest wavelength. Similar results were also obtained with the same absorption value at 290 nm but with ethanol as a solvent [7]. The boron-pyridoxine complex resulted in a new absorption in the 237 nm region. The oxygen atom in pyridoxine and boron from borax is negatively charged so the negative charge of boron will attack the free electrons of oxygen in the O-H bond. As a result, will be released the H atom so that the pyridoxine will be locally protonated due to the negatively charged nature of boron [2]. The new absorption of the boron-pyridoxine complex in the 237 nm region allows for charge transfer from electrons in boron to π* orbitals.

Optimization of Pyridoxine Borax Complexation

The interaction time, temperature, and pyridoxine quantity effects on the boron-pyridoxine complex were the three parameters that made up the optimization.

Effect of Interaction Time

The effect of interaction time will determine the amount of obtained product and it is expected that the boron can react completely during the reaction. A certain amount of time is required to form an optimal boron-pyridoxine derivative complex. The effect of various interaction times between boron and pyridoxine is shown in **Figure** 2. The optimum interaction time is 40 minutes with the highest absorbance value. However, after 50 minutes it decreased because the reaction formation of the boron-pyridoxine complex becomes unstable and bonds are formed easily to fall back on.

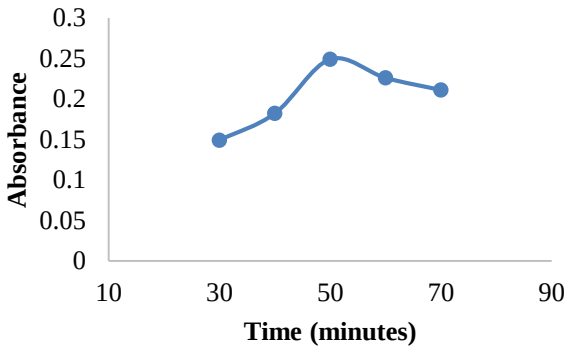

Figure 2. The effect of interaction time on the absorbance of the boron-pyridoxine complex

Effect of Temperature

The temperature effect was carried out to determine the reaction temperature that would affect the rate of the derivative reaction. The effect of temperature interactions between boron and pyridoxine is shown in **Figure** 3.

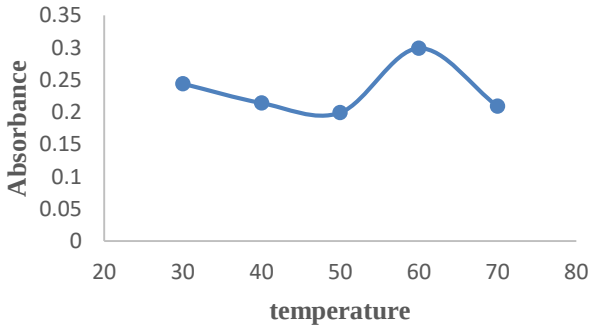

Figure 3. Effect of Temperature on Absorbance of the boron-pyridoxine Complex

Based on **Figure** 3, the optimum temperature for the reaction is 60˚C with the highest absorbance value but at a temperature of 70ºC the absorbance obtained decreases, this occurs because with increasing temperature, the reaction for the formation of the boron-pyridoxine complex begins to become unstable and the complex bonds formed easily detached.

Effect of amount of Pyridoxine

The effect of the amount of pyridoxine is shown in **Figure** 4. The absorbance of the solution initially increased and then reached the optimum with the addition of 2 mL of pyridoxine 100 mg/L. Further addition of the pyridoxine amount did not affect the absorbance because the complex is no longer formed.

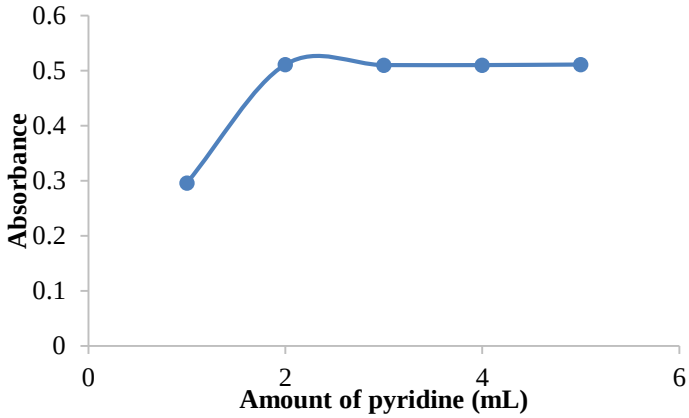

Figure 4. Effect of the amount of pyridoxine on the absorbance of the boron-pyridoxine Complex

Identification Using The FT-IR Spectra

FTIR spectra of the borax, pyridoxine, and Boron-Pyridoxine complex compounds are shown in **Figure** 5.

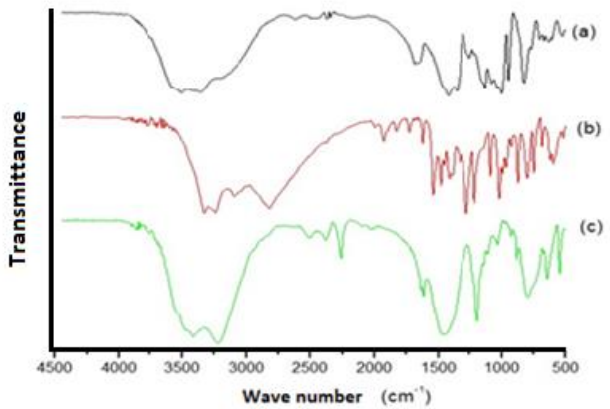

Figure 5. FTIR Spectra of (a) Borax, (b) Pyridoxine, and (c) Complex Boron-pyridoxine

Figure 5 depicts a vibration with a broad band in the wave number area 3606–3352 cm^{-1}, in borax **(a),** indicating a -OH group. The presence of a B-O group is shown by absorption in wave numbers 1031–1354

cm^{-1} and 947 cm^{-1} [8]. Vibration with a broad band in the wave number range 3240–3325 cm^{-1}, in the pyridoxine spectrum (b) shows the existence of a -OH group. A band in the wave number region of 3093 cm^{-1} belongs to an aromatic CH group whereas a band with a wave number of 2821 cm^{-1} corresponds to an aliphatic CH group. Absorption at wave numbers 1543-1624 cm^{-1}, 1728-1928 cm^{-1}, and 1328-1438 cm^{-1} correspond to an aromatic C=C group, C=N group, and an aliphatic C=C group respectively. The band in wave number 1018-1215 cm^{-1} is a phenolic C-O group of pyridoxines [9]. A widening vibration in the wave number region 3217-3414 cm^{-1} of the complex boron-pyridoxine spectrum **(c)** due to OH groups. Absorption in wave numbers 1618 cm^{-1} and 1452 cm^{-1} indicate aromatic C=C group and aliphatic C-C group respectively. The presence of a B-O group is shown by absorption in wave numbers 1109-1193 cm^{-1}, whereas the presence of B-H stretching is indicated by absorption in wave number 2515 cm^{-1}.

XRD (X-Ray Diffraction) Characterization

Pyridoxine, borax, and Boron-pyridoxine were characterized using X-ray diffraction. The diffractogram pattern of the Pyridoxine, borax, and Boron-pyridoxine is depicted in **Figure** 6.

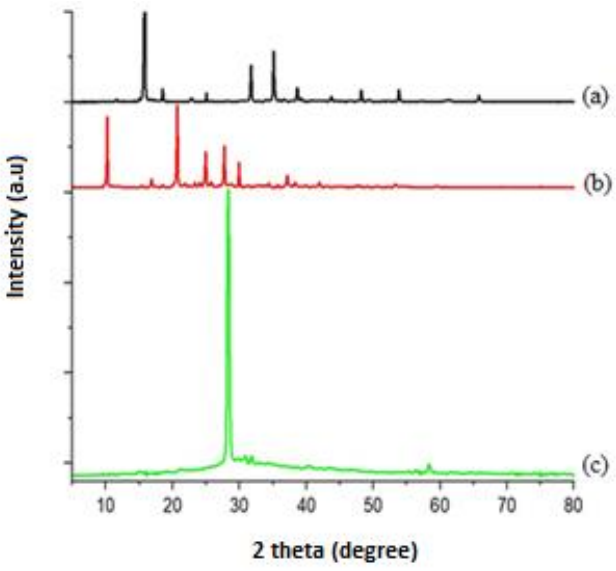

Figure 6. Diffractogram for a) Borax, b) Pyridoxine, and c) Complex Boron-pyridoxine

Based on **Figure** 6, the X-ray diffractogram of borax **(a)** reveals the presence of a sharp peak at 2θ = 15°, a minor peak at 2θ = 25° corresponding to the borate ions; and the peak is around 2θ at 55° [10, 11]. The diffractogram of pyridoxine **(b)** reveals the presence of the highest intensity peak at 2θ = 20.686° [12]. The Boron-Pyridoxine complex compound shows a new peak at an angle of 30.93°.

CONCLUSION

1. Optimization reaction conditions between boron and pyridoxine were 40 minutes, 60 °C and the amount of pyridoxine 100 mg/L was 2 mL.
2. The characterization of Boron-pyridoxine complex compounds by FTIR showed by absorption of B-O in the 1031-1354 cm^{-1} region, and B-OH in the 881-1109 cm^{-1} region. Characterization of the boron-pyridoxine complex by XRD obtained new diffraction angles of 30.93°

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