

Letter to Editor

# Preliminary Results of Purification of Dairy Sewage by Photocatalysis on Titania

W. Zmudziński\*

Faculty of Commodity Science, Poznań University of Economics,  
Aleja Niepodległości 10, 61-875 Poznań, Poland

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## Abstract

Photodegradation of milk solutions (dairy sewage substitutes) occurred both in the presence and absence of TiO<sub>2</sub> photocatalyst, as it was monitored using COD measurements. At lower milk concentration the photoreaction rates were directly proportional to the concentration. Small additions of hydrogen peroxide enhanced greatly milk photodegradation, especially in the presence of titanium dioxide photocatalyst.

**Keywords:** photocatalysis, dairy sewage, TiO<sub>2</sub>

## Introduction

The dairy industry is one of the most important branches of food production and preservation because of the variety of nutritional products. However, as other branches of food processing, it produces a lot of waste. In addition, the wastes are complex due to production diversity. First of all they are composed of all milk components, namely milk proteins, lipids, lactose and minerals. They also contain washing, disinfectant and hygienic agents, among others [1, 2]. According to literature data BOD (biological oxygen demand) of dairy sewage can vary between 40 and 10,000 mg O<sub>2</sub>/dm<sup>3</sup> (mean value, 2,300 mg O<sub>2</sub>/dm<sup>3</sup>) and COD (Chemical Oxygen Demand) between 80 and 95,000 mg O<sub>2</sub>/dm<sup>3</sup> (mean value, 4,500 mg O<sub>2</sub>/dm<sup>3</sup>), depending on type of production, applied technology and the method of sewage purification [3].

Biological methods, e.g. the method of activated sludge, are utilized first of all for purification of dairy sewage [4]. In older dairies the sewage is purified by simplified biological method, i.e. the method of oxidation ditch. However, because of high load of the sewage with organic matter an anaerobic method (a fermentation chamber) is recommended, in which

the organic wastes undergo decomposition mainly to methane and carbon dioxide [2, 4].

The studies are developed along the application of AOP (advanced oxidation processes) for purification of dairy sewage. For that purpose the methods utilize highly reactive OH<sup>•</sup> radicals generated *in situ* in various ways. In the case of organics composed of C, H and O, oxidation products consist only of CO<sub>2</sub> and H<sub>2</sub>O [3, 5-7].

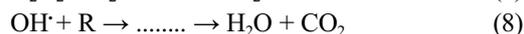
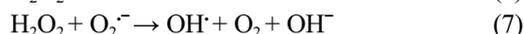
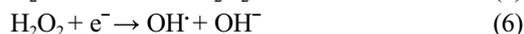
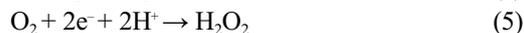
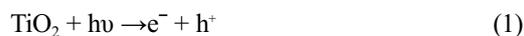
Among the AOP's, photocatalysis on semiconductors seems to be the most promising. The process needs only a photoactive semiconductor and appropriate light - the UV part of the solar spectrum is sufficient for excitation of semiconductor electrons. Titanium dioxide serves mainly as the semiconductor; the compound, besides its high photoactivity, is very stable chemically and photochemically, is non-toxic and relatively cheap [2, 8, 9]. Many compounds such as carboxylic acids, organic dyes, phenols, pesticides, surfactants, some inorganic compounds, and many others are fully mineralized by photocatalysis on TiO<sub>2</sub>, see e.g. [10, 11].

Illumination of a semiconductor with the light of an appropriate energy ( $h\nu \geq E_g$ ,  $E_g$  - width of a semiconductor forbidden band) causes the formation of free electrons (electrons in semiconductor conduction band) and holes in semiconductor valence band. If their lifetime is sufficiently

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\*e-mail: w.zmudzinski@ue.poznan.pl

long they can react with some molecules to reduce (electrons) or oxidize (holes) them. Mechanisms of such processes proceeding on the surface of titania are shown below [12-14]:



In aqueous environments the holes react with water molecules or with OH- groups adsorbed on TiO<sub>2</sub> surface, forming very active hydroxyl radicals (reactions 2 and 3). Excited electrons reduce oxygen molecules dissolved in water; note that oxygen reduction also leads to hydroxyl radicals (see reactions 4-7). The highly active OH<sup>·</sup> radicals attack any organic matter dissolved in the solution-causing formation, via many one-electron reactions, carbon dioxide and water. Therefore, the overall reaction is similar to ordinary burning of organic matter:



In contrast to other water purification methods, in the case of water contaminants containing only C, H and O atoms, the heterogeneous photocatalytic processes do not introduce to the environment any additional impurities except CO<sub>2</sub> and H<sub>2</sub>O.

The paper presents preliminary results of application of TiO photocatalytic processes to purification of dairy sewage.

## Experimental

Diluted solutions of full-fat powdered milk (26.5% fat) were used as substitutes for dairy wastes. Depending on the experiment, concentrations of powdered milk were as follows: 0.32, 0.40, 0.60, 0.80, 1.0 or 1.4 g·dm<sup>-3</sup>. The milk solutions were prepared by simple dissolution of an appropriate weight of milk powder in doubly distilled water. For photocatalytic experiments 165 cm<sup>3</sup> of an appropriate solution of the powdered milk was mixed with 0.05 g TiO<sub>2</sub> (99.9%, Aldrich, anatase) and sonicated for 5 minutes. Then the homogeneous slurry was transported to an air lift loop photoreactor (Pyrex made, 200 cm<sup>3</sup> volume) described elsewhere [15-17]. The contents of the photoreactor were mixed by an air lift (50 cm<sup>3</sup>·min<sup>-1</sup>) controlled by a narrow draft tube placed in the centre of the tube reactor. The conical bottom of the reactor was equipped with a septum through which the air stream was fed to the reactor with a needle, the loop of which reached the bottom of the draft tube. The reactor was illuminated from the side wall with two 300W xenon lamps (OSRAM). The bulbs were placed 50 cm from the reactor. Pyrex walls of the reactor deter-

mined lower limit of entering light (about 300 nm cutoff filter). The photoreactor was cooled by an air stream, the temperature was maintained at 30°C.

Photocatalytic experiments were performed in a non-continuous mode (batch reactor); before each experiment the reaction slurry was aerated for 15 minutes. The photoreactions were conducted for 3 hours. In some cases a defined amount of hydrogen peroxide solution was added prior to illumination. After the illumination had been stopped, several cm<sup>3</sup> of the reaction slurry (depending on initial milk concentration) was analyzed for COD using a dichromate method [18]. Each photocatalytic experiment was repeated at least twice, and each reaction solution (slurry) was analyzed for COD at least twice – prior to and after illumination.

The water used for photocatalytic studies was doubly distilled in a quartz still. Prior to distillation the water was de-ionized on a special column. All chemicals were of p.a. purity.

Anatase titania (99.9%, Aldrich) used as a photocatalyst had a BET-specific surface area of 11.9 m<sup>2</sup>·g<sup>-1</sup> as measured on a Micromeritics apparatus. It showed a typical anatase spectrum with the adsorption onset at about 400 nm (taken on a Specord M-40 spectrophotometer). Average particle size of the TiO<sub>2</sub> powder was about 0.1 μm (89% of the particles were in the range 0.07-0.2 μm). The size of titania particles was measured using a granulometric method and water as a liquid medium.

## Results and Discussion

As mentioned above, the goal of this study was to check the possibility of application of heterogeneous photocatalysis on TiO<sub>2</sub> for mineralization of the components of dairy sewage. Application of diluted powdered milk as a sewage substitute seemed to be well founded – the solutions contained all milk ingredients, such as proteins, fat, lactose, mineral salts, and more. However, the ratios of the ingredients were rather different than in ordinary dairy sewage. Moreover, some other pollutants also are present in real sewage, such as e.g. detergents, disinfectants, etc.

Progress of photomineralization of dissolved powdered milk was followed by determination of COD (chemical oxygen demand) prior to and after illumination of the solutions. Although time consuming, the COD dichromate method seemed to be the only one suitable for these studies - it was possible to determine at the same time the compounds present in water and adsorbed on titania grains. It was checked in blank experiments that the presence of small titania admixture did not influence the results of COD measurements. It was also assumed in these studies that the observed decrease of COD, caused by illumination, was proportional to the loss of total organic carbon (or, in other words, to carbon dioxide evolved during the photocatalytic process). Therefore, although the rate of photocatalytic mineralization of each milk ingredient could be different, the results were expressed either as a percentage of COD decrease or in grams, as the amount of milk mineralization.

Table 1. Degradation of milk during three-hour illumination of 165 cm<sup>3</sup> of the solution in the presence of TiO<sub>2</sub>.

Milk concentration		Drop of COD	Milk mineralized
[g/dm <sup>3</sup> ]	[g/165 dm <sup>3</sup> ]	[%]	[g/165 dm <sup>3</sup> ]
0.32	0.053	13	0.0069
0.4	0.066	12.8	0.0084
0.6	0.099	13.1	0.013
0.8	0.132	13.9	0.0183
1	0.165	12.7	0.0209
1.4	0.231	9.1	0.021

Table 2. Milk degradation under illumination of milk solution with and without TiO<sub>2</sub> admixture.

Milk concentration	With TiO <sub>2</sub> admixture		Without TiO <sub>2</sub> admixture	
	COD Drop	Milk mineralized	COD Drop	Milk mineralized
[g/dm <sup>3</sup> ]	[%]	[g/165 dm <sup>3</sup> ]	[%]	[g/165 dm <sup>3</sup> ]
0.32	13	0.0069	6.5	0.0034
0.60	13.1	0.013	8.0	0.0079

Table 3. Influence of 3% H<sub>2</sub>O<sub>2</sub> added prior to illumination on milk degradation in the solutions with and without TiO<sub>2</sub> admixture.

Milk concentration	3% H <sub>2</sub> O <sub>2</sub> added	Milk mineralization	
		with TiO <sub>2</sub>	Without TiO <sub>2</sub>
[g/dm <sup>3</sup> ]	[cm <sup>3</sup> ]	[g/165 dm <sup>3</sup> ]	
0.6	0.5	0.038	0.0095
0.6	1	0.018	0.005

The results of previous studies conducted in this laboratory [15-19] were the base for setting the reaction conditions: 165 cm<sup>3</sup> of the reaction solution, 0.05 g TiO<sub>2</sub>, air stream rate 50 cm<sup>3</sup>·min<sup>-1</sup>. There were two reasons for the choice of milk concentration:

- 1<sup>o</sup> practical possibility of determination and registration of COD changes caused by illumination, and
- 2<sup>o</sup> the fact that at too high concentrations of organics in water the photoreaction rate could be reduced and even totally inhibited.

COD of the solution having 1.40 g/dm<sup>3</sup> milk concentration was 1986 mgO<sub>2</sub>·dm<sup>-3</sup>.

The results of three-hour illumination of diluted solutions, having various concentrations of the milk in the pres-

ence of TiO<sub>2</sub> photocatalyst, are shown in Table 1. Some explanations should be done here. In the last column of Table 1 there are shown the amounts of totally mineralized milk, i.e. to CO<sub>2</sub> and H<sub>2</sub>O. The values were calculated taking into account initial milk concentrations and COD drop after three-hour illumination of the reaction suspension. One must remember, however, that in fact many particles of milk ingredients are only partly oxidized: note that the process proceeds via many one-electron reactions. Nonetheless, the calculated values shown in Table 1 characterize well the progress of the reaction of milk photodestruction.

It follows from the data shown in Table 1 that three hour illumination of milk solutions with TiO<sub>2</sub> admixtures causes slow mineralization of the milk. Moreover, for lower milk concentrations, 0.32-1.00 g·dm<sup>-3</sup>, the extent of the substrate mineralization is directly proportional to its initial concentration in the solution: in each case the loss of milk amounted to 13% vs. its initial concentration. It follows from the above that the process of the photocatalytic milk mineralization fulfils 1<sup>st</sup>-order reaction kinetics. The dependence of the amount of milk mineralized during three-hour illumination vs. initial concentration and appropriate equation describing the resulting straight line are shown in Fig. 1.

It can be added here that the process of heterogeneous photocatalytic oxidation of any organic substance contained in water is generally regarded as fulfilling 1<sup>st</sup>-order kinetics (see [20] and references therein). However, at higher concentrations of degraded substrates the kinetics of the process can change to zero order. The explanation is as follows: the rate of generation of OH· radicals by illuminated titania is constant under constant light flux. Therefore, the reaction extent is restricted by the amount of OH· produced and cannot exceed that amount. Note that the amounts of milk mineralized are practically the same at 1.0 and 1.4 g·dm<sup>-3</sup> of initial substrate concentration.

In order to find real influence of the catalytic effect of illuminated TiO<sub>2</sub>, it was also of interest to study direct milk photolysis. The results are shown in Table 2; for comparison, the results obtained in the presence of TiO<sub>2</sub> are also inserted in Table 2.

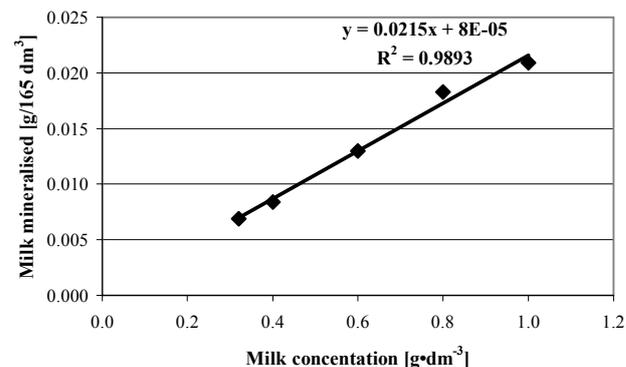


Fig. 1. Dependence of the amount of milk mineralized after three-hour illumination vs. initial concentration.

One can see from Table 2 that the yield of direct milk photolysis, which leads to full mineralization, is about 50% of that in the presence of TiO<sub>2</sub>. Moreover, the rate of the direct photolysis is also proportional to initial milk concentration. Therefore, the observed drops in COD shown in Table 1 consist of COD decrease caused both by direct photolysis and by TiO<sub>2</sub> photocatalytic effect. Both processes are directly proportional to initial milk concentration. Therefore, the overall process fulfils 1<sup>st</sup>-order reaction kinetics as it shown above.

Oxidation reactions in the presence of H<sub>2</sub>O<sub>2</sub>, especially under UV illumination, go *via* OH<sup>•</sup> radicals. Therefore, additions of hydrogen peroxide to the above-slurries described of TiO<sub>2</sub>/diluted milk should result in reaction rate enhancement. The results of investigations are collected in Table 3.

Let's compare the data of Table 3 to those shown in Tables 1 and 2 (obtained for the same milk concentration). H<sub>2</sub>O<sub>2</sub> small additions (0.5 cm<sup>3</sup>) rise threefold reaction rate in the presence of illuminated TiO<sub>2</sub>. Also, the yield of direct milk photolysis increases a little, about 20%. On the contrary, the addition of 1 cm<sup>3</sup> 3% H<sub>2</sub>O<sub>2</sub> raises the rate of the reaction in the presence of TiO<sub>2</sub> to a lesser extent (about 40%) and lowers the rate of direct milk photolysis by about 37%. However, it should be added here that at admixture of 1 cm<sup>3</sup> 3% H<sub>2</sub>O<sub>2</sub> a precipitate was observed during prolonged illumination. The precipitate consisted probably of casein milk proteins that underwent gelation under lower pH; it was observed that at the same time pH solution dropped from initial value of 7.15 to 4.5.

In conclusion, illumination of diluted milk solutions (dairy sewage substitutes) in the presence of titanium dioxide with the light of Xe lamps causes both their direct photolysis and photocatalytic oxidation. The observed reaction rates were directly proportional to the concentration (1<sup>st</sup>-order kinetics). The addition of a small amount of 3% H<sub>2</sub>O<sub>2</sub> prior to illumination greatly enhanced the milk photodegradation rate, especially in the presence of TiO<sub>2</sub>.

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