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EFFECT OF VARIOUS AGENTS ON STABILITY OF 2-PHENYLBENZIMIDAZOLE-5-SULFONIC ACID

Abstract

The subject of this study is 2-phenylbenzimidazole-5-sulfonic acid (PBSA), which is one of 26 filters used for personal protection in the European Union. The aim of the study was to investigate the stability of 2-phenylbenzimidazole-5-sulfonic acid and its sodium salt under the influence of various agents. The study has shown that UV radiation, pH value, hydrogen peroxide are important factors limiting the stability of PBSA. The significance of the study is expanding the knowledge about the stability of PBSA.

Key words

PBSA, UV filter, emerging pollutants, photodegradation, oxidation.

Introduction

UV filters, also known as sunscreens, are chemicals applied in personal protection products. The main task of UV filters is to protect skin from excessive exposure to solar radiation [1]. At present, there are 26 active substances acting as UV filters, accessible for the use in cosmetics in the European Union [2]. One of the filters commonly used in sun creams is 2-phenylbenzimidazole-5-sulfonic acid (PBSA). Due to its high absorption ability in the range from 290 to 320 nm, it is used as a UV-B filter [3].

It is noted, however, that PBSA is characterized by toxic ecological properties such as estrogenic [3,4] and phytotoxic activities [5]. Therefore, PBSA is classified as an emerging pollutant (EP) by the Environmental Protection Agency of the United States [6] and recognized as one of the endocrine disrupting chemicals (EDCs) in the environment [7]. PBSA is identified in surface waters at high concentration levels ($109\text{-}2679\text{ ng}\cdot\text{L}^{-1}$). It is caused by introducing personal products containing PBSA into the water [8]. When PBSA is released into the water environment it can also undergo various reactions. Little knowledge about the behaviour of filters and their fate in the environment prompted recent studies on the impact of environmental factors on the stability of UV filters [9]. Previous studies have shown that PBSA is susceptible to photodegradation in the aquatic environment by sunlight that is scattered in surface water. Photolysis of PBSA proceeds both directly or indirectly with the participation of water matrix components. An effect of organic humic substances and nitrate ions NO_3^- on the acceleration of the indirect PBSA photodegradation process is demonstrated [10]. However, Jammoul and Canonica find that $\text{HCO}_3^-/\text{CO}_3^{2-}$ ions are the quenchers of excited states PBSA [11, 12]. Therefore, their presence in water environment contributes to slowing down the photodegradation processes of organic UV filters. Also, iron ions slightly inhibit photodegradation of PBSA [13]. The effect of iron ions can be significantly higher in surface waters, where concentration of iron ions can reach $1\text{-}5\text{ mg}\cdot\text{L}^{-1}$ due to the elution of this element from soil and rocks [13].

Another important aspect of environmental pollution with UV filters is household waste water. UV filters get into sewage as a result of laundering, being washed away from skin during baths and removed with urine [14]. It has been shown, however, that UV filters occurring in wastewater at $\mu\text{g}\cdot\text{L}^{-1}$ levels are only partially degraded since conventional technologies in waste water treatment plants are not adapted to their removal [15]. Therefore, the attention was focused on finding the most effective methods to inactivate or eliminate sunscreens from wastewater [16]. The researchers find that photochemical degradation of PBSA is one of the effective methods of degradation [16-19]. The studies on PBSA show that UV irradiation of acid generates the formation of several free radicals and active oxygen forms ($^1\text{O}_2$ lub $\text{O}_2\cdot^-$, $\text{OH}\cdot$) [20-22]. One of the most common methods of PBSA photochemical degradation is the use of UV/ H_2O_2 system [17, 23]. Research has shown that degradation and mineralization of PBSA occur as a result of a selective attack of $\text{OH}\cdot$ radicals. The effectiveness of oxidation with hydrogen peroxide in the presence of UV radiation depends on the dose of H_2O_2 as well as on the range and intensity of UV radiation [17,18]. However, the presence of other pollutants in the water matrix can result in a lower oxidation efficiency [17]. An effective solution is also homogeneous

photocatalysis with Fenton's reagents. $\text{SO}_4^{\bullet-}$ has strong oxidizing properties at different pH values of solutions and it is recommended for decomposition of organic compounds with high stability. Another popular method is heterogeneous photocatalysis with TiO_2 . Titanium dioxide causes a significant acceleration of photodegradation and is a promising solution for PBSA removal from wastewater. The researchers also emphasize that photolysis of PBSA is highly dependent on pH. Based on previous studies, it can be concluded that, in an acidic and alkaline medium, a PBSA molecule is excited and more easily undergoes degradation [20]. Therefore, using the knowledge that the pH of the solution contributes to the rate of degradation of the compound, and that one of the most important degradation factors is radiation, the authors propose an analysis of the effect of pH, radiation and oxidizing agents.

The aim of this study is to determine the chemical stability of 2-phenylbenzimidazole-5-sulfonic acid and its salt under the influence of such factors as radiation, hydrogen peroxide, pH and the system hydrogen peroxide/chloride ion.

Materials and methods

Materials

All chemicals were purchased from commercial suppliers and used without purification. 2-phenylbenzimidazole-5-sulfonic acid (PBSA, CAS: 5466-77-3) was obtained from Sigma-Aldrich (USA). H_2O_2 (30%) was obtained from POCh (Poland), HCl (35-38%) was obtained from POCh (Poland), buffer solutions (pH 4, pH 5, pH 8, pH 12) were obtained from POCh (Poland).

Reaction conditions

- Determination of the stability of PBSA and its sodium salt (Na-PBSA);
- PBSA solution at concentration of $3.5 \cdot 10^{-5}$ mole/L was prepared by dissolution of 9.6 mg of acid in 1L of distilled water. The solution of PBSA sodium salt at concentration of $3.5 \cdot 10^{-5}$ mole/L was prepared by dissolution of 9.6 mg of PBSA and 1.6 mg of NaOH (molar ratio 1:1) in 1L of distilled water. The prepared salt was left in a dark place for 24 hours to ensure that the neutralization reaction by ionic replacement of hydrogen ion of the acid with sodium ion of hydroxide will proceed. The reaction of two mixtures was adjusted to pH 5 with buffer;
- Effect of hydrogen peroxide on the stability of Na-PBSA salt;
- The excess of hydrogen peroxide in the molar ratios of 1:2; 1:5 and 1:10 (Na-PBSA: H_2O_2) was introduced into the initial solution of PBSA sodium salt at the concentration of $3.5 \cdot 10^{-5}$ mole/L;
- Effect of pH on the stability of PBSA sodium salt;
- Buffer solutions were introduced into the initial solution of PBSA sodium salt at the concentration of $3.5 \cdot 10^{-5}$ mole/L in order to obtain pH of the mixtures studied on the level of 4, 5, 8 and 12;
- Effect of hydrogen peroxide/chloride ion (oxychlorinating system) on the stability of PBSA sodium salt;
- Hydrogen peroxide and hydrochloric acid in molar ratios of 1:5:10; 1:10:5 and 1:10:10 (Na-PBSA: H_2O_2 :HCl) were introduced into the initial solution of PBSA sodium salt at the concentration of $3.5 \cdot 10^{-5}$ mole/L. The reaction of all the mixtures was adjusted with buffer to pH 5;
- Irradiation process and spectrophotometric analysis;
- The tested solutions were introduced into a cylindrical reactor of Heraeus. The reactor was placed on a magnetic stirrer. The reactor was equipped with a medium pressure mercury lamp (150W) emitting radiation in the range of 200-600nm. The lamp was cooled with water when performing analysis, which guaranteed a constant temperature during measurement (21-25°C). Analysis of the solutions was carried out by a spectrophotometer UV/Vis Academy Spectra View 2100 (Fig. 1.).

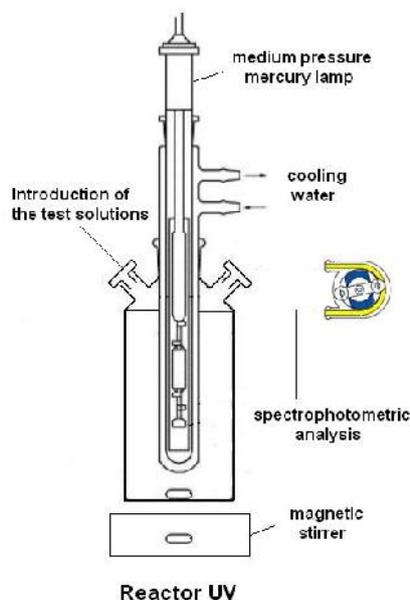


Fig. 1. Research diagram
Source: Author's

The tested solution was pumped by a low flow peristaltic pump of 304 type into a flow cell QS; Hellma Analytics, 175.000-QS, 10 nm Z.15. Prior to determinations, a zero sample was introduced and then the studied solutions were analysed. The data were recorded every 1 minute.

Results and discussion

It is found that PBSA filter and its salt Na-PBSA are resistant to degradation because their concentration is unchanged without access to light. An essential factor limiting the stability of PBSA is radiation. It results from the findings that PBSA acid is less stable than its sodium salt and undergoes faster photochemical degradation. After an hour of irradiation, the degree of degradation for PBSA is 75%, while for Na-PBSA it is 50% (Fig. 2.). Similar results are obtained by Ji et al., who claims that without radiation, degradation of PBSA practically does not occur [21]. As it results from their own observation and from the literature [19], transformation of 2-phenylbenzimidazole-5-sulfonic acid into its sodium salt not only increases the stability, but also solubility in water and prevents crystallization of the compound. Therefore, further studies on the impact of different factors are carried out for Na-PBSA.

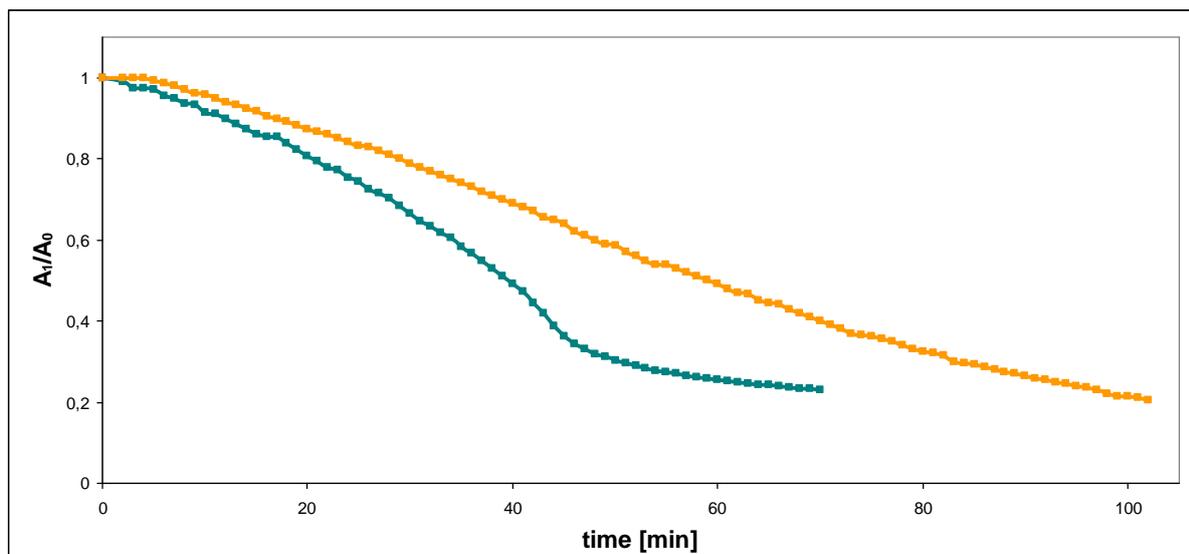


Fig. 2. Comparison of the rate of degradation for PBSA and Na-PBSA
Source: Author's

The next stage is to investigate the effect of hydrogen peroxide in the presence of UV radiation on Na-PBSA salt (Fig. 3.). It is observed that, on adding H_2O_2 to the system, the reaction of sunscreen decomposition is accelerated. The fastest degradation proceeds at 10-fold excess of hydrogen peroxide. It is found that the loss in sunscreen in the reaction mixture with 10-fold excess of H_2O_2 after 40 minutes is 77%, with 5-fold excess is 63% and with 2-fold excess 55%, respectively.

The results suggest that the degradation process of Na-PBSA can occur using an oxidation reaction by a radical pathway. It is known that hydrogen peroxide in the presence of light forms reactive hydroxyl radicals, which creates possibilities for oxidation of organic compounds, and consequently leads to the formation of new compounds [24, 25]. The formation of degradation products is such an important aspect because between the substrate and the metabolites competing reactions may occur, resulting in a non-selective attack $HO\bullet$ relative to the parent compound and by-products of decomposition. Consequently, the availability of $HO\bullet$ during photodegradation of the parent compound can decrease because the concentration of intermediate products increases [17]. In addition, after a certain period of photochemical degradation, H_2O_2 concentration decreases, which leads to the decrease in radical generation and hence a decreased degradation rate. The above information can explain the slowing-down of the decomposition reaction of Na-PBSA mixture with H_2O_2 after 40min.

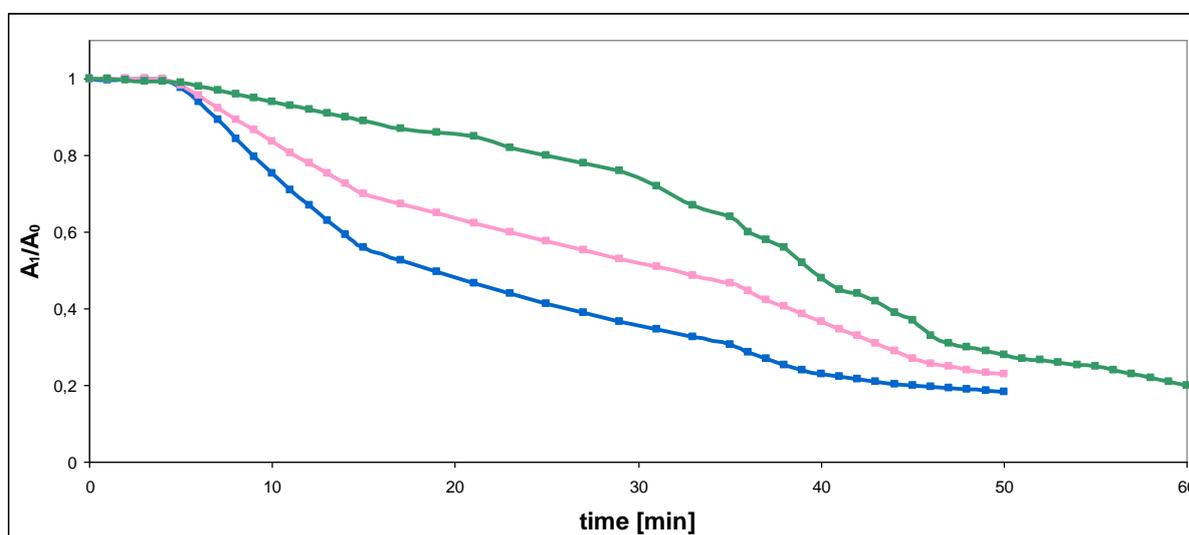


Fig. 3. Effect of hydrogen peroxide on the stability of sodium salt of PBSA: Na-PBSA/ H_2O_2 [1:10] ; Na-PBSA/ H_2O_2 [1:5] ; Na-PBSA/ H_2O_2 [1:2]

Source: Author's

In the next stage of studies, the effect of pH on stabilization of Na-PBSA subjected to UV radiation is investigated. Testing is performed at pH ranges from 4 to 12. A solution of PBSA sodium salt is degraded within the whole pH range (Fig. 4.) However, the most effective degradation occurs in a basic medium at pH 12. As soon as after 20 min of exposition, 78% of the investigated solution is degraded. For comparison, during the same time period, 34% of solution at pH 8; 30.5% of solution at pH 4 and only 12.2% of solution at pH 5 are degraded. During the first 20 minutes, the course of Na-PBSA degradation at pH 4 and 8 is similar, only after 40 minutes of irradiation, it is observed that at pH 4 the absorption value decreases from the initial value by about 80 % and at pH 8 by 60 %. The results obtained are in accordance with the studies conducted by other authors [21, 26, 27].

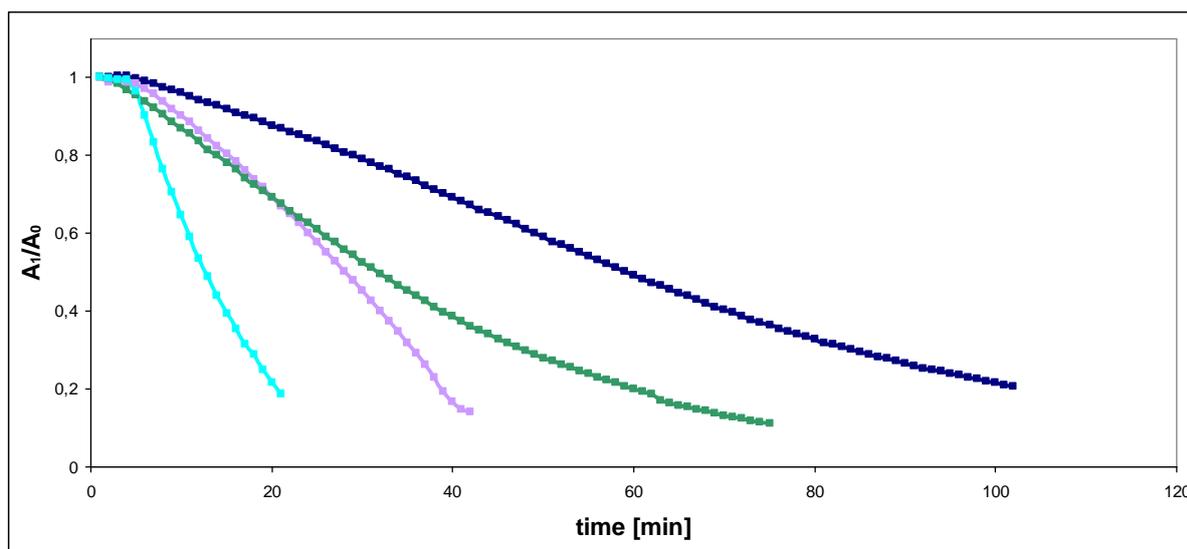


Fig. 4. Effect of pH on the stabilization of PBSA sodium salt: . pH=5 ; pH=12 ; pH=4 ; pH=8
Source: Author's

Ji et al. have shown that quantum yield in acidic or basic medium is much higher than in neutral medium, which affects the direct photolysis of PBSA and accelerates degradation of the compound [21, 22]. Researchers have found that, at acidic pH, O_2^- is protonated to formation of H_2O_2 , which under irradiation forms a stronger oxidant $HO\cdot$ [21, 28]. Therefore, the acceleration of PBSA photolysis in acidic pH can be attributed to an alternative degradation pathway caused by $HO\cdot$ [20, 21].

In contrast, in basic pH, a bathochrome shift (i.e. the absorption spectrum shift) to a longer wavelength caused by dissociation of imine group to form dianion (PBSA-2H) can be observed [21]. On shifting, maximum absorption overlaps with the emission spectrum of the lamp, which can further result in more efficient degradation of the compound (Fig. 5.).

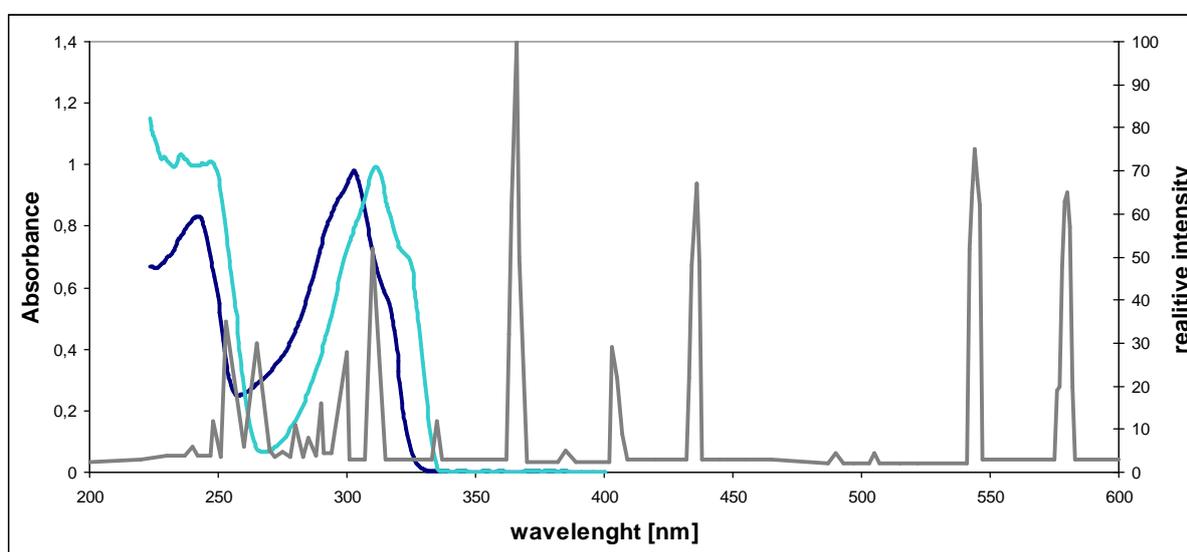


Fig. 5. Absorption spectra of PBSA sodium salt (pH=5 ; pH=12) superimposed on the emission spectrum of a medium-pressure lamp
Source: Author's

To verify the impact of chlorinating and oxidizing agents on the stability of Na-PBSA, hydrogen peroxide and hydrogen chloride are introduced into the system. The resulting system hydrogen peroxide / chloride ion is highly reactive and affects organic compounds such as UV filters, which are emerging pollutants [17, 22, 25]. Based on the findings, it is observed that molar ratios of H_2O_2/HCl have a significant impact on the degradation of NaPBSA. The reaction runs most rapidly in the systems of PBSA salt/ H_2O_2 / HCl [1:10:10] and PBSA salt/

H₂O₂ / HCl [1:10:5]; after 30 min degradation in these systems is about 80%. However, the slowest reaction was in the system with 10-fold and 5-fold excess of hydrochloric acid since the loss in concentration of sunscreen is about 50% after the same time (Fig. 6.). Similar results are obtained while studying the effect of oxychlorinating systems on the conversions of another sunscreen EHMC [25]

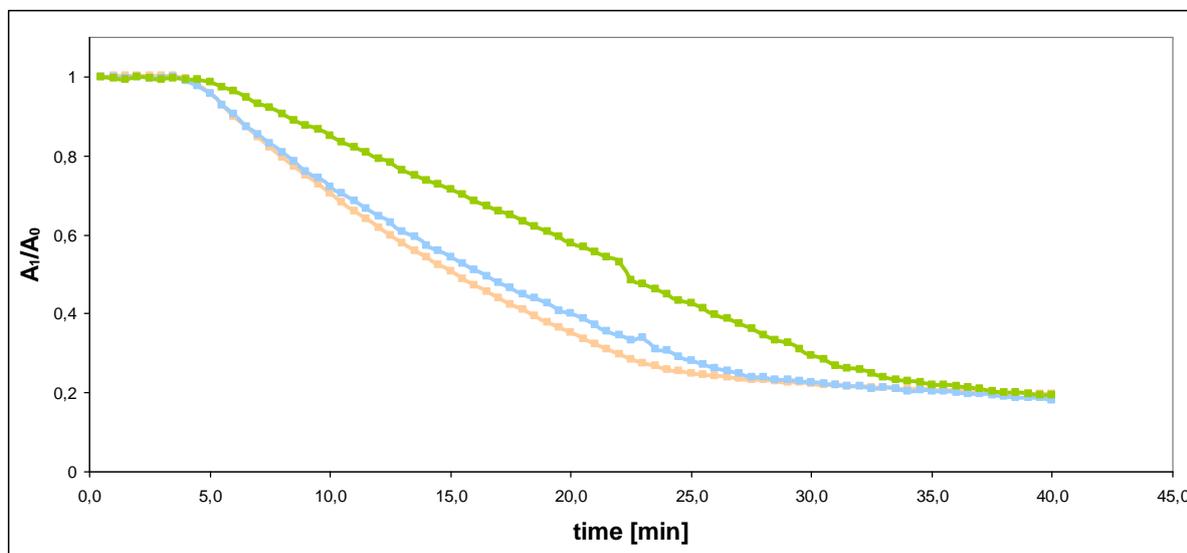


Fig. 6. Effect of hydrogen peroxide on the stability of PBSA sodium salt: Na-PBSA/H₂O₂/HCl [1:10:10] ;
Na-PBSA/H₂O₂/HCl [1:10:5] ; Na-PBSA/H₂O₂/HCl [1:5:10]

Source: Author's

The above results can be explained by the fact that hydrogen peroxide in the presence of UV radiation is a source of reactive oxygen forms and leads to faster degradation of the compound discussed. According to Zhang, additional introduction of a chlorine ion into the system can cause further conversions, as a result of which the reactive forms of chlorine can also be formed [24]. The chloride ion in the H₂O₂/UV system can be converted to reactive Cl• (with a high redox potential of 2.4 V) or to HOCl•. Abdelraheem has shown that these radicals are able to attack selectively the organic compounds and lead to increase in the total efficiency of decomposition [15]. However, in our experiment, chloride ions do not affect the decomposition of PBSA sodium salt and this mechanism has not been confirmed.

Conclusions

The study has shown that UV radiation is an important factor limiting the stability of PBSA. It is found that Na-PBSA is characterized by better photochemical stability than PBSA. The medium of the system in which photolysis was carried out had a significant influence on the time of PBSA salt disintegration. It is proven that pH value is another factor determining the stability of the compound. Alkaline (pH = 12) and acidic (pH = 4) medium of the analysed solution distinctly accelerates the degradation reaction of the filter analysed. It is shown that hydrogen peroxide significantly accelerates photodegradation of Na-PBSA. It is also noted that the increase in concentration of the reactants affects the rate of PBSA decomposition.

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