



Degradation of Food industrial pollutants by photocatalysis with immobilized titanium dioxide



Andrea Hinkova^{*}, Svatopluk Henke, Zdenek Bubnik, Vladimir Pour, Alena Salova, Marcela Slukova, Evzen Sarka

Institute of Chemical Technology, Department of Carbohydrates and Cereals, Technicka 5, Prague 6, 166 28, Prague, Czech Republic

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ABSTRACT

The paper deals with application of advanced oxidation processes in degradation of surfactants, which represent large group of pollutants in food industrial waste waters. The photocatalytic degradation of two surfactants, an anionic sodium dodecyl sulphate (SDS) and cationic N-cetyl-N,N,N-trimethylammonium bromide (CTAB), was tested in a lab-scale UV reactor (Mikropur, Czech Republic) with immobilized titanium dioxide catalyst (P25, Degussa). Various conditions were verified, e.g. initial detergent concentrations (1.2–18.7 mg/l), oxygen flow rates (0 or 72.2 ml/min) and amount of catalyst used. The degradation in a presence of catalyst, oxygen and UV irradiation was the fastest process with maximum achieved rate constants of 0.0503 min^{-1} at anionic surfactant degradation and 0.342 min^{-1} at cationic detergent degradation. The energy demands for SDS degradation were also calculated and possible scale-up into large industrial scale discussed.

Industrial relevance: Due to the relatively high organic content, food industrial waste waters contribute to the overall pollution problem. A need for water purification at low cost and energy with limited use of chemicals is still rising. Therefore, new advanced oxidation processes (AOPs), which are capable to oxidize and mineralize almost any organic contaminant, represent rapidly developing field of recent technological research. This study deals with possible application of photocatalysis with immobilized TiO₂ in degradation of surfactants, which are quite common pollutants in food industrial waste waters, and compares this method with others. The energy balance of the process and an outline of possible industrial application were mentioned as well.

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1. Introduction

Food industry requires large volumes of water of different quality, which implies production of significant amounts of wastewaters (see Table 1). It is estimated that food industry's contribution to the total wastes produced is at least 10% (Doble & Kumara, 2005). Most of the present compounds (see Table 2) are biodegradable substances (i.e. carbohydrates, proteins, lipids); however some other undesirable components like soil, organic suspended solids (i.e. fruit and vegetable pits, seeds, skins, pulp) or chemicals used during the technological process may occur as well.

Conventional methods for water treatment are disinfection and decontamination, however these techniques are often energetically and operationally demanding, requiring intensive chemical treatments, whose residuals can even increase the problems with pollution and decontamination (Malato, Fernandez-Ibanez, Maldonado, Blanco, & Gernjak, 2009). New techniques, such as advanced oxidation processes

(AOPs), might improve the effectiveness of traditional water purification process due to the low energy demands and no chemicals used.

The main feature of these technologies is the production of highly reactive hydroxyl radical ($\cdot\text{OH}$) which initiate consequential reactions resulting in the destruction and removal of organic compounds. The rate constant of most reactions involving hydroxyl radicals in aqueous solutions is in order of 10^6 – $10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$. These technologies are also non-selectively attacking and versatile, which is useful and necessary in waste water treatment (Malato et al., 2009). These methods use different ways to produce hydroxyl radicals. Some of them utilize UV photolysis of H₂O₂ and ozone to produce $\cdot\text{OH}$. Others, such as heterogeneous photocatalysis and homogeneous photo-Fenton process, use the photocatalyst in a presence of H₂O₂ and irradiation with UV-VIS light.

The photo-Fenton process is probably the most applied technology from AOPs. The Fenton reaction (1) can occur in sunlit waters because both H₂O₂ and Fe²⁺ are photo-chemically produced resulting in hydroxyl radicals' formation:



The photocatalytic reaction is based on the illumination of semiconductor particle (e.g. TiO₂, ZnO, ZrO₂, CeO₂, CdS, ZnS) with photon, whose

^{*} Corresponding author at: Institute of Chemical Technology in Prague, Department of Carbohydrates and Cereals, Technicka 5, 166 28 Prague 6, Czech Republic. Tel.: +420 220 44 3111; fax: +420 220 44 5130.

E-mail address: andrea.hinkova@vscht.cz (A. Hinkova).

Table 1
Pollution from food processing industry in Denmark; biochemical oxygen demand (BOD).

	Production tons/year	m ³ waste water/ton of product	Million m ³ waste water/year	BOD ₅	10 ⁵ persons equivalents ^a
Abattoirs	600,000	20	12	1,500	8.0
Dairies	5,000,000	1.5	7.5	1,800	6.0
Fish filleting plants	100,000	2	0.2	5,500	0.5
Potato starch production	25,000	30	0.75	5,500	1.9
Breweries	600,000	10	6	1,500	4.0

^a 60 g BOD₅/24 h per inhabitant (Jørgensen & Johnsen, 1989).

energy must be at least equal to the difference of energies between the conduction and the valence bands (band-gap energy, E_G).

This leads to the excitation of electrons e^- from the valence to the conduction band, thus there are free photoelectrons available in the conduction band and positive photoholes (h^+) in the valence band. Then, in gas or liquid medium, the charge carriers can migrate to the surface of the photocatalyst to react with substances, which are adsorbed on the photocatalyst's particle.

The photocatalytic process does not depend on the intensity of the radiation, but only on its energy. Thus, even a small amount of photons is able to run the photocatalytic oxidation and subsequently leads to rapid redox reactions.

Advanced oxidation processes can be used for degradation of many residues from food industry, such as organic acid (Quici, Morgada, Gettar, Bolte, & Litter, 2007), nitrogen compounds, which represent high risk of water eutrophication (Herrmann, 1999), organic dyes (Malato et al., 2009), or residuals of pesticides and herbicides, which are not biodegradable (Malato et al., 2002). Heavy metals can be removed as crystallites deposited on the photocatalyst (Herrmann, 1999) and phenols, which are highly toxic to water ecosystems, can be decomposed by solar TiO₂ photocatalysis (Gernjak et al., 2004). Hydroxyl radicals ($\cdot OH$) formed during the photocatalysis using TiO₂ as a catalyst remove microorganisms in waste waters. This method is suitable for removal of bacteria, viruses, fungi and algae (Kim, Kim, Cho, & Cho, 2003), or even bacteria spores; e.g. *Clostridium perfringens* and *Escherichia coli* (Dunlop, McMurray, Hamilton, & Byrne, 2008).

Surfactants represent another large group of chemicals used in food industry. It is estimated that food industry and agrochemicals consume about 400 thousand tonnes of surfactants every year (Hargreaves, 2003). Some surfactants are harmful to organisms living in water, and they may cause water eutrophication. Their presence in industrial waste waters can be reduced by sorption on activated carbon (Bautista-Toledo, Rivera-Utrilla, Méndez-Díaz, Sánchez-Polo, & Carrasco-Marín, 2014) and by biodegradation with activated sludge. Biodegradation decomposed 97% of sodium dodecyl sulphate (SDS) during 12 days in river-water die-away test (Okpokwasili & Olisa, 1991). The removal percentage of 99% with the average half-life less than 2 days was observed in aerobic degradation of SDS in sea water (Pérez-Carrera, León, Lara-Martín, & González-Mazo, 2010).

Despite their biodegradability, surfactants may cause problems in waste water treatment; they are known to reduce the activity of

activated sludge hence slow down the biodegradation, the foaming limits the biological degradation and large quantities of surfactants remain in the sludge, which is partly discharged back to the environment. Scott and Jones (2000) suggest that sewage sludge may contain 0.5–4% of linear alkylbenzene sulfonates (LAS) in dry weight, and about 16% of sludge is applied to land.

Therefore, the photocatalytic degradation of SDS, which leads to formation of SO_4^- , water and carbon dioxide (Lea & Adesina, 1998), is an efficient tool in total surfactant degradation. Amat, Arques, Miranda, and Segu (2004) tested the solar degradation of anionic surfactants SDS and dodecylbenzenesulfonate (DBS) both in laboratory scale and pilot plant. The results showed that the most effective method in lab-scale experiments was the photo-Fenton process using the Fe(II) at pH 2.8, however the results from TiO₂ photocatalysis were also satisfactory. During the solar pilot plant experiments the degradation yield of more than 80% was achieved mostly in less than 3 hours. The study of SDS photo-oxidative degradation with suspended titanium particles revealed that the reaction is characterized by the activation energy of 41 kJ.mol⁻¹ (Lea & Adesina, 1998).

This work is focused on photocatalytic decomposition of anionic surfactant SDS and cationic surfactant N-cetyl-N,N,N-trimethylammonium bromide (CTAB) using immobilized TiO₂ as a catalyst in a lab-scale reactor. The rate of decomposition of SDS was compared with other degradation methods, such as biodegradation, adsorption or solar degradation with suspended TiO₂. The overall energy balance of the process was calculated as well.

2. Material and methods

2.1. Photocatalytic reactor

All experiments were carried out in a UV photocatalytic reactor (Fig. 1) manufactured by the Mikropur Company (Hradec Kralove, Czech Republic).

The cylindrical feeding vessel (volume 500 ml) is a glass duplicator equipped with outlets and inlets of the thermostat/cooling circuit, sensors, reaction mixture circulation and feeding. The feeding inlet also serves for removal of gaseous products formed during the reaction. The photocatalytic cell is equipped with a stainless steel cooling jacket as well. The UV lamp (Teslamp, Czech Republic, 250 W, peak wave length 350–370 nm) is inserted into the photocatalytic cell together

Table 2
Composition of waste fractions and effluents from various branches of food industry; COD: chemical oxygen demand, BOD: biochemical oxygen demand, TS: total solids.

	Slaughterhouse waste ^a	Slaughterhouse waste ^b	Restaurant, fruit and vegetable waste ^a	Dairies ^b
pH	5.9	–	4.5	8–11
Total solids (TS)	13%	1,300–1,400 mg.l ⁻¹	21%	675 mg.l ⁻¹
Volatile solids	96% of TS	–	95% of TS	635 mg.l ⁻¹
Total nitrogen	1.0% of TS	114–148 mg.l ⁻¹	3.8% of TS	55 mg.l ⁻¹
Total phosphorus	0.3% of TS	20–30 mg.l ⁻¹	0.4% of TS	35 mg.l ⁻¹
Oil and grease	–	100–200 mg.l ⁻¹	–	–
Total carbon	60% of TS	–	49% of TS	–
COD	–	4,200–8,500 mg.l ⁻¹	–	4,000 mg O ₂ /l
BOD	–	1,600–3,000 mg.l ⁻¹	–	2,600 mg.l ⁻¹

^a Murto, Björnsson, & Mattiasson, 2004.

^b Doble & Kumara, 2005.

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