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The Level of Knowledge on The Use of Titanium Dioxide As a Photocatalyst in Bosnia and Herzegovina

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ABSTRACT: *We are witnesses that every year a growing number of studies related to the use of titanium dioxide as a photo catalyst in advanced oxidation processes. The aim of its use is reducing the organic pollutants in water and air treatment. As a result of extensive research, we have a large number of publications on this topic in the past 20 years. However, despite of all mentioned above, the level of knowledge on this issue in Bosnia and Herzegovina is not at a high and satisfied level. Namely, the* survey covers students, *representatives from the industry, as well as the teaching staff of the University. The results of these studies show that there is great interest in acquiring new knowledge and conducting research on this topic. The aim of this paper is to show to developed countries that in Bosnia and Herzegovina there is the potential of knowledge, and everyone interested in cooperation can help in a developing of a single laboratory for this type of research in which the staff of the University of Tuzla and students would take active participation.*
Keywords: *knowledge, titanium dioxide, water treatment.*

I. INTRODUCTION

By early 1990, in the focus of interest and subject to constant monitoring in the environment were non-polar dangerous substances and heavy metal ions. Today, the subject of interest of scientists is "new contaminants": pesticides, drugs, colors, agents for personal hygiene, plasticizers, various industrial additives, and flavors and similar. The industrial wastewaters are often overloaded with organic compounds such as: various aromatic and aliphatic hydrocarbons, intermediates for different industrial processes, chlorinated hydrocarbons, and others.

Advanced oxidation processes, in particular, photocatalysis by using titanium dioxide (TiO_2) can be an alternative to conventional methods for the treatment of industrial wastewater, and the justification for their use is reflected in:

- using the sunlight for their activation,
- replacement of stoichiometric amounts of reagents by catalytic cycles
- the reduction of waste.

Photocatalytic oxidation, has attracted great attention in recent years due to its excellent efficiency of removing pollutants, low cost, photochemical stability and without using toxic chemicals [1, 2]. Among all semiconductors, TiO_2 is mostly used as a photocatalyst in heterogeneous photocatalysis because of its photostability, non-toxicity, low cost and stability in water under various environmental conditions [3].

Because of the serious impact on the environment, industrial wastewaters are of particular concern. Comparing with the municipal wastewaters, industrial wastewaters generally contain a high concentration of toxic or non-biodegradable pollutants, such as fats, oils, heavy metals, phenols and ammonia [4]. Suspended solids (SS), biological oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC) are some of the parameters that determine the water quality of wastewater [5].

These parameters are usually very high in industrial wastewaters which significantly reduce the efficiency of conventional methods for waste water treatment. Industrial effluents are much more complex composition than other wastewater. Then, the water quality of industrial wastewaters varies from one to the other industries. For example, wastewater from the iron and steel industry has a large amount of ammonia, cyanide, benzene, naphthalene, phenol and cresol, resulting in the coke production in the reduction reaction in the blast furnace [6]. Conversely, dispersed colors are considered to be the dominant pollutants in wastewater of the textile industry and paper industry, which usually contain a high concentration of suspended solids and BOD [7].

Due to the high concentrations of toxic pollutants and variety of water quality, treatment of industrial wastewater is a major challenge. Currently, the textile wastewater is one of the most important sources of pollution. Features of these wastewaters are higher value of color, BOD and COD, complex composition and difficult to degrade. If they are discharged without treatment, these are serious harmful consequences for the environment. Because of the danger of colored wastewaters, many countries have adopted strict standards, but currently there are no uniform standards.

II. TITANIUM DIOXIDE (TIO_2)

2.1 Basic concepts

Titanium (IV) oxide (TiO_2) belongs to the group of transition metal oxides [8]. TiO_2 is a white solid insoluble in water and has the following physical characteristics: molecular weight: 79.87 g mol^{-1}, density: 4.23 g cm^{-3} and a melting point of 1870 °C. At the beginning of the 20^{th} century began the industrial production of TiO_2 and this oxide began to be used as a pigment in white paint instead of previously used toxic lead oxide. Today, the annual production of TiO_2 is more than 4 million tons [9]. TiO_2 is most widely used as a white pigment in paints (51% of total production), plastic (19%) and the paper (17%). In recent years, the use of TiO_2 as a pigment in small sectors is increased: textiles, food, leather, pharmaceuticals (dyeing drugs, toothpaste, UV absorber with sunscreen to protect from the sun and other cosmetic products) and various titanate pigments (mixed oxides $ZnTiO_3$, $ZrTiO_4$, etc.). TiO_2 is a chemically stable, non-toxic and has a low cost. Due to the high refractive index, the thin films of the oxide are used in silicon solar cells and in many optical devices [10].

2.2 Electronic and crystal structure

The energy difference between the valence and conductive band, ie. electronic energy gap, E_g TiO_2 for anatase form is 3.23 eV or for rutile form is 3.02, which corresponds to the energy of photons of UV light. At pH = 7, the standard potential of valence band in which occurs the excess positive charge, and the oxidation takes place is 2.53 V, whereas the standard potential of the conducting band is -0.52 V (relative to a standard hydrogen electrode). These values indicate that photogenerated electrons in the conduction band have the ability to reduce water to elemental hydrogen ((E^0 H_2O/H_2 = -0,413 V), while holes in the valence band have the ability to oxidize water to oxygen (E^0 O_2/H_2O = 1,23 V) [11].

The main crystal structures of TiO_2 are anatase, rutile and brookite. Stability of phases depends on the particle size of the TiO_2. Rutile is the most stable phase for particles larger than 35 nm, anatase is the most stable phase for particles below 11 nm, while brookite is the most stable phase for particles of 11-35 nm [12].
Rutile phase is thermodynamically more stable than anatase phase and by heating to an elevated temperature, a transition from anatase to rutile phase occurs. Enthalpy of anatase-rutile transformation is low (from -1.3 to - 6.0 kJ mol^{-1}). Transition temperature is in the range from 600 ° C to 1000 ° C.

2.3 TiO_2 as a photocatalyst

An important application of the TiO_2 is as a photo catalyst in a variety photocatalytic processes. TiO_2 is chemically and biologically inert, photocatalytic stable, easy to prepare and use, photoactive, cheap and without risk to the environment and people. The only drawback of “pure” TiO_2 is that it does not absorb the visible part of the spectrum. Scientific research of the photocatalytic effect of TiO_2 dates back to the period 1930-1965. when the studies mainly deal with understanding the process of site allocations of pigment colors of binder, ie. "chalking" phenomenon and degradation of color. Several studies have also dealt with the study of specific reactions that were largely sporadic and did not have any scientific contribution or commercial interest in using TiO_2 as photoactive materials.

The revolutionary discovery in the field of photo catalysis came from scientists Fujishima and Honda who discovered in 1972. possibility of photocatalytic decomposition of water molecules using UV irradiation and TiO_2 anodes in combination with platinum electrode immersed in an aqueous solution of electrolytes [13]. Frank and Brad are first investigated the possibility of using irradiated TiO_2 in water treatment. [14]. These scientists have investigated the reaction of photocatalytic oxidation of cyanide to cyanate and sulphite to sulphate and developed a new area called heterogeneous photo catalysis. The research was later extended to a large number of organic and inorganic species. It was concluded that the photo catalysis can be used successfully in degradation of organic and inorganic pollutants, and the photo-assisted organic synthesis.

III. RESEARCH AND DISCUSSION

3.1 Research methods

In the framework of the project entitled "Development of new photocatalytic materials based on titanium dioxide," funded by the Federal Ministry of Education and Science Bosnia and Herzegovina was conducted an anonymous survey. The survey was included companies throughout Bosnia and Herzegovina that have wastewaters, then undergraduate students and several professors at the University of Tuzla.

3.2 Results and discussion

We wanted to get the information of across Bosnia and Herzegovina companies by which matters are overloaded wastewaters, as well as which methods they use in the purification and how much money they invest in wastewater treatment. We also wanted to find out whether they have a desire for new methods of water purification. The total number of examined companies was 12.
In Table 1 there are processes used in water treatment in these companies.

Table 1. Type of used treatment process.

Type of used treatment process	Number of companies
biological processes	2
biological and precipitation processes	2
mechanical removal of solids and biological process	1
physical-chemical processes	1
precipitation process	4
remove grease and oil	1
does not use any process	1

Therefore, the survey results showed that two companies are using biological processes, two companies are using biological and precipitation processes, one company mechanical removal of solids and biological process, one company physical-chemical processes, four companies precipitation process, one company use remove grease and oil and one company any process does not use.

Also, the survey results show that the volume of produced wastewater ranges in the value from 0.250 to 7,500 m^3. The results show also that the money that they invest or have a plan to invest in the wastewater treatment range from 500 Euros to 2.5 million Euros.
Pollutant by which are contaminated wastewaters are mainly: oil and grease, heavy metals, inorganic substances, suspended solids, solid matter, nitrogen and phosphorus.
In Table 2 there are questions and answers of the surveyed companies. Answers are expressed numerically and by percentage.

Table 2. The questionnaire for the companies and their answers.

No	Question	Answer	
		Yes	No
1	Have you think about the introduction of new methods for the treatment of wastewater?	1 8,3%	11 91,7%
2	Have you heard for the term "photocatalytic processes"?	1 8,3%	11 91,7%
3	Do you know what opportunities provide an application of photocatalytic processes in wastewater treatment?	0 0%	12 100%
4	Would you like to learn more about the photocatalytic processes?	7 58,3%	5 41,7%
5	Are you interested in the development of new photocatalytic materials?	6 50%	6 50%
6	Did you know that someone is using photocatalytic processes for the purification of water?	0 0%	6 100%
7	Do you know something about the use of titanium dioxide?	0 0%	9 100%

The results of the survey clearly show that the surveyed companies:
1 are not interested in the introduction of new methods for wastewater treatment,
2. never heard before for the term photocatalytic processes
3. do not know what possibilities provides an application of photocatalytic process in wastewater treatment
4. the desire to learn more about photocatalytic processes expressed 58.3% examinee
5. for the development of new photocatalytic materials are interested 50% examinee
6. nobody do not know that someone is using photocatalytic processes for water treatment
7. nobody do not know anything about using of titanium dioxide.

Questions in Table 3, which relate to the students, we received the following answers expressed numerically and by percentage.

Table 3. The questionnaire for the students and their answers.

No	Question	Answer	
		Yes	No
1	Have you heard for the term "photocatalytic processes"?	8 66,7%	4 33,3%
2	Do you know what opportunities provide an application of photocatalytic processes in wastewater treatment?	0 0%	12 100%
3	Would you like to learn more about the photocatalytic processes?	8 66,7%	4 33,3%
4	Are you interested in the development of new photocatalytic materials?	8 66,7%	4 33,3%
5	Did you know that someone is using photocatalytic processes for the purification of water?	8 66,7%	4 33,3%
6	Do you know something about the use of titanium dioxide?	8 66,7%	4 33,3%
7	Is it your opinion photocatalysis the future to reduce pollution?	8 66,7%	4 33,3%

From the survey results it is clear that the students:

a) are previously heard for the term of photocatalytic processes, but they do not know what possibilities provides application of photocatalytic processes in wastewater treatment.
b) It is commendable that they are interested in the development of new photocatalytic materials and that they want to learn more about these processes.

It is interesting that 66.7% of examinee students have heard for the term of photocatalytic processes while 91.7% of examinee from companies never heard of them. The study also shows that students are 10% more interested in learning more about the photocatalytic processes and the development of photocatalytic materials than examinee from companies across the country.
The results of the survey after a scientific-education workshop are presented in Table 4.

Table 4. The questionnaire and answers of participants after workshop.

No	Question	Answer	
		Yes	No
1	Have you heard for the term "photocatalytic processes"?	8 100%	0
2	Would you like to learn more about the photocatalytic processes?	8 100%	0
3	Did you know that someone is using photocatalytic processes for the purification of water?	3 37,5%	5 62,5%
4	Do you know something about the use of titanium dioxide?	6 75%	2 25%
5	Are you interested in further education in this field?	7 87,5%	1 12,5%
6	Would you participate in research of this kind?	5 62,5%	3 37,5%
7	Did you learn something new today after the workshop?	8 100%	0

IV. CONCLUSION

From the results of the research it is possible to see that the surveyed participants heard for the term of titanium dioxide. However, representatives from the industry do not know much about it, while students and teachers show a large percentage of knowledge and they are very interested in research in this field. Results of the research show that in Bosnia and Herzegovina does not have a lot of researchers who deal with these issues, but it is good that there is interest in further training and research in this direction. The problem in Bosnia and Herzegovina is that there are no funds for scientific research to acquire appropriate equipment and chemicals that are necessary to make this kind of research carried out in laboratories and educate students through practical exercises in this area. We believe that solar photocatalytic TiO_2 method may provide a promising way for the complete degradation of pollutants in industrial wastewaters.

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