Waste Water Disinfection by Titanium Dioxide (Tio_2) Solar Photocatalysis

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ABSTRACT
The task of achieving suitable wastewater disinfection without formation of dangerous disinfection by products by chemical disinfectants, as well as increasing need for a versatile wastewater disinfection and reuse systems demands for a new technologies for efficient disinfection and microbial control mechanism. Titanium dioxide (TIO_2) a metal oxide semiconductor nanomaterial has proved as a powerful antibacterial, antiviral and antifungal properties through diverse mechanism of photo catalytic production of reactive hydroxyl and oxygen species on their surfaces in the presence of solar photons hvwhich inhibits enzyme activity and DNA synthesis ,damages the bacterial cell components and viruses in wastewater that contains these pathogenic agents. This paper reviews the antimicrobial mechanism and disinfection efficiency of Titanium dioxide (TIO20 nanoparticle, discusses their merits, limitations and applicability for wastewater disinfection, and highlights research needs by involving more people in order to exploit innovative TIO2 nanomaterial in wastewater disinfection

INTRODUCTION
The world health organization (WHO) requires suitable disinfection of wastewater to protect public health and ecosystem(WWAP, 2014). The development of new technology to achieve suitable disinfection of wastewater without formation of dangerous disinfection by product such as organo chlorine compound formed during chlorination disinfection of water containing organic matter(Veniri, D Mantzavinos, D. , 2012)Nowadays worldwide, access to safe water of about 3.5 billion people are not fulfilled, nearly 2.5 billion people do not have admittance to improved sanitation and around 768 million people do not have admittance to improved source of water (WWAP,2014). According to some estimation, through 2050 more than 40% of global population will live in conditions of severe water stress. The population growth, economic development and urban expansion will increase demand of freshwater in the future, which in turn will affect water-intensive industries. Among the most water-intensive industries, thermal power plants, steel plants and pulp and paper are dominating. For instance, according to different sources pulp and paper industry can require from 5 to 20 m^3 of water per ton of product (Peter N. Williamson, Hudson, QC,2007) and in some cases up to 1000 m^3 per ton of product, while in sugar industry about 15 m^3 is needed per ton of sugar (Ranade,V.V and Bhandari, VM, 2014) It is worth making a point that during recent decades environmental impact of pulp and paper industry on water, air and soil was reduced by 80 - 90% [6]. However, environmental policy regarding quality of discharged wastewater is tightening, leading to necessity of new solutions for water treatment not only for pulp and paper industry but for all water-intensive industries as well as industries discharging hazardous wastewater.Water treatment using photocatalysis has gained extensive attention in recent years. Photocatalysis is promising technology from green chemistry point of view. The most

widely studied and used photocatalyst for decomposition of pollutants in water under ultraviolet irradiation is TiO_2 because it is not toxic, relatively cheap and highly active in various reactions(Mantzavinos, D. and Veniri, D. 2011)

Other existing water disinfection methods

The widely known conventional methods of water disinfection are chlorination, ozonisation and ultraviolet (UV) irradiation. Chlorination is the application of chlorine and its related compounds such as elemental chlorine, (chlorine gas), sodium hypochlorite solution or dry hypochlorite . Even though chlorine as disinfectant is cost effective, but cyst forming microorganism survive disinfection using chlorine. Another disadvantages of using chlorine for water disinfection is that, chlorine chlorine was found to react with natural organic matter in wastewater to form undesirable chlorinated disinfection by product (DBP) such as trihalomethane and halo acetic acid where many of these products were reported to be carcinogenic(Malatos*, et al* 2009). Furthermore, chlorine in water was reported to be associated with unpleasant taste and odour not only by chlorine its self but also from the odorous by product so formed (Malato*et al*, 2009).

Ozonisation

This is another method of disinfection where ozone (O3) is produced or generated on site at a treatment plant by passing dry oxygen through a system at high voltage electrode system. Ozone (O3) is reported to be the strongest oxidizing agent with a very strong disinfection ability and was reported to be very effective against pathogenic microbes than chlorination. But, more costly and difficult to monitor and control the process under different conditions(Pillai, S., Seery, M., Pelaez, M., 2012)

Ultraviolet Water Treatment system(UV Irradiation)

The ultraviolet germicidal irradiation is a wastewater disinfection method that uses ultraviolet light of short wave length produced from special type of lamp known as germicidal lamp to kill microorganism in wastewater(Zang, Y., Chai, X., and Zeng, J., 2011). Ultraviolet wastewater treatment system has been reported to have a very high effectiveness in removing protozoa, for example *cryptosporidium, Giardia;* bacteria for example, *campylobacter, salmonella, shigella, E.coli;* Viruses for example*, Entric, Hepatitis A, Norovirus , Rotavirus*; but reported not effective in removing chemicals from wastewater (Zhang et al, 2012)

Titanium dioxide (TIO_2) solar photo catalytic wastewater disinfection method

The Tio2 solar photocatalytic wastewater disinfection method is a new innovation disinfection technology which employs semiconductor titanium dioxide (TIO_2) as a catalyst and photon energy from the sun in the presence of solar concentrating reactors. This technology relies on photochemically induced damages by chemical species generated on the Tio_2surfarce to the pathogenic agent in contact with the catalyst in wastewater (Pillai et al, 2012). The following researchers reported the successful application of solar photocatalytic treatment of engineering scale treatment of induatrial non-biodegradable persistent water contaminant (Malato*et al,* 2009). It has been reported that disinfection by photocatalysis is exceptionally effective due to several

mode of action that can be brought to bear on the pathogenic organism which include viruses, bacteria,fungi and algae. Each of these pathogenic agents is associated with challenges in terms of structure and defence mechanism such as cyst formation by microorganism can be effectively by this method(Mantzavinos*et al,* 2012). Malato*et al*, 2009 reported the main advantages TIO_2 as a catalyst of choice in photocatalytic water disinfection as it operates under ambient temperature and pressure , but mainly it has the possibility of using solar light as radiation source.

Forms of Titanium dioxide (TIO_2)

Titanium dioxide chemically written as TIO_2 is also known as titanium(IV) oxide or titania is a naturally occurring oxide of titanium which exist in three different forms as ores. The three different polyforms of TIO_2 are anatase, rutile and bookite. Rutile form is orthorhombic and the most table form, while anatase and bookite are tetrahedron crystal with a band gap of 3.2 and 3.0 electron volt (ev) respectively (Pillai*et al*, 2012)

Research groups and countries involved in titanium dioxide (TIO_2) solar photocatalytic wastewater disinfection method.

Research groups who are mostly involved in studying the TIO_2photcatalytic disinfection process composed mainly of chemists, chemical engineers who are mostly familiar with the terms in photochemistry and reactor issues associated with photocatalytic system. Studies has shown the gradual growth of TIO_2 disinfection research from basic research on laboratory scale to to first trial with real disinfection application(Malato*et al,* 2009;Blake *et al,* 2010; Tsai *et al*, 2010). The countries involved in the research on photocatalytic disinfection method are mostly European countries example Germany, Spain and in Asia, Japan.

Fundamentals and mechanism of TIO_2photocatalysis

The basics of photo physics and photochemistry underlying the heterogenousphotocatalysis employing the semiconductor titanium dioxide TIO_2 ctalyst have been extensively reported(Mantzavinos et al 212). According to (Jin et al, 2010)when photon energy (hv) which is greater than or equal to band gap energy of the TIO2 is illuminated on the TIO2 surface , usually 3.2 for anatase or 3.0 ev for (rutile), the electron will be photo exited to the empty conduction band .

Within this review unmodified and modified TiO_2 materials (powders and thin films) were prepared (Irina, L. 2016). Physico-chemical properties of photocatalytic materials were characterized with UV-visible spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectrometry (XPS), inductively coupled plasma optical emission spectroscopy (ICP-OES), ellipsometry, time-of-flight secondary ion mass spectrometry (ToF-SIMS), Raman spectroscopy, goniometry, diffuse reflectance measurements, thermogravimetric analysis (TGA) and nitrogen adsorption/desorption. Photocatalytic activity of prepared samples in aqueous environment was tested using model compounds such as phenol, formic acid and metazachlor. Also purification of real pulp and paper wastewater effluent was

studied. Concentration of chosen pollutants was measured with high pressure liquid chromatography (HPLC). Mineralization and oxidation of organic contaminants were monitored with total organic carbon (TOC) and chemical oxygen demand (COD) analysis. Titanium dioxide powders prepared via sol-gel method and doped with dysprosium and praseodymium were photocatalytically active for decomposition of metazachlor. The highest degradation rate of metazachlor was observed when Pr-TiO_2 treated at 450ºC (8h) was used. The photocatalytic LED-based treatment of wastewater effluent from plywood mill using commercially available TiO_2 was demonstrated to be promising post-treatment method (72% of COD and 60% of TOC was decreased after 60 min of irradiation). The TiO_2 coatings prepared by atomic layer deposition technique on aluminium foam were photocatalytically active for degradation of formic and phenol, however suppression of activity was observed. Photocatalytic activity of TiO_2/SiO_2 films doped with gold bipyramid-like nanoparticles was about two times higher than reference, which was not the case when gold nanospheres were used.

Treatment of wastewater containing organic matter

The total amount of wastewater (sewage, industrial and agricultural) globally discharged to water bodies is tens of millions of cubic meters per day (Corcoran, E., C. Nellemann, E. Baker, R. Bos, D. Osborn, H. Savelli, 2010) According to some estimation, about 80 – 90 % of all wastewater in developing countries is not treated (World Water Assesment Programme,2009). For instance, an estimated treatment capacity for sewage generated in major cities in India is only about 30 % (R. Kaur, B. Pal,2015) Whereas in EU about 82 % of all generated urban wastewaters have received secondary treatment in 2009-2010 (European Comission,2013. Amount of industrial wastewater varies significantly from country to country. It should be noted that in general almost all water utilized for industrial purposes ends up as wastewater. In developing countries quantities of wastewater generated by the same type of industry are generally higher. For instance, in developed countries steel industry consumes 8 – 10 times lower amount of water per ton of steel than in India. The highest contribution to generation of industrial wastewaters is made by water-intensive industries. The thermal power plants, steel plants and pulp and paper industry were reported to be the most water-intensive industries .

Usually before discharge wastewater is treated by primary clarification followed by biological process Tertiary/advanced treatment is not often applied due to high cost of the processes . Despite applied treatment, wastewater effluent is characterized by high concentration of organic materials, high adsorbable organic halogens (AOX), suspended solids, metal ions, tannins, lignin and derivatives, fatty acids, etc Very often COD value of pulp and paper wastewater effluent exceeds discharging limits and/or recommendations in EU. Thus, according to best available techniques published by the European commission the mean COD value is 103 mg L^{-1}[30]. While reported values of COD in pulp and paper effluents varies significantly starting from 592 mg L^{-1} up to 9065 mg L^{-1} depending on the type of the process(V.K. Saharan, D.V. Pinjari, P.R. Gogate,2014) Hence, additional treatment should be applied in order to reach discharging limits and/or recommendations and minimize and/or prevent negative effect to the environment.
Titanium dioxide (TIO_2) solar photo catalytic wastewater disinfection method

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Heterogeneous photocatalysis is widely studied phenomenon especially in energyrelated issues, purification of water and air, etc. Only in last ten years the number of scientific papers containing word photocatalysis or photocatalyst in the title exceeds 9000(J. Herrmann,1999). And each year number of articles devoted to photocatalysis is increasing (J. Herrmann,1999). It is not surprising because photocatalytic properties of some semiconductors are successfully used worldwide for self-cleaning and antifogging surfaces (J.M. Buriak, P.V. Kamat, K.S. Schanze,2014) cancer therapy, outdoor air purification, deodorization of indoor air, wastewater purification, etc (T.N. Rao, D.A. Tryk, A. Fujishima,2003). Photocatalysis can be defined as a chemical reaction induced by absorption of photons by solid material known as photocatalyst (B. Ohtani,2011). It should be mentioned that photocatalyst does not undergo any chemical changes during and after reaction. In the literature term catalyst is often used instead of photocatalyst. Probably it occurs because some photocatalysts are sometimes used in catalytic reactions as catalysts. But, from thermodynamic point of view the concept of catalysis and photocatalysis is different. Thus, energy-storing reactions can be driven by photocatalysis ($\Delta G>0$) while catalysis is limited to thermodynamically possible reactions ($\Delta G<0$) [10]. Absolute or relative reaction rate in the field of photocatalysis is usually referred as photocatalytic activity (B. Ohtani,2011). Photocatalytic process in water can be divided on five steps(J. Herrmann, 1999): Transfer of reactants in water to the surface of photocatalysts Adsorption of reactants on the surface
Photonic activation of surface of photocatalyst and reaction in the adsorbed phase

Desorption of reaction products

Elimination of reaction products from the interface region.
Generally accepted eexplanation of the main principle of photocatalysis with TiO_2 is often presented as shown in Figure 1

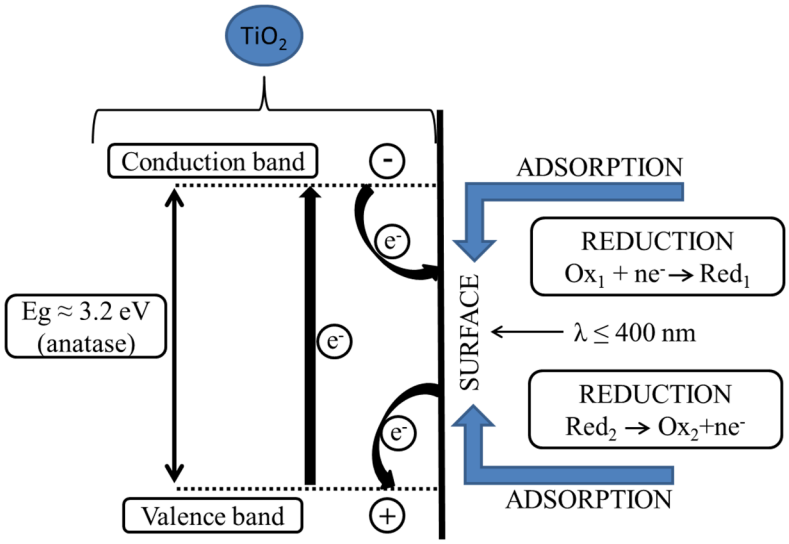

Figure 1: Simplified scheme of TiO_2photocatalysis (J. Herrmann, 2010)

As shown in Figure 1, when photocatalyst (in present case TiO_2) absorb the light with energy equal or greater than band gap energy of photocatalyst, formation of electronhole pairs occurs. The last dissociate into positively charged holes (h^+) in valence band (VB) and electrons (e^-) in conduction band (CB). These charge carriers in the CB and VB reduce and oxidize compounds adsorbed on the surface of photocatalyst, respectively. However, recombination of these charge carriers can occur (Figure 2) causing absence of chemical reaction. Often in the literature decrease or increase of photocatalytic activity is explained by enhanced or supressed electron-hole recombination, respectively (B. Ohtani,2013). As it was mentioned in recent review (B. Ohtani,2013) no direct confirmation of electron-hole recombination during heterogeneous photocatalysis was reported, which may appear surprising. However, detection of electron-hole recombination is not easy because it proceed with heat liberation.

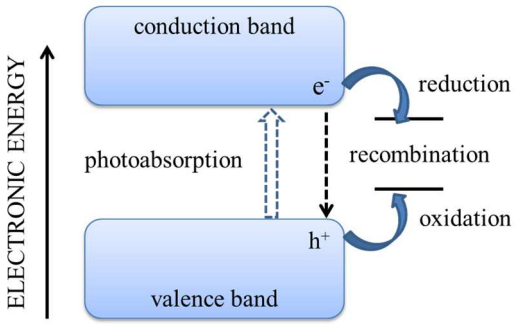

Figure 2: Simplified diagram of electron-hole (e^-/h^+) recombination (B. Ohtani,2013)

There are five main physical parameters which are known to influence photocatalytic activity (J. Herrmann,2010). Reaction rate as a function of these parameters is shown in Figure 2.

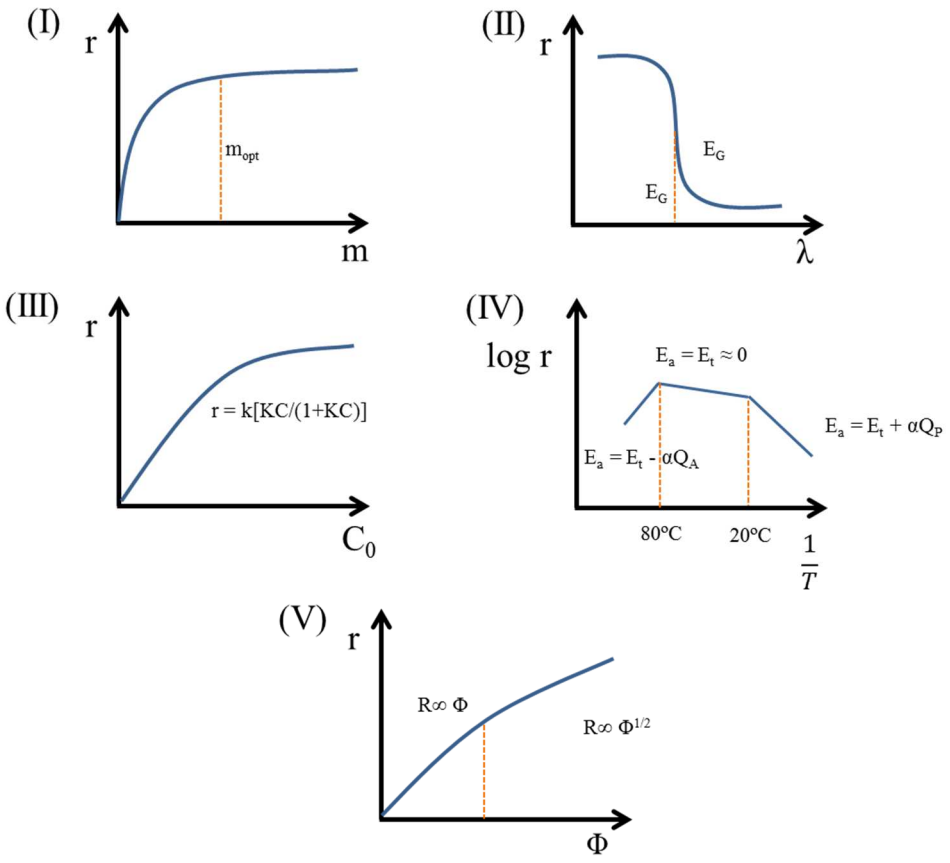

Figure 2: Effect of (I) mass of photocatalyst, (II) wavelength, (III) initial concentration, (IV) temperature and (V) radiant flux on photocatalytic activity (J. Herrmann, 2010)

As it was reported, initial rates of photocatalytic reaction are directly proportional to mass of photocatalyst till certain value after which the function $r = f(m)$ reach plateau (full absorption of photons). Optimal mass of photocatalyst (m_{opt}) depends on operating conditions and reactor geometry (J. Herrmann,2010). Photocatalytic activity strongly depends on the wavelength of the irradiation source (Figure 3.4 II). For instance, for TiO_2 with band energy 3.20 eV the irradiation with $\lambda \leq 400$ nm is required. Generally kinetics of photocatalytic reactions is described in literature using Langmuir-Hinshelwood mechanism, probably due to its usefulness in modelling process:

$$r = K \frac{KC}{1+KC} \qquad \text{equation 1}$$

where r is true rate constant, K is the constant of adsorption at equilibrium and C is the momentary concentration. However, it was demonstrated that rate constants of Langmuir-Hinshelwood mechanism have no physical meaning for photocatalysis (S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, W. Gernjak,2009).The optimum temperature range for photocatalytic reactions (Figure 2 IV) is between 20ºC and 80ºC. At very low temperatures photocatalyticactivity

decreases and desorption of final product becomes rate limiting step. At elevated temperatures (above 80ºC) exothermic adsorption of reactant is becoming rate limiting step and activity is decreasing (J. Herrmann,2009). Hence, photocatalytic reactions in aqueous media are attractive since no heating is required. As presented in Figure 2 (V), the photocatalytic activity is proportional to radiant flux (Φ) till certain value. This value significantly varies depending on experimental conditions. For instance, when Philips HPK 125 UV lamp was used critical flux was estimated to be 25 mW/cm^2. Interestingly, under solar irradiation critical flux is about 2 – 3 mW/cm^2 (S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, W. Gernjak,2009). After this value reaction rate is proportional to square root of radiant flux ($\Phi^{1/2}$). Thus, the optimal use of irradiation corresponds to area where photocatalytic activity is proportional to radiant flux.

Advanced materials for photocatalysis

Desired properties and design of photocatalysts

As it was reported previously (O. Carp, C.L. Huisman, A. Reller, 2004) ideal photocatalyst should be chemically and biologically inert, stable in photocatalytic reactions, easy to produce and use, cheap, not dangerous for humans and environment and efficient under sun irradiation. Thus, titanium dioxide, the most studied material for photocatalytic applications (J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, D.W. Bahnemann, 2014) is almost ideal photocatalyst. Moreover, TiO_2 (P25) is used as reference photocatalyst. Many excellent review papers were devoted to titanium dioxide and its photocatalytic properties (R. Fagan, D.E. McCormack, D.D. Dionysiou, S.C. Pillai,2016). However, photocatalytic activity of TiO_2 and other photocatalytic materials is limited leading to low quantum yields (≤ 10%) (B. Ohtani,2008). Generally the main limiting factors are (B. Ohtani,2008)
recombination of electron-hole (e^-/h^+) pairs;
requirement of ultraviolet light (UV) at a wavelength shorter than ca. 390 nm(X. Lin, J. Xing, W. Wang, Z. Shan, F. Xu, F. Huang, 2007);
low rates of mass transport between active centers of TiO_2 and organic pollutants.

Numerous attempts to design photocatalytic materials with activity higher than that of TiO_2 were made recently (J.M. Coronado, F. Fresno, M.D. Hernández-Alonso, R. Portela,2013). Lin et al. suggested that efficient photocatalyst can be designed by combination of n-type semiconductor (with good electron conductivity) with hole-accepting semiconductor with relatively high structure openness degree (J.M. Coronado, F. Fresno, M.D. Hernández-Alonso, R. Portela,2013). In order to prove this suggestion Bi_2O_3 (n-type semiconductor) was combined with $BaTiO_3$ (dielectric and ferroelectric material) and enhanced photocatalytic activity of this material was reported for decomposition of methyl orange and methylene blue. The improvement of photocatalytic activity was associated with electric-field-driven electron-hole separation. Other coupled semiconductors or heterojunctions such as SnO_2/TiO_2, TiO_2/ZrO_2, $CdSe/TiO_2$, $BiVO_4/TiO_2$, BiOCl/BiOI, Bi_2S_3/TiO_2 and CdS/TiO_2(C. Liu, T. Yang, C. Wang, C. Chien, S. Chen, C. Wang, W. Leng, Y. Hwu, H. Lin, Y. Lee, C. Cheng, J.H. Je, G. Margaritondo,2009) etc. were studied for photocatalytic applications.

Another way to design photocatalytic materials is to use metal nanoparticles with surface plasmon

resonance (SPR) as co-catalysts (Y. Yu, P. Zhang, L. Guo, Z. Chen, Q. Wu, Y. Ding, W. Zheng, Y. Cao,,2014). The metal nanoparticles with SPR can absorb light in the semiconductor and possibly enhance photocatalytic activity. Depending on desired SPR particle size, shape and dielectric environment should be modified. The most used co-catalysts for this purpose is gold and silver nanoparticles because of intense optical absorption and scattering properties. Thus, many scientists reported enhanced photocatalytic activity of TiO_2 modified with Au nanoparticles in UV and/or visible light region(E. Kowalska, R. Abe, B. Ohtani, 2009;(T. Okuno, G. Kawamura, H. Muto, A. Matsuda,2014).

An interesting approach for design of advanced photocatalytic materials were reported by Yu et al. (M. Sharma, D. Das, A. Baruah, A. Jain, A.K. Ganguli, 2014). In this work electronic band structures and density of states for TiO_2nanosheets, nanotubes and nanoparticles were calculated using density functional theory (DFT). After that TiO_2nanosheets, nanotubes and nanoparticles were synthesized and tested for decomposition of 4-chlorophenol. Experimentally obtained band structures and photocatalytic activities of prepared materials were in agreement with theoretical calculations. Thus, photocatalytic activity ranks in order of nanosheets> nanotubes > nanoparticles.

Materials and methods

Photocatalytic materials

Synthesis

Sol-gel technique and atomic layer deposition (ALD) were used for preparation of photocatalytic materials. Thin films of TiO_2 were deposited on aluminium foam substrate (thickness 3.2 mm, bulk density 0.2 g cm^{-3}, purity 98.5 % and porosity 93%). Before deposition, surface of the substrates was cleaned ultrasonically in water and ethanol and dried at 100°C. Thin films were deposited on 7.5 cm × 2.5 cm substrate. As a precursor $TiCl_4$ was used, H_2O was a source of oxygen. The reactor was operated under pressure of about 1 mbar and at temperature 300°C with nitrogen as a carrier and purging gas. Thin film of Al_2O_3 with thickness about 40 nm was deposited on aluminum foam prior TiO_2 in order to avoid corrosion of substrate The surface of aluminum foam was uniformly coated allowing maintaining the porosity and gas permeability of the support.

Experimental setup

Reactor design

For experiments performed with coatings and powder photocatalysts different types of reactor were used. Powder photocatalysts were tested in batch mode with recirculation (Irina, L. 2016) using tubular glass reactors (borosilicate glass, inner diameter 0.6 cm) attached to the LEDs. The total volume of tubular reactors was 10.7 mL. The volume of model solutions or effluents treated using this reactor design was chosen according to experimental time, required volume and number of samples. An equation (given in fig. below) was used for calculation of contact time.

$$t_{cont} = \frac{(V_r \cdot t)}{V_w} \qquad \text{equation2}$$

Where t_{cont} is contact time (min), V_r – volume of the reactor (mL), t – sampling time (min) and V_w – volume of the water in the system at certain sampling point.

DISCUSSION

Photocatalytic activity of TiO_2 powder

Commercial TiO_2 Degussa P25 (without modifications) under UVA irradiation (LEDs) was found to be feasible for posttreatment of pulp and paper wastewater received from local plywood mill (Irina, L. 2016). Formic acid was a model compound for optimization of experimental parameters because it is often found as one of the final intermediates of degradation of more complex organic pollutants. Optimal mass of photocatalyst was defined as 0.5 g L^{-1} based on photocatalytic tests performed with formic acid as demonstrated on below in fig 3

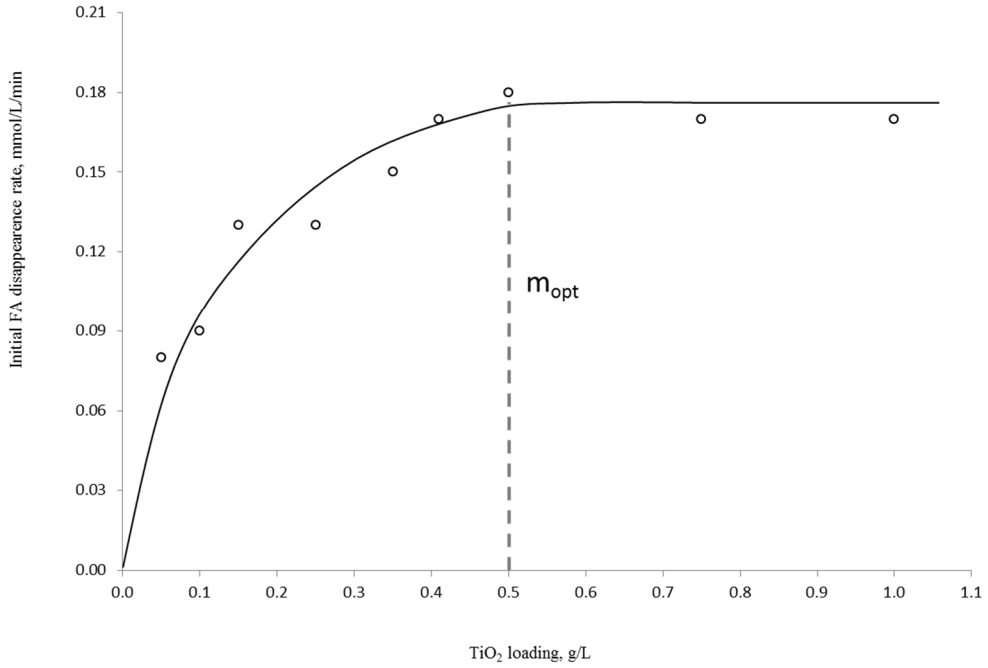

Figure 3: Initial rate of formic acid degradation as a function of mass of TiO_2 (Irinam L, 2016)

Initial rates of formic acid degradation were estimated according to zero order kinetics for 1 min of contact time. From the Figure 5.1 it was concluded that absorption of efficient photons was reached at loading of TiO_2 0.5 g L^{-1}. Optimal mass of TiO_2 obtained in this work is in agreement with other studies conducted with model compounds (R. Wu, C. Chen, C. Lu, P. Hsu, M. Chen A.2010; Rincón, C. Pulgarin,2004) and real pulp and paper industrial wastewaters (M.Y. Ghaly, T.S. Jamil, I.E. El-Seesy, E.R. Souaya, R.A. Nasr,2011; E.C. Catalkaya, F. Kargi, 2008). Therefore, this optimal mass of photocatalyst was used in further experiments with phenol and plywood mill wastewater. In optimal conditions initial degradation rate of phenol was 0.033 mmol L^{-1} min^{-1} and it was almost completely eliminated after 6 min under irradiation. Detected by-products of photocatalytic phenol decomposition were hydroquinone, benzoquinone, catechol and formic acid. Formation of hydroquinone, benzoquinone and catechol during phenol decomposition using TiO_2/UV system was reported earlier (A.M. Peiró, J.A. Ayllón, J. Peral, X. Doménech, 2001). According to some studies (A.M. Peiró, J.A. Ayllón, J. Peral, X. Doménech,2001) there are about 20 byproducts generated during photocatalytic decomposition of phenol. Results of TOC measurements confirmed that not all intermediates were determined (Figure 5.2).

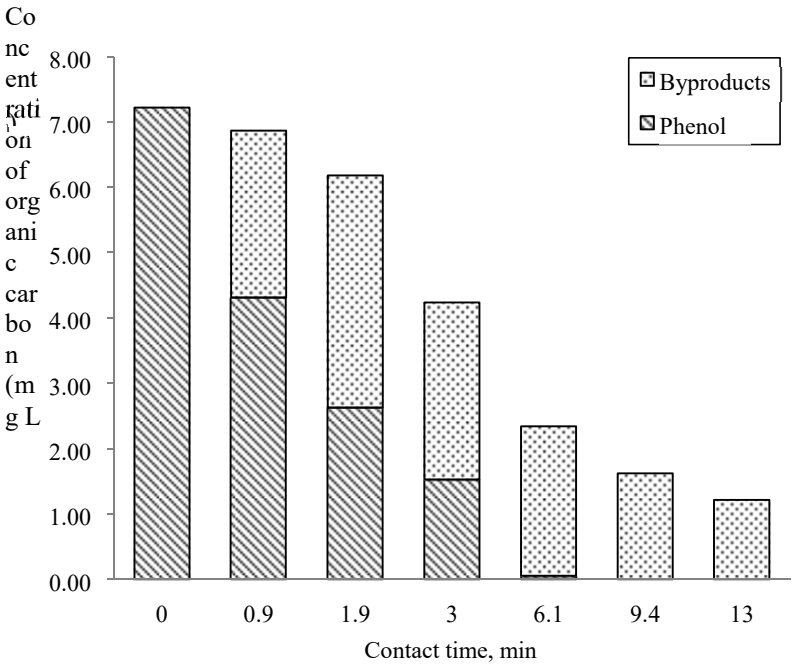

Figure 4: TOC results of photocatalytic phenol degradation

As can be seen from Figure 4, after 6 min of irradiation amount of phenol was about 0.7%, while amounts of benzoquinone, catechol, hydroquinone and formic acid were 20%, 7.9%, 6.2% and 2.9%, respectively. Thus, amount of organic carbon corresponding to detected by-products after 6 min of contact time was equal to 37.7%, which means that rest 62.3% of TOC is unidentified intermediates. After 13 min of contact time mineralization in terms of TOC and COD was 74% and 69%, respectively. Apparent quantum yields (QY) for phenol and formic acid degradation under optimal conditions were estimated to be 0.98% and 0.8% , respectively. Achieved values of QY are in agreement with reported earlier values of about 1% for majority of photocatalytic reactions in aquatic environment(A. Mills, S. Le Hunte,1997).

The tannic acid present in plywood mill wastewater effluent (initial concentration
0.0088 mM) was fully decomposed after 43 min of contact time. Due to photosensitization properties of humic substances (like tannic acid)(F. Han, V.S.R. Kambala, M. Srinivasan, D. Rajarathnam, R. Naidu,2009), about 45% of this compound was eliminated after 60 min of photolysis. Mineralization of organic pollutants presented in wastewater in terms of TOC and COD is demonstrated on Figure
5.

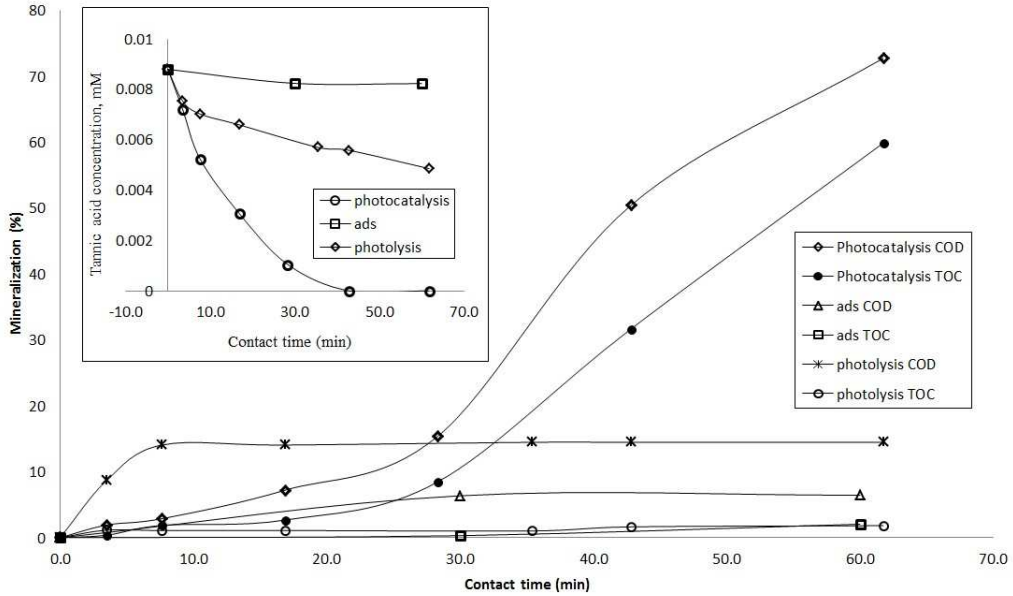

Figure 5: Mineralization of organic pollutants in plywood mill wastewater effluent as a function of contact time. Insert – degradation of tannic acid vs contact time. Source Irina L,2016

As shown in Figure 5, Irina L, reported thatafter 60 min of photocatalytic wastewater treatment TOC and COD removal reach values 60% and 72%, respectively. During first 30 min of contact time average TOC removal per power unit of LEDs emission was about 0.14 mg TOC/W. With the increase of contact time this value increased up to 1 mg TOC/W and then declined. Calculated average oxidation state of carbon atoms (AOSC) confirmed oxidation of organic compounds in wastewater leading to changes in AOSC value from -0.8 in the beginning of photocatalytic test to +0.7 in the end. Thus, UVA-LED based photocatalytic treatment can be considered as promising technique for advanced treatment of post-treatment of industrial pulp and paper wastewater effluents.

CONCLUSION

Photocatalysis is an efficient method which can address environmental issues such as purification of water and air. The field of photocatalysis is constantly developing. Scientists are preparing new photocatalytic materials in order to improve photocatalytic activity of titanium dioxide known as benchmark material. In spite of this fact, titanium dioxide is one of the most studied photocatalysts nowadays. This work was devoted to review on disinfection researches conducted by group of researchers from Matsunga et al,(1985) to date on TiO_2 and modified TiO_2 materials for photocatalytic water treatment. Materials were prepared in the form of powders and thin films. Feasibility of UVA-LED based photocatalytic treatment of plywood mill wastewater effluent was demonstrated by Irina L, (2016)Commercially available TiO_2 (Degussa P25) was used as a photocatalyst. Results suggest that photocatalysis can be successfully applied as post-treatment method for industrial effluents (pulp and paper, refinery, textile, etc.) containing organic compounds some of which can be recalcitrant. What has been observed in all TIO2 disinfection research are all related to reactive oxygen species such as those normally associated with irradiated

TIO2. Based on the information obtained from the result by recently conducted research, we can only conclude that disinfection conditions are highly dependant on reactor configuration, light source, type of of TIO2 and organism as reported by various researchers.

RECOMMENDATIONS

It is important for researchers on TIO2 solar catalytic disinfection of wastewater to continue to strive for clearly defined condition for experiments so that comparison can be made between targeted organism. The effectiveness of some light sources used for irradiating TIO2 that are not rated to have output within the band gap of anatase or rutile phase of the TIO2 suggests that cell killing might be effective at very low dose of ultra violet (UV) light.Therefore, far it appears that the more we move away from controlled laboratory media, the more challenging it become to destroy pathogenic agent because pathogenic agents equip themselves in the wild with with defenses which are difficult to overcome. There are multiple mode of destructive action which are characteristic to solar TIO2 photocatalytic disinfection method that can operate simultaneously, such as absorption/ trapping, reactive oxygen species and direct and indirect photochemistry.Finally, for TIO2 solar photocatalytic disinfection process to lead to industrial or large scale application according to (Chong, M.N.,Jin, B., and Saint, C., 2010) who reported that recent TIO_2 disinfection research that focuses more on disinfection applied to more resistant microorganism. It is critical to develop the process up a level where the process is robust that is minor to moderate changes to water stream which does not strongly affects the plant efficiency, is cheap compared to other disinfection methods, suistainable, easy to implement, easy to maintain and operate such as in the less developed countries of the world especially in Afirica, low risk regarding health and safety for staff handling TIO2, safe regarding environment.

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