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Optimal Configuration of a Photocatalytic lab-reactor by using Immobilized Nanostructured TiO_2

Ibrahimova Seynure[a], Fagan Aliyev[a], Marco Stoller[b], Angelo Chianese*[a]

[a]Azerbaijan University of Architecture and Construction, Ayna Sultanova 5, AZ 1073, Baku
[b]Sapienza University of Rome,Dept. Chemical Engineering, via Eudossiana 18, I00184 Rome, Italy
angelo.chianese@uniroma1.it

In this study, TiO_2 nanoparticles (NPs) and glass balls coated by an N-doped TiO_2 nanostructured layer were used for photocatalytic degradation of organic compounds in aqueous solutions. Preliminary batch photocatalytic experiments were carried out on the degradation of methylene blue (MB) in aqueous solutions by using two types of reactor: the first one was a cylindrical vessels fitted with a mechanical stirrer where the TiO_2 NPs were suspended, whereas the second one consisted of a rectangular box with the glass spheres located at the bottom. For an initial MB concentration of 7 ppm a conversion of around 50 % was detected after 120 min for both the cases. An UV lamp was used for the light irradiation. Then, the catalytic effectiveness of the coated glass balls was checked on a system of industrial interest: the reduction of the organic compounds in an olive mill wastewater (OMW) stream. In this case a more performing configuration of the reactor was adopted by positioning the glass balls over a wire and feeding an air stream under the wire itself, moreover a visible light lamp was used alternatively to the UV lamp. For an initial COD of the OMW equal to 1100 mg/l, a conversion of 57 % was obtained after 120 minutes by using the UV lamp and a conversion of 99% with the use of a visible lamp. This latter result demonstrated the possibility of a strong purification of OMW by using the developed N-doped immobilized TiO_2 catalyst under visible light.

1. Introduction

Photocatalysis is one of the most effective operation to degrade organic compounds in wastewater streams (Luo et al.,2013). Among the various materials used for photocatalysis TiO_2 is the most usual one for wastewater purification for its relatively low cost and high stability (Tu et al., 2013). The photocatalysts may consist of nanoparticles suspended in the liquid phase or a nanostructured layer coating a fixed support. The first system is usually more powerful since it provides a very high surface area, but it has a great drawback, that is the recovery of the used nanoparticles and their recycling in order to reduce the operating cost of the depuration process. On the contrary the use of an immobilized nanostructured catalyst can be less effective at constancy of the catalyst mass, but it seems to be more viable from the point of view of its application in an industrial process, because of the fixed support.
This work reports the application of photocatalysis assisted by TiO_2 nanoparticles and glass spheres coated by a nanostructured layer of titanium dioxide. Two organic aqueous solutions were considered: a very dilute solution of methylene blue (MB) and an olive oil vegetation wastewater (OMW). The purification of this wastewater has a great importance in the Mediterranean area because of its high pollution (COD 40 -150 mg/l) and its big amount, i.e. more than 4 millions of tons per year. In spite of many efforts of applied research works an economic definitive solution for this latter problem has not yet achieved. In particular membrane processes appears to miss the required purification targets for discharge in the municipal sewer systems (500 mg/l of COD), producing RO permeates characterized by a residue COD value equal to 1000 mg/l (Stoller et al., 2013). On the other side, the RO permeate appears to be almost transparent, thus not requiring the use of suspended magnetic nanoparticles for the recovery (Ruzmanova et al., 2013a) but relying on immobilized catalysts systems
The first series of runs concerning the MB degradation was mainly due to compare the effectiveness of the two considered catalytic systems, that is Nps and coated glass spheres, by using always undoped TiO_2. After

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verifying that both the catalysts should provide comparable results, in the second series of data, focused on the degradation of OMW, the immobilized doped titania catalyst was adopted and the process performances were examined by using an UV lamp and a visible lamp, respectively. The purpose of this second series of runs was in fact to evaluate the feasibility of using visible light instead the UV one, with a significant reduction of fixed and operating energy cost (Ruzmanova et al., 2013b). The innovative aspect of the work is mainly to show the feasibility of effective performances of an immobilized photocatalyst if the reactor is carefully designed.

2. Experimental

Two types of catalysts were produced: titanium oxide nanoparticles and nitrogen doped sol-gel material to be used for the coating of glass spheres 4 mm in size.

2.1 Materials

Chemicals used in the experimental procedure are as follows: ethanol, 96 % in purity, from Carlo Erba, hydrogen peroxide, ≥35 % in purity from Sigma Aldrich, tetraisopropoxide ($Ti[OCH(CH_3)_2]_4$), 97 % in purity from Sigma Aldrich and N-ethylmethylammine ($C_2H_5NHCH_3$) , 97 % in purity, from Sigma Aldrich.

2.2 Synthesis of undoped TiO2 nanoparticles and N-doped TiO2 sol-gel material

TiO_2 nanoparticles were produced by hydrolysis of titanium tetraisopropoxide (TTIP) and subsequent precipitation. The reaction was carried out by separately pouring into a cylindrical beaker the two reagent solutions, respectively TTIP and 0.1 M nitric acid (NAS) under agitation provided by a three blade marine propeller rotating at high speed. The obtained suspension was submitted to centrifugation at 7000 rpm for 5 minutes and the nanoparticles are separated from the surnatant and washed three times by distilled water. The NPs were put in an oven where they were firstly dried at 110 °C, then calcinated at 450 °C to obtain a prevalent anatase phase.

2.3 Coating of Glass Spheres by TiO_2 Sol-Gel material

To produce the sol-gel material, a suspension of TiO_2 NPs, produced by the above mentioned procedure, was added drop-wise by a fixed amount of hydrogen peroxide 30% b.w. . The precipitate dissolved completely by reaction with hydrogen peroxide and formed a transparent orange sol of titanium-hydrogen peroxide complex. The produced sol was added drop by drop in a cold water bath by a N-ethyl methylamine solution, previously prepared by using 97% N-ethyl methylamine solution. The color of the solution changed from orange to the yellowish. The solution was kept under stirring for 2 hours before its use for coating.
Glass spheres of 4 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 10 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 distilled water and dried again at 85°C. As a final step, the spheres coated with non-doped gel were calcined 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 as much as possible the loss of nitrogen.

2.4 Characterization

The size distribution of the TiO_2 NPs was determined by means of a Brookhaven Plus 90 nanosizer. A very narrow NPs distribution with an average value of 15 nm was observed, as shown in Fig. 1.
The nature of the obtained layer coating was characterized by X-ray diffraction. The X-rays diffraction of TiO_2 nanostructured layer was performed and it was ascertained that anatase was the dominant crystalline phase. The analysis of the methylene blue aqueous solution was performed by using an UV spectrometer at a wavelength of 633 nm. To evaluate the organic degradation of the OMW chemical oxygen demand (COD) was measured before and after each experiment. COD was measured by COD kits supplied by Dr. Hach-Lange and a LASA100 photometer.

Figure 1: Size distribution of the produced TiO_2 nanoparticles

2.5 The experimental set-up

For the experiments made by using TiO_2 NPs as catalyst a cylindrical vessel 0,5 l in capacity, fitted with a three blade marine propeller rotating at 1500 rpm were adopted. Under the bottom of the vessel an UV lamp, 10 W in power, was located to provide the photons necessary for the photocatalytic process.
A more sophisticated apparatus, shown in Fig. 2, was implemented to carry out the photocatalysis by using the coated glass spheres. The reactor consists of a rectangular box fitted with some baffles, whose bottom was covered by 20 g of glass spheres. The box was pushed in a bath maintained at a constant temperature of 20 °C. A 7 ppm Methylene Blue (MB) aqueous solution was continuously recirculated by a volumetric pump through an external jacketed vessel, also maintained at 20 °C, in order to cool down the reagent solution, which is heated up by the UV lamp. The overall volume of the MB solution was equal to 300 ml. The above mentioned UV lamp was put over the reactor vessel 10 cm far from the liquid layer.

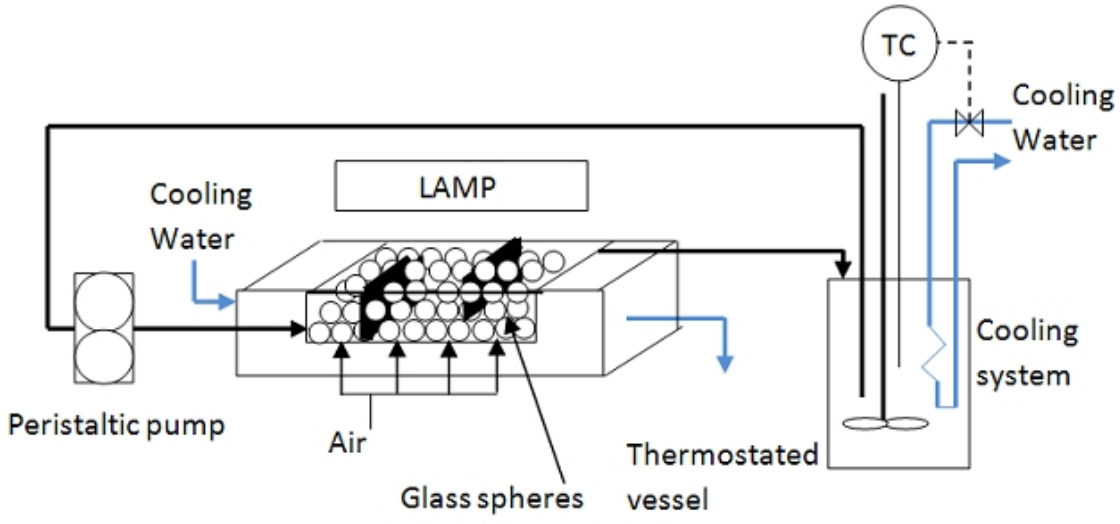

Figure 2: Scheme of the set-up adopted when the coated glass spheres were used as catalyst and the air is fed under the grid where the glass spheres are located

3. Experimental results and Discussion

3.1 Degradation of MB

Experimental runs were performed with the two photocatalytic systems to evaluate the degradation of MB at 20 °C under the above mentioned UV lamp. In preliminary runs, replicated twice, we evaluated a good reproducibility of each run.
The experimental data obtained by using the NPs and the coated glass spheres are reported in table 1 and 2, respectively. In fig. 3 the obtained results with the two kind of catalysts are compared.

Table 1: Experimental data on the MB degradation by using NPs catalyst

Time [min]	0	30	60	90	120	150	180	210	240	270	300	330	360	390	420	450
ppm	7,0	5,3	4,6	3,8	3,5	3,3	2,9	2,8	2,4	2,0	1,8	1,5	1,2	1,0	0,8	0,5

Table 2: Experimental data on the MB degradation by using coated glass sphere catalyst

Time [min]	0	30	60	90	120	150	180
ppm	7,0	6,5	5,3	4,8	3,8	3,0	2,3

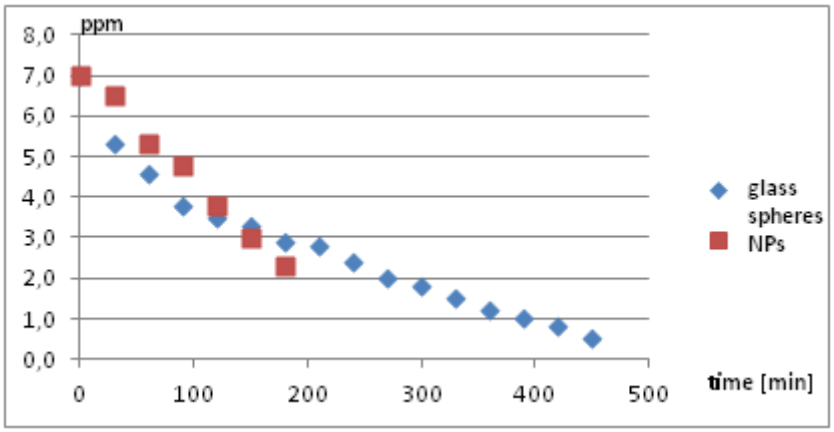

Figure 3: Concentration of MB throughout the runs performed with the NPs and the coated glass spheres

The trend observed in the two runs are quite similar for the first 180 minutes. An attempt was made to correlate the two series of data by a kinetics of the pseudo first order, that is expressed by the equation:

$$r = k\, C_{MB} \qquad (1)$$

where r is the reaction rate in ppm MB per minute, C_{MB} is the MB concentration in ppm and k the kinetic constant. By the best fitting of the data, a kinetic constant value equal to 0,005 min^{-1} and 0,0055 min^{-1} for the coated glass spheres and for the NPs, respectively, was estimated. The determination coefficient R^2 is equal to 0.92 for both the cases.

3.2 Degradation of the organic compounds in the OMW

In this case the catalyst was the glass spheres coated by the doped titania and the reactor was the rectangular box with the two external circuits, above described. In order to improve the degradation process a more efficient air-gas contact system was implemented. The glass spheres were situated over a steel wire located at the bottom of the reactor and the air was fed at fixed flow rate under the wire by a sparger consisting of a tube with a series of holes over its surface.
The examined OMW sample was diluted with respect to the original sample down to a COD value equal to 1112 mg/l, to operate with a more transparent polluted stream.

The use of the nitrogen doped coating allowed to adopt also visible light for the photocatalytic degradation of the organic compounds. Thus, we have used two types of light source an UV light lamp, equal to that one above mentioned, and a visible light lamp, 50 watt in power.
The obtained experimental data are reported in Table 3. The evolution of the COD throughout the two experimental runs are shown in Fig. 3.
The following consideration could be made on the obtained results:
A. The adopted nitrogen doping procedure allows an effective absorption of energy in the visible light range.
B. The use of the visible light lamp allows much better performances, as a consequence of both the higher power with respect to the UV lamp and of the wavelength range of the effective radiation extended beyond that one of the UV range.
C. The degradation of the organic compounds in an OMW stream characterized by a COD of around 1,1 g/l is almost quantitative. This good result relies on the efficiency of both the adopted set-up and the used N-doped catalyst.
D. The visible light seems to be effective particularly during the second half of the run.

Table 4: Evaluation of COD of OMW for experiments performed by using UV lamp and visible light lamp

UV light		**Visible light**	
Time [min]	COD [mg/l]	Time [min]	COD [mg/l]
0	1112	0	1112
15	940	15	897
30	725	30	658
60	563	60	482
90	530	90	133
120	472	120	9

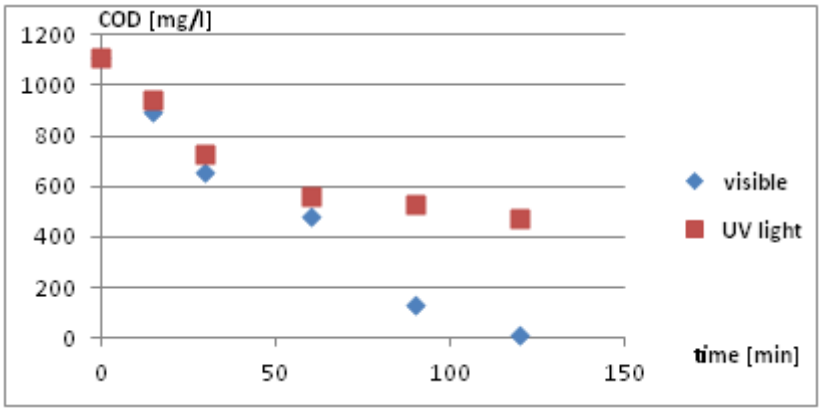

Figure 4: Reduction of COD by photocatalysis under irradiation of UV and visible light

The experimental data have been handled to evaluate the kinetic coefficient of a first order reaction kinetics. The obtained values of the kinetic constant of eq. 1 has been evaluated equal to 0,0076 min^{-1} and 0,0287 min^{-1}, respectively.

4. Conclusion

This study deals with the degradation of organic compounds by TiO_2 assisted photocatalysis. The experimental work was addressed to two objectives. The first one was to compare the effectiveness of the photocatalysis performances when nanoparticles or a nanostructured coating layer was used. Undoped TiO_2 was used under UV light. The experiments carried out on the degradation of 7 ppm MB aqueous solutions exhibited an almost equal conversion, around 50 %, in both the cases. The main aim of this result was to find

out that the two catalytic systems may be equivalent and an immobilized catalyst may be adopted instead of NPs, so overcoming the hard recovery operation required by the NPs use . The second objective was to check the possibility to irradiate the immobilized catalyst with visible light instead of UV light, in order to decrease the photocatalysis process operating cost. In order to allow the absorbance of radiation in the visible light range TiO_2 doped by nitrogen was used, moreover a new reactor configuration was adopted to improve the air-catalyst contact . The examined solution was the olive oil vegetation wastewater with a COD value equal to 1112 mg/l. The run performed under visible light was very successful allowing an almost quantitative degradation of the organic compounds. This result was due to the following factors: a good N-doping of TiO_2 and a very good contact air-immobilized catalyst.

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