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PHOTOCHEMICAL DEGRADATION OF PHENOL WITH THE PARTICIPATION OF TiO₂ NANOPARTICLES AND ETHYL-3,3,5,5-TETRACIANO-2-HYDROXIDE-2-METIL-4,6-DIPHENYL CYCLOHEXANE CARBOXYLATE

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The photochemical decomposition of phenol with the participation of TiO₂ nano-particles and ethyl-3,3,5,5-tetraciano-2-hydroxide-2-metil-4,6-diphenyl cyclohexane carboxylate by UV spectroscopy was studied for the first time. It has been shown, that UV irradiation of this mixture during 1 hour brings to 52% decomposition of phenol.

Keywords: *UV decomposition, photocatalysis, ethyl-3,3,5,5-tetraciano-2-hydroxide-2-metil-4,6-diphenyl cyclohexane carboxylate, phenol, waste water solution.*

doi

Introduction

The contamination of water basins with high toxic organic substances is considered as global ecological issues recently and therefore the works in the direction of the solution of this problem are very topical. In modern era heterogenic photocatalysis is considered one of the most effective processes in the environmental protection and treatment of waste waters from phenol-type contamination. This is because conventional classical chemical methods do not provide complete removal of contaminants [1–2].

By looking through the world literature, recently treatment methods by nano-composites are encountered very much: i.e. graphene oxide GO/Al₂O₃ nano-composite has been prepared with spin locking method for better treatment of phenol from waste water; at that time graphene oxide layer has been tightly covered with Al₂O₃-nanoparticles, it was possible to treat phenol from waste water by 99,9% on the basis of this obtained composite [3]. There are also other references in the viewed works [4–6].

Phenol is present always in waste water of various productions: petroleum chemistry, medicine, plastics, coal, and color change and paper production. Generally, phenol is one of the most important contaminants, because of high toxicity in the regard of its weak biological decomposition, being in high concentration and harmful influence to environment for a long time. As it is

noted, gradual reduction of clean water and increase of contamination are already among the significant ecological issues in the world. Currently, millions of people are suffering from the shortage of fresh water in the world. So far many methods have been used for removal of phenol from waste water. Usage of physical, chemical and biological methods is less trendy today. During the chemical processing intervening products are obtained so that they are also harmful for environment. Biological processing methods are less influencing for the acceleration of biological reactions, and in physical treatment absorption and membrane filtration methods are mainly used. Membrane filtration is a unique method for treatment of water from contaminating substances, i.e.; currently, the method of membrane filtration is paid much attention as an effective process in the regard of ecology and energy effectiveness for the water treatment. However at this time degradation of toxic substances in the composition of water requires other methods. Therefore, the subject of working out new methods does not lose its actuality.

Experimental part

The irradiation was carried out with using of photochemical reactor ALDKITTOO. The electron absorbtion spectra was recorded on UV/VIS spectrophotometer Varian Cary 50 Scan.

Ethyl-3,3,5,5-tetracyano-2-hydroxide-2-methyl-4,6-diphenyl cyclohexane carboxylate (II) was obtained by condensation of three-component system: benzaldehyde, acetylacetic acid ester and malonodinitrile with the participation of trichloroacetic acid at room temperature during 1–2 hours. The process was controlled by

20 ml of phenol solution (1mg in 1000 ml of water) was mixed with suspension of 0.05 g TiO_2 nanoparticles and 0.05 g ethyl-3,3,5,5-tetracyano-2-hydroxide-2-methyl-4,6-diphenyl cyclohexane ethyl carboxylate in 5 ml of water. The obtained reaction mixture was placed into photochemical reactor ALDKITTOO and exposed during 1 hour.

After the photolysis process the dependence of the absorption coefficient of the reaction solution on the wavelength has been measured in UV-VIS spectrophotometer. On the basis of the obtained curves the photolytic decomposition has been proved.

II substance is obtained by us for the first time. X-ray structural data have been published early [8]. The information related to the crystal structure of II compound has been uploaded in Cambridge structure base under the number of CCDC 1839026, at the same time can be received from www.ccdc.cam.ac.uk.

Analysis of the results

It may be noted by referring the information that TiO_2 nanoparticles has very good photo-dissociative activity together with chemical compounds, which contain with C, N atoms

thin-layered chromatography method. The yield 63%, M.p. 120–124°C. Found, %: C 76.10, H 5.37, N 6.83. Calculated for $\text{C}_{26}\text{H}_{22}\text{N}_4\text{O}_3$, %: C 76.32, H 5.22, N 8.68 [7].

The scheme of the reaction has been shown below:

[9–11]. And why has namely the usage of TiO_2 been paid less? The matter is that we have considered more appropriate TiO_2 nanoparticles as the works to be done by us have been carried out in the participation of UV radiation, since TiO_2 nanoparticles gets excited only during UV radiation ($\lambda < 387 \text{ nm}$), it has only 5% excitement in the visible region. Furthermore, TiO_2 is chemically sustainable, it is obtained in soft condition, that's easily in the viewed case, and the most important is that it is considered ecologically clean [12].

TiO_2 nanoparticles prepared for the process has been determined by TEM method and the results has been given in Figure 1. As seen from Figure 1, the sizes of the obtained nanoparticles are homogenous and vary between 10–30 nm. The purity and crystalline properties of the TiO_2 nanoparticles were investigated by powder X-ray diffraction (XRD) method. Figure 2 shows the XRD patterns of the synthesized TiO_2 nanopowders. All the XRD peaks were well defined and corresponded to TiO_2 at rutile phase. From the line broadening of the (101) diffraction peak by Scherrer's method, the average crystal size of TiO_2 is about 10–30 nm. This

result is according to TEM data. The specific surface areas for TiO_2 is $159.6 \text{ m}^2/\text{g}$. In the pattern all lines can be indexed, using the ICDD (PDF-2/ Release 2011 RDB) DB card number 00-001-1292. The pattern of TiO_2 nanopowder has characteristic peaks at 27.90° (110), 36.01° (101), 41.58° (111), 54.71° (211) [8].

It should be noted that it was not found any toxic influence of II substance. According to this, obtained II substance is used in the photo-catalytic dissociation of phenol. For this purpose the following solution has been prepared.

On Figure 4 it was given the absorption spectrum of initial solution, containing TiO_2 , phenol and ethyl-3,3,5,5-tetracyano-2-hydroxide-2-metil-4,6-diphenyl cyclohexane carboxylate before the radiation. The phenol absorption band is observed at 270 nm.

On Fig. 5 it is given the comparison of the curves obtained during photolysis process (60 minutes). It is seen from the graphic that the curves which are characteristic for phenol (270 nm) are reducing gradually so that it is the decomposition of the certain part of phenol in the process.

Fig. 1. TEM micrograph of the TiO_2 nanopowders.

Fig. 2. XRD patterns of the TiO_2 nanopowders.

Fig.3. Molecular structure of ethyl-3,3,5,5-tetracyano-2-hydroxide-2-metil-4,6-diphenyl cyclohexane carboxylate according to XRA

Fig.4. UV-VIS spectrum of the phenol, ethyl-3,3,5,5-tetracyano-2-hydroxide-2-metil-4,6-diphenyl cyclohexane carboxylate and nanoparticles of TiO_2 mixes in water solution before the radiation.

Fig.5. The change of UV-VIS spectrum during photolysis process: 1 – $\text{TiO}_2/\text{org.comp.}$ + phenol (before photolysis); 2 – $\text{TiO}_2/\text{org.comp.}$ + phenol (40 min radiation); 3 – $\text{TiO}_2/\text{org.comp.}$ + phenol (50 min radiation); 4 – $\text{TiO}_2/\text{org.comp.}$ + phenol (after 60 min. radiation).

Conclusion

This article has been directed to the solution of ecological problems for the environmental protection. So, the decomposition of toxic substances in contaminated water using nanoparticles is considered one of the most important and topical issues. In this work we have been studied the photocatalytic decomposition of phenol in the presence of ethyl-3,3,5,5-tetracyano-2-hydroxide-2-metil-4,6-diphenyl cyclohexane carboxylate and TiO_2 and shown, that UV light irradiation ($\lambda \geq 400\text{nm}$) during 60 minutes results in 52% degradation of phenol.

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TiO_2 NANOHİSSƏCİKLƏRİ VƏ ETİL-3,3,5,5-TETRASIANO-2-HİDROKSİD-2-METİL-4,6-DİFENİL TSİKLOHEKSAN KARBOKSİLAT İŞTİRAKINDA GEDƏN FOTOKİMYƏVİ REAKSIYA

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TiO_2 nanohissəciklərinin və etil-3,3,5,5-tetrasiano-2-hidroksid-2-metil-4,6-difenil tsikloheksankarboksilat iştirakında ilk dəfə olaraq fenolun fotokimyəvi reaksiyası aparılmışdır. Proses 60 dəqiqə davam etmişdir, reaksiyanın getməsi UB şüalandırıcı cihazda çəkilmiş əyrilərlə təsdiqlənmişdir. Prosesdən sonra fotoli zməhsulu kütlə spektroskopiyası üsulu ilə tədqiq edilmiş və fenolun 52% parçalanması müəyyən edilmişdir.

Açar sözlər: UV radiasiya, etil-3,3,5,5-tetraciano-2-hidroksid-2-metil-4,6-difenil tsikloheksankarboksilat, fenol, kütləspektroskopiya.

ФОТОХИМИЧЕСКАЯ РЕАКЦИЯ В ПРИСУТСТВИИ НАНОЧАСТИЦ TiO_2 И ЭТИЛ-3,3,5,5-ТЕТРАЦИАНО-2-ГИДРОКСИД-2-МЕТИЛ-4,6-ДИФЕНИЛ ЦИКЛОГЕКСАН КАРБОКСИЛАТА

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Впервые проведена фотохимическая деградация фенола с участием нано частиц TiO_2 и карбоксилата этил-3,3,5,5-тетрациано-2-гидроксида-2-метил-4,6-дифенилциклогексана. Процесс длился 60 мин, фотохимическая диссоциация фенола была подтверждена кривыми, полученные в аппарате УФ-излучения. В конце процесса с использованием масс-спектропии был анализирован раствор фотолита и было определено 52% разложение фенола.

Ключевые слова: УФ излучение, этил-3,3,5,5-тетрациано-2-гидроксид-2-метил-4,6-дифенил циклогексан карбоксилат, раствор фенола, масс-спектропия.