Decomposition of 3-chlorophenol on nitrogen modified TiO_2 photocatalysts

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ABSTRACT

Photocatalytic activity of nitrogen modified TiO_2 calcined at temperatures of 100–350 °C toward 3-chlorophenol (3-CP) degradation was studied. In the experiments the fluorescent UV lamp and the incandescent lamp emitting mainly Vis light were applied. The degradation efficiency was evaluated on a basis of changes of 3-CP, total organic carbon and Cl^- concentration. A significant improvement of the photoactivity of the N-modified photocatalysts compared to the reference sample was observed. The rate of 3-CP degradation increased with the calcination temperature, and the highest efficiency was achieved for TiO_2 annealed at 350 °C. After 5 h of UV irradiation in the presence of TiO_2/N-350 and reference TiO_2 the 3-CP concentration decreased for 77% and 36%, respectively. The 3-CP removal after 24 h of Vis irradiation was 30% and 12% for the N-modified and reference samples, respectively. The 3-CP decomposition and mineralization were greatly influenced by pH of the solution, achieving the highest rate at pH 7 for the modified photocatalysts. An increase of the calcination temperature resulted in an increase of the rate of •OH formation. The photocatalytic activity of the N-modified TiO_2 remained unchanged during repeated photocatalytic degradation cycles.

1. Introduction

Chlorinated organic compounds, especially chlorophenols are pollutants, which have become a great environmental concern [1–3]. Most of them are toxic and can act as mutagenic or carcinogenic agents [4,5]. Chlorophenols present in water create serious problems such as death of aquatic life in inland water bodies or inhibition of the normal activities of microbial population in wastewater treatment plants. They are also readily absorbed by gastrointestinal tract of human [6]. Depending on their structure, chlorophenols exert different toxic effect to mammalian and aquatic life [7]. The LD_{50} values determined in mice indicated that 2-chlorophenol (2-CP) and 3-chlorophenol (3-CP) were considerably more toxic than dichlorophenols [8], whereas the increase of the chlorine atom number in chlorophenols enhanced their toxicity to fish [9]. Tests based on algal growth inhibition indicated that the level of toxicity among monochlorophenols depended on the organisms they affected [10].

Chlorophenols are introduced in the environment by chemical and pharmaceutical industries [11,12], during chlorination of municipal water or through degradation of other organic compounds [13]. Chlorophenols in natural water pose a serious risk because of a persistence and an accumulation in the environment

[14,15]. Biological treatment procedures for the decomposition of chlorinated phenols are slow or nondestructive due to their resistance to biodegradation [15]. Direct photolysis of chlorophenols do not also undergo in natural environment since they absorb light below 290 nm [16]. Hence, a demand for the efficient and economical water treatment method exists. In general, the presence of chlorine in the phenyl ring contributes to an increase of the resistance of an organic substance to degradation [17,18]. However, heterogeneous photocatalysis is one type of an advanced oxidation process (AOP), which can be successfully used as a method for the degradation of these compounds [19–21]. Commonly used catalyst in photocatalysis is titanium dioxide [22]. Unique photocatalytic properties of anatase TiO_2 such as high reactivity and stability as well as relatively low cost make it suitable for the oxidation of organic pollutants present in wastewater and water.

There are some literature data concerning photocatalytic degradation of chlorophenols such as pentachlorophenol [23] or monochlorophenols [24–34] in the presence of TiO_2. Usually 2-CP and 4-chlorophenol (4-CP) have been selected as target compounds [26–29]. A high effectiveness of photocatalytic removal of these substances under UV irradiation was previously reported [4,30–33]. The results obtained during the photocatalytic oxidation of monochlorophenols in H_2O_2/UV/TiO_2 system [11] revealed a complete 3-CP and 4-CP degradation after 30 min, while total 2-CP decomposition was achieved after 2 h.

Pure TiO_2 can be photoexcited under UV light irradiation, which is only about 2–4% of sunlight [35]. Therefore, an increase of

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absorption of TiO_2 in the visible region to improve its visible response is desired. Doping of TiO_2 with metals, metal oxides as well as nonmetal elements are the main methods of preparation of visible light active photocatalysts. It was proved by numerous researches that doping with nonmetals such as N, C, Br, Cl, F, J is especially beneficial for enhancement of visible light activity of TiO_2.

The pioneering paper, which reported doping of TiO_2 with nitrogen as a method of preparation of visible light active photocatalysts was published in 2001 by Asahi et al. [36]. The authors prepared the $TiO_{2-x}N_x$ films by sputtering the TiO_2 target in N_2/Ar gas mixture and subsequent annealing at $550\,°C$ in N_2 atmosphere. Diwald et al. [37] prepared Vis active TiO_2/N photocatalysts by high-temperature treatment of TiO_2 with NH_3 gas. Ammonolysis was found to be a promising method of preparation of the so-called second-generation photocatalysts [38].

The enhancement of photocatalytic activity in the visible region by doping with N is usually attributed to changes in electronic structure of photocatalysts [39–42]. The visible light activity can be due to [43]: (1) the substitutional doping of N, which causes a band gap narrowing driven by mixing of N 2p states with O 2p states or (2) N 2p states isolated above the valence band of TiO_2. Incorporation of nitrogen into TiO_2 lattice can be substitutional (Ti–N–Ti) or interstitial (Ti–O–N and/or Ti–N–O) [44]. Peng el al. [45] indicated that both substitutional and interstitial N impurities can enhance the photoactivity in visible light. Moreover, the photocatalytic activity of interstitial N-doped TiO_2 was found to be higher than that of substitutional N-doped TiO_2.

The influence of nitrogen precursor on photoactivity of N-doped TiO_2 during degradation of chlorophenols under both UV and Vis irradiation was previously observed [44,46]. For example, Ananpattarachai et al. [44] reported that among three nitrogen dopants: urea, triethylamine and diethanolamine the latter one provided the interstitial N-doped TiO_2 with highest visible light absorption ability and highest efficiency in 2-CP degradation. A comparison of the efficiency of 4-CP photodegradation in the presence of N-doped TiO_2 and pure TiO_2 showed that the nitrogen atoms in the structure of the photocatalysts were responsible for the visible light photocatalytic activity and higher effectiveness under UV light as well [47]. Nevertheless, the literature data concerning application of TiO_2/N for degradation of monochlorophenols such as 3-CP under Vis irradiation are limited.

There are still some important issues concerning nitrogen modified TiO_2 photocatalysts, which require further studies. They include: (1) determination of the influence of preparation conditions on photocatalytic activity of TiO_2/N; (2) evaluation of •OH radicals formation on TiO_2/N surface and (3) investigation on the photostability of the nitrogen modified photocatalysts under cyclic performance.

During the present work the photocatalytic activity of nitrogen modified TiO_2 toward degradation of 3-CP under irradiation of fluorescent UV lamp and incandescent lamp emitting mainly Vis light was investigated. The influence of calcination temperature of the photocatalysts on the efficiency of decomposition and mineralization of the model compound was especially studied. Moreover, the effect of solution pH on the photocatalytic removal of 3-CP was determined. The influence of •OH generation rate on 3-CP degradation efficiency was also investigated. Finally, the stability of TiO_2/N during cyclic performance was evaluated.

2. Experimental

2.1. Materials

3-chlorophenol with purity of 98% (Sigma–Aldrich) was used as a model organic compound in the photocatalytic tests. Ammonia water (25%) was purchased from Chempur (Poland).

A commercial titanium dioxide dried at $100\,°C$ was used as the reference/starting material. The photocatalyst was supplied by the Chemical Factory "Police" S.A. in Poland.

The preparation of the photocatalysts was carried out using HEL Ltd. "Autolab" E746 installation. 600 g of commercial TiO_2 and $350\,cm^3$ of diluted NH_4OH solution (2.5%) were placed in a temperature–pressure reactor. The reactor was closed and the mixture was blended using a magnetic stirrer. The photocatalysts were heated up to $100\,°C$ for 4 h. Afterwards, the samples were dried in air for 4 h at six different temperatures in the range of $100–350\,°C$ (photocatalysts denoted later as TiO_2/N-100 to TiO_2/N-350). Finally, the obtained photocatalysts were ground with a mortar to form a fine powder. The nitrogen modified titania samples were used as photocatalysts for decomposition of 3-CP in water.

The physico-chemical characteristics of the reference material and the prepared TiO_2/N photocatalysts were presented in our earlier work [48]. In order to complete the characterization of the photocatalysts the zeta potential and point of zero charge (pH_{pzc}) were measured using Zetasizer Nano-ZS equipped with Multi Purpose Titrator MPT–2 and degasser (Malvern Company).

2.2. Experimental procedures

Photocatalytic decomposition of 3-CP was carried out in a glass beaker containing $500\,cm^3$ of aqueous solution of the model compound and 0.1 g of a photocatalyst. The initial concentration of the model solution was equal to $10\,mg/dm^3$ unless otherwise stated. The pH of 3-CP solution amounted to pH 3 (adjusted with HCl), pH 4.8 (no pH adjustment) or pH 7 (adjusted with NaOH). The reaction solution was continuously mixed with a magnetic stirrer.

During the first series of experiments a UV light source built of 6 fluorescent lamps (Philips Cleo, 20 W) with total UV irradiation intensity of $154\,W/m^2$ was used. In the second series of experiments an incandescent lamp (Philips, 100 W) emitting Vis light with intensity of $385\,W/m^2$ was applied. The irradiation spectrum of the incandescent lamp contained less than 0.05% of UV component (UV intensity: $0.2\,W/m^2$). Since the intensity of UV light was very low, it can be assumed that the photodegradation was mainly due to action of Vis light. It is also worth noting that the UV contribution was about hundred times lower than in case of solar light, which typically contains UV flux in the range of $20–30\,W/m^2$ [49]. The term "UV light" used later in the text refers to the light emitted by the fluorescent lamp whereas the term "Vis light" means the light emitted by the incandescent lamp.

The photodegradation of 3-CP was conducted for 5 h or 24 h under the UV or Vis light, respectively. The concentration of 3-CP in the solution was evaluated on the basis of UV–Vis spectra ($\lambda_{max} = 275\,nm$, Jasco V-530 spectrometer, Japan). The total organic carbon (TOC) concentration was measured using the "multi N/C 2000" analyzer (Analytik Jena, Germany). The chloride ion concentration was monitored using potentiometric method (Orion 920A with an ion-selective electrode). Prior to the measurements the reaction mixture was filtered through a $0.45\,\mu m$ membrane filter. For identification of the intermediate products of 3-CP photocatalytic degradation HPLC and GC–MS methods were applied. HPLC analyses were performed using HPLC LaChrom Elite (Hitachi, Japan) equipped with the PUROSPHER STAR RP-18e ($5\,\mu m$) Merck column and UV/Vis detector. The mobile phase consisted of 30% of CH_3OH and 70% of water. The flow rate of eluent was $0.8\,cm^3$/min. GC–MS system consisted of THERMO TRACE GC ULTRA gas chromatograph coupled with a DSQ mass spectrometer. The Restek RTX-5MS (30 m, $0.25\,\mu m$) column was used. Analytes were extracted from samples and concentrated prior to analysis using solid-phase extraction (SPE) Supelclean™ ENVI™ Chrom P filters.

The formation of hydroxyl radicals on a photocatalyst surface in the aqueous solution was investigated by the fluorescence spectroscopy. Terephthalic acid was used as a compound, which upon reaction with the hydroxyl radicals generates a highly fluorescent probe. It should be noted, however, that this method allows only to determine the relative ability of a photocatalyst toward •OH generation. The absolute concentration of the hydroxyl radicals on the surface of a photocatalyst cannot be measured by using this technique. The solution of terephthalic acid (5×10^{-4} mol/dm^3) was prepared in a diluted (2×10^{-3} mol/dm^3) NaOH solution in order to ensure the solubility as indicated by Ishibashi et al. [50]. Terephthalic acid reacted with the surface •OH radicals and generated highly fluorescent hydroxy product 2-hydroxyterephthalic acid. Fluorescence spectra of the 2-hydroxyterephthalic acid were measured using F-2500 Hitachi (Japan) spectrofluorometer. 2-hydroxyterephthalic acid was identified as a peak with the maximum at 420 nm. The excitation wavelength amounted to 314 nm. During all the experiments, a 0.02 g of a photocatalyst and 100 cm^3 of terephthalic acid solution were irradiated with UV or Vis light. The solution was continuously mixed during the reaction by means of a magnetic stirrer.

3. Results and discussion

3.1. Photocatalytic degradation of 3-CP under UV light

3.1.1. The influence of solution pH on photodegradation of 3-CP in the presence of the TiO$_2$/N photocatalysts

During the first step of the present research the influence of solution pH on the effectiveness of decomposition and mineralization of 3-CP in the presence of TiO$_2$/N calcined at various temperatures was investigated. The results are shown in Fig. 1a–c. The decomposition of 3-CP under UV light in the absence of photocatalysts was not observed, thus the reaction was conducted in a pure photocatalytic regime.

Before the UV lamp was switched on a 30 min adsorption in the dark was carried out (Fig. 1a–c). Experimental study of the adsorption of phenol on anatase reported by Bekkouche et al. [51] indicated that the adsorption was chemisorption in a monolayer and obeyed the Langmuir model. It should be stressed that the solution pH plays an important role in the adsorption and photocatalytic processes. The pH influences the electrostatic interactions between a semiconductor surface, solvent molecules and substrate. In addition, protonation and deprotonation of organic pollutants takes place depending on the solution pH [52].

In order to determine the izoelectric point the surface charge of the modified photocatalysts at different pH was measured. The results obtained for TiO$_2$/N calcined at the lowest (100 °C), medium (200 °C) and the highest (350 °C) applied temperatures are shown in Fig. 2. The pH$_{pzc}$ determined for TiO$_2$/N-100, TiO$_2$/N-200 and TiO$_2$/N-350 was 5.83, 5.89 and 5.88, respectively. The data reveal that the TiO$_2$/N surface is positively charged at pH < 5.9, whereas it is negatively charged at pH > 5.9. Therefore, in the former case adsorption of negatively charged molecules is favored, whereas in the latter case the positively charged species are easily adsorbed.

The results presented in Fig. 1a–c show that within the pH range used in the experiments the amount of 3-CP adsorbed on the photocatalysts surface was very low. However, it can be also observed that under strongly acidic pH (pH 3) the amount of the adsorbed 3-CP was slightly higher compared to that at pH 7, in which case the 3-CP adsorption was negligible. The pK_a of 3-CP is 8.98 [53], which means that under the conditions applied in the research the model compound was mainly in its molecular form. The 3-CP molecule undergoes deprotonation becoming negatively charged in basic media, which were not considered in this work. Taking this
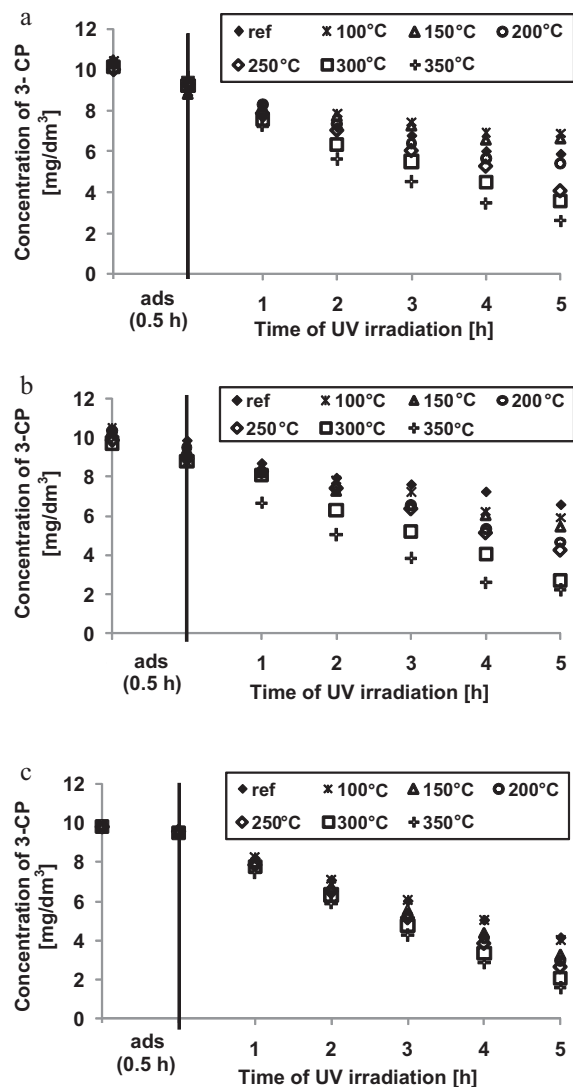

Fig. 1. The changes of 3-CP concentration during photocatalytic decomposition under UV irradiation using reference sample and nitrogen modified TiO$_2$ calcined at different temperatures: (a) pH 3; (b) pH 4.8; (c) pH 7; 3-CP concentration: 10 mg/dm^3; photocatalyst loading: 0.2 g/dm^3.

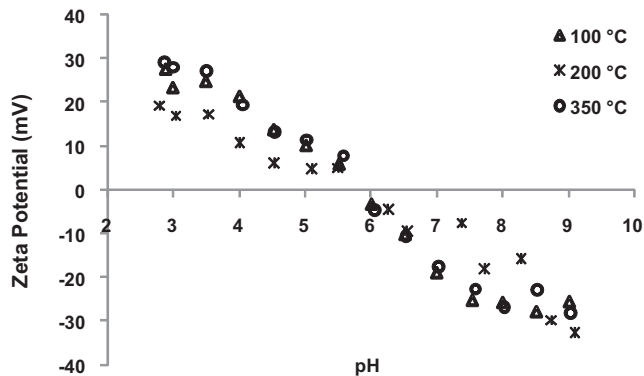**Fig. 2.** Zeta potential–pH plots of TiO$_2$/N calcined at different temperatures.

into account, the observed decrease of the amount of the adsorbed 3-CP can be attributed to the surface charge of the photocatalysts. At pH 7, which is above the pH$_{pzc}$ of TiO$_2$/N the photocatalyst surface is negatively charged. Under such conditions the water molecules can block the photocatalyst surface thus reducing the 3-CP
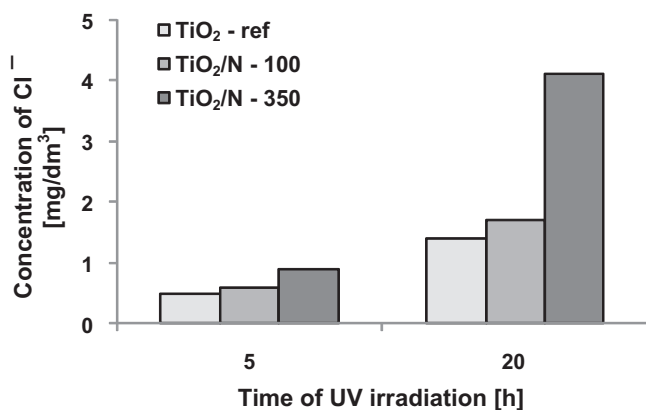
Fig. 3. Concentration of Cl^- in 3-CP solution after 5 h and 20 h of UV irradiation in the presence of different photocatalysts; 3-CP concentration: 20 mg/dm^3; photocatalyst loading: 0.2 g/dm^3.

Fig. 4. The influence of solution pH on the effectiveness of 3-CP mineralization under UV irradiation in the presence of reference sample and TiO$_2$/N calcined at different temperatures; 3-CP concentration: 10 mg/dm^3; photocatalyst loading: 0.2 g/dm^3; time of the processes: 5 h.

adsorption [53]. On the opposite, at pH 3 the photocatalyst surface was positively charged which was more beneficial for adsorption of unionized 3-CP molecules. A similar enhancement of adsorption in acidic compared to neutral media was also observed in case of phenol [54].

After adsorption in dark the light source was switched on and the photocatalytic reaction was started. Fig. 1a–c shows the results obtained during photocatalytic decomposition of 3-CP in the presence of different photocatalysts. A gradual increase of the photocatalytic activity of the modified TiO$_2$ with the increase of calcination temperature can be observed. The tendency was maintained at all the pH applied. The removal of 3-CP after 5 h of UV illumination was found to be 25–40% higher for TiO$_2$/N calcined at 350 °C than that for TiO$_2$/N-100, depending on pH.

On the contrary to the adsorption results an improved effectiveness of 3-CP photocatalytic decomposition with increasing pH was observed. The effectiveness of 3-CP removal after 5 h of irradiation in the presence of the TiO$_2$/N-350 sample was ca. 74%, 77% and 84% for pH 3, 4.8 and 7, respectively. The tendency can be explained by a greater extent of surface coverage by OH^- ions at higher pH. The OH^- ions can be oxidized to $^\bullet OH$ radicals, which take part in oxidation of 3-CP.

In order to compare the results an additional experiment of 3-CP decomposition in the presence of the commercially available AEROXIDE® TiO$_2$ P25 (Evonik, Germany) was performed. It was found that after 4 h of irradiation the concentration of 3-CP decreased to 0 mg/dm^3.
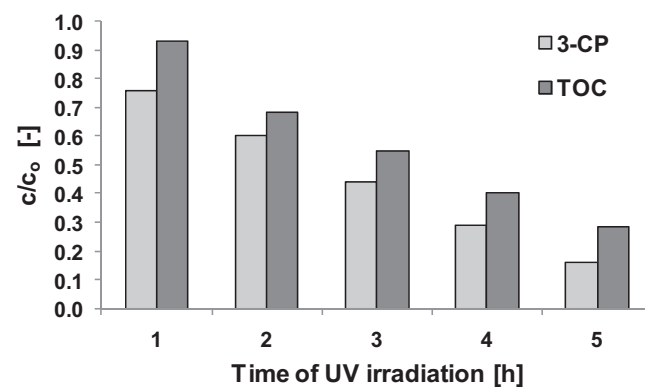
3.1.2. Mineralization of 3-CP in the presence of the TiO$_2$/N photocatalysts

The effectiveness of 3-CP mineralization was evaluated on a basis of Cl^- as well as TOC concentration measurements. It was observed that the concentration of chloride ions increased in time of the process. Fig. 3 shows Cl^- concentration after 5 and 20 h of degradation of 3-CP conducted with application of TiO$_2$ without modification and TiO$_2$/N calcined at the lowest (100 °C) and the highest (350 °C) temperatures applied. In order to emphasize changes of chloride content the concentration of 3-CP was set at 20 mg/dm^3. The most significant increase of the Cl^- concentration was observed for TiO$_2$/N calcined at 350 °C. The concentration of Cl^- amounted to 0.9 and 4.1 mg/dm^3 after 5 and 20 h of the process, respectively. This is in agreement with the results presented in Fig. 1, which show that this catalyst was the most active in 3-CP decomposition.

Fig. 4 shows effectiveness of 3-CP mineralization expressed in terms of TOC removal after 5 h of UV irradiation in the presence
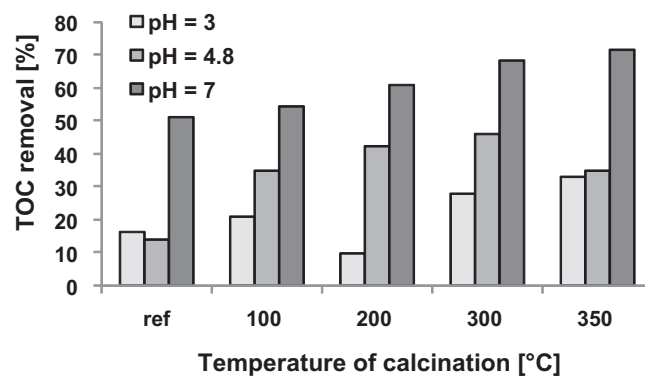
Fig. 5. A comparison of the effectiveness of decomposition and mineralization of 3-CP in the presence of TiO$_2$/N-350 under UV irradiation; 3-CP concentration: 10 mg/dm^3; photocatalyst loading: 0.2 g/dm^3.

of different photocatalysts. Additionally, the influence of pH was taken into account. It should be stressed that the graph represents the removal of not only the initial substrate but all organic degradation intermediates present in the reaction mixtures as well.

Similarly as in case of 3-CP decomposition (Fig. 1) the removal of TOC was the most efficient at the highest pH applied. Under acidic conditions (pH 3) the photocatalytic mineralization of 3-CP was found to be very low and ranged from 21% to 33% for TiO$_2$/N-100 and TiO$_2$/N-350, respectively. At pH 4.8 the effectiveness of mineralization was improved significantly. TOC was removed for 35–46%, dependent on the photocatalyst applied. Adjustment of pH to pH 7 resulted in remarkable increase of TOC removal, which reached ca. 72% for TiO$_2$/N calcined at 350 °C. The lowest effectiveness of mineralization exhibited the reference sample.

According to Krýsa et al. [30] the mineralization kinetics of 4-CP could be approximated by a zero order function. It is caused by the fact that a large number of reaction products may be produced by reactions of $^\bullet OH$ radicals with benzene derivatives. These intermediate products in turn can undergo further reaction with $^\bullet OH$, indicating complex reaction sequences. As a result TOC removal proceeds with a notable delay in comparison with 3-CP removal, which was also observed in our investigations. In Fig. 5 a comparison of the efficiency of 3-CP decomposition and mineralization during photocatalytic process under UV irradiation using TiO$_2$/N-350 is presented.

In order to identify the oxidation products formed during the photodecomposition of 3-CP the GC–MS and HPLC analyses were performed (Table 1). In the 3-CP solution after 5 h of UV

Table 1
Intermediates of photocatalytic degradation of 3-CP under UV and Vis irradiation in the presence of the TiO$_2$/N photocatalysts.

Intermediates	UV irradiation	Vis irradiation
Chlorohydroquinone	+	
Hydroquinone	+	
Benzoquinone		+
Resorcinol	+	+
Catechol	+	+
Phenol	+	+
Formic acid	+	
Acetic acid	+	
Maleic acid	+	

irradiation in presence of TiO$_2$/N some amounts of chlorohydroquinone, hydroquinone, resorcinol, catechol and phenol, except from 3-CP were identified. Moreover, the presence of aliphatic carboxylic acids such as formic, acetic and maleic was observed. The generation of the reaction intermediates can be explained by $^\bullet$OH radical attack on 3-CP molecule.

3.1.3. The influence of physico-chemical properties of TiO$_2$/N photocatalysts on their photocatalytic activity

A detailed characteristics of the prepared TiO$_2$/N photocatalysts was presented in the previous paper [48]. The most important physico-chemical properties of the samples are summarized in Table 2. The presence of nitrogen groups on the surface of the modified samples was confirmed by XPS analysis which revealed that concentration of N atoms in TiO$_2$/N-350 was about 0.85 at.%. It was suggested that the nitrogen atoms were present in the environment of O–Ti–N linkages at interstitial sites between the TiO$_2$ lattices [48].

The observed improvement of photocatalytic activity with increasing annealing temperature of the photocatalysts was associated with their physico-chemical properties. The crystallite size and the content of the anatase phase increased with the increase of the calcination temperature (Table 2). Consequently, a decrease of the specific surface area S_{BET} took place. Taking into consideration that higher S_{BET} value means that larger surface is accessible for photocatalytic reaction, the TiO$_2$/N-100 (S_{BET} = 235 m^2/g) should be more active than TiO$_2$/N-350 (S_{BET} = 94 m^2/g). The results show, however, that the highest photoactivity exhibited the sample calcined at 350 °C. Therefore, the crucial factors responsible for photocatalytic activity of the prepared photocatalysts were found to be phase composition and crystallite size of anatase. The heat treatment of the samples contributed to transformation of amorphous phase to anatase phase (Table 2). The content of anatase increased from 31.9% in case of TiO$_2$/N-100 to 47.8% in case of TiO$_2$/N-350. Furthermore, an increase of crystallite size of anatase from 6.1 nm for 100 °C up to 10.3 nm for 350 °C was observed (Table 2). It was previously reported that a decrease in crystallite size of TiO$_2$ leads to the reduction of volume recombination [55]. This might suggest that the TiO$_2$/N-100 should be more active than TiO$_2$/N-350. However, it was also found [55,56] that when the size is extreme small, surface recombination becomes an important process. This is because in the regime of ultrafine particle size most of the e$^-$/h$^+$ pairs are generated close to the surface. In such a case they may quickly reach the surface and undergo rapid surface recombination mainly due to abundant surface trapping sites and the lack of driving force for e$^-$/h$^+$ pairs separation [57]. Taking the above discussion into account it might be concluded that the high activity of TiO$_2$/N-350 was due to both higher anatase content and larger anatase crystallite size in case of this photocatalyst compared to TiO$_2$/N-100.
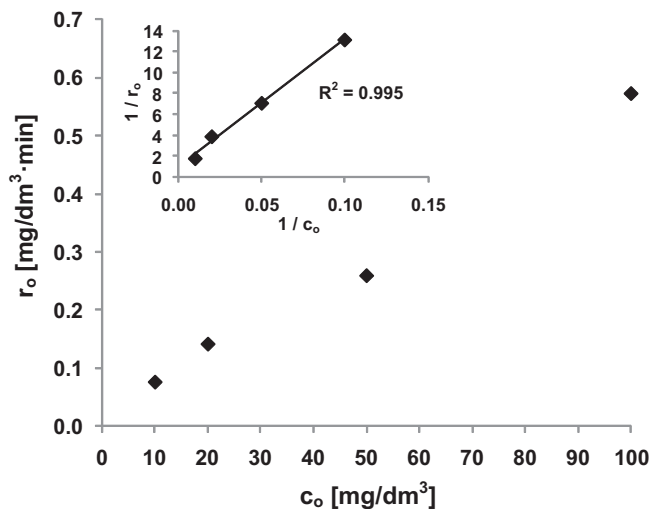
Fig. 6. Initial rate of 3-CP photocatalytic decomposition (r_o) under UV light as a function of initial concentration (c_o); photocatalyst loading: 0.2 g/dm^3.

3.1.4. Effect of initial 3-CP concentration

The influence of initial concentration of 3-CP on its decomposition rate was examined with application of the TiO$_2$/N-350, which was the most active from all the photocatalysts prepared during this work. The obtained results (Fig. 6) revealed that the initial degradation rate (r_o) increased with increasing 3-CP concentration and amounted to 0.0759, 0.1413, 0.2592 and 0.5734 mg/dm^3 min for c_o of 10, 20, 50 and 100 mg/dm^3, respectively.

The photodecomposition of organics in the presence of TiO$_2$ is usually described by the Langmuir–Hinshelwood (L–H) kinetics [30,58]. Rideh et al. [21] proposed the L–H model as the only one appropriate to describe the photooxidation of 2-CP. Therefore, in the present work the L–H model was applied for calculation of the reaction rate constant (k) and the constant of adsorption equilibrium (K):

$$r_o = \frac{-dc}{dt} = \frac{kKc_o}{1 + Kc_o} \qquad (1)$$

The expression can be rearranged into linear form as follows:

$$\frac{1}{r_o} = \frac{1}{kK} \cdot \frac{1}{c_o} + \frac{1}{k} \qquad (2)$$

In order to find the k and K constants values, the $1/r_o$ vs. $1/c_o$ was plotted, as shown in the inset in Fig. 6. A linear correlation between $1/r_o$ and $1/c_o$ up to 100 mg/dm^3 with R^2 = 0.995 was observed. The calculated rate constant k of the 3-CP photocatalytic decomposition in the presence of TiO$_2$/N-350 was 1.076 mg/min, while the adsorption constant K was found to be as low as 7.6×10^{-3} dm^3/mg. The rate constant obtained in this work was found to be significantly higher compared to that obtained by Peiró et al. [59], who studied the kinetics of phenol and substituted phenolic compounds degradation in aqueous suspensions of TiO$_2$.
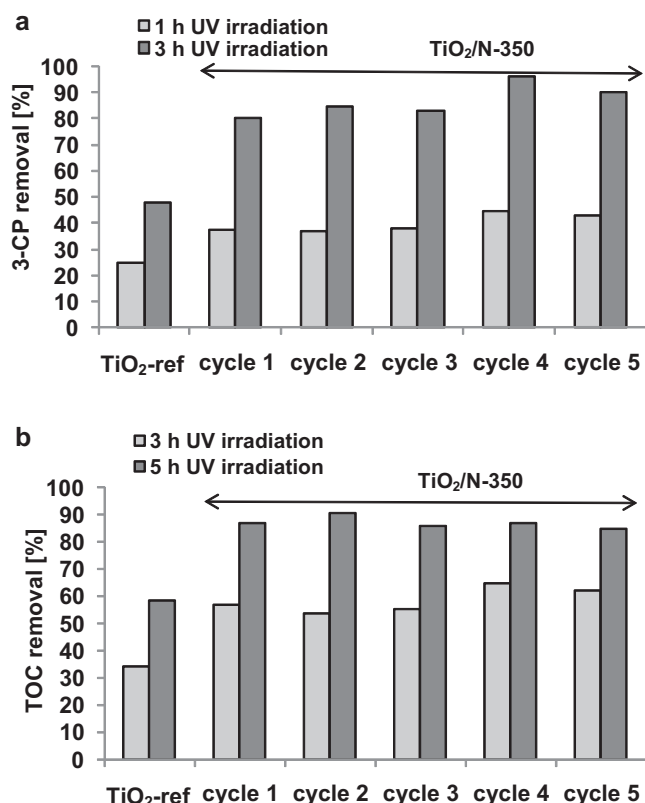
3.1.5. Photostability of the TiO$_2$/N photocatalysts

The photostability of the photocatalysts is one of the most important properties of these materials [60,61]. The substrate degradation rate was often found to be degressive with an increase in cycle times [62]. A significant decrease of photocatalytic activity of N-doped TiO$_2$ was reported by Nosaka et al. [63]. The authors explained the lack of photocatalyst stability by the fact that the surface of the photocatalyst was covered with some by-products or the doped nitrogen atoms were released from TiO$_2$ lattice. According to Lai et al. [64] N-doped TiO$_2$ nanotube array film showed no apparent change in surface morphology after repeating photocatalytic

Table 2
Physico-chemical properties of TiO_2/N photocatalysts.

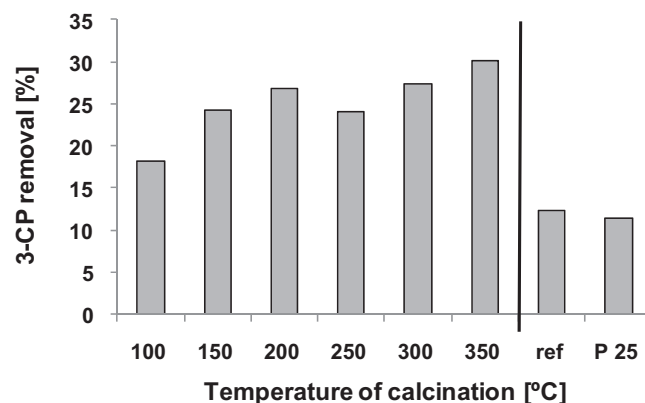| Photocatalyst	Mean crystallite size [nm]	Mean particle size [nm]	S_{BET} [m²/g]	Relative fraction of TiO_2 phases [%]		
				Amorphous	Anatase	Rutile
TiO_2/N-100	6.1	167.6	235	65.1	31.9	3
TiO_2/N-150	6.7	167.6	238	61.0	36.0	3
TiO_2/N-200	7.8	235.3	205	57.0	40.0	3
TiO_2/N-250	8.2	193.9	172	55.9	41.1	3
TiO_2/N-300	9.4	289.6	139	38.8	58.2	3
TiO_2/N-350	10.3	271.0	94	49.2	47.8	3

Adapted from Ref. [48].

Fig. 7. Stability of TiO_2/N-350 during repeated photodegradation cycles under UV light (a) effectiveness of 3-CP decomposition; (b) effectiveness of mineralization; 3-CP concentration: 5 mg/dm³; photocatalyst loading: 0.2 g/dm³.

Fig. 8. Effectiveness of 3-CP decomposition after 24 h of Vis irradiation in the presence of different photocatalysts; 3-CP concentration: 10 mg/dm³; photocatalyst loading: 0.2 g/dm³.

cycles. Additionally, only a slight reduction of photoactivity (ca. 8%) toward dye removal was observed.

In order to examine the stability of the most active TiO_2/N-350 in subsequent cycles the 3-CP at concentration of 5 mg/dm³ was applied. After a complete mineralization of 3-CP the photocatalyst was separated by filtration, dried at 70 °C for 20 h and then reused in the next cycle of photodegradation of 3-CP. The results of both, degradation and mineralization of 3-CP in five subsequent cycles are shown in Fig. 7. The removal of 3-CP was higher than TOC removal. This results from the fact that the parameter defined as TOC refers to all organics present in the sample, i.e. both 3-CP and intermediates of its decomposition. After 3 h of photocatalytic process the removal of 3-CP was about 80–90%, whereas after 5 h of UV irradiation TOC was removed for about 90%.

For comparison purpose, the results obtained in the presence of pure TiO_2 as a reference sample are also shown in Fig. 7. It can be observed that the efficiency of 3-CP decomposition after 3 h of UV irradiation in the presence of the reference TiO_2 was about two times lower compared to the N-modified sample and amounted to ca. 48%. Similarly, the mineralization was less efficient in case of

the unmodified TiO_2. After 5 h of irradiation the concentration of TOC decreased for less than 60%.

The results presented in Fig. 7 revealed that the efficiency of 3-CP decomposition and mineralization was stable during all five of the cycles. Thus, the obtained N-modified TiO_2 could be successfully reused without losing its photocatalytic activity.

3.2. Photocatalytic degradation of 3-CP under Vis light

In the next step of the investigations the photocatalytic degradation of 3-CP in aqueous solution in the presence of the TiO_2/N under Vis irradiation was examined. As was explained in Section 2, since the irradiation emitted by the applied light source contained less than 0.05% of UV light (0.2 W/m²), it can be assumed that the degradation of 3-CP was mainly due to Vis light action. The reaction solutions containing 10 mg/dm³ of 3-CP at natural pH were illuminated for 24 h. The photolysis of 3-CP under Vis light was found negligible.

Fig. 8 shows that the photocatalysts modified with nitrogen were more active than both the reference sample and the TiO_2 P25 under the conditions applied. The improvement of photocatalytic activity of the TiO_2/N photocatalysts under the Vis irradiation in comparison with the reference sample was very significant. Phase transformation from amorphous to anatase form as well as modification with nitrogen were the main factors responsible for the improved photocatalytic performance. However, the data shown in Fig. 8 revealed also that the unmodified TiO_2 and P25 exhibited a low photoactivity toward 3-CP decomposition. This phenomenon could be attributed to the presence of low intensity UV light emitted by the incandescent lamp (Section 2.2), particularly because the experiment was carried out for 24 h.

Incorporation of nitrogen in catalyst structure in case of the sample treated at 100 °C resulted in an enhancement of its activity for ca. 30% compared to the unmodified TiO_2 annealed at the
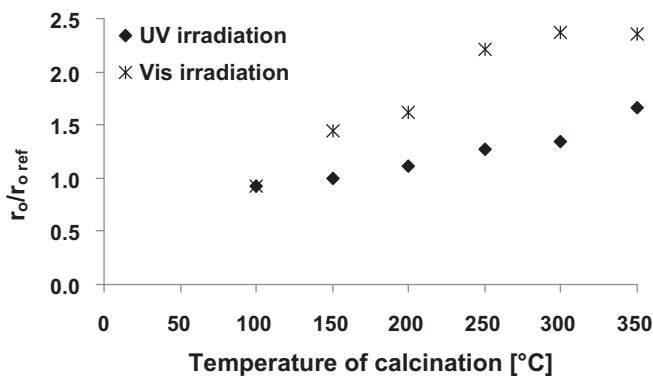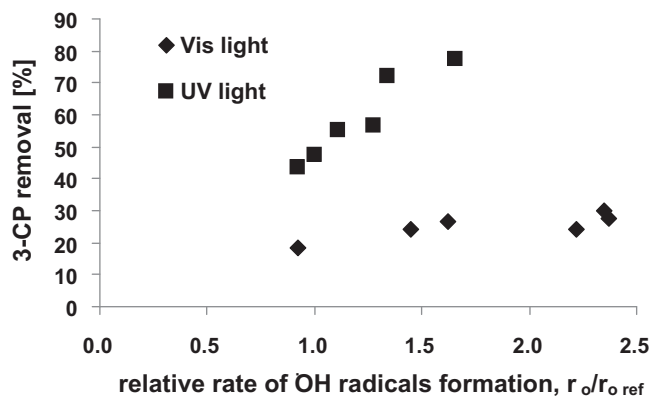
Fig. 9. The influence of calcination temperature of the photocatalysts on the effectiveness of generation of hydroxyl radicals under UV and Vis irradiation; r_o – initial rate of •OH generation on TiO$_2$/N; $r_{o\,ref}$ – initial rate of •OH generation on reference TiO$_2$; $r_{o\,ref\,UV}$: 1986 [a.u./min]; $r_{o\,ref\,Vis}$: 15 [a.u./min].

Fig. 10. The influence of the relative rate of •OH radicals generation on the effectiveness of 3-CP photodecomposition under UV and Vis light; time of irradiation: 5 h (UV) or 24 h (Vis).

same temperature. The 3-CP removal was about 18.2% and 12.4% in case of the two samples, respectively. An increase of treatment temperature up to 350 °C led to ca. 60% improvement of 3-CP decomposition rate compared to the reference TiO$_2$ (30.1% vs. 12.4%). However, on a basis of the measurement of TOC concentration after 24 h of Vis irradiation it was found that mineralization of organics was not efficient. For photocatalysts TiO$_2$/N calcined at temperatures <250 °C TOC concentration was maintained on the same level as in the initial solution. Application of the photocatalysts treated at higher temperatures (above 250 °C) resulted in improvement of TOC removal, although the mineralization efficiency was still very low. After 24 h of irradiation in the presence of TiO$_2$/N-300 and TiO$_2$/N-350 TOC was removed for 6.9% and 7.6%, respectively. The results show that although decomposition of 3-CP under Vis light was significant, the mineralization was not efficient and organic compounds were still present in the treated solution. On a basis of HPLC analysis the presence of resorcinol, benzoquinone, catechol, phenol and 3-CP was confirmed. The main difference between the products of 3-CP degradation detected under UV and Vis irradiation was the lack of low molecular organic acids in the latter case, as shown in Table 1. Similar results were reported by other authors [65]. Moreover, in case of the experiments conducted under Vis illumination no hydroquinone or chlorohydroquinone were detected. One reason for the lack of aliphatic acids among intermediates detected under Vis irradiation might be their very low concentration. As was explained above, the mineralization efficiency after 24 h of Vis irradiation was 6.9–7.6% only. In such case aliphatic acids might have not been detected by the analytical techniques applied. However, in order to state it unequivocally further extensive investigations are necessary.

3.3. The influence of •OH radicals formation rate on the effectiveness of 3-CP degradation

In order to investigate the effectiveness of generation of •OH radicals on the surface of the nitrogen modified TiO$_2$ the fluorescence method was applied. Terephthalic acid solutions containing a fixed amount of different photocatalysts were magnetically stirred and illuminated under UV and Vis light. The observation of the intensity of fluorescence peak attributed to 2-hydroxyterephthalic acid, which corresponds to the number of hydroxyl radicals formed on the catalyst surface revealed a linear increase of the amount of •OH in time of the UV or Vis irradiation. Fig. 9 illustrates the initial rates (r_o) of •OH radicals generation calculated for different photocatalysts. Each r_o value is presented with reference to the initial rate of •OH formation determined for the unmodified TiO$_2$ ($r_{o\,ref}$). The $r_{o\,ref}$ under UV irradiation was equal

to $r_{o\,ref\,UV}$ = 1986 [a.u./min] and under Vis light was $r_{o\,ref\,Vis}$ = 15 [a.u./min]. The arbitrary unit [a.u] refers to the intensity of the fluorescence peak which corresponds to the amount of •OH radicals, as was explained earlier.

It can be clearly seen that under both UV and Vis irradiation an increase of the calcination temperature of photocatalysts resulted in an increase of the rate of •OH species formation. The influence of calcination temperature on the •OH radicals generation was especially observable for Vis irradiation. The $r_o/r_{o\,ref}$ in this case for the TiO$_2$/N treated at 100 °C was equal to 0.9 only whereas in case of the sample annealed at 350 °C the ratio amounted to 2.3. The enhancement of •OH generation with increasing annealing temperature could be attributed to the improvement of crystallinity of the sample [66,67]. In photocatalysis the electrons and holes generated in the irradiated TiO$_2$ particles are trapped at the surface forming free radicals [68]. The •OH radicals have been proposed as the main oxidative species in photocatalytic degradation of organic compounds [69]. The influence of the TiO$_2$ crystalline phase and crystallite size of anatase on the production of •OH radicals under UV light was investigated by Hirakawa et al. [70] and Tryba et al. [55]. It was found that formation of •OH on rutile was significantly lower compared to anatase. Moreover, it was reported [55] that with decreasing lattice strain (improving crystallinity) with heat treatment the formation of •OH radicals was accelerated and then tended to decrease with the proceeding transformation from anatase to rutile. The results shown in Fig. 9 are consistent with the above mentioned literature data. An increase of photoactivity of the synthesized TiO$_2$/N photocatalysts toward •OH formation with an increase of calcination temperature could be attributed to their improved crystallinity, as was discussed in Section 3.1.3.

The increase of •OH radicals generation rate entailed higher 3-CP removal, which confirms the •OH radicals reaction mechanism of 3-CP photooxidation (Fig. 10). It should be emphasized here that the amount of hydroxyl radicals generated under UV light was significantly higher compared to that under Vis irradiation. For example, the ratio of initial rates of •OH formation on TiO$_2$/N-350 under UV and Vis amounted to $r_{o\,UV}/r_{o\,Vis}$ = 94, which means that the $r_{o\,Vis}$ was only ca. 1.1% of the $r_{o\,UV}$. Such significant difference in the rates of hydroxyl radicals formation can explain lower effectiveness of 3-CP decomposition under Vis compared to UV light. Low concentration of •OH under Vis light might also explain why the difference between 3-CP decomposition on the TiO$_2$/N calcined at different temperatures was not very significant (Fig. 8).

Additionally, it should be noted that the dependence between the rate of •OH formation and 3-CP removal under both sources of irradiation was not linear. This lack of linearity can be attributed

to formation of intermediate products during degradation. The organic intermediates play very important role in the 3-CP decomposition by consuming •OH radicals as discussed previously. The competing reactions decrease the 3-CP decomposition rate by reducing the number of •OH radicals available for the main substrate.

4. Conclusions

A significant influence of the presence of nitrogen on the photocatalytic activity of TiO_2 under UV and Vis irradiation was found. The photoactivity was also affected by calcination temperature applied during preparation of the photocatalysts. The efficiency of 3-CP decomposition at pH 4.8 in the presence of the most active TiO_2/N calcined at 350 °C was higher for ca. 41% (UV) and 18% (Vis) in comparison with the reference sample. The highest efficiency of 3-CP degradation was observed at pH 7. Since the adsorption of 3-CP under neutral conditions was negligible, the improved efficiency of the photodegradation of the model compound at pH 7 was attributed to more efficient formation of hydroxyl radicals. The rate of •OH radicals generation on the surface of the modified photocatalysts increased with temperature of calcination. The increase was more significant under Vis than under UV irradiation. However, the amount of •OH radicals formed under Vis was significantly lower than under UV light. In case of the most active TiO_2/N-350 the initial rate of •OH formation in the presence of UV was ca. 94 times higher than under Vis irradiation. As a result the 3-CP photodegradation under Vis light was not as efficient as under UV light. Nonetheless, the nitrogen modified photocatalysts were significantly more active than pure TiO_2. The by-products identified during photodegradation of 3-CP under UV light were chlorohydroquinone, hydroquinone, resorcinol, catechol, phenol and aliphatic acids. In case of Vis irradiation the presence of chlorohydroquinone, hydroquinone and organic acids was not observed. The activity of the N-modified TiO_2 remained constant after 5 cycles of 3-CP degradation, which confirms that the photocatalyst can be successfully reused.

Acknowledgment

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