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Visible light active N-doped TiO₂ immobilized on polystyrene as efficient system for wastewater treatment



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ABSTRACT

The photocatalytic activity of N-doped TiO₂ particles supported on polystyrene (PS) surface by using a solvent-cast method at ambient temperature was evaluated on methylene blue (MB) dye decolourization. Subsequently, the effect of the new photocatalyst was evaluated in the inactivation of an antibiotic resistant (AR) *Escherichia coli* (*E. coli*) strain selected from the effluent of the biological process of an urban wastewater treatment plant. N-doped TiO₂ particles supported on PS were characterized by UV–vis DRS reflectance and Laser Raman spectra measurements. The results of photocatalytic tests with MB water solutions showed that MB can be successfully degraded (83–100%) under visible light after 180 min of irradiation. The system was also effective in the phenol photocatalytic degradation. Moreover, photocatalytic process effectively inactivated AR *E. coli* strain which was reduced by 97% after 30 min treatment. The developed preparation method could be a promising simple and low cost procedure for preparing immobilized photocatalysts for large scale commercial applications to wastewater treatment under direct solar light.

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1. Introduction

Advanced Oxidation Processes (AOPs) have been increasingly and successfully investigated in the removal of different contaminants from water [1] and wastewater [2]. Additionally, since conventional chemical disinfectants (such as chlorine gas, hypochlorites, chlorine dioxide and ozone) produce toxic disinfection by-products, AOPs have been also investigated as alternative disinfection processes for the inactivation of different microorganisms [3–5]. In particular, AOPs have been recently investigated in the inactivation of antibiotic resistant bacteria [6,7] to control the spread of antibiotic resistance (AR) into the environment, one of the main challenges in urban wastewater treatment and reuse [3,8]. AOPs rely on the capacity of producing highly reactive radical species (in particular hydroxyl radicals) which can degrade pollutants and inactivate microorganisms. Among AOPs, heterogeneous photocatalysis has proven to be an effective water and wastewater treatment process, and titanium dioxide (TiO₂) is the

most widely used and investigated photocatalyst for the removal of recalcitrant and photo-stable organic contaminants in wastewater treatment [9]. TiO₂ has an excellent photocatalytic activity, no toxicity, long-term stability and cheap production costs. However, there are two drawbacks that limit the application of the photocatalytic process based on the use of TiO₂. From one side, pure TiO₂ (band gap is 3.2 eV in anatase form, 3.0 eV in rutile form) absorbs only ultraviolet (UV) light in an effective way, thus making solar driven applications not competitive with other processes. Moreover, if photocatalysts are used as suspended aggregates of nanoparticles in the liquid reaction medium, they can damage the recirculation pumps and, after treatment, a separation process for photocatalyst removal is needed [10]. To solve the problems related to the low efficiency of TiO₂ under visible light, doping method is a very promising approach to increase the spectral performance of TiO₂ in the visible region [11–13]. Recently, B, C, N, S, and F have been used to extend the photo-response from the UV to the visible light region [11,14–16]. Among all options, the N-doped TiO₂ seems to be the most promising photocatalyst active under visible light irradiation [11,17–19]. Moreover, in order to avoid expensive particles separation processes after the treatment,

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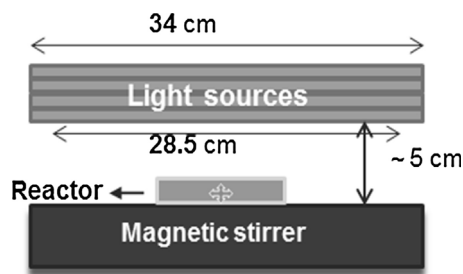


Fig. 1. Photocatalytic system.

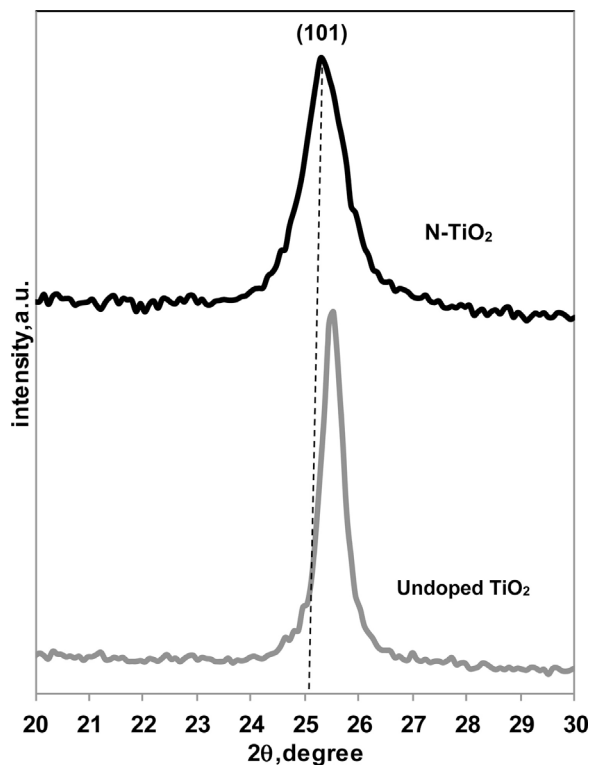


Fig. 2. XRD patterns of undoped TiO_2 and N-TiO_2 particles in the range $20\text{--}30^\circ$.

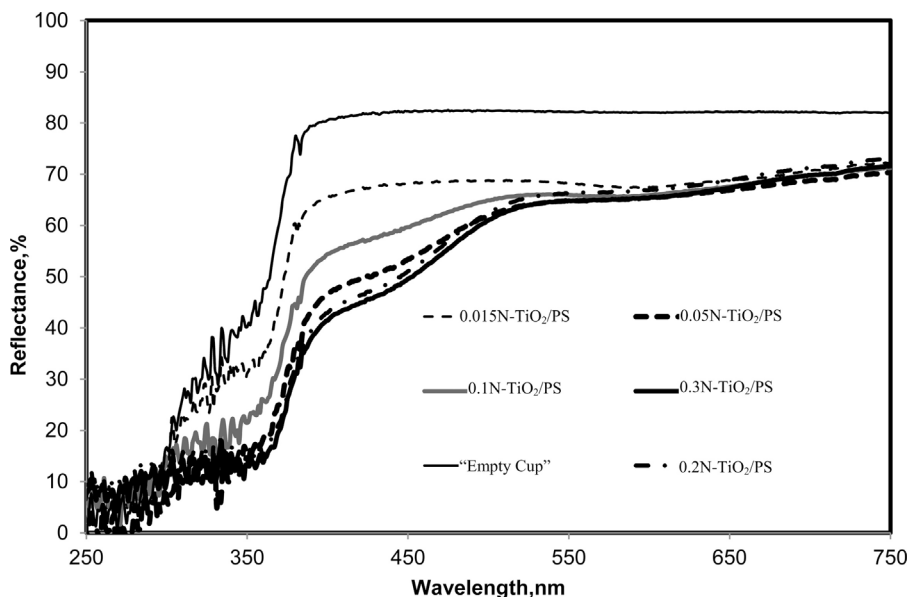


Fig. 3. Reflectance spectra of "Empty Cup" and $x\text{N-TiO}_2/\text{PS}$ samples.

the immobilization of the photocatalyst over suitable supports could be a valid solution.

Recent studies have been focused on the immobilization of doped TiO_2 with various substrates such as hollow glass spheres [10], reactor walls [20], synthetic fabrics [21], natural fabrics [22] and polymers [23,24]. Among the latter, polystyrene (PS) is a cheap, inert, non-toxic and low density thermoplastic polymer, widely used in food service and retail industry [25]. The methods for fixing titania particles on the chosen substrate may vary from as simple as dip-coating or sol-gel techniques [9] to more complex, specialized and expensive methods like chemical vapor deposition [26], thermal treatment method [27], hydrothermal methods [28] and gelation of catalyst in a polymeric substrate and subsequent extraction with supercritical CO_2 [24].

In order to simplify and make cheaper the preparation method of an immobilized photocatalyst, in this work, a visible active N-TiO_2 photocatalyst was immobilized by solvent-casting method on PS plates. The photocatalytic performances of $\text{N-TiO}_2/\text{PS}$ under visible light irradiation were first investigated in the degradation of methylene blue and phenol. Moreover, to evaluate the possible application of $\text{N-TiO}_2/\text{PS}$ photocatalytic system as tertiary treatment of urban wastewater, the inactivation of an AR *Escherichia coli* (*E. coli*) strain selected from real urban wastewater was investigated.

2. Materials and methods

2.1. Photocatalysts preparation

N-TiO_2 photocatalyst was prepared by sol-gel method starting from titanium tetraisopropoxide (TTIP by Sigma Aldrich) and adding ammonia aqueous solution at 30 wt.% supplied by Carlo Erba, with a molar ratio $\text{N/Ti} = 18.6$ [15]. In particular, 100 mL of ammonia aqueous solution was added to 25 mL of TTIP at 0°C , while the solution was vigorously stirred to form a white precipitate. Finally, the precipitate was washed with water, centrifuged and calcined at 450°C for 30 min. The N-TiO_2 sample was deeply characterized in our previous papers. In particular, it resulted in a yellow appearance and presented an energy band-gap of 2.5 eV [3,15] with a specific surface area (evaluated by BET method) of $30\text{ m}^2\text{ g}^{-1}$ [29]. In addition FT-IR characterization was

carried out showing bands attributed to the N atoms embedded in the TiO₂ network [3,30].

PS was used as polymeric substrate for the deposition of different amount of N-TiO₂ particles through solvent-casting method. Acetone was used as solvent for the preparation of the samples. In particular, a certain amount of N-TiO₂ was added to 10 mL of acetone (Sigma Aldrich). The obtained N-TiO₂ suspension was stirred for two minutes at room temperature and then dropped on the PS supports (Petri dishes, I.D. = 8.5 cm, weight = 7.187 g, provided by Microglass Heim).

In order to remove the excess of N-TiO₂ particles not immobilized on PS surface, several cycles in an ultrasonic bath (CEIA-CP104) were performed on N-TiO₂/PS until to reach a stable loading of the sample. After ultrasonic treatment, the samples were dried for 48 h at room temperature. The final obtained samples were named xN-TiO₂/PS where x indicates the amount of N-TiO₂ (in grams) immobilized on PS surface. “Empty Cup” is a Petri dish without N-TiO₂ particles. The final content of N-TiO₂ on PS was in the range 0.2–4.2 wt%.

2.2. Photocatalysts characterization

For the characterization of N-TiO₂ particles and xN-TiO₂/PS samples several techniques were used. Wide-angle X-ray diffraction (WAXD) patterns with nickel filtered Cu-K α radiation were obtained with an automatic Bruker D8 Advance diffractometer, in reflection. Laser Raman spectra were obtained by Dispersive Micro-Raman (Invia, Renishaw), equipped with a laser emitting at 514 nm in the range of 100–2000 cm⁻¹ Raman shift. A Perkin Elmer spectrophotometer (Lambda 35) equipped with a RSA-PE-20 reflectance spectroscopy accessory (Labsphere Inc., North Sutton, NH) was used for the UV–vis DRS reflectance measurements.

2.3. Photocatalytic activity tests

Photocatalytic tests for the degradation of MB, phenol and *E. coli* inactivation were carried out in the functionalized PS Petri dishes, directly used as photoreactor. The bottom surface of the photoreactor was covered by a photoactive layer (Fig. 1). The total volume of the solution in the photoreactor was 30 mL. The solution was continuously stirred during the irradiation of the overall Petri dish surface. The irradiation of the photoreactor was carried out with three visible light lamps (Beghelli, 8W) with wavelength emission in the range 400–800 nm.

A cooling fan was positioned near the photocatalytic system in order to control the temperature, which was always lower than 35 °C. The initial concentration of MB and phenol was 10 and 50 mg/L, respectively.

The liquid samples were collected at fixed time intervals, and analyzed by a Perkin Elmer UV–vis spectrophotometer at $\lambda = 663$ and 270 nm to measure MB and phenol concentration, respectively. The total organic carbon (TOC) of aqueous solutions was measured by the high temperature combustion method on a catalyst (Pt-Al₂O₃) in a tubular flow microreactor operated at 680 °C, with a stream of hydrocarbon free air to oxidize the organic carbon [31].

AR *E. coli* inactivation experiments were performed in 30 mL of deionised water with a saline solution of an AR *E. coli* strain (initial concentration of 10⁵ CFU mL⁻¹). The *E. coli* strain was selected according to its resistance to a mixture of three antibiotics (namely ampicillin, ciprofloxacin and tetracycline) from the effluent of the biological process of an urban wastewater treatment plant, according to a procedure explain elsewhere [32]. AR *E. coli* inactivation was monitored by means of standard plate counting method after 24 h incubation at 37 °C. Tryptone Bile X–glucuronide Agar (TBX) was used as selective growth medium.

3. Results and discussion

3.1. Photocatalyst characterization

Before analyzing xN-TiO₂/PS samples, XRD spectrum of N-TiO₂ particles was obtained and compared with undoped TiO₂ prepared with the same procedure but adding distilled water instead of ammonia aqueous solution (Fig. 2). It is worthwhile to note that the diffraction peaks related to (101) plane of N-TiO₂ in anatase phase shifted to a lower value of 2θ (25.29 °) with respect to the diffraction peaks at 25.53 ° (related to the same (101) plane) of undoped TiO₂. Possibly, N replaced O in the TiO₂ structure due to differences in binding properties [33] meaning that the crystalline structure of anatase was doped with nitrogen.

UV–vis DRS spectra of the samples can be observed in Fig. 3. The “Empty Cup” absorbed a fraction of the radiation in the UV range due to the PS properties [25], while it is completely transparent to the visible range, meaning that the used support does not subtracts

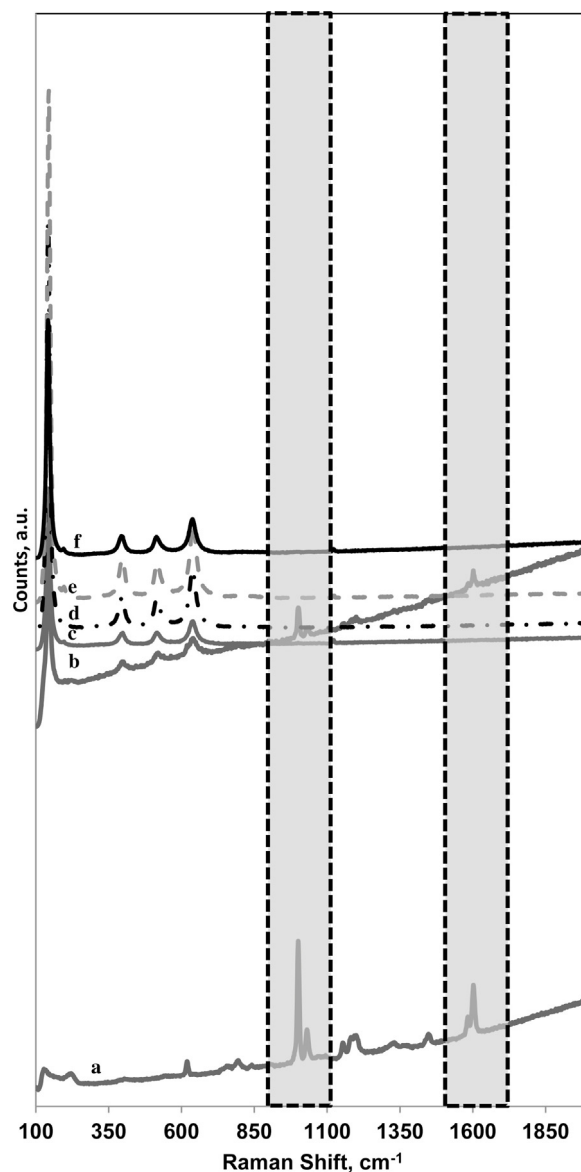


Fig. 4. Raman spectra of the sample: (a) “Empty Cup”; (b) 0.015N-TiO₂/PS; (c) 0.05 N-TiO₂/PS; (d) 0.1 N-TiO₂/PS; (e) 0.2N-TiO₂/PS and (f) 0.3N-TiO₂/PS.

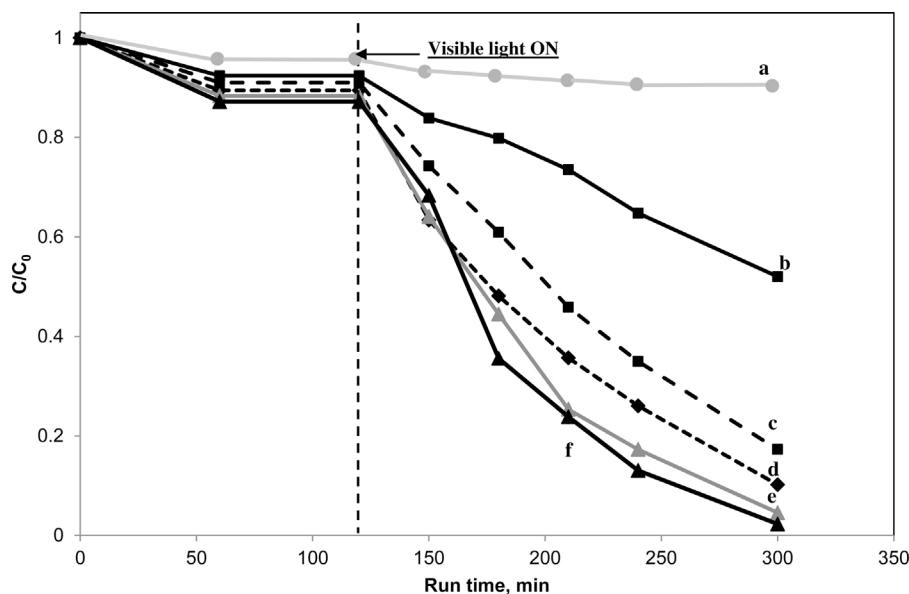


Fig. 5. Photocatalytic activity test in the decolourization of MB: influence of different amount of N-TiO₂ (a) “Empty Cup”; (b) 0.015N-TiO₂/PS; (c) 0.05 N-TiO₂/PS; (d) 0.1 N-TiO₂/PS; (e) 0.2N-TiO₂/PS and (f) 0.3N-TiO₂/PS.

photons useful to activate the N-TiO₂ particles [25]. The increase of N-TiO₂ loading on PS surface leads to spectra similar to those of pure N-TiO₂ [3] that clearly shows the ability of the photocatalyst to absorb visible light because of the electronic transition from the isolated N 2p level to the conduction band [34].

The sample 0.015N-TiO₂/PS shows a spectrum similar to that one of the “Empty Cup”, meaning that PS surface is only partially covered by N-TiO₂ particles. As the N-TiO₂ amount was increased from 0.05 to 0.3 g, the reflectance of the samples in the visible region, decreased as the mass of the photocatalyst was increased, thus making evident that almost a complete coverage of PS surface was achieved.

The results from the characterization of the samples through Raman (Fig. 4) spectra showed strong Raman modes around 998, 1026 and 1599 cm⁻¹ for the “Empty Cup”. These bands are still present for the sample 0.015N-TiO₂/PS, while totally disappeared for the other samples that exhibited only the characteristic Raman-active modes of the anatase TiO₂ phase [3], indicating that the overall PS surface is covered by N-TiO₂ particles, thus confirming the UV–vis DRS results. Moreover, it is important to underline that the solvent-casting method did not change the Raman modes of unsupported N-doped TiO₂.

3.2. Photocatalytic activity: effect on MB

To evaluate the effect of the amount of N-TiO₂ deposited on PS support, photocatalytic tests were carried out with MB dye solution (initial concentration of 10 mg/L) under visible light irradiation. The samples were left for two hours under dark conditions to get the MB adsorption equilibrium. Under this condition, MB concentration decreased in the first hour and remained unchanged in the second hour (Fig. 5), meaning that the adsorption-desorption equilibrium of MB dye was achieved. After the dark period, the solution was irradiated with visible light. No decolourization of MB solution was observed for the “Empty cup” due to photolysis of MB under visible light irradiation [15]. This control test confirmed that any photocatalytic activity takes place when N-TiO₂ is not present on PS surface.

For all xN-TiO₂/PS samples an initial adsorption step in dark conditions was observed leading to MB decolourization in the range 8–12.9%. When the solution was irradiated with visible light, the behavior was completely different compared to the results obtained with the “Empty cup”. In fact, under light irradiation 0.015N-TiO₂/PS, 0.05N-TiO₂/PS, 0.1N-TiO₂/PS, 0.2N-TiO₂/PS and 0.3N-TiO₂/PS catalysts showed a significant photocatalytic activity (MB decolourization as high as 26, 54, 65, 75 and 77%, respectively), after 90 min of irradiation time. More in detail, up to N-TiO₂ amount of 0.05 g (0.05N-TiO₂/PS), photocatalytic activity markedly increased indicating that the overall N-TiO₂ dispersed on the PS surface is effectively irradiated. For 0.3 g of N-TiO₂ (0.3N-TiO₂/PS), photocatalytic decolourization rate was almost the same of that one obtained with 0.2 g of N-TiO₂ (0.2N-TiO₂/PS). This means that the amount of N-TiO₂ effectively irradiated did not change, because the additional N-TiO₂ particles mask the layers below N-TiO₂. Thus, the best sample chosen to investigate the stability as well as to compare with N-TiO₂ in powder form was 0.2N-TiO₂/PS (Fig. 6). According to the results achieved under visible light (Fig. 6a), the photocatalytic activity of 0.2N-TiO₂/PS was similar to that one obtained using the same amount (0.2 g) of N-TiO₂ powder deposited on the PS surface.

The photocatalyzed decolourization process can be described by a first-order kinetic (Eq.(1)) with respect to the concentration of MB after dark adsorption [35]:

$$-\ln\left(\frac{C}{C_{dark}}\right) = k_i \cdot t \quad (1)$$

where:

C = concentration of MB at any given time [mg/L];

C_{dark} = concentration of MB after dark adsorption [mg/L];

t = irradiation time [min];

k_i = apparent kinetic constant [1/min].

The obtained results are plotted in Fig. 6b. It is worthwhile to note that the values of k_i are very similar (0.014 and 0.015 min⁻¹). According to these results, the photocatalytic activity of 0.2N-TiO₂/PS was unaffected by diffusional limitations [36]; the reaction proceeded under chemical regime and photoactivity is to be

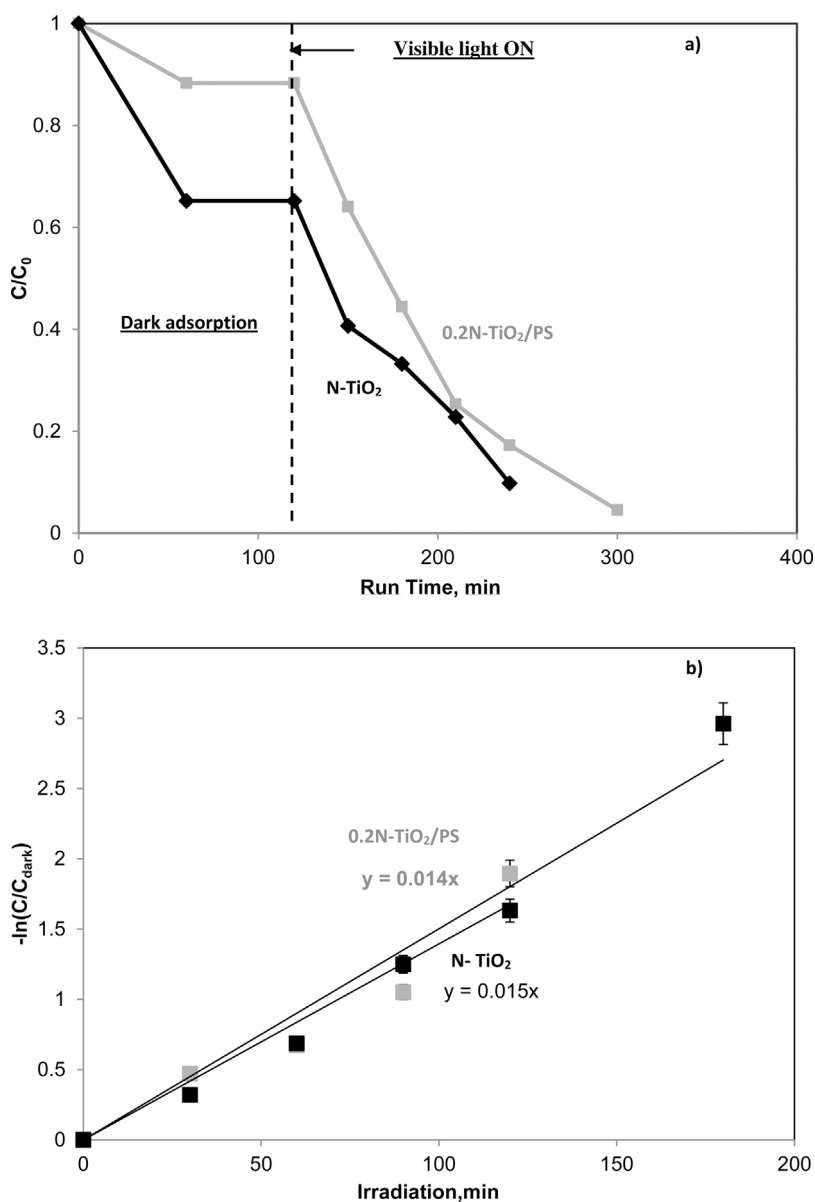


Fig. 6. Comparison between the photocatalytic activity of 0.2N-TiO₂/PS and N-TiO₂ in powder form. a) Decolourization of MB and b) evaluation of decolourization kinetic.

ascribed only to the deposited N-TiO₂ as active phase where the reaction takes place.

The photocatalytic test was repeated up to four cycles (Fig. 7) to investigate the reusability of 0.2N-TiO₂/PS sample, and a significant reduction of decolourization percentage in 30 min of irradiation from the fresh sample to the first reuse was observed. The decrease in the decolourization rate may be due to the weakening of the dye adsorption ability. However, it is worth noting that, from the first to third reuse, the photocatalytic activity of 0.2N-TiO₂/PS was nearly the same, reaching the total decolourization after 180 min of irradiation. This last result confirms that the stability of N-TiO₂ coated on PS support was achieved.

Moreover, the stability of 0.2N-TiO₂/PS was evaluated by subjecting the sample to a cycle of 500 h of visible irradiation and monitoring the weight change of the sample over time. No variation in the sample weight was observed, indicating that the polymeric support has high stability in the presence of the photocatalyst dispersed on its surface.

3.3. Photocatalytic activity: effect on phenol

Photocatalytic test with 0.2N-TiO₂/PS sample under visible light was performed using phenol as colorless organic pollutant to exclude sensitization phenomena of N-TiO₂ surface by MB dye (Fig. 8).

No photocatalytic activity was observed for “Empty Cup” sample. On the contrary, 0.2N-TiO₂/PS was effective in the degradation of phenol reaching a degradation of about 72% after 180 min of visible light irradiation. In addition TOC removal of about 60% was achieved after the same irradiation time. This last result evidenced that the 0.2N-TiO₂/PS photocatalyst was also effective in the mineralization of phenol to CO₂ and H₂O.

3.4. Inactivation of *E. coli* by photocatalytic process

The control test in dark (only catalyst) did not show any AR *E. coli* removal (data not shown), and the control test with visible

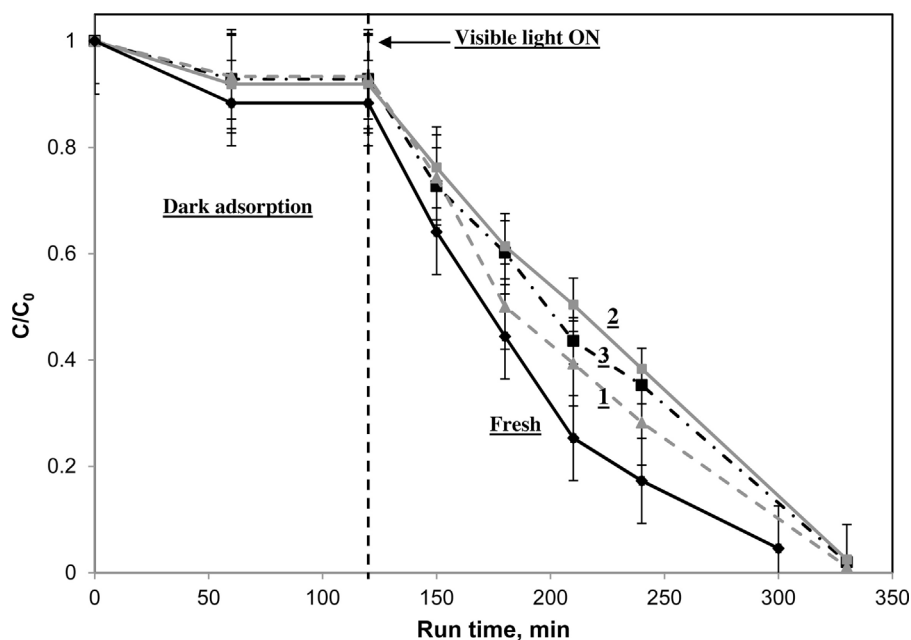


Fig. 7. Evaluation of MB decolourization performances obtained on 0.2N-TiO₂/PS after 3 recycling experiments.

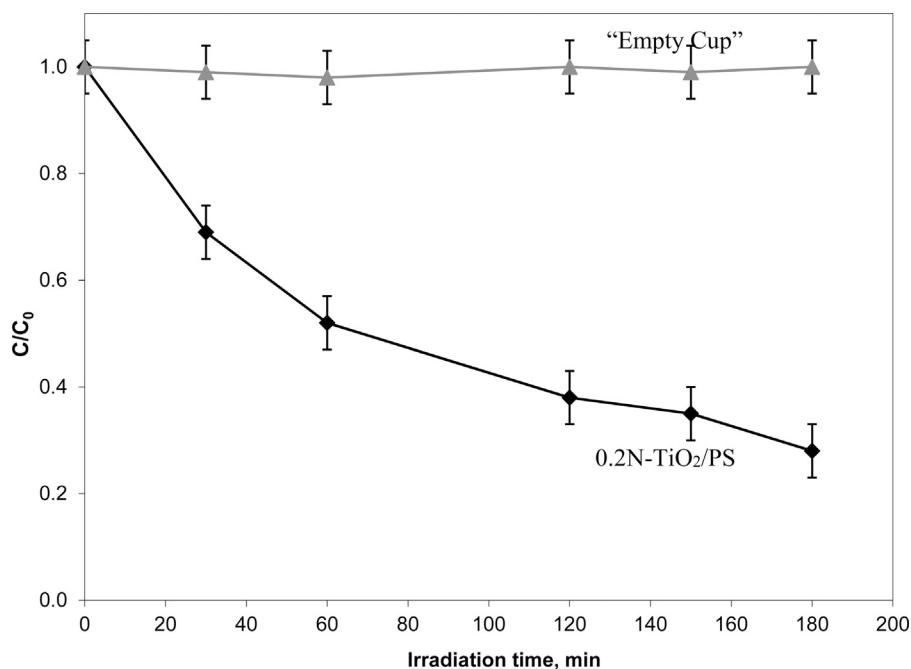


Fig. 8. Phenol degradation on "Empty Cup" and on 0.2N-TiO₂/PS.

light (as standalone process) resulted in a quite poor AR *E. coli* inactivation (approximately 10% after 10 min irradiation, then any significant change was observed till 60 min irradiation) (Fig. 9). Actually, this result is consistent with the light source used (visible light lamp emitting radiation between 400 and 800 nm) because it does not emit radiation in the UV-C range, which is effective as bactericidal radiation. Unlike of visible radiation, photocatalytic process drastically decreased initial AR *E. coli* concentration, which was reduced by 97% after 30 min treatment (Fig. 9). Photocatalytic process results in the production of reactive oxygen species (in

particular hydroxyl radicals), which can effectively attack bacterial cell wall, thus inactivating *E. coli* under visible light too [37].

Moreover, photocatalytic process efficiency in *E. coli* inactivation under visible light can be drastically improved in the presence of No-metal doping [38]; however, in spite of the improved efficiency, the effect of N-doped TiO₂ in the inactivation of lab cultured *E. coli* suspensions was quite lower (approximately 40% after 30 min treatment) compared to our results. But when N-doped TiO₂ powder irradiated by a wide spectrum 250 W lamp (350–450 nm emission spectrum) was investigated in the

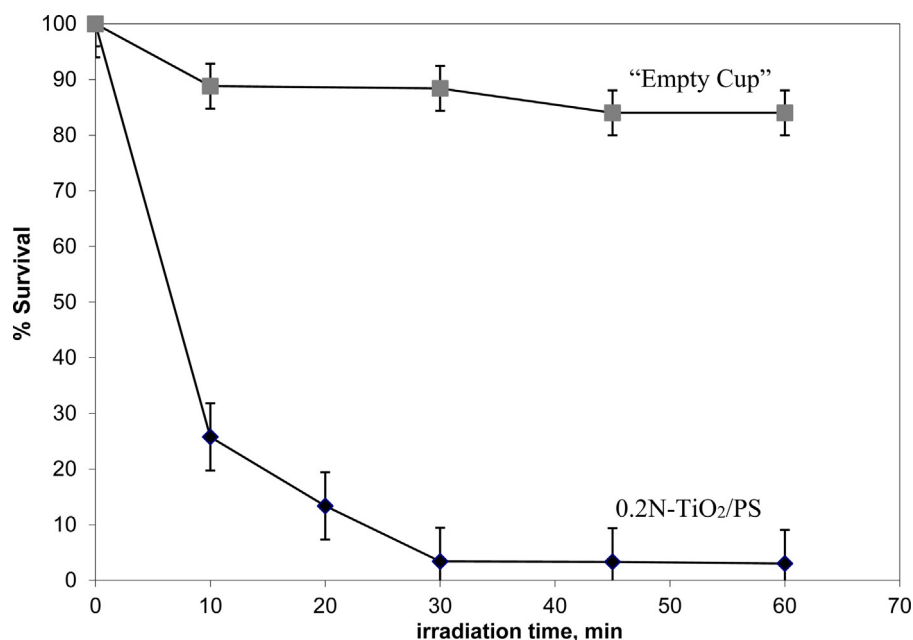


Fig. 9. Percentage of AR *E. Coli* inactivation on “Empty Cup” and on 0.2N-TiO₂/PS.

inactivation of an antibiotic resistant *E. coli* strain, a higher photocatalytic disinfection efficiency was observed (7 log unit inactivation in 60 min treatment) [3] compared to our work.

4. Conclusions

Visible active N-doped TiO₂ photocatalyst has been successfully immobilized on polystyrene based macroscopic support by solvent-casting method. The structured photocatalysts were tested in the photocatalytic degradation of methylene blue, chosen as model pollutant. The optimal amount of immobilized photocatalyst, which led to the complete decolorization of MB solution after 180 min of visible light irradiation, was found to be 0.2 g. Moreover, the optimized structured catalyst was successfully investigated in the photocatalytic degradation of phenol (72% in 180 min of treatment) and in the inactivation of an AR *E. coli* strain (97% removal in 30 min of treatment). The structured photocatalyst obtained by the solvent-casting method is easy to produce and it looks to be a promising option for photocatalytic applications under visible light to wastewater treatment.

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