

# Application of modified concrete to remove surfactants from water

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**Abstract.** In these studies two types of modified concretes in photocatalytic mineralization of anionic surfactant sodium dodecylbenzenesulfonate (NaDBS) were used. Commercial TiO<sub>2</sub>-P25 and nitrogen modified TiO<sub>2</sub>-N as photocatalysts for concrete modification were employed. The studies were conducted in the special designed reactor which was a simple model of the secondary settler used at the sewage treatment plant. The mineralization of anionic surfactant NaDBS after 18 h of UV light irradiation amounted to 48% for concrete modified by TiO<sub>2</sub>-P25 and 37% for concrete modified by TiO<sub>2</sub>-N.

## 1 Introduction

Active surface agents are the group of organic compounds most commonly used in various industries, services and households. In the industry, they are used for washing and dyeing (textile) as wetting substances - for example: for foundry molds (metallurgy), in the production of pesticides, synthetic resins, paints and varnishes (chemical industry), plastics, cellulose and paper, food (food industry) and moreover in printing, photography, cosmetics, pharmacy, zootechnics and medicine. In households surfactants are mainly used as washing agents [1-3]. The market research institute Ceresana Research expects the global active surface agents market to generate revenues of more than 41 billion US dollars in 2018 – translating to an average annual growth of 4.5% [4].

Surfactants can be divided on: ionic (cationic, anionic), non-ionic and amphoteric, depending on their structure. Structure of surfactants consisting of hydrophilic part (ionic or strongly polar) and hydrophobic part, which is usually a hydrocarbon chain [5]. One of the most commonly used anionic surfactants are linear alkylbenzenesulphonates (LASs), introduced in the 1960s to substitute the hardly biodegradable tetrapropylbenzenesulfonate. In plants, which are treating households wastewater mainly, LAS concentration under 10 mg/L can be found [6]. This concentration can expressly increase when municipal wastewater are also receiving wastes from industrial washing processes [7]. Some works has been reported to estimate the biodegradability and environmental safety of LASs directly and their intermediates degradation products [8]. As biodegradability has been proven, linear alkylbenzenesulphonates removal from wastewater

has generally been limited to conventional processes, like biological treatments. Percent of LAS removed in popular biological systems is usually between 90 and 95% by activated sludge and almost 70% by biological filter wastewater treatment [9]. However, biological treatment make some difficulties. For concentrations over 20 mg/L the pH self-regulation of the wastewater decreases and, as a consequence additional neutralization is required [10]. Moreover, in biological processes long retention time is needed to accomplish surfactant removal [9] which may create the need to reduce an amount (or time) of others conventional treatment methods (physical and chemical treatment, chemical oxidation).

An alternative to the conventional methods are the advanced oxidation processes (AOPs). Final products of surfactants decomposition by AOPs are CO<sub>2</sub>, H<sub>2</sub>O and inorganic residue. One of best known AOP method is heterogeneous photocatalysis based on semiconductors, such as most popular titanium(IV) oxide (TiO<sub>2</sub>).

The role of the electron acceptor in the photocatalysis process perform O<sub>2</sub> forming in reduction reaction reactive oxygen radical O<sub>2</sub><sup>•-</sup>. Pair electron-hole which is photogenerated on the catalyst surface, may serve formation of the hydroxyl radicals by the oxidation reaction of the adsorbed molecules H<sub>2</sub>O or OH<sup>-</sup> [11] or can lead to oxidation of the adsorbed organic compounds [12]. An Amount of •OH radicals produced on the catalyst surface (surface hydroxylation) [13] is one of the important methods for determining its photocatalytic potential [14] and is next to adsorption (electron hole oxidation), significant oxidation way in whole photocatalysis process.

One of the methods of using the titanium dioxide is to use it to create a composite of common building

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materials, such as gypsum [15] or concrete [16] with self-cleaning properties by its superhydrophilic surface. This is a simple method that does not require additional work and extra costs in the future. These photoactive materials can be effectively use against air or water pollution while retaining their original mechanical properties or even improving them [17].

In this study, the possibilities of sodium dodecylbenzenesulfonate (NaDBS) surfactant remove from water were investigated. For this purpose, concrete enriched with commercial and new, modified with nitrogen titanium dioxide under the UVA irradiation in laboratory scale were tested.

## 2 Materials and methods

### 2.1 Materials

An anionic surfactant from a group of LAS, sodium dodecylbenzenesulfonate (Sigma-Aldrich Company, Germany) as model surfactant was used. The molecular mass of this compound is 348.48 g/mol. The critical micellar concentration (CMC) in room temp. equal 554 mg/L [18].

Nitrogen modified TiO<sub>2</sub> (TiO<sub>2</sub>/N) were obtained at the Institute of Inorganic Technology and Environment Engineering, West Pomeranian University of Technology in Szczecin, in the AutoLab installation E746 (HEL Ltd). 600 g of TiO<sub>2</sub> (Azoty, Police Chemical Factory S.A.) were placed reactor in 350 ml of 2.5% solution of NH<sub>4</sub>OH. The modification was carried out at 100°C for 4 h. The photocatalyst was dried for 4 h at 100°C in an air atmosphere. Reference TiO<sub>2</sub> material was Aeroxide P25 (Evonik Company, Germany). Detailed information about semiconductors are presented in Table 1.

**Table 1.** Characteristic of used photocatalysts.

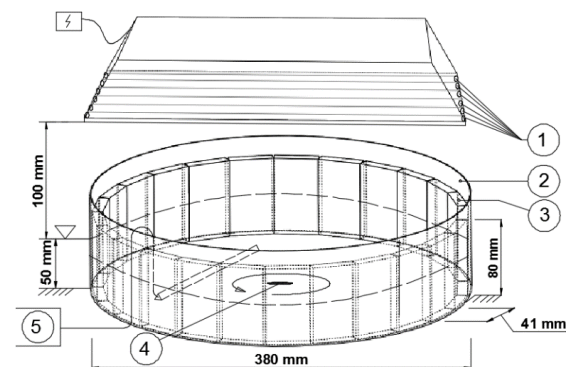
Photo-catalyst	S <sub>BET</sub> [m <sup>2</sup> /h ]	avg molecular size [nm]	phase content	pH <sub>PZC</sub>
TiO <sub>2</sub> /N	345	190	67% amorphous, 30% anatase, 3% rutile	6.7
TiO <sub>2</sub> -P25	56	26	75% anatase, 25% rutile	5.9

The concrete (WB-80, Cekol) was used for modified concrete preparation. It was a mixture of aggregate - quartz sand, cement, carbonate meal and modifying additives. It consisted 20% of Portland cement and ~80% of quartz sand with maximum grain size of 4 mm. Bulk density of mixture was 1700 kg/m<sup>3</sup> ± 5%. The ratio of deionized water added to the dry mixture was, according to the manufacturer's recommendations, in all composites 0.12. The mortar fills the requirements of the PN-EN 13813 CT-C20-F5 standard. The photocatalyst used to create composite was

always accounted to 10% wt/wt of cement (2% whole mixture) in the composite.

### 2.2 Photocatalytic activity tests

In Fig. 1 the scheme of photocatalytic reactor used in this study was shown.



**Fig. 1.** Scheme of photocatalytic reactor (1. 6x 15 W UVA lamps; 2. steel reactor; 3. concrete plates; 4. magnetic stirrer 5. oxygen concentrator).

The reactor was simple model of the secondary settler, and was stainless steel tank, volume 10 L. A source of UV-Vis light was Magic 836 set (Efbe-Schott GmbH) equipped with six UVA - Vis (UV300 < λ < VIS600) Cleo ISOLde lamps (Phillips), each 15 W. Lamps were 100 mm above the water, parallel to the water surface.

Concrete slabs were laid in a reactor along a steel wall, forming a regular polygon. A dimensions of all concrete plates were the same – 41 x 80 x 10 mm. A number of plates in each reaction was set to 25. The total active surface of photocatalytic underwater area was 512.2 cm<sup>2</sup>. In the middle of the bottom of the reactor was placed a magnetic stirrer, ensuring a mixing of the solution. In reactions which using additional oxygenation, it was provided by an oxygen concentrator (Everflo, Phillips) by continuously dosing oxygen at concentration up to 95%, through diffuser with a volume flow of 300 L/h. Due to the necessity of gas injection, in all processes using additional O<sub>2</sub> dosing, prior to the addition of solution to reactor were carried out 1 h photolysis of surfactant molecules by 150 W medium pressure UV lamp. The effect of this process was to reduce foaming of solution to level which allowed to begin the reaction.

All photocatalytic activity studies were made for pure concrete, concrete with 10% wt/wt TiO<sub>2</sub>/N and the concrete with 10% wt/wt TiO<sub>2</sub>-P25 composite. Photoactivity was examined in the oxidation reactions of the NaDBS surfactant at initial concentrations of 20 mg/L and at unmodified pH. After adding the surfactant solution to the reactor, for 0.5 h at darkness was achieving the equilibrium concentration of organic compound by dynamic adsorption/desorption processes on concrete plates surface. Concentration of total organic carbon (TOC) and UV200-300 absorbance (ABS) value after this process was treated as initial (TOC<sub>0</sub> and ABS<sub>0</sub>).

After that, the reactions were started. Studied processes were carried out for 6 or 18 h. The initial TOC concentration of 20 mg/L NaDBS solution was 12 mg/L. The initial concentration of TOC of UV pretreatment 20 mg/L NaDBS solution was 11.8 mg/L.

The efficiency of the each process was determined as the ratio of the TOC concentration and ABS value in the reaction time to their initial values ( $TOC_t/TOC_0$  and  $ABS_t/ABS_0$ ). UV absorbance spectrum of the reaction mixture samples were determined by UV-Vis spectroscopy (Spectroquant Pharo 300, Merck Millipore). The TOC concentrations were measured on Multi N/C 2100 S (Analytik Jena).

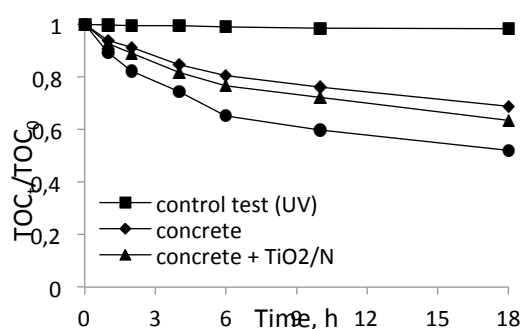
### 3 Results and discussion

#### 3.1 Decompositon of NaDBS molecules

The oxidation efficiency of material composite consisting nitrogen modified  $TiO_2$  compared to composite with reference  $TiO_2$ -P25, pure concrete and control test without any building materials under UV irradiation were presented in Fig. 2. All tested processes lasted 18 h and were oxidized only with natural air circulation. The pH and conductivity changes in time in Table 2 were presented.

**Table 2.** pH and conductivity changes after 6 and 18 h of UV light irradiation.

Reaction time [h]	Control tests	Con-crete	Con-crete + $TiO_2$ -P25	Con-crete + $TiO_2$ /N
<b>pH</b>				
0	6.2	10.4	11	10.6
6	6.38	11.05	11.49	10.82
18	6.35	11.01	11.6	10.52
<b>Conductivity [<math>\mu</math>S/cm]</b>				
0	16	100	216	147
6	19	441	916	550
18	21	346	733	527



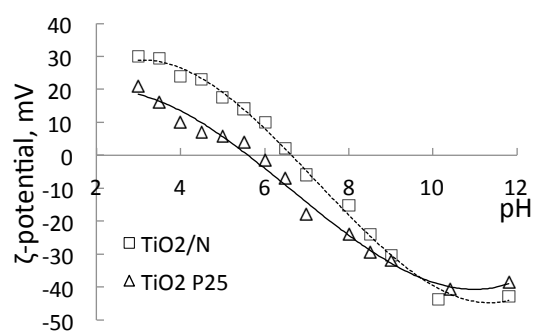
**Fig. 2.** Changing of TOC content as a function of time during NaDBS 20 mg/L solutions photodecomposition.

In photolysis control test had not been noticed any oxidation reactions. In all others reactions, significant

photooxidation processes have taken place. As it can be seen, the most active composite in this condition is the concrete with commercial  $TiO_2$ -P25. The mineralization degree after 18 h of reaction with this building material reached 48% of initial TOC. The TOC removal after 18 h in reaction with  $TiO_2$ /N/concrete composite was 37%, and 31% in pure concrete. The significantly higher  $TiO_2$ -P25/concrete decomposition potential than in the other tested water purification methods was also evidenced by much more intense changes in oxidized solution conductivity (Table 2). The high growth of conductivity testifies to the appearance of a large amount of ionic reaction intermediates and therefore, indirectly, higher degree of surfactant molecule fragmentation. After 6 h of reaction the conductivity value reached 0.91 mS/cm, while in analogous time of reaction with concrete and  $TiO_2$ /N catalyst, cond. was much lower and stopped at 0.55 mS/cm.

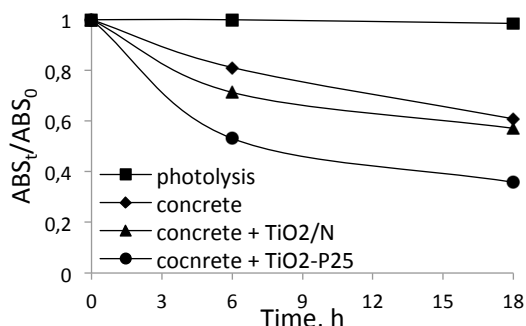
One of the normal properties of new concrete in is increasing the pH value of water. It is mostly due to calcium hydroxide, which is a normally by-product of cement hydration. In Table 2 was presented, how the value of pH were changing in time of studied reactions. Besides of control test, all of these processes were carried out at very alkaline pH, what could have had a significant impact on the course of the reactions. When the concentration of  $OH^-$  ions is higher, the ability to consequently trapping holes increasing, resulting in more photogenerated  $\bullet OH$  radicals. More effective semiconductor in the surface production of OH radicals than  $TiO_2$ /N, as proved Bubacz et al. [19] is  $TiO_2$ -P25. An interesting phenomenon is, how effective in oxidation process is pure concrete. This also may be related to the ability to surface-forming OH radicals but it requires further, more in-depth research.

At alkaline pH, also the ability to oxidize the anionic surfactant directly on the surface is reduced by lower degree of adsorption because of repulsive effect of same charges (catalyst surface – anionic part of surfactant molecule). This is due to the high negative electrokinetic potential of these two catalysts, with a higher value on  $TiO_2$ /N under these pH conditions (Fig. 3). This relationship, in addition to a lower surface hydroxylation capability, have had a decisive effect on  $TiO_2$ /N lower efficiency in TOC oxidation. The efficiency of photodecomposition processes can be verified by studying the change in UV absorbance intensity in time.



**Fig. 3.** Relationship between  $\zeta$ -potential and solution pH value for  $TiO_2$ /N and  $TiO_2$ -P25.

Changes in UV absorbance spectra at 223 nm in NaDBS 20 mg/L solutions photodecomposition by various methods in Fig. 4 are presented.



**Fig. 4.** Changes in UV absorbance spectra at 223 nm in NaDBS 20 mg/L solutions photodecomposition by various methods.

The UV-Vis absorbance spectra of NaDBS during light irradiation showed reveal strong absorption band, centered at and 223 nm, and a second but weak band at ~260 nm. It was found, that they are caused by the  $\pi - \pi$  electronic transitions of C=C bonds in the aromatic ring of NaDBS. Intensive reduction of the absorbance in these areas proves the decomposition of the organic compound, which also results in a reduction in the propensity to produce foam by the solution. Changes in absorbance at the 223 nm wavelength allow us to suppose that there are changes in the aromatic rings of the surfactant particles. From the analysis of changes in the absorption spectrum of the NaDBS solution during its photooxidation, it follows that the reduction of the absorption band intensity from the maximum at 223 nm is accompanied by an increase in absorption in the range  $\lambda \leq 215$  nm. This indicates the formation of reaction products whose absorption spectra are within the analyzed spectral range and overlap with the NaDBS absorption spectrum.

As in the case of TOC mineralization, in reducing the intensity of absorbance also the most effective composite was the one formed from the addition of P25 to concrete and after 18 h resulting in 64% reduction of absorbance at 223 nm wavelength. In concrete with TiO<sub>2</sub>/N reaction the reduction of absorbance at this wavelength was 43%, and 39% in pure concrete respectively.

## 4 Conclusions

Two different types of photocatalysts were studied, commercial TiO<sub>2</sub>-P25 and nitrogen modified TiO<sub>2</sub> which were used for two types of modified concretes preparation. It was proved that use of photocatalytic concrete can be successfully applied to reduction of concentration and mineralization of anionic surfactants compounds. Higher activity under UVA irradiation due to its properties was observed with TiO<sub>2</sub>-P25 reactions than TiO<sub>2</sub>/N catalyst. The mineralization of anionic surfactant NaDBS results achieved by them after 18 h of reactions were respectively: 48% and 37%.

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