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Photocatalytic Treatment of Olive Mill Wastewater by N-doped Titanium Dioxide Nanoparticles under Visible Light

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In this work N-doped TiO_2 sol-gel material was successfully synthesized and used for coating on glass spheres of 1 mm in diameter. The composite material was characterized by dynamic light scattering (DLS) and X-ray diffraction (XRD).The catalytic activity of the obtained photocatalyst was investigated in terms of degradation of organic compounds in diluted and undiluted olive mill wastewater (OMWW) samples. The tests were performed in a batch photoreactor, irradiated by a 150W visible light lamp. The reduction of chemical oxygen demand (COD) was chosen as key parameter of the organic matter degradation. The obtained results showed that the adopted doping and the number of coating layers influences the outcome.

1. Introduction

Heterogeneous photocatalysis is used as an effective method for different origin wastewater cleaning (Huang D. et al., 2012). Titanium dioxide (TiO_2) is one of the most promising materials for that (Papoulis D. et al., 2010) due to its high activity, chemical stability, and it is inertia to photo corrosion (Simonsen M. E. et al., 2012). However, it has a relatively wide band gap (3.2 eV for anatase). That's why TiO_2 can be excited only with UV light, which accounts for only a small fraction of solar light (3–5%). Therefore, it is highly desirable to develop TiO_2-based photocatalysts with enhanced activities under visible light (Hu S. et al., 2010). Doping of TiO_2 with metal/non-metal species is considered an efficient way to enhance photocatalytic activity under visible light irradiation by providing defect states in the band gap (Bangkedphol S. Et al., 2010). Asahi et al. were among the first researchers who mentioned N-doped TiO_2 materials. N-doping showed effective UV and visible light activity (Avisar D. et al., 2013). Recently a lot of studies have been done to examine the preparing procedures of N-doped TiO_2, such as sputtering (Nejand B.A. et al., 2011, Lee S.-H. et al, 2010), sol–gel preparation (Guo X. et al, 2012, Wang Z.-B. et al, 2012, Nishikiori H. et al., 2011), ion implantation (Zhang S.J. et al., 2012, Han L. et al., 2010), pulsed laser deposition, plasma surface modification, solvothermal synthesis (He H.Y. et al,2010), and hydrothermal synthesis (Hu S. et al., 2010). Among these methods sol-gel synthesis is the most simple, quick, and effortless procedure (Spadavecchia F. et al, 2012). Nanocrystalline TiO_2 immobilized on supporting materials such as glass, sand, or zeolite can improve the solid-liquid separation efficiency (Ye M. et al., 2010). In this work, the photoactivity of the produced photocatalyst was checked on the organic matter degradation of an olive mill wastewater stream. This wastewater is characterized by high organic load, with COD values up to 80 g/l, high salinity, acid pH values and a high content of polyphenols. Olive mill wastewater results to be strongly phitotoxic, and thus it is not possible to decompose the organic matter by biological process. As a consequence this wastewater represents a hard environmental problem which requires prompt solution feasible from a technical and economic point of view. In this respect, membrane technologies to be a promising technique to treat different kind of wastewater streams containing organic matter (Stoller M. et al., 2006, Iaquinta M. et al., 2009, Ochando-Pulido J.M. et al., 2012). One of the main problem in applying this technique is membrane fouling (Stoller M., 2011, Stoller M., Chianese A., 2006, Stoller M., Bravi M., 2010). Methods to inhibit membrane fouling involves both the search of optimal operating conditions as well as the application of suitable pretreatment processes (Stoller M., Chianese A.,

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2007, Stoller M., 2008, Stoller M. 2009, Stoller M. et al., 2013). Photocatalysis appears to be a very efficient pretreatment process both for fouling inhibition purposes on membranes purifying wastewater streams containing organic matter and for a post-treatment of the permeate coming out from a sequence of membrane process adopted for the OMWW purification. In fact, the purified water from the OMWW process has to exhibit a COD less than 500 mg/l to be dispose in a civil sewer, but this target is not always assured by the membrane processes. The photocatalysis assisted by TiO_2 catalyst sensitive to visible light may represent an easy and economic operation for the last degradation step of the organic compounds in the OMWW in order to reach the required COD target.

2. Experimental procedure

2.1 Materials

Chemicals used in the experimental procedure are reported in Table 1.

Table 1: The chemicals used in the experimental procedure

Chemicals	Formula	Brands	Purity (%)
Ethanol	C_2H_5OH	Carlo Erba	96
Hydrogen peroxide	H_2O_2	Sigma Aldrich	≥35
TTIP	$Ti[OCH(CH_3)_2]_4$	Sigma Aldrich	97
N-ethylmethylamine	$C_2H_5NHCH_3$	Sigma Aldrich	97

2.2 Synthesize of the N-doped TiO_2 nanoparticles

Ttitanium tetraisopropoxide (TTIP) was dissolved in ethanol and then hydrolyzed with distilled water. The white precipitate of hydrous oxide was instantaneously produced; the mixture was then stirred for 10 min. The amorphous precipitate was separated by centrifugation and washed three times with distilled water for complete removal of alcohol. Afterwards, a fixed amount of hydrogen peroxide was added drop-wise (Jagadale et al., 2008). The precipitate dissolved completely by reaction with hydrogen peroxide and formed a transparent orange sol of titanium-hydrogen peroxide complex. The produced sol was doped by adding drop by drop in the cold water bath of N-ethylmethylamine solution, previously prepared by using 97% N-ethylmethylamine solution. The colour of the solution changed from orange to the yellowish. The solution was kept under stirring for 2 hours before its use for coating.

2.3 Coating of Glass Spheres by TiO_2 Sol-Gel material

Glass spheres of 1 mm in diameter were put into a dip coater. Non-doped or doped sol was poured in the dip coater and maintained in contact with the spheres for 15 min. At the end of this period of time, the sol material was slowly withdrawn from the dip coater. The coated spheres were firstly dried for one hour in a furnace at 85˚C, then washed with distillated water and dried again at 85˚C. As a final step, the spheres coated with non-doped gel were calcinated 15 min in 450˚C in order to obtain TiO_2 in anatase form. Otherwise, the spheres coated with doped gel was calcinated for 15 min at the lower temperature, that is 300°C, in order to obtain the anatase phase of TiO_2, by avoiding the as much as possible the loss of nitrogen.

3. Characterization

Dynamic light scattering was used to measure the modal particle size. The DLS measurements were performed in a nanosizer, model PLUS 90, supplied by Brookhaven. Moreover, the obtained nanoparticles were characterized by X-ray diffraction. The X-rays diffraction of TiO_2 nanocrystals was performed to check if anatase was the dominant crystalline phase. Chemical oxygen demand reduction was adopted as key parameter to characterize the photocatalytic activity. COD was measured by COD kits supplied by Dr. Hach-Lange and a LASA100 photometer.

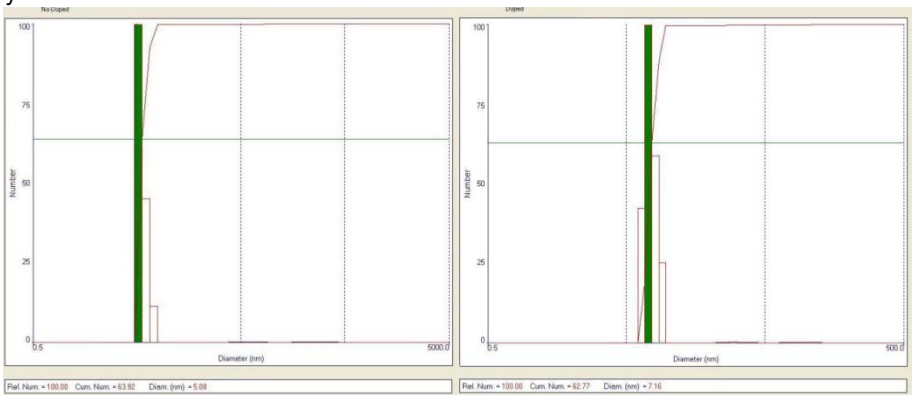
4. Photocatalytic activity

The reactor used for the photocatalytic tests consists of a rectangular box whose base is covered by the coated glass spheres. The wastewater to be treated was recycled at a fixed flow rate through the box by using a peristaltic pump. The reactor was put in thermostated vessel in order to maintain the constancy of the operating temperature around 30°C. A 150 W Halogen Lamp was placed at 10 cm from the liquid surface. The depth of the liquid layer into the reactor was adjusted at 1.5 cm or 3.0 cm. 2 runs were performed to investigate the effect of the liquid depth. Each run lasted 2 hours. At fixed interval of 15 minutes a sample of wastewater was withdrawn and its COD measured.

20 g of coated glass spheres were located in the reactor, whereas the volume of liquid was of 150 or 300 ml, according to the chosen liquid depth. The used wastewater was the clarified stream coming out from a flocculation operated on an OMWW sample, and diluted by distilled water at a ratio equal to 1:20.

5. Results and discussion

Non-doped and N-doped TiO_2 particles size distribution in the sol-gel material used for coating were measured by a nanosizer based on dynamic light scattering. Figure 1 shows the size distribution measurements of non-doped and N-doped TiO_2 particles. The modal size resulted 5nm and 7nm, respectively.



(a) (b)

Figure 1: Particle size distribution for non-doped (a) and N-doped (b) nanocatalyst.

The XRD patterns of obtained non-doped and N-doped TiO_2 nanocrystals were measured. The results show the formation of nanocrystallineTiO_2 in the form of anatase in both samples. The shift of the exothermic picks of N-doped TiO_2 diagram in comparison with non-doped TiO_2 ones was observed. The obtained data can be justified by a change of the morphological structure of TiO_2 due to the doping. The results are shown in Figure 2.

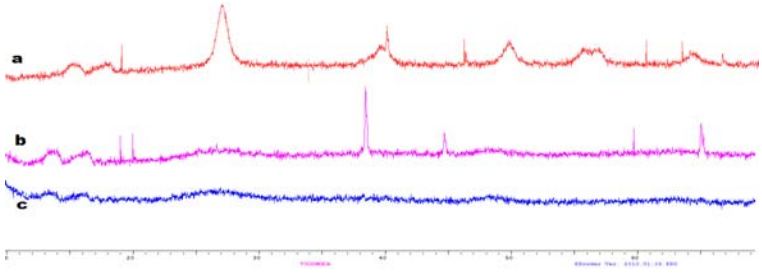


Figure 2: XRD patterns of non doped TiO_2 (a), N-doped TiO_2 nanocrystals (b) and amorphous TiO_2 (c)

In order to confirm that the photocatalytic activity of doped-TiO_2 is better than non-doped TiO_2 under visible light, some photocatalytic experiments were performed on the treatment of olive mill waste water. The adopted OMWW sample has a relatively high organic content, in terms of COD equal to 28 g/l. The experimental investigation was focused on the effect on the organic compounds degradation of the following parameters: the reaction batch time, the initial wastewater concentration and the thickness of the liquid in the reactor vessel, or, expressed in other words, the volume to be treated by each batch run.
Figure 3 shows the COD percentage reduction of the OMWW at a dilution rate of 1:20 with distilled water, for one coating layer catalysts. The liquid depth was equal to 1.5 cm. Along the time a progressive decrease of COD is noticed, but the decrease rate is much more for the diluted waste water because its greater transparency, which allows a deeper penetration into the liquid of the photons provided by the lamp. Figure 3 reports the effects of the subsequent coating and the dopant on the photocatalytic reaction. Both the dopant and the number of coatings improves the reaction performances. By doping, the absorbance band of TiO_2 was shifted to the more visible range that is toward wavelengths higher than 400nm (Sacco et al. 2012). This may justify the improved performances achieved by the doped particles.

Finally, Figure 4 compares the performances of two runs performed on an OMWW sample without dilution, for liquid depth values equal to 1.5 and 3.0, respectively. A higher COD decrease was obtained for the lower depth, since better photon penetration into the liquid is guaranteed by smaller liquid thickness.
The higher degradation rate for a smaller value of COD observed in this work is well known from the literature. In fact, operating with a COD of 1960 mg/l a maximum conversion of 58% was found by Baransi et al. (Baransi et al., 2012), whereas for an initial COD value of 118 mg/l the degradation grade reached a value of 70% as reported by Badawy et al. (Badawy et al., 2009). We would like emphasize the results achieved in this work of the effect of a multiple coating, leading to a higher catalitic surface.

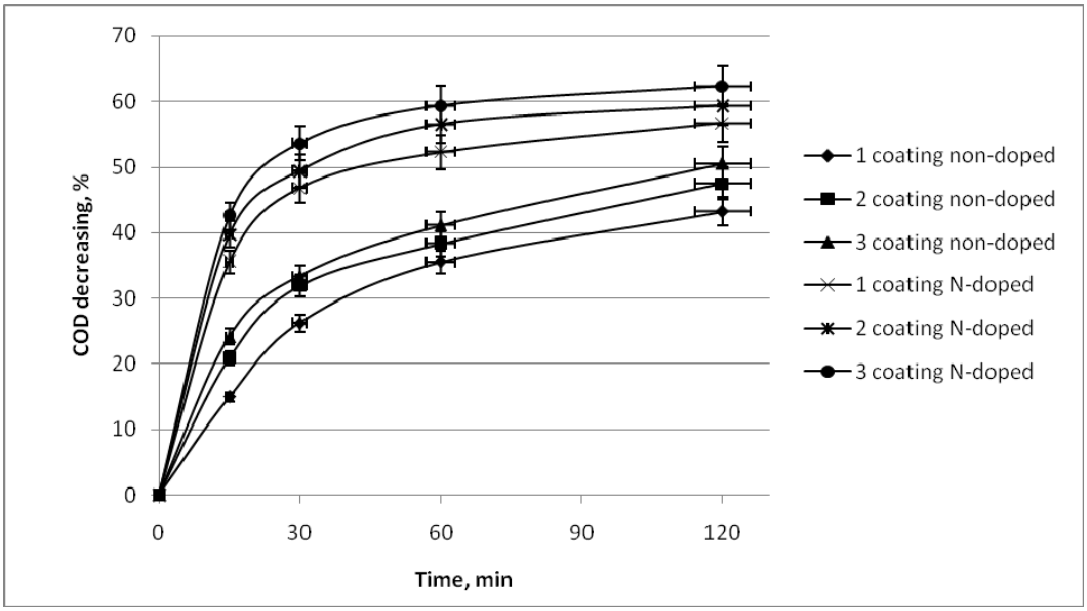


Figure 3: COD reduction by using doped and non-doped spheres

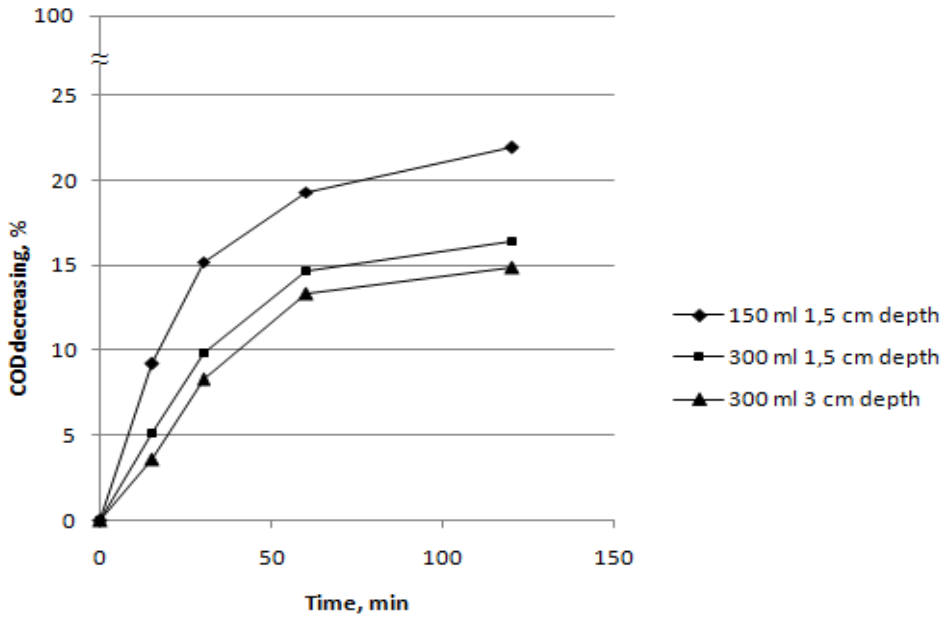


Figure 4: Influence of different parameters on the photocatalytic process

OMWW is a complex solution which contains a wide range of organic compounds of different origin (Hajjouji H. El et al. 2008). During the photocatalytic process secondary organic compounds are formed as product of the primary reactions. As a consequence, changes of the reaction kinetic coefficient throughout

the degradation process must be expected. As a matter of fact COD changes much more in the first 30 minutes after the run start then later on, as shown in Table 2, this is because organic compounds in the first reaction period of time have higher molecular weight and are more prone to degradation. The slope change of the COD vs time curve cannot be justified by the COD variation. As a consequence the fitting of the COD reduction by a first order reaction cannot be reasonably adopted for the examined runs.

Table 2: Kinetic of the OMWW degradation process.

Time, min	Non doped 1 coating		Non doped 2 coating		Non doped 3 coating		N-doped 1 coating		N-doped 2 coating		N-doped 3 coating	
	$\overline{C}$	ΔCi/Δti	$\overline{C}$	ΔCi/Δti	$\overline{C}$	ΔCi/Δti	$\overline{C}$	ΔCi/Δti	$\overline{C}$	ΔCi/Δti	$\overline{C}$	ΔCi/Δti
0-15	1305	840	1262,5	1180	1240	1360	1160	2000	1130	2240	1110,5	2396
15-30	1120	640	1037,5	620	1005	520	830	640	782	544	732,5	628
30-60	975	260	915	180	885,5	218	711,5	154	664	200	614	160
60-120	855,5	105	805	130	764,5	133	642	62	594	40	552,5	43

6. Conclusion

In this study, the photocatalytic activity of immobilized nanostructured N-doped and non-doped TiO_2 catalyst was investigated. N-ethylmethyamine was used as dopant. Glass spheres, adopted as catalytic supports, were coated by TiO_2 by using a sol-gel method. For the photocatalytic tests, diluted and undiluted olive mill wastewater samples were used. The results shows that the percentage of organic matter reduction is proportional to the batch time, the number of performed coating on the support and inversely proportional to the liquid thickness and the initial wastewater COD value. Moreover, the adopted doping procedure was validated under visible light, exhibiting higher performances if compared to those obtained using non-doped particles.

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