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THE ROLE OF VITAMIN B_6 IN THE CHEMICAL SELF-PURIFICATION PROCESSES OF AQUATIC SYSTEMS

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ABSTRACT. Water resources can constantly renew themselves due to their self-purification capacity, but anthropogenic activities reduce the intensity of these self-purification processes. One of the organic substances present in water is vitamin B_6, which is present in surface waters as a result of biological processes in water bodies or as a result of anthropogenic impact. So, the changes in vitamin B_6 were examined using test systems that included substances involved in the self-purification of natural waters: dissolved oxygen, hydrogen peroxide, and copper (II) ions. Analysis of the results obtained shows that vitamin B6 efficiently degrades by reacting with dissolved oxygen in the presence of copper ions. This indicates that the substrate is not persistent and can be easily removed from the aqueous environment.

Keywords: *vitamin B_6; pyridoxine; dissolved oxygen; hydrogen peroxide, copper (II) ions.*

INTRODUCTION

Water is an essential component of the natural environment and the basis of many types of industrial activities. In recent decades, there has been a growing concern about the quality of natural water and various problems associated with the availability, use, and management of water resources.

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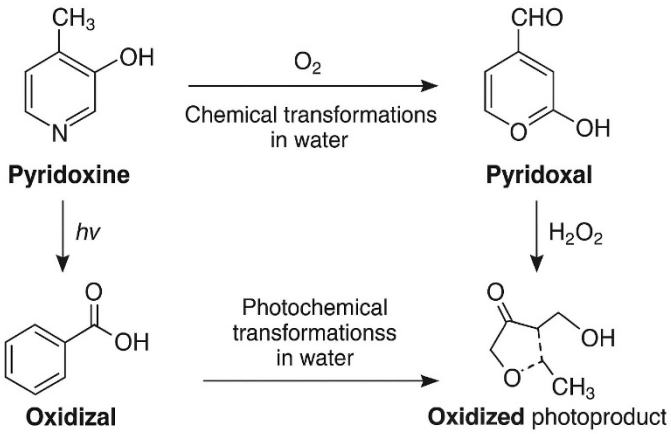
Water quality assessment has become an important issue, since scientists predict that fresh water will become a scarce resource in the future. Deterioration of water quality is a serious degradation of the environment due to anthropogenic load. The presence of organic substances of various kinds in natural waters is an urgent global problem that requires constant assessment and study. When these substances significantly reduce the self-purification capacity of natural waters, the problem intensifies [1]. Self-purification of natural waters is a complex process that simultaneously includes physical, chemical, and biological processes. Self-purification of water and improvement of its quality are necessary for the self-sustaining of the aquatic ecosystem. Therefore, it is important to study the participation of various substances with reducing properties in the processes of chemical self-purification of water bodies.

Vitamin B_6 (pyridoxine), a biologically active organic compound, can enter surface waters through both natural and anthropogenic pathways. Anthropogenic inputs come from industrial effluents, wastewater discharge, and agricultural runoff, whereas natural sources include phytoplankton, aquatic bacteria, and decomposing plant matter. Despite its low concentration, vitamin B_6 can be found in a variety of chemical forms, including phosphorylated derivatives of pyridoxine, pyridoxal, and pyridoxamine [2].

The concentration of vitamin B_6 in natural waters is generally very low and varies depending on the water source and environmental conditions [3, 4]. Data on vitamin B6 concentrations in various aquatic systems are limited. A study conducted in the Western Atlantic Ocean (at the mouth of the Amazon River) reported vitamin B_6 concentrations ranging from undetectable levels to 36 pM, equivalent to 0–7.4 ng/L [3]. In another study on the Osun River (Nigeria), pyridoxine concentrations ranging from 71.6 to 622.8 μg/L, or approximately $4.26 \cdot 10^{-4}$ to $3.68 \cdot 10^{-3}$ M, were detected. These higher values may be attributed to anthropogenic activities and the presence of specific phytoplankton species [4].

The behavior of vitamin B_6 in aquatic environments is a little-studied topic. However, it is known that vitamin B6 is unstable in water, being readily degraded in the presence of light and oxygen [5-10]. Under aerobic conditions, pyridoxine can be oxidized to form pyridoxal (Scheme 1), a process that is favored by alkaline pH and the presence of transition metals (Fe^{3+}, Cu^{2+}), which catalyze redox reactions [5–8].

Exposure to UV light (260–320 nm) causes cleavage of the pyridoxine side chain, leading to the formation of degradation products such as aldehydes, carboxylic acids, and other compounds. These photochemical products resulting from pyridoxine degradation no longer possess biological activity [9–11].



Ehrenshaft et al., 2006, Gregory, 1998, Combs, 2012

Scheme 1. Chemical and photochemical transformations of pyridoxine [7, 9]

Studies have shown that vitamin B_6 exhibits significant antioxidant properties. Therefore, it is important to investigate its role in aquatic environments.

The aim of this study is to evaluate the contribution of vitamin B_6 to the self-purification processes of aquatic systems. We undertook the following tasks to attain this objective:

- to study the efficiency and mechanisms of redox transformations of vitamin B_6 using model systems;
- to determine the kinetic parameters of redox reactions involving vitamin B_6 and assessing its persistence in aquatic systems.

RESULTS AND DISCUSSION

Dissolved oxygen is the most common oxidizing agent in natural waters, typically present at concentrations ranging from 0 to 15 mg/L. However, under normal conditions, it is relatively inert due to its triplet ground state. Therefore, to participate in oxidation processes, it must first be activated—either by sunlight or by interaction with substances possessing reducing properties [11]. Given its constant presence in surface waters, it is of interest to study its interaction with vitamin B_6 in aqueous solutions.

To investigate this, a simplified system (1) was modeled: B_6-$H_2O_{dist.}$-O_2. During the experiments, the concentration of dissolved oxygen in the system was maintained at $3.0 \cdot 10^{-4}$ M. To study the oxidation of vitamin B_6 by dissolved oxygen, five subsystems were modeled in which the initial concentration of the

vitamin varied from $1.0 \cdot 10^{-5}$ M to $5.0 \cdot 10^{-5}$ M, while the oxygen concentration remained constant—corresponding to its saturation level at 20 ºC (approximately $3.0 \cdot 10^{-4}$ M).

Analysis of the kinetic data showed that vitamin B_6 is resistant to oxidation by dissolved oxygen alone. Only a slight decrease in vitamin concentration over time was observed, and the reaction rates were very low ($W_{300} \approx 10^{-10}$ M/s).

Given that natural waters also contain transition metal ions—particularly Cu(II) ions [12]—these were added to the simulated systems at concentrations consistent with those found in natural environments (10^{-7} to 10^{-6} M). To investigate catalytic processes involving dissolved oxygen, the following system was modeled: *vitamin B_6-$H_2O_{dist.}$-O_2-Cu(II)* (system *2)*. In this system, a series of subsystems was created by varying the concentration of one component at a time while keeping the others constant. For determination of partial order with respect to all components of the modeled systems, the method of initial rates using logarithmic transformation was applied. Thus, for determination of partial order with respect to vitamin B_6, in the system 2, the initial concentration of vitamin $(2.48\text{-}8.92) \cdot 10^{-4}$ M was varied, and the concentration of Cu(II) ions was kept constant. The graphical representation of *log W* (initial rate) versus the log of the system's initial vitamin B_6 concentration was used to calculate the partial order with respect to vitamin B_6 (Figure 1). The data for determining the reaction order with respect to vitamin B_6 during catalytic oxidation with dissolved oxygen are presented in the Table S.1.1.

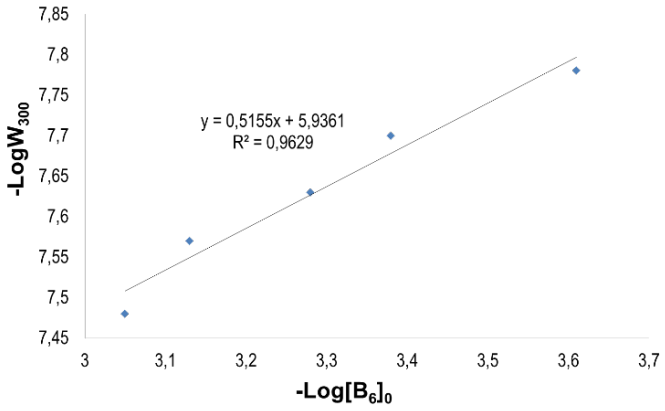


Figure 1. Determination of the partial order (log-log plot of rate vs. [B_6]) for the catalytic oxidation with dissolved oxygen ([Cu(II)]=*const.*=$3 \cdot 10^{-6}$ M, 20ºC, pH=*const.*=7) [own data]

From Figure 1 it was established that the partial order with respect to vitamin B_6 is ≈ 0.5.

In the same way, the partial order of reaction towards Cu(II) ions was determined by varying their concentration in the system and keeping the concentration of vitamin B_6 constant (Figure 2).

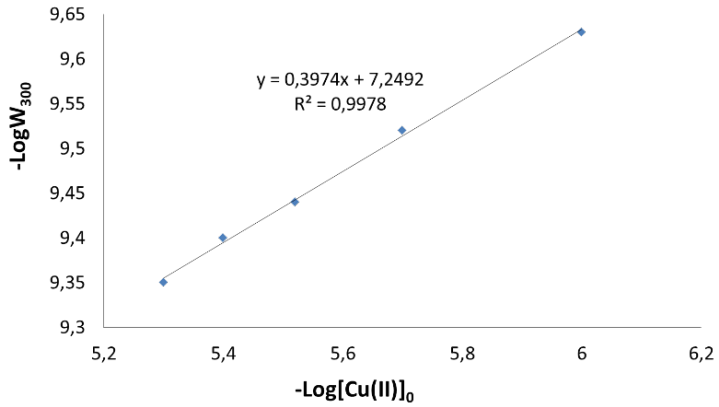


Figure 2. Determination of the partial order (log-log plot of rate vs. [Cu(II)]) for the catalytic oxidation with dissolved oxygen ([B_6]=*const.*=$3\cdot10^{-4}$ M, 20ºC, pH=*const.*=7) [own data]

The data for determining the reaction order with respect to Cu(II) ions during catalytic oxidation with dissolved oxygen are presented in the Table S.1.2.

From Figure 2 it was established that the partial order with respect to vitamin Cu(II) ions is ≈ 0.4, and the apparent constant in these systems is $2\cdot10^{-5}$ s^{-1}.

Using chemical kinetics methods, a rate equation (equation 1) was derived to express the rate-law dependence of the reaction rate on the concentrations of the system's components:

$$W=k\cdot[B_6]^{0,5}\cdot[Cu(II)]^{0,4} \quad (1)$$

where k is the rate constant (s^{-1}), which is influenced by the temperature, the concentration of dissolved oxygen in the water, and the pH value. Thus, it was found that this is a first-order reaction. Based on the law of first-order reactions, the reaction constant and half-life were calculated.

The average value of the effective constant was also calculated, which is equal to $5.31 \cdot 10^{-5}$ s^{-1}. Based on the obtained value of the effective constant k, the half-life was established to be (218 ± 0.23) min.

Hydrogen peroxide is one of the important oxidizing agents in natural waters, participating in various reactions that influence the redox state of aquatic systems. Numerous studies indicate that average hydrogen peroxide concentrations in surface waters range from 10^{-7} to 10^{-5} M [13–15]. The highest concentrations of H_2O_2 typically occur during the day under solar radiation, while the lowest levels are observed at night in the absence of sunlight. To investigate the transformation processes of vitamin B6, the following system was modeled (3): *vitamin* B_6-$H_2O_{dist.}$-H_2O_2. For this model system, kinetic patterns were established, and a rate equation was derived to describe the dependence of the vitamin transformation rate on the concentrations of the system's components.

Using the calculated partial reaction orders of the system components (Figure 3 (A) and (B)), the following kinetic equation (equation 2) was obtained, reflecting the power-law dependence of the reaction rate on component concentrations:

$$W = k \cdot [B_6]^{0.7} \cdot [H_2O_2]^{0.5} \quad (2)$$

where k is the rate constant (s^{-1}), which is influenced by the temperature, the concentration of dissolved oxygen in the water, and the pH value.

The data for determining the reaction order with respect to vitamin B_6 and H_2O_2 during oxidation with hydrogen peroxide are presented in the Tables S.2.1 and S.2.2.

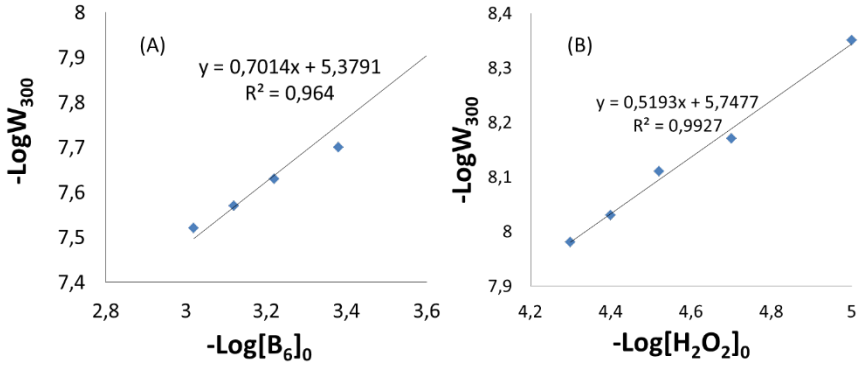


Figure 3. Determination of the partial order in the system *vitamin* B_6-$H_2O_{dist.}$-H_2O_2, for the oxidation with hydrogen peroxide: *A* - log-log plot of rate vs. [B_6], [H_2O_2]=*const.*=$3 \cdot 10^{-5}$ M; B - log-log plot of rate vs. [H_2O_2], [B_6]=*const.*=$3 \cdot 10^{-4}$ M; 20ºC, pH=*const.*=7 [own data]

For the oxidation of vitamin B_6 by hydrogen peroxide, the effective rate constant was calculated to be $3.55 \cdot 10^{-5}$ s^{-1}. Based on this rate constant (k), the half-life ($\tau_{1/2}$) of the process was determined to be (325±0.65) min.

Metal ions with variable valence, particularly Cu(II) ions, play an important role in reactions involving hydrogen peroxide. In the presence of dissolved oxygen, these metal ions remain in an oxidized state and are involved in the activation of both oxygen and hydrogen peroxide. Once activated, these species interact with various substrates, facilitating their transformation and acting as catalysts in oxidation processes [11, 12]. Therefore, it is important to study the oxidation of vitamin B_6 by hydrogen peroxide in the presence of Cu(II) ions.

As in the previous experiments, a system (4) was modeled consisting of the following components: *vitamin B_6-$H_2O_{dist.}$-H_2O_2-O_2-Cu(II)*. The principles of chemical kinetics were applied to this system to determine the partial reaction orders (Figure 4 (A), (B) and (C), derive an expression for the reaction rate, and calculate the effective rate constant.

Thus, the kinetic equation can be expressed as in equation 3:

$$W = k \cdot [B_6]^{1.2} \cdot [H_2O_2]^{0.5} \cdot [Cu(II)]^{0.3} \quad (3)$$

The effective rate constant at different concentrations of components in the systems is $4.22 \cdot 10^{-5}$ s^{-1}, which is influenced by the temperature, the concentration of dissolved oxygen in the water, and the pH value. Based on this rate constant (k), the half-life ($\tau_{1/2}$) of the process was determined to be (274±0.75) min.

The data for determining the reaction order with respect to vitamin B_6, H_2O_2 and Cu(II) ions during catalytic oxidation with hydrogen peroxide are presented in the Tables S.3.1, S.3.2 and S.3.3.

The experimental data can be interpreted as follows. In the presence of copper ions, oxygen oxidizes pyridoxine significantly faster than in their absence. This acceleration occurs because copper ions act as catalysts, facilitating the activation of molecular oxygen and enhancing the transfer of electrons from pyridoxine to oxygen.

Molecular oxygen itself is a relatively weak oxidizing agent under normal conditions. Consequently, the oxidation of pyridoxine proceeds very slowly and typically requires either elevated temperatures or extended reaction times. However, in the presence of copper ions, pyridoxine forms coordination complexes with copper, which can activate molecular oxygen and promote its conversion into more reactive species, such as the superoxide anion (O_2^-•), hydroxyl radical (•OH), and hydrogen peroxide (H_2O_2). These reactive oxygen species efficiently oxidize pyridoxine to pyridoxal or other products [16–19].

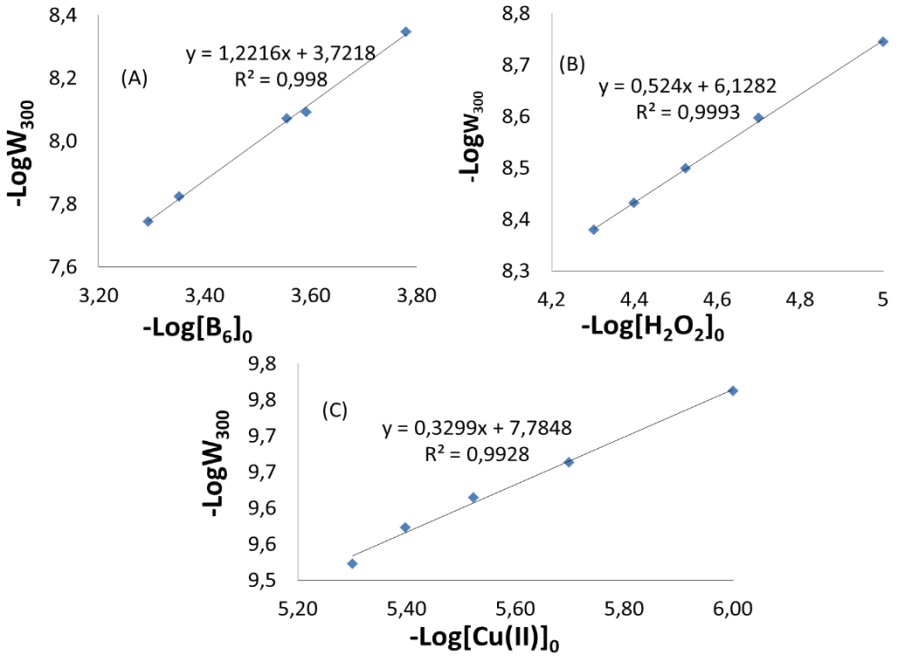


Figure 4. Determination of the partial order in the system B_6-$H_2O_{dist.}$-H_2O_2-O_2-*Cu(II),* for the catalytic oxidation with hydrogen peroxide: *A* - log-log plot of rate vs. [B_6], [H_2O_2]=*const.*=$3\cdot10^{-5}$ M, [Cu(II)]=*const.*= $3\cdot10^{-6}$ M; B - log-log plot of rate vs. [H_2O_2], [B_6] =*const.*= $3\cdot10^{-4}$ M, [Cu(II)]=*const.*=$3\cdot10^{-6}$ M; C - log-log plot of rate vs. [Cu(II)], [B_6]=*const.*=$3\cdot10^{-4}$ M, [H_2O_2]=*const.*=$3\cdot10^{-5}$ M; 20ºC, pH=*const.*=7 [own data]

Taking into account the structural features of pyridoxine and by analogy with similar systems, the following mechanism of its oxidation in the presence of copper ions and oxygen can be proposed:

1. Complexation and reduction of Cu^{2+} to Cu^{+}:

Pyridoxine coordinates with Cu^{2+} ions to form an active complex. When pyridoxine (vitamin B_6) interacts with copper(II) ions (Cu^{2+}), a complexation reaction occurs, resulting in the formation of coordination complexes, reaction 4. These complexes are stable in aqueous solutions and can contain one or two pyridoxine ligands per copper ion:

$$Cu^{2+} + n\ PN \rightleftharpoons [Cu(PN)n]^{2+} \qquad (4)$$

where PN is pyridoxine; *n=1* or *2,* depending on the reaction conditions and *pH* of the medium.

The interaction mechanism includes three main stages [16–18]:

- coordination of donor atoms:
  pyridoxine contains several donor centers: a hydroxyl group, an amino group, and a pyridine ring. Copper(II) ions can coordinate to the nitrogen atom of the pyridine ring and to the oxygen atoms of the hydroxyl groups;
- complex formation:
  the formation of both 1:1 and 1:2 complexes (metal:ligand) in aqueous solution was observed, especially at pH 5–7. This conclusion is supported by spectrophotometric and conductometric data;
- reduction of Cu^{2+} to Cu^{+}, reaction 5:
  pyridoxine can act as a reducing agent by interacting with copper(II) ions, reducing them to copper(I), while itself undergoing oxidation:

$$Cu^{2+}+PN \rightarrow Cu^{+}+PN^{\cdot+} \quad (5)$$

where $PN^{\cdot+}$ is the oxidized pyridoxine cation radical.

2. Oxygen activation:

Further interaction of Cu^{+} with molecular oxygen can lead to the formation of reactive oxygen species, reaction 6:

$$Cu^{+}+O_2 \rightarrow Cu^{2+}+ O_2^{\cdot-} \quad (6)$$

In addition, copper(II) ions can bind with superoxide anions to form superoxide complexes, reaction 7 [20]:

$$Cu^{2+}+ O_2^{\cdot-} \rightarrow [Cu^{2+}(O_2^{\cdot-})]^{+} \quad (7)$$

This process is accompanied by the formation of reactive oxygen species such as hydroxyl radicals (•OH) and hydrogen peroxide (H_2O_2), which participate in subsequent oxidation reactions [21].

3. Substrate oxidation:

The reactive intermediates transfer electrons from pyridoxine to oxygen, resulting in its oxidation to corresponding products such as pyridoxal or pyridoxic acid.

The non-catalytic oxidation of pyridoxine by hydrogen peroxide is a complex process that has not been sufficiently studied in the scientific literature. This reaction proceeds very slowly under neutral conditions and typically requires either highly acidic environments or elevated temperatures [22–23].

However, there are studies focusing on the interaction of pyridoxine with H_2O_2 in the presence of catalysts, as well as general information on the oxidation of pyridine derivatives [24–30].

The catalytic oxidation of pyridoxine by hydrogen peroxide in the presence of copper ions is an intriguing process that may have applications in both biochemical research and environmental chemistry. Although direct studies on this specific reaction are limited, existing data suggest a possible mechanism.

Analogies with the oxidation of other compounds in the presence of copper ions and hydrogen peroxide suggest the following mechanism [27–28]:

1. *Complexation*:

Pyridoxine coordinates with copper(II) ions to form an active complex (4).

2. *Activation of hydrogen peroxide*:

The copper(II) complex reacts with H_2O_2 to form reactive copper-peroxide intermediates, reactions (8) and (9). This step is analogous to the formation of complexes capable of electrophilic or nucleophilic reactions with organic substrates [29–30]:

$$[Cu^{2+}(PN)]+H_2O_2 \rightarrow [Cu^{+}(PN)]+HO_2^{\cdot}+H^{+} \quad (8)$$

$$[Cu^{+}(PN)]+H_2O_2 \rightarrow [Cu^{2+}(PN)]+OH^{-}+{\cdot}OH \quad (9)$$

1. Oxidation of pyridoxine:

The active intermediates transfer electrons from pyridoxine to oxygen, resulting in its oxidation to corresponding products such as pyridoxal, reactions (10) and (11) [31]:

$$PN\text{-}CH_2\text{-}OH+{\cdot}OH \rightarrow PN\text{-}CH^{\cdot}\text{-}OH+H_2O \quad (10)$$

$$PN\text{-}CH^{\cdot}\text{-}OH+{\cdot}OH \rightarrow PN\text{-}CHO+ H_2O \quad (11)$$

2. Catalyst regeneration:

The reduced copper(I) ion is oxidized back to copper(II), completing the catalytic cycle, reaction (12):

$$[Cu^{+}(PN)]+H_2O_2 \rightarrow [Cu^{2+}(PN)]+OH^{-}+{\cdot}OH \quad (12)$$

The experimental data and the key relationship for the catalytic oxidation of the substrate show that Cu (II) ions not only help speed up the reaction but also take part in the changes happening during the process. The partial order of reaction after Cu (II) ions, which is valued at 0.3, indicates its insignificant influence on the transformation of vitamin B_6, but it still exists. In this case, the oxidation proceeds according to a cyclic mechanism, in which the role of the active particle that directly participates in the oxidation of the substrate is played by the metal ion in the oxidized form. In this case, oxygen or hydrogen peroxide mainly helps to turn the metal back into its oxidized form after it has been changed to its reduced form during the oxidation of the substrate.

Schematically, these transformations can be presented as follows [11, 32]:

- oxidation of the substrate and reduction of the transition metal ion (Cu^{2+}):

$$2Cu^{2+} + DH_2 \rightarrow 2Cu^{+} + D + 2H^{+} \quad (13)$$

- regeneration of the oxidized form of the metal:

$$2Cu^{+} + O_2(H_2O_2) + 2H^{+} \rightarrow 2Cu^{2+} + H_2O_2\ (2H_2O) \quad (14)$$

Thus, the copper ion cyclically switches between oxidation states II and I, activating O_2 or H_2O_2 and continuously generating oxidizing radicals that convert pyridoxine to pyridoxal.

CONCLUSIONS

The most efficient process for vitamin B_6 oxidation is the catalytic oxidation by dissolved oxygen in water, which exhibits the highest rate constant and the lowest half-life. The slowest oxidation occurs with hydrogen peroxide, with a half-life of 5 h 25 min 25 s. When copper ions are added to the B_6-H_2O_2 system, the reaction rate increases significantly, confirming the catalytic role of copper ions in surface waters.

The rate of oxidation in the B_6-O_2-Cu (II) system is higher than in the B_6-H_2O_2-Cu (II) system. This indicates that vitamin B_6 is more readily oxidized by catalytically activated dissolved oxygen than by hydrogen peroxide. Considering that the concentration of hydrogen peroxide varies throughout the day and may sometimes be absent in surface waters, while dissolved oxygen is always present, this scenario ensures the continuous catalytic decomposition of vitamin B_6. Consequently, chemical self-purification via redox transformations involving vitamin B_6 occurs both day and night.

Since vitamin B_6 is effectively oxidized catalytically by dissolved oxygen, its degradation in the aqueous medium can lead to the accumulation of additional hydrogen peroxide, which is an active intermediate product of oxygen reduction. The presence of copper ions positively influences the redox processes involving vitamin B_6, with catalytic activity being most pronounced in the B_6-O_2-Cu (II) system.

The analysis of the results indicates that the presence of vitamin B_6 in the aqueous medium can positively influence chemical self-purification processes. The following points support this assertion:

a) vitamin B_6 is effectively degraded by dissolved oxygen in the presence of copper ions, which is beneficial because it does not require additional reagents or special conditions. Moreover, the short half-life suggests that the substrate is not persistent, enabling its easy removal from the aqueous medium.

b) the efficient oxidation of vitamin B_6 by dissolved oxygen produces additional hydrogen peroxide. The accumulation of extra H_2O_2 helps maintain the oxidative state of the water and supports hydrogen peroxide's role in redox reactions involving peroxidase substrates.

c) the fact that hydrogen peroxide and Cu(II) ions do not significantly accelerate vitamin B_6 oxidation is advantageous for the aquatic environment, as these components remain available to participate in other biochemical processes.

EXPERIMENTAL SECTION

To study the kinetics of vitamin B_6 transformations in aqueous solutions using model systems, a direct spectrophotometric method was employed, utilizing a phosphate buffer at pH 7. The optical density of the solution was measured at 328 nm to determine substrate concentrations. Under laboratory conditions, the following redox systems were modeled: *Vitamin B_6-$H_2O_{dist.}$-O_2 (1); Vitamin B_6-$H_2O_{dist.}$-O_2-Cu(II) (2); Vitamin B_6-$H_2O_{dist.}$-O_2-H_2O_2 (3); Vitamin B_6-$H_2O_{dist.}$-O_2-H_2O_2-Cu(II) (4)*. All systems were investigated under aerobic conditions, with dissolved oxygen acting as a key oxidant in the aquatic environment. Hydrogen peroxide (H_2O_2), a naturally occurring oxidant in surface waters, was added in systems (3) and (4). The addition of copper(II) compounds in systems (2) and (4) is justified by their environmental relevance and the catalytic role of Cu(II) ions in the redox transformations of pollutants.

Kinetic regularities were studied for each modeled system by varying the concentration of a single component while keeping the others constant. As a result, partial reaction orders were determined, rate equations were derived,

and effective rate constants and substrate half-life values were calculated. The concentrations of components in the model systems were selected to reflect natural conditions: hydrogen peroxide at approximately 10^{-5} M, Cu(II) ions at 10^{-6} M, and vitamin B_6 at 10^{-5} M, ensuring optimal optical density values.

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