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REMOVAL OF NADOLOL USING COUPLED NANOMATERIALS BASED ON TITANIUM AND CARBON

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Abstract: Nadolol (NAD), one of the representatives of β-blockers, is used to treat cardiovascular diseases such as angina and hypertension. Due to its frequent use, it has been detected in hospital wastewater from which it is not removed efficiently enough, so it reaches natural waters. The lack of a satisfactorily efficient method for removing NAD from wastewater has created a need to find a more efficient way for its removal. This paper aims to investigate the efficiency of photocatalytic degradation of NAD by two TiO_2-C nanocomposites with different carbon content (9 and 20 wt%) under UV radiation. The applied nanocomposites, synthesized by the sol-gel hydrothermal method, showed significant efficiency in removing NAD compared to direct photolysis. Also, the reaction rate constant, according to which the decomposition of NAD in the presence of TiO_2-C takes place in the pseudo-first order, was calculated. The degradation of NAD was monitored by HPLC–PDA technique.

Keywords: Nadolol, Photocatalytic degradation, Kinetics.

1. INTRODUCTION

Pharmaceuticals are organic compounds synthesized to be resistant to typical biotransformation mechanisms in order to prolong their existence in the organism. This means that they are highly stable compounds, and municipal sewage treatment plants cannot entirely eliminate them. Since the treatment process is inefficient, effluent waters are a significant source of pharmaceuticals in the environment [1].

ß-blockers are representatives of cardiovascular pharmaceuticals used for the treatment of abnormal heart rhythms, high blood pressure, and angina pectoris [2]. Their presence in the aquatic environment has been confirmed, leading to questions about decomposition, potentially harmful effects on aquatic organisms, and accumulation in the food chain [3]. Nadolol ((2R,3S)-5-[3-(tert-butylamino)-2-hydroxypropoxy]-1,2,3,4-tetrahydronaphthalene-2,3-diol, NAD) is widely used β-blocker which is partially metabolized in the body. About 24.6% was found to be excreted by urine [4]. Precisely because of this, it was not surprising that it was detected in effluent and influent wastewater at concentrations of 23.3 to 167 ng/dm^3 [3]. This proves that conventional processes are insufficiently effective for its removal, so alternatives are considered.

Advanced oxidation processes (AOPs) have attracted significant interest in the field of wastewater remediation because of their superior removal capability and quick reaction times. AOPs refer to processes relying on highly reactive free radicals with high oxidative power. Free radicals have the ability to degrade organic pollutants found in aqueous media, and some AOPs in which they can be formed are ozonation, Fenton oxidation, photocatalysis, ultrasound irradiation, etc. [5].

Organic contaminants may be efficiently decomposed into less hazardous chemicals via photocatalytic degradation. Nanopowder TiO_2, one of the most significant photocatalytic materials, offers many benefits, including excellent chemical stability, high photocatalytic activity, non-toxicity, low cost, and reusability [6]. TiO_2 is an n-type semiconductor with a band gap ranging from 3.0 to 3.2 eV, which means that UV irradiation is suitable for its activation as photocatalyst. When UV irradiation induces the formation of reactive species on the surface of the TiO_2, such as $^{\bullet}OH$ radical, the photocatalytic transformation of a pollutant occurs. Although TiO_2 is already effective in removing organic pollutants, researchers are still trying to improve its catalytic activity. Doping TiO_2 with non-metallic components, such as nitrogen, carbon, sulfur, and others, is one technique [7]. Carbon materials with distinctive structure and morphology, high surface areas, and strong conductivity, such as carbon nanotubes, activated carbon, graphene, and carbon black (C), are leading candidates as photocatalyst support. Among the above-mentioned, carbon black is more easily accessible and less expensive than other carbon compounds, giving it an advantage as a doping material [8].

This paper investigated the efficiency of photocatalytic degradation of NAD by two TiO_2-C nanocomposites with additional carbon content (9 and 20 wt%) under UV radiation. The applied nanocomposites, synthesized by the sol-gel hydrothermal method, showed significant efficiency in removing NAD compared to direct photolysis. Also, the reaction rate constant, according to which the decomposition of NAD in the presence of TiO_2-C takes place in the pseudo-first order, was calculated. The degradation of NAD was monitored by HPLC–PDA technique.

2. MATERIALS AND METHODS

2.1. Materials

NAD ($C_{17}H_{27}NO_4$, $M_r = 309.4$, ≥99% purity) was purchased from Sigma–Aldrich and was used without additional purification. The standard solutions of NAD (0.05 mmol/dm^3) were made using ultrapure water (UPW, pH = 6.56, $\kappa = 0.055$ µS/cm). The solutions were stored in a dark, light-free environment at a temperature of 4 °C. Chemicals, such as 99.9% acetonitrile (ACN, C_3H_3NO, Sigma-Aldrich, pro analysis) and 85% orthophosphoric acid (H_3PO_4, Lachema, Neratovice, Czech Republic, pro analysis), that were employed as mobile phase components for liquid chromatography, were also used without purification. TiO_2 nanoparticles with different amounts of carbon black were synthesized using the sol–gel hydrothermal method [9]. TiO_2-C9 and TiO_2-C20 refer to samples of TiO_2 containing 9 and 20 weight percent of carbon black, respectively.

2.2. Degradation procedures

A Pyrex glass cell with a plain window on which the light beam was focused (total volume of *ca.* 40 cm^3) was used for photocatalytic degradation of NAD. Experiments were performed using 20 cm^3 of 0.05 mmol/dm^3 NAD containing 1.0 mg/cm^3 of TiO_2-C9 or TiO_2-C20. Before irradiation, the reaction mixture was sonicated for 15 min in the dark to establish adsorption/desorption equilibrium. Also, before irradiation, the reaction mixture was thermostated at 25 °C using water circulating jacket in a stream of O_2 (3.0 cm^3/min). During all experiments, the solution was stirred using a magnetic stirring bar under continuous gas flow. A high-pressure mercury lamp (125 W, Philips, HPL-N, emission bands at 290, 293, 296, 304, 314, 335, and 366 nm, with maximum emission at 366 nm) was used as the UV radiation source.

2.3. Analytical procedures

Aliquots of 0.50 cm^3 were taken from the reaction mixture at the beginning of the experiment and at regular time intervals to monitor the kinetics of NAD removal with High Performance Liquid Chromatography with Diode Array Detection (HPLC−PDA, Shimadzu) equipped with an Eclipse XDB−C18 column (150 mm × 4.6 mm i.d., particle size 5 µm, 30 °C). The reaction mixture's highest volume variation due to aliquot sampling was *ca.* 10%. The solutions were filtered through Millipore (Millex-GV, 0.22 µm) membrane filters. The absence of NAD adsorption on the filters was initially examined. Afterward, a 20 µL sample was injected and analyzed using a HPLC–PDA. The UV/vis PDA detector was set at 210 nm (suitable NAD adsorption wavelength). The gradient method of analysis was utilized in HPLC–PDA. The mobile phase (flow rate 0.7 cm^3/min) was a mixture of ACN and water (0 min 15% ACN, which increased to 25% ACN for 6 min, after which 30% ACN was constant for the next 2 min; post time 1 min), the water being acidified with 0.1%

H_3PO_4. The reproducibility of repeated runs was around 3−10%. The retention time for NAD was 5.2 ± 0.1 min. A combination of glass electrode (pH-Electrode SenTix 20, WTW) connected to a pH meter (pH/Cond 340i, WTW) was used to measure the pH.

3. REZULTS AND DISCUSION

The heterogeneous photocatalytic degradation of NAD in water was investigated in the presence of two photocatalysts, TiO_2-C9 and TiO_2-C20, under UV irradiation. First, in order to determine the contribution of UV radiation to the degradation of NAD, the efficiency of direct photolysis for NAD under UV irradiations was examined. Using UV radiation, only 4.7% of NAD was degraded after 120 min of irradiation which means that direct photolysis using UV radiation wasn't efficient for the removal of NAD from water (Figure 1a). Although the adsorption spectrum of the NAD and the spectrum of the UV radiation source overlap to a certain degree, it is not enough for the efficient degradation of NAD. Further, the effectiveness of TiO_2-C9 and TiO_2-C20 was examined, and as can be seen from Figure 1, both catalysts show significantly higher efficiency in NAD degradation compared to direct photolysis. TiO_2-C20 showed higher efficiency compared to TiO_2-C9, where 81.0% and 65.4% of NAD was degraded after 120 min, respectively. The results obtained by Raman scattering measurements indicate that higher carbon content probably enhances carbon crystallization during hydrothermal synthesis. Also, it was noted that the proportion of the anatase phase in TiO_2-C20 is higher than in TiO_2-C9 [9]. All of the above implies a higher amount of carbon contributes to the improvement of the photocatalytic activity of TiO_2. The pH change was monitored throughout each experiment (Figure 1b). First, the initial pH values in direct photolysis and photocatalytic degradation are different, which means that the presence of the catalyst affects the pH. Further, as can be seen, during direct photolysis, the pH value increases slightly from 7.7 to 8.8 after 120 min of irradiation, while in the case of photocatalytic degradation, the situation is reversed, the pH value decreases slightly from 8.0 to 7.5 for TiO_2-C9 and from 8.0 to 7.2 for TiO_2-C20. This indicates that alkaline intermediates were formed during direct photolysis, while acidic intermediates were formed during photocatalytic degradation, which lowered the pH to a neutral value. If we take into account that the complete degradation of organic compounds leads to their mineralization to CO_2 and H_2O, lowering the pH from alkaline to neutral during photocatalytic degradation is reasonable. Namely, with the use of TiO_2-C9 and TiO_2-C20, a high degradation efficiency was achieved, which means that the mineralization and the formation of CO_2 may have occurred, which lowered the pH.

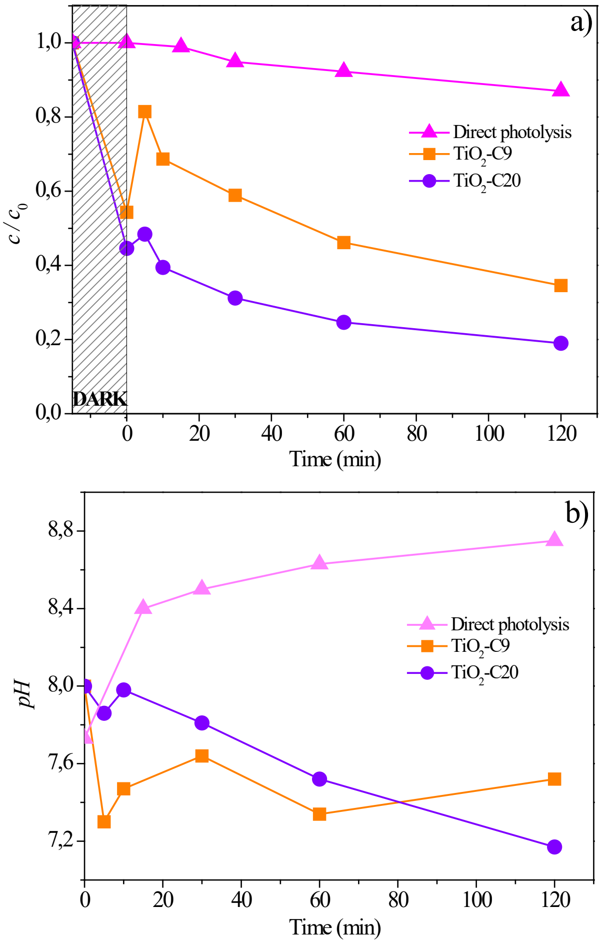

Figure 1. *Degradation efficiency of NAD (0.05 mmol/dm³) in the presence of TiO_2-C9 and TiO_2-C20 under UV irradiation (a) and change of pH during the processes(b)*

Figure 1a shows that after 15 min of sonification in the dark, NAD has adsorbed to the surface of TiO_2-C9 and TiO_2-C20 to 45.7% and 55.42%, respectively. Also, during the first five minutes of irradiation, NAD desorbs from the surface of the photocatalysts, and during the next 115 min, degradation takes place. It is important to note that with the TiO_2-C20, desorption occurs to a minor degree, probably because degradation occurred more quickly, which is the consequence of the photocatalyst's higher efficiency. Since adsorption occurs using TiO_2-C9 and TiO_2-C20 before UV irradiation, the adsorption efficiency of both photocatalysis was further investigated in the dark (Figure 2a). As can be seen, NAD is again most adsorbed during 15 min of sonification. After 5 min from the start of mixing the suspension, NAD desorbs from the surface of the photocatalysts, after which adsorption/desorption equilibrium is established. A higher percentage of adsorption was observed with TiO_2-C20 than with TiO_2-C9, which can be related to the carbon content. It is known that carbon black has a high adsorption capacity [10], which explains the higher adsorption of NAD using a photocatalyst with a higher carbon black content. Figure 2b shows the change in pH value during the adsorption of NAD in the presence of TiO_2-C9 and TiO_2-C20 in the dark. In the presence of TiO_2-C9 the pH increased from 8.0 to 8.2, while in the presence of TiO_2-C20 the pH decreased from 8.0 to 7.7. These slight changes in pH imply that the carbon content in the photocatalyst affects the change in pH.

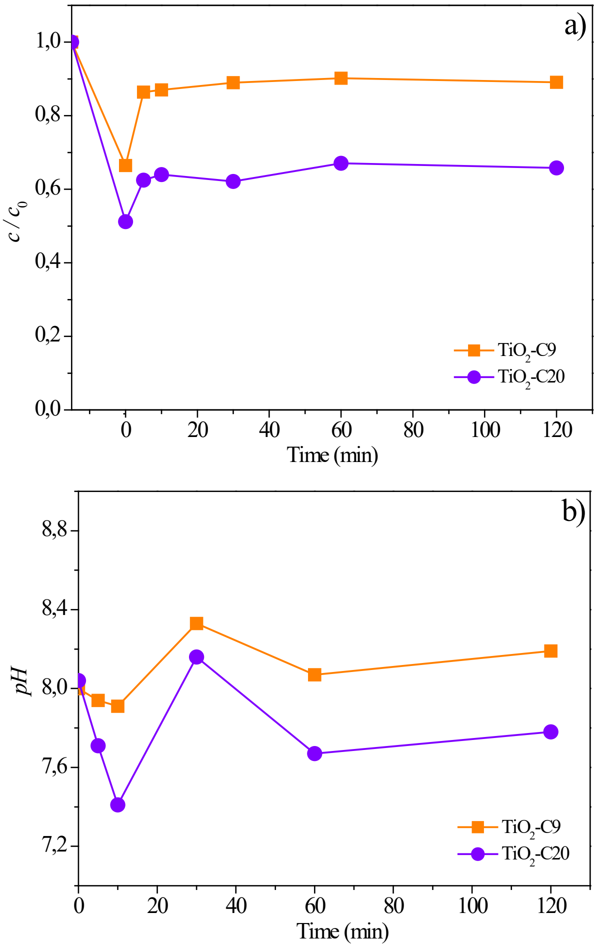

Figure 2. *Adsorption efficiency of NAD (0.05 mmol/dm^3) in the presence of TiO_2-C9 and TiO_2-C20 in the dark (a) and change of pH during the processes (b)*

The photocatalytic degradation kinetics of NAD in the presence of TiO_2-C9 and TiO_2-C20 fit the Langmuir–Hinshelwood model:

$$-\frac{dc}{dt}=\frac{kKC}{1+KC} \qquad (1)$$

where k is the intrinsic reaction rate constant (mmol/(dm^3 min)), K is the Langmuir–Hinshelwood adsorption constant (dm^3/mol), and C is the concentration of the substance. When the concentration of the substance is very low, the term $KC << 1$ and Eq. (1) simplifies to a pseudo-first-order kinetic law:

$$-\frac{dc}{dt}=k_1C \qquad (2)$$

where k_1 is the pseudo-first-order rate constant which can be calculated from the linear dependence of ln(c/c_o) vs. irradiation time. The first five minutes after the degradation started were excluded from the constant calculation since this was when the equilibrium between adsorption and desorption was established (Figures 2 and 3). The rate constants for kinetics of photocatalytic degradation of NAD with TiO_2-C9 and TiO_2-C20 under UV irradiation were calculated as $6.96\cdot10^{-3}$ 1/min and $7.47\cdot10^{-3}$ 1/min with the linearity correlation coefficient of 0.97 and 0.95, respectively.

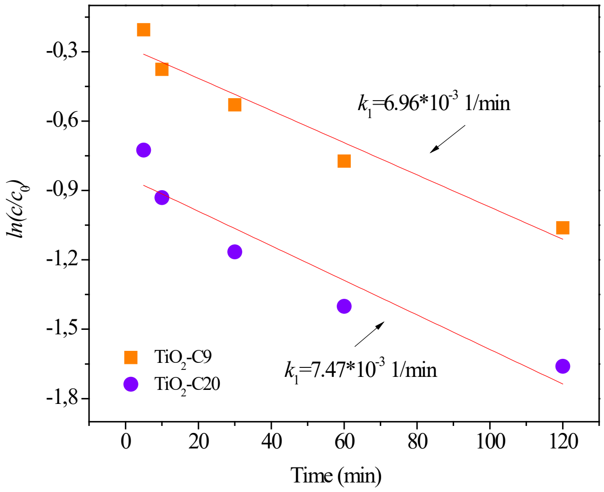

Figure 3. *Determination of the reaction rate constant (k_1) of NAD degradation in the presence of TiO_2-C9 and TiO_2-C20 under UV irradiation*

Considering all that has been said so far, it is certain that TiO_2-C20 is a more effective photocatalyst for the degradation of NAD than TiO_2-C9. However, both TiO_2-C9 and TiO_2-C20 show significant efficiency under UV irradiation compared to direct photolysis. Also, changes in pH imply that intermediates formed by applying TiO_2-C9 and TiO_2-C20 are similar. Adsorption occurs with both photocatalysts, which can be explained by the presence of carbon black, which is proven to be a promising adsorbent.

4. CONCLUSION

The presence of pharmaceutical compounds in surface waters is a growing environmental problem that is partly a consequence of the municipal sewage treatment plants that have difficulties in effective removal of pharmaceuticals from hospitals and industrial and domestic wastewater. In this context, sewage treatment methods must be improved. Recently, heterogeneous photocatalysis, one example of AOPs, has received lots of attention because of its ability to completely mineralize very stable pollutants by using highly reactive $^{\bullet}OH$ radicals.

The subject of this paper is the determination of the efficiency of photocatalytic degradation of NAD under UV irradiation with TiO_2 catalysts with different carbon content (TiO_2-C9 and TiO_2-C20). HPLC–PDA technique was used to monitor the degradation kinetics, and a pH meter was used to monitor the pH change. First, the direct photolysis of NAD under UV radiation was investigated and shown to be inefficient, wherein 4.7% of NAD was degraded after 120 min of irradiation. Further, the kinetics of photocatalytic degradation using TiO_2-C9 and TiO_2-C20 under UV irradiation was monitored. The obtained results showed that TiO_2-C20 is more efficient in the photodegradation of NAD than TiO_2-C9, where 81.0% and 65.4% of NAD was degraded after 120 min, respectively. In all cases, photocatalytic degradation of NAD followed the pseudo-first order. Because the adsorption of NAD on the surface of both photocatalysts was observed on the degradation kinetic curves, the adsorption efficiency of NAD in the dark was investigated. After 120 min, 10.9% and 34.2% of NAD was adsorbed on the surface of TiO_2-C9 and TiO_2-C20, respectively.

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УКЛАЊАЊЕ НАДОЛОЛА ПРИМЕНОМ КУПЛОВАНИХ НАНОМАТЕРИЈАЛА НА БАЗИ ТИТАНА И УГЉЕНИКА

Сажетак: Надолол (НАД), један од представника β-блокатора, употребљава се у лечењу кардиоваскуларних болести као што су ангина и хипертензија. Због честе употребе детектован је у отпадним водама болница из којих се не уклања довољно ефикасно, због чега је детектован и у природним водама. Недостатак задовољавајуће ефикасне методе за уклањање НАД из отпадних вода створио је потребу да се пронађе ефикаснији метод за његово уклањање. Циљ овога рада је испитивање ефикасности фотокаталитичке разградње НАД применом два TiO_2-C нанокомпозита са различитим садржајем угљеника (9 и 20 вт%), у присуству УВ зрачења. Примењени нанокомпозити, синтетисани сол-гел хидротермалном методом, показали су значајну ефикасност приликом уклањања НАД у односу на директну фотолизу. Такође, израчуната је и константа брзине реакције према којој се разградња НАД у присуству TiO_2-C одвија по псеудопрвом реду. Разградња НАД праћена је HPLC–DAD техником.

Кључне речи: надолол, фотокаталитичка разградња, кинетика.

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