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PHOTOCATALYTIC PROPERTIES OF FLUORINATED TETRAARYLANTIMONY CARBOXYLATES

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Organic dyes are widely used in different kinds of manufacturing. As a result, they become common organic contaminants, and lead to water pollution. Therefore, the search of effective methods for such compound destruction is of interest. One of such methods is the photocatalytic destruction by antimony organic compounds. It has been found out that the incorporation of tetraarylantimony monocarboxylates ($Ar_4SbOC(O)R$, Ar = Ph, R = C_6F_5 (**1**), $CF_2CF_2CF_3$ (**2**), CF_2Br (**3**); Ar = p-Tol, R = CF_2CF_3 (**4**), $CF_2CF_2CF_3$ (**5**)) and further irradiation of solutions with UV radiation causes photocatalytic degradation of organic dyes methylene blue (MB) and methyl violet (MV) in their aqueous solutions. The change of concentration of organic dyes could be seen due to change in peak intensity at 554 nm and 665 nm in the UV spectra of MB and MV. Tetraphenylantimony carboxylates **1**–**3** showed higher photocatalytic activity than tetra(p-tolyl) antimony carboxylates **4**, **5**. Thus, MB decomposition was 90.5–98.8 %, MV: 97.7–100 % after 60 min irradiation of aqueous solutions containing compounds **1**–**3**. While in the presence of **4**, **5**, decomposition of MB and MV was 55.1–53.2 % and 71.2–78.7 %, respectively. In both cases, methyl violet was susceptible to more total destruction than methylene blue. The experiments showed the probability of repeatable use of the photocatalysts. After full decay of the pigment, tetraarylantimony carboxylate precipitated by centrifugation, the precipitate was decanted and used for the next cycle. As a result of two photodegradation processes, the mass of tetraarylantimony carboxylates decreased on average by 50 % after washing and drying, but the carboxylates were still effective, which proved the possibility of the photocatalyst repeatable use and their stability.

Keywords: tetraarylantimony carboxylates, organic dyes, methyl violet, methylene blue, photocatalysis.

Introduction

A large range of organic contaminants introduced into natural water supplies or waste water treatment systems are known to be residual dyes from various sources. Organic dyes are widely used in the textile, cosmetic, pharmaceutical, tannery, paper and mining industries [1, 2]. At present, the scientific community is actively discussing the problem of extracting dyes from wastewater in order to reduce their impact on the environment [3–5]. The main problem when dyes get into water is their stability because of their complex aromatic composition and synthetic origin [6–9].

Another problem is their accumulation of dyes in water body resulting in the loss of dissolved oxygen, which creates anoxic environments that are toxic to marine organisms [10–12]. According to the literature, some organic dyes are very toxic, they may cause carcinogenic, allergic and dermatic effects [13].

Nowadays, different methods for water purification and the organic dyes decomposition are used. For example, use of biological [14–16], physical [17] or chemical treatment. The last includes the dyes degradation caused by polyurethane [18], nanoparticles [19–23]. Dye degradation generally means dye decolorization and mineralization in textile waste water. Decolorization is the destruction of the dye molecule chromophore group; organic compounds are also degraded into CO_2 and H_2O [24].

Earlier, the photocatalytic activity of triarylantimony carboxylates has been studied [25].

In this work, we studied the possibility of photocatalytic destruction of organic dyes methylene blue and methyl violet in their aqueous solutions by adding tetraarylantimony monocarboxylates and further irradiation of the solutions with UV radiation.

Experimental

Photocatalytic Activity Test

The photocatalytic activity of tetraarylantimony carboxylates was estimated by photodegradation of aqueous solutions of methylene blue (MB) and methyl violet (MV) dyes at room temperature (298 K). Experiments were performed according to the general procedure [25]: 20 mg of tetraarylantimony carboxylates of the general formula $Ar_4SbOC(O)R$, Ar = Ph, R = C_6F_5 (**1**), $CF_2CF_2CF_3$ (**2**), CF_2Br (**3**); Ar = p-Tol, R = CF_2CF_3 (**4**), $CF_2CF_2CF_3$ (**5**) (synthesized by the reaction of pentaarylantimony with a proper carboxylic acid 1:1) were added to 50 ml of an aqueous solution of MB or MV (concentration 4 mg/L). To establish adsorption-desorption equilibrium, the resulting suspension was stirred in the dark for 30 minutes. Then the suspension was irradiated under a UV lamp with constant stirring for one hour. The concentration of MS and MV was measured by UV spectroscopy every 15 minutes. The collected samples were centrifuged to separate tetraarylantimony carboxylates.

The visible UV diffuse reflectance spectrum (UV-Vis.) was obtained in the region of 200 to 800 nm using a Shimadzu UV2700 spectrometer. Barium sulfate with a reflectance of 100 % was used as a standard.

Results and Discussion

A change in the peak intensity at 554 nm and 665 nm for MV and MB, respectively, in their UV spectra, indicated a change in the concentration of dyes in the solution (Fig. 1 a, b). In a control experiment carried out under similar conditions in aqueous solutions without the addition of tetraarylantimony monocarboxylates, no decomposition of the MB and MV dyes occurred.

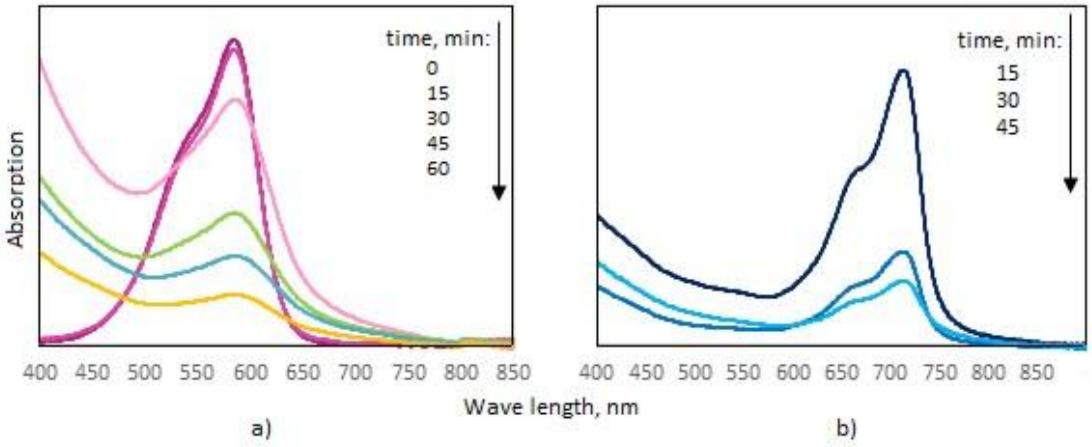

Fig. 1. (a) Absorption spectrum of MV solution in the presence of 4; (b) absorption spectrum of MB solution in the presence of 1

It has been found that the photocatalytic activity of the compounds under study is different. Tetraphenylantimony carboxylates **1**–**3** exhibited higher photocatalytic activity than tetra(p-tolyl)antimony carboxylates **4**, **5** (Fig. 2).

Thus, upon 60 min irradiation of solutions containing compound **1**–**3**, the decomposition of MB was 90.5 %, 97.3 %, 98.8 %, MV: 97.7 %, 99.5 %, 100 %, respectively. Tetra(p-tolyl)antimony monocarboxylates **4**, **5** exhibit relatively low photocatalytic activity: in the presence of compound **4**, the decomposition of MB and MV occurred by 53.2 % and 78.7 %, respectively; in the presence of **5** – by 55.1 % and 71.2 %, respectively. The photocatalytic efficiency of all complexes is obviously higher for the decomposition of MV than MB. In general, the photocatalytic activity of **1**–**3** is comparable to those of triphenylantimony *bis*(trifluoromethylbenzoates), studied earlier. Thus, triphenylantimony *bis*(trifluoro-2-methylbenzoate) leads to the destruction of 90.5 % MB, and 90.6 % MV after 150 min and 90 min of irradiation, respectively [25].

To assess the possibility of the repeatable use of the photocatalysts, we studied the process of circulating photocatalysis of MB and MV under the treatment with **2**, **4** and **5**. After complete decay of the dyes, tetraarylantimony carboxylates were precipitated by centrifugation, the precipitates were decanted and used for the next cycle (Fig. 3). As a result of two cycles of photodegradation, the mass of

tetraarylantimony carboxylates after washing and drying decreased on average by 50 %. However, as the graphs show, all the compounds were still effective towards dye decomposition and lead to the destruction of 49.5 % of MB, and 80.5 % – 90.0 % of MV after 1 hr irradiation.

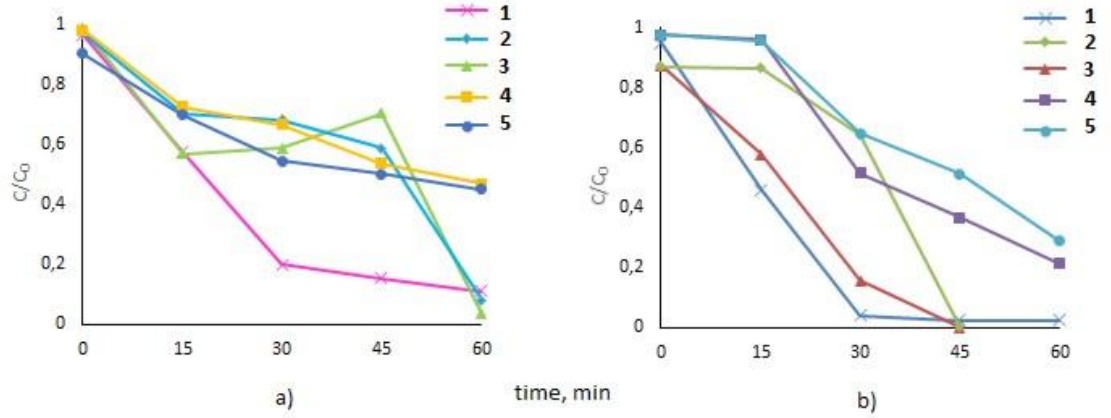

Fig. 2. Change in the reduced concentration (C / C0) under UV irradiation (t, min) of solutions of MV (a) and MB (b) dyes in the presence of tetraarylantimony carboxylates 1–5

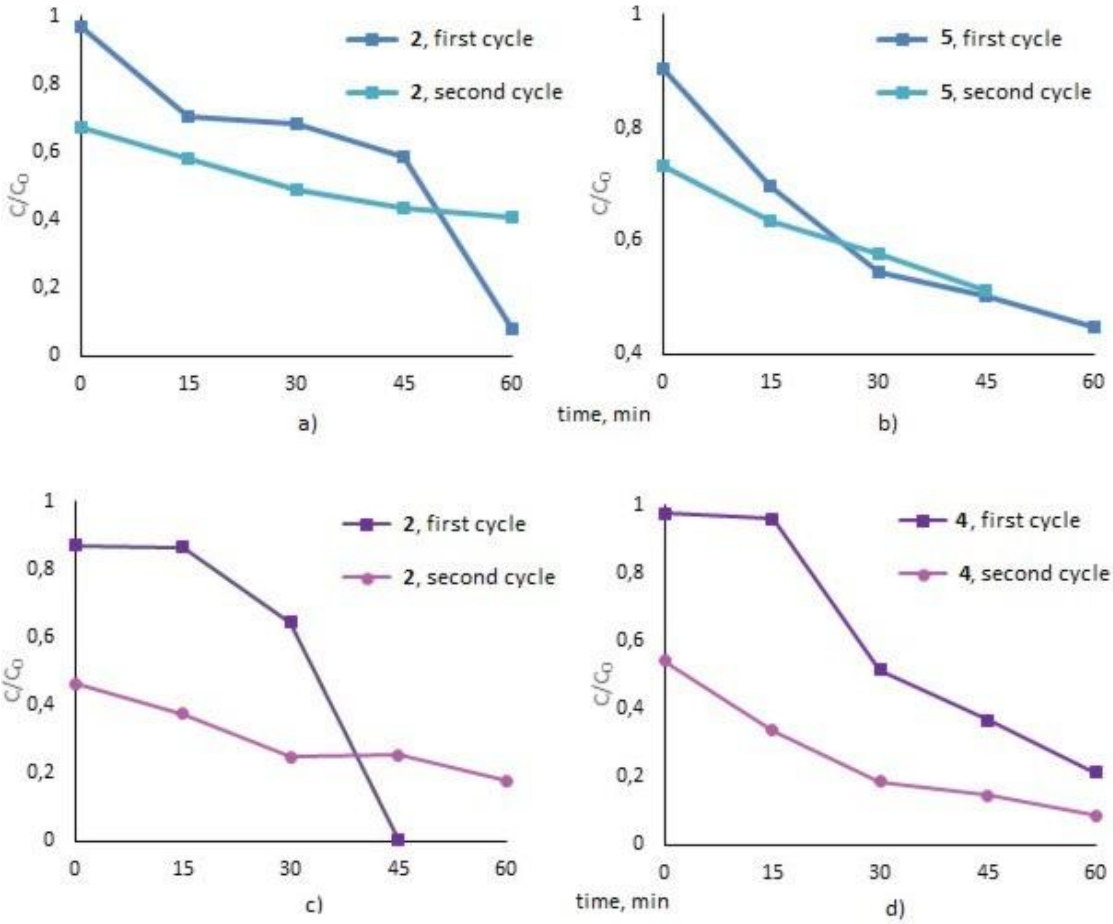

Fig. 3. Photocatalytic decomposition of MB with 2 (a), 5 (b), MV with 2 (c), 4 (d) (1 and 2 cycles)

Conclusion

Fluorinated tetraarylantimony carboxylates can be good candidate for the photocatalytic degradation of organic dyes: methylene blue and methyl violet. Meanwhile, tetraphenylantimony carboxylates are more effective towards both dyes, in comparison to tetra(p-tolyl)antimony compounds. However, methyl violet undergoes a fuller destruction than methylene blue.

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ФОТОКАТАЛИТИЧЕСКИЕ СВОЙСТВА ФТОРИРОВАННЫХ КАРБОКСИЛАТОВ ТЕТРААРИЛСУРЬМЫ

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Органические красители широко используются на производстве. Как результат, в настоящее время они являются распространенными загрязняющими веществами, приводящими к загрязнению воды. Поэтому представляет интерес поиск эффективных методов деструкции таких соединений. Одним из таких методов является фотокаталитическая деструкция с использованием органических соединений сурьмы. Установлено, что использование монокарбоксилатов тетраарилсурьмы ($Ar_4SbOC(O)R$, Ar = Ph, R = C_6F_5 (**1**), $CF_2CF_2CF_3$ (**2**), CF_2Br (**3**); Ar = p-Tol, R = CF_2CF_3 (**4**), $CF_2CF_2CF_3$ (**5**)) и дальнейшее облучение растворов УФ-излучением вызывает фотокаталитическую деструкцию органических красителей метиленового синего (МС) и метилового фиолетового (МФ) в их водных растворах. Изменение концентрации органических красителей наблюдается по изменению интенсивности пиков при 554 нм и 665 нм в УФ-спектрах МС и МФ. Карбоксилаты тетрафенилсурьмы **1**–**3** оказались более активными, чем карбоксилаты тетра(п-толил)сурьмы **4**, **5**. Так, разложение МС составило 90,5–98,8 %, МФ – 97,7–100 % после 60 мин облучения водных растворов, содержащих соединения **1**–**3**. В присутствии **4**, **5** разложение МС и МФ составило 53,2–55,1 % и 71,2–78,7 % соответственно. В обоих случаях МФ был подвержен более полной деградации, чем МС. Эксперименты подтвердили возможность повторного использования фотокатализаторов. После полного разложения красителя

карбоксилатом тетраарилсурьмы осадок центрифугировали, декантировали и использовали для следующего цикла. В результате двух циклов фотодеструкции масса карбоксилатов тетраарилсурьмы после промывки и сушки уменьшилась в среднем на 50 %. Однако карбоксилаты тетраарилсурьмы оставались фотокаталитически активными, что доказывало возможность их многократного использования и их стабильность.

Ключевые слова: карбоксилаты тетраарилсурьмы, органические красители, метиловый фиолетовый, метиленовый синий, фотокатализ.

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