We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

4,900
Open access books available

124,000
International authors and editors

140M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Heterogeneous Photocatalysis Remediation of Wastewater Polluted by Indigoid Dyes

Enrico Mendes Saggioro, Anabela Sousa Oliveira and Josino Costa Moreira

Additional information is available at the end of the chapter

Abstract

Organic dyes constitute one of the largest groups of wastewater's pollutants. In general, they are released into the environment by textile industries. Approximately 100,000 dyes are widely used in the textile industry, and a large wastewater of dyestuff is generated annually. Among these, indigoid class is commercial dyes used mostly for cotton cloth dyeing. Indigo carmine (IC) is also one of the oldest dyes and still one of the most used in textile industry and is considered as a very toxic indigoid dye. Most toxic dyes are recalcitrant to biodegradation, causing a decrease in the efficiency of biological wastewater treatment plants. Titanium dioxide is a well-known photocatalyst mostly used in suspensions in photoreactions for wastewater treatment. The use of TiO_2 has some advantages such as ease of handling, low cost, low toxicity, high photochemical reactivity, and non-specific oxidative attack ability. In this way, it can promote the degradation of different target organic compounds with little change of operational parameters. The aim of this chapter is to present the different approaches already used in our team for the remediation of waters containing IC mainly through heterogeneous photocatalysis with TiO_2. Adsorption over activated carbon (AC) and photocatalytic degradation of IC mediated by titanium dioxide will be revised as well as some studies on the phototoxicity of the photoproducts with aquatic and terrestrial organisms. This chapter makes a comprehensive approach to the different results on the remediation of model effluents containing IC undertaken by this team of researchers.

Keywords: photocatalysis, titanium dioxide, wastewater treatment, Indigo carmine, ecotoxicology

1. Introduction

Textile industry process generates a significant amount of wastewaters containing 5–15% of an untreated dye, which can be released into the environment. Around 100,000 dyes are

currently in use by the global textile industry, and 7×10^5 ton of dyestuff is produced annually worldwide. Moreover, the effluent of textile industries has intense color, chemical oxygen demand (COD), suspended solids, and several refractory compounds like heavy metals [1]. Discharges of untreated dye effluent into the water body produce colored effluents that not only cause esthetic deterioration but also affect oxygen and nitrogen cycles through photosynthesis, and they may also be toxic to aquatic biota [2]. Indigo is a commercial dye used mostly for cotton cloth dyeing (blue jeans), and the main constituent is indigotin that is extracted from the leaves of *Indigofera tinctoria* [3–5]. Indigo carmine (IC; 3,3-dioxo-2,2-bis-indolyden-5,5-disulfonic acid disodium salt) is also one of the oldest dyes and still employed extensively today for dyeing cotton with annual consumption around 33 million kg [6]. The wastewater-containing indigo is characterized by a dark blue color due to cross-conjugated system or H-chromophore, consisting of a single –C=C– double bond substituted by two NH donor groups and two CO acceptor groups [7]. The structure of IC is shown in Figure 1.
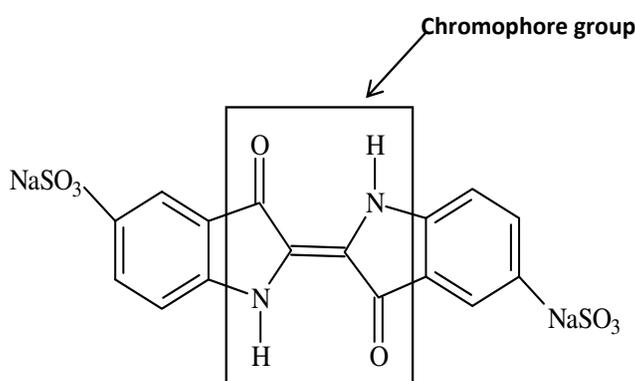

Figure 1. Chemical structure of Indigo carmine.

IC is a toxic dye once its contact with skin and eyes can cause permanent injury to cornea and conjunctiva. Moreover, the oral exposure can cause a disturbance in the reproductive, developmental, and neuronal systems [8]. Most toxic dyes are recalcitrant to biodegradation, causing a decrease in the efficiency of biological wastewater treatment plants. Furthermore, traditional physical–chemical methods have some operational problems such as sludge generation, membrane fouling, and phase change of the pollutants [2, 9]. To avoid these problems, the use of advanced oxidative processes (AOPs) for wastewater treatment from textile industries has been proposed. AOPs are emergent and promising processes for removal of persistent organic pollutants. The main factor in the degradation of pollutants is by the generation of highly oxidant and nonselective hydroxyl radicals ($^\bullet$OH) that promote the reaction of different classes of organic compounds. This technology can lead the complete mineralization or promote the formation of more biodegradable intermediates. The AOPs can be applied to a large set of different matrixes and that decontamination occurs through pollutants of degradation instead of their simple phase transfer. These methodologies become even more attractive when they use the sunlight as the source of energy [10, 11]. Although different advanced oxidation processes use several different reaction systems, all of them have the same chemical characteristic, i.e., the production and use of $^\bullet$OH [12–14].

Among AOPs, heterogeneous photocatalysis has been very attractive because the use of sunlight activated the process, allowing energy economy [15]. Heterogeneous photocatalysis produces oxidizing species able to promote degradation of organic pollutants through semiconductor as the catalyst. Typically, TiO_2, ZnO, CdS, and ZnS semiconductors are employed in photocatalysis due to the electronic structure. It has a fully occupied valence band (VB) and an empty conduction band (CB). In this way, excited electrons can be transferred to chemicals into the semiconductor particle environment, and at the same time, the catalyst accepts electrons of oxidized species [12, 13]. Photocatalysis action mechanism can be visualized in Figure 2.

The semiconductor (TiO_2) absorbs photons equal or higher than that of the band gap to promote an electron from the VB to the CB. Consequently, an electron/hole pair is formed as described by the following set of equations:

$$TiO_2 + \ hu \rightarrow h^+_{VB} + e^-_{CB} \tag{1}$$

The hole produced in the VB can oxidize the water presents in the medium producing $^\bullet OH$ and oxidize hydroxide ions or the substrate itself, according to Figure 2.
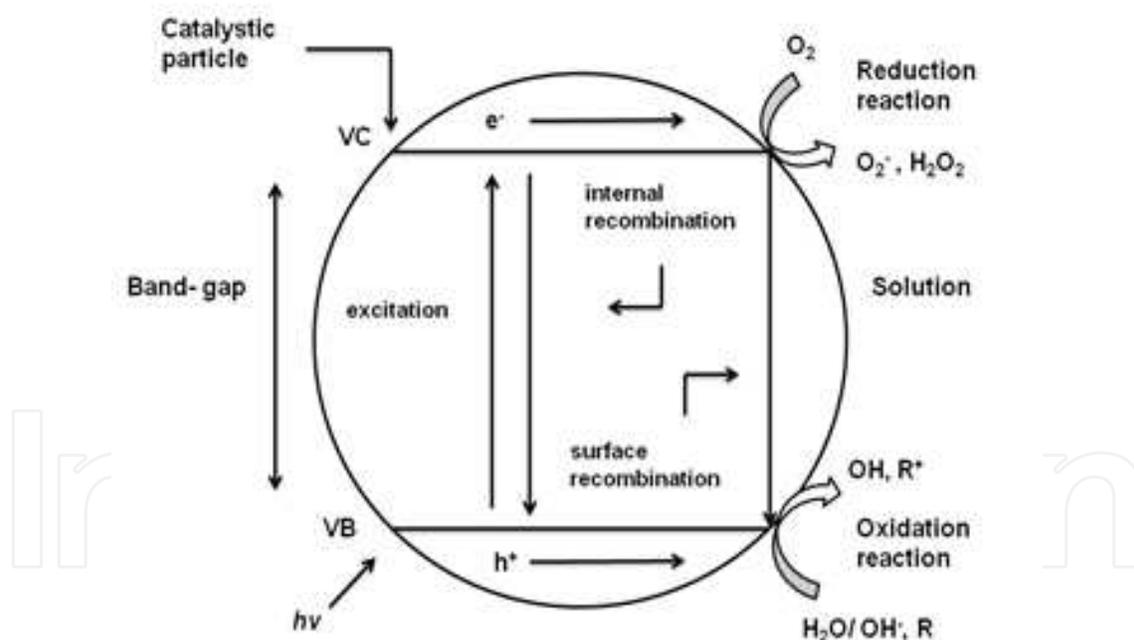

Figure 2. Mechanism of semiconductor (TiO_2) particle surface.

$$TiO_2\left(h^+_{VB}\right) \ + \ H_2O_{adsorv} \rightarrow TiO_2 + {}^\bullet OH_{adsorv} + \ H^+ \tag{2}$$

$$TiO_2\left(h^+_{VB}\right) \ + \ OH^-_{adsorv} \rightarrow TiO_2 + {}^\bullet OH_{adsorv} \tag{3}$$

$$TiO_2\left(h^+_{VB}\right) + RX_{adsorv} \rightarrow TiO_2 + RX\bullet^+_{adsorv} \tag{4}$$

Moreover, the electrons promoted to the CB are also able to reduce the oxygen available for superoxide radicals. Thus, the presence of oxygen is essential in all oxidative processes:

$$TiO_2\left(e^-_{CB}\right) + O_2 \rightarrow TiO_2 + O_2\bullet^- \tag{5}$$

Titanium dioxide is a well-known photocatalyst mostly used in photoreactions for wastewater treatment [16]. Fujishima and Honda [17] studied the heterogeneous photocatalysis of water extensively by TiO_2. As a consequence, several studies have reported the use of titanium dioxide as process able to degrade all persistent pollutants [18–23] and wastewater textile dyes from industries [24, 25]. The TiO_2 has low cost and toxicity, high photochemical reactivity, and non-specific oxidative attack. In this way, it can promote the degradation of organic compounds with little change of operational parameters [26]. TiO_2 has significant advantages for environmental application at the fact converted persistent organic molecules to safe oxidation products such CO_2 and H_2O [27]. Additionally, it can be used as an antibacterial agent due to its strong oxidation activity and hydrophilicity [28].

To perform a heterogeneous photocatalytic reaction is necessary to use semiconductors with the adequate "band gap" to be activated by solar energy. TiO_2 has a high band gap, of 3.2 eV, being consequently activated only by radiation below 380 nm. On the other hand, metal oxides, such as TiO_2, are resistant to photocorrosion with an adequate application on photocatalysis [28].

The decolorization of a model water effluent containing IC dye mediated by TiO_2 indicated that IC photodegradation depends on various parameters, e.g., the initial concentration of the dye, the amount of TiO_2, pH of the solution, the presence of inorganic anions, temperature, and the addition of different concentrations of hydrogen peroxide. Furthermore, the efficiency of the photocatalytic process strongly depends on the geometry of the photoreactor, which should enable all photocatalyst particles to be fully illuminated. Different photoreactors under artificial and solar irradiation were used, and their efficiency tested on the photodegradation of IC dye. On the other hand, photocatalytic degradation may generate photoproducts more toxic than their parent compounds. Thus, it is important to assess the toxicity of the resultant solution after treatment to determine potential threats to biodiversity of the treated waste to be released into the environment.

Although most of the experiments with IC reported in the literature were performed with the photocatalysts dispersed in water to enable the post-treatment photocatalysts removal, it is most important to use an immobilized catalyst. This chapter makes a comprehensive approach to the different results on the remediation of model effluents containing IC dye.

2. Heterogeneous photocatalysis degradation of Indigo carmine dye

2.1. Degradation of Indigo carmine dye under different geometry reactors

Heterogeneous photocatalysis processes require the maximum utilization of photons gener-ated by artificial light or solar irradiation. The photochemical solar technology included the geometry design reactors for efficient solar photon collections to promote the photodegrada-tion of organic pollutants presents on wastewater effluents [6]. The degradation of the IC dye was studied under different irradiation source and geometry reactors. Figure 3 shows the reactors that have been used to study the degradation at a laboratory bench top scale. First, Figure 3A shows a batch magnetically stirred reactor, irradiated with a high pressure of 125 W mercury vapor lamp (Reactor 1). Due to lamp geometry, a single point of stirring is applied. Second, Figure 3B shows a batch magnetically stirred with irradiation being ensured by four parallel 20 W daylight lamps; as light distribution is always identical below the lamps, multipoint stirring can be used (Reactor 2). The reactor presented on Figure 3C consists of a glass tubular continuous-flow reactor illuminated by one 20 W daylight lamp, fitted inside the tubular reactor (Reactor 3). The dye solution is pumped through this reactor, between lamp and inside's reactor wall, circulating to/from a storage beaker.
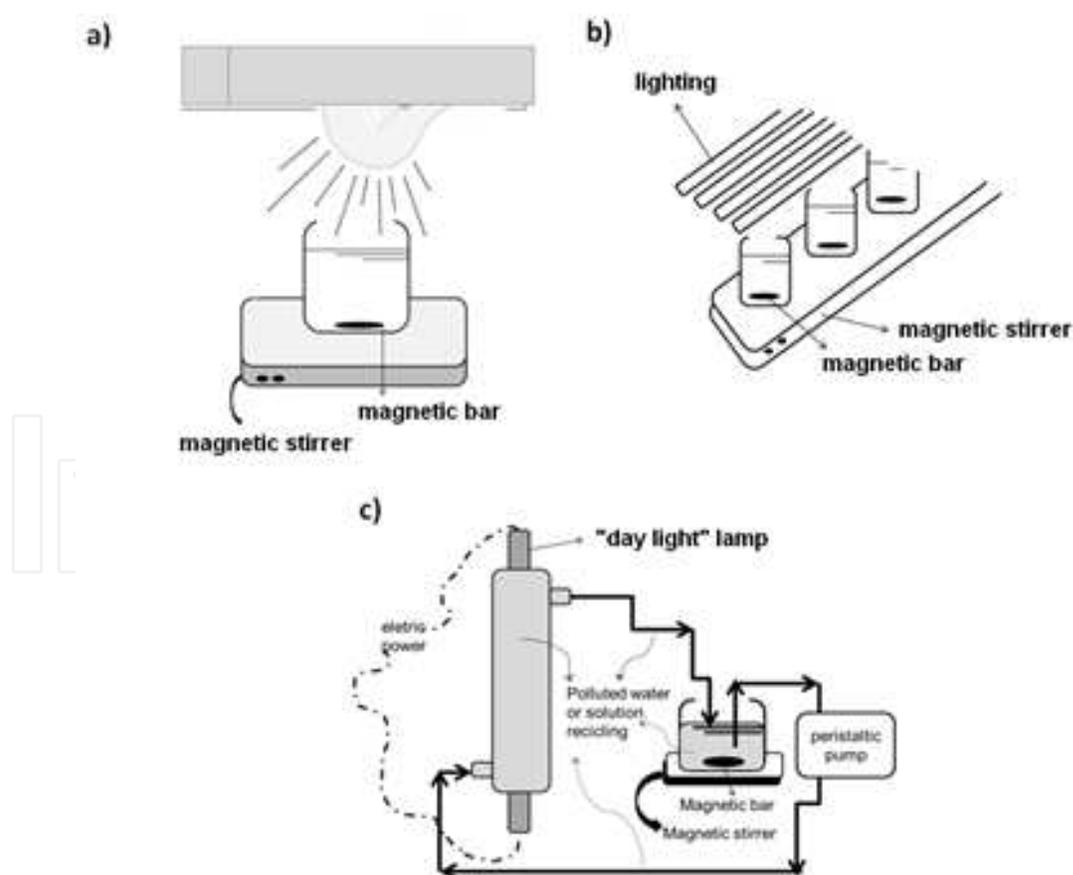

Figure 3. Reactors used on photocatalytic degradation of Indigo carmine dye in water [29].

In all cases, the efficiency of photocatalytic degradation of IC was directly related to the amount of photocatalyst. The optimum concentration of TiO$_2$ (i.e., the minimum photocatalyst concentration enabling the highest photodegradation rate) depended on the geometry of the photoreactor that should enable all photocatalyst particles to be fully illuminated. For improvement of the photocatalysis efficiency, especially under solar irradiation, an equipment that makes a more efficient collection of photons could be applied. This equipment, already a pilot plant reactor, is a solar collector coupled to the tubular reactor where degradation itself takes place, and it usually represents the largest source of operating costs of a photocatalysis unit for treatment of effluents. This reactor, whose simplified diagram is presented in Figure 4, is a tubular reactor with compound parabolic solar concentration. These reactors are static parabolic collectors with a parabolic reflective surface that have their axis (where sunlight concentrates the most) a tubular reactor, where wastewater to be remediated flows through as shown in Figure 4. They had demonstrated to provide an excellent efficiency in the treatment of low pollutant's concentration effluents [29].
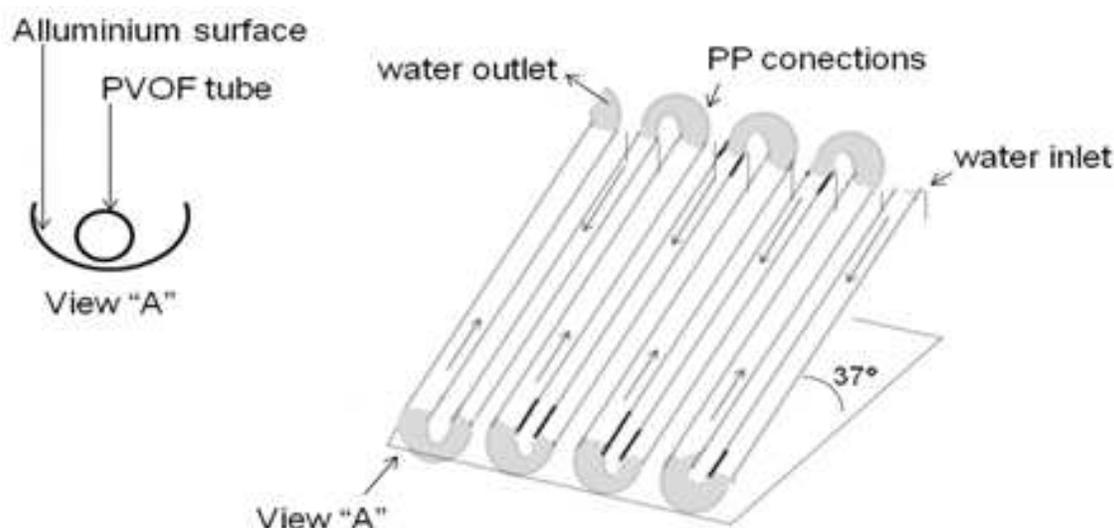

Figure 4. Simplified diagram of a compound parabolic collecting (CPC) reactor (CPC) [29].

Reactor 1 demonstrated the best results in photocatalytic degradation for IC. Photocatalysis efficiency at 96% and 92% was achieved in 30 minutes for concentrations of 1 g L^{-1} and 1×10^{-1} g L^{-1} of TiO$_2$, respectively. On the other hand, the photodegradation on Reactors 2 and 3 was very slower with 100% of IC degradation at 1440 minutes of irradiation time under the same TiO$_2$ concentrations [29]. The results obtained for Reactor 1 were very similar to the ones obtained under sunlight irradiation during summer because the photon flux used in both processes was similar. It is possible to replace artificial light source by natural solar light irradiation with the same efficiency. Furthermore, experiments carried out in winter months also demonstrated reasonable efficiencies. The photolysis of the dye was negligible for the compound parabolic reactor (CPC) like for the experiments in batch lab reactors. On the other hand, in distilled water, its photodegradation was observed to be complete for an accumulated UV energy of 15 kJ L^{-1}, correspondingly approximately to only 12 minutes of irradiation time [29].

The absorbance of the IC dye at 610 nm decreased gradually with prolonged light exposure due to an increase in decolorization and light-induced degradation. Figure 5 shows the fast decolorization of 610 nm and also the changes of the spectra in the UV region. The decolorization of IC solutions is associated with the cleavage of double-bond carbon (–C=C–), characteristic of indigoid dye molecules (Figure 1) [30]. Absorption in the UV region can be assigned to the aromatic rings and exhibited peaks at 286 and 250 nm [31]. The intermediates may have been formed as demonstrated the changes of indigo dye UV–visible spectra. Lower molecular weight (MW) organic compounds or carbon dioxide probably is the most intermediates formed by oxidation of original IC structure [32].
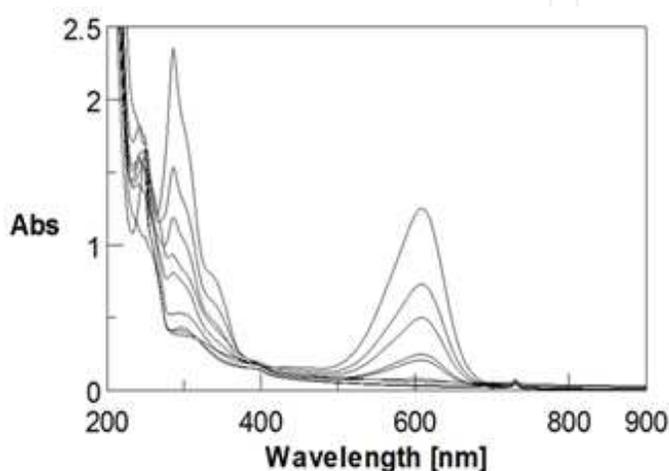

Figure 5. Time dependent UV–visible spectrum of Indigo carmine. Initial concentration of IC: 30 mg L^{-1}; dosage of TiO$_2$: 1×10^{-2} g L^{-1}. Spectra from top to bottom correspond to irradiation times of 0, 15, 30, 45, 60, 90, 120, 180, and 300 min, respectively. Experiments performed with Reactor 1, in Figure 3A [29].

The solar irradiation batch lab experiments were very helpful to establish the best conditions for different geometries and light source for the photodegradation of IC dye. It facilitates the correspondence between various reactors with artificial irradiation and solar irradiation on the photodegradation of IC dye [29]. The summarized results indicate the feasibility of solar photocatalysis with TiO$_2$ to the treatment of IC effluents from a textile industry, mainly in regions with available sunlight throughout the year. Moreover, titanium dioxide application to be activated by sunlight is compatible with the green chemistry principles [32].

2.2. Influence of different parameters on the photodegradation of Indigo carmine dye

2.2.1. Effect of catalyst amount

The effect of the TiO$_2$ amount on the photocatalytic degradation of IC was evaluated. Moreover, the significance of adsorption on the catalyst surface should also be assessed from results obtained in the absence of light. The IC adsorption on TiO$_2$ was found to be about 10% after 90 minutes of contact, and adsorption/desorption equilibrium time was 30 minutes in the dark. The color of indigoids dyes is influenced by the presence of associated chromophores and

auxochromes groups. IC can be oxidized by positive hole or $^\bullet$OH or reduced by electrons in the CB where all processes were leading to the decrease in the color of water [7].

The photocatalysis efficiency is apparently directly proportional to the amount of photocatalyst used, according to Figure 6. These results can be rationalized regarding an availability of active sites on TiO_2 surface and on the light penetration for activation of TiO_2 suspensions [24]. Moreover, in suspensions containing 1 g L^{-1} of TiO_2 (first-order kinetic = 0.8442 min^{-1}), the depth of light penetration is considerably smaller than in those containing only 0.1 g L^{-1} of TiO_2 (first-order kinetic = 0.9002 min^{-1}). However, the availability of active sites is much higher. Additionally, agglomeration and sedimentation of TiO_2 particles also occur in suspensions containing a high concentration of TiO_2 [33]. In this way, the optimum amount of TiO_2 has to be determined for each solution to be treated to avoid the unnecessary use of a catalyst in excess.
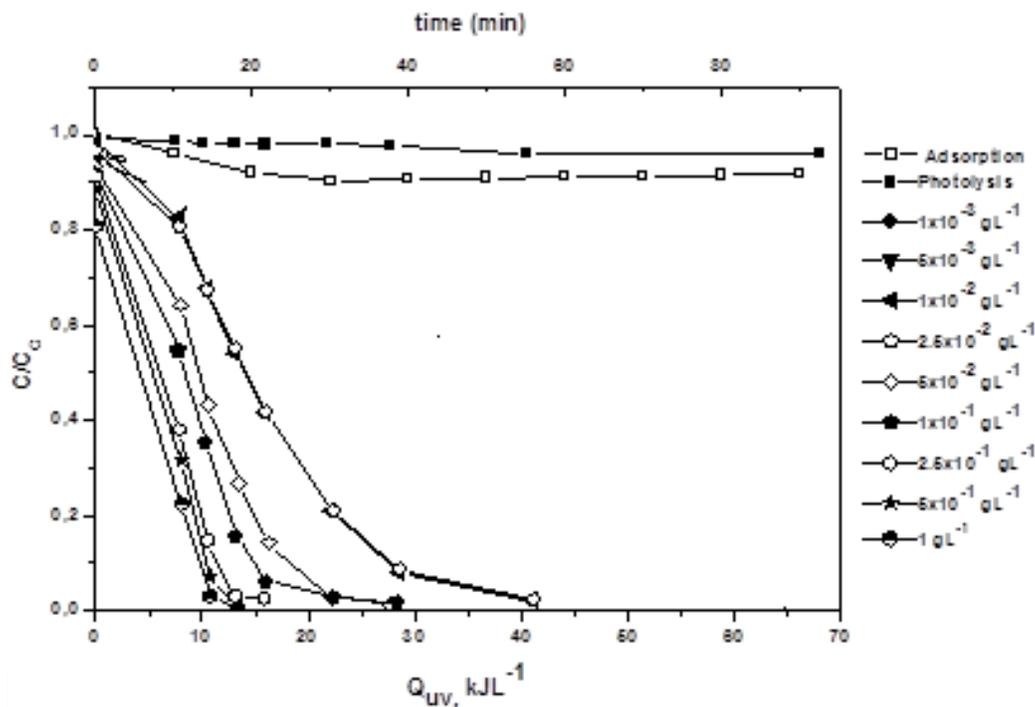

Figure 6. Effect of TiO_2 suspension concentration on the photocatalytic degradation of 30 mg L^{-1} of IC [34].

2.2.2. Effect of initial dye concentration

The photocatalytic degradation of the dye decreased with increase in its concentration in the sample solution. The reduction in the photodegradation rate constant can be attributed to adsorption of dye molecules on the catalyst surface and consequent decrease on the generation of $^\bullet$OH radicals because the active sites were occupied by dye cations [35]. Also, a significant amount of light may be absorbed by the indigo dye rather than TiO_2. Probably reducing the efficiency of the catalytic reaction, the concentration of oxidant species decreases [36]. Another possible cause of the decline of decolorization is the competition between intermediate

products formed in photocatalytic processes for the limited adsorption and catalytic site on the surface of TiO_2 [37].

2.2.3. Effect of inorganic ions

Several anions commonly used in dye-containing industrial wastewater such as Cl^-, HCO_3^-, SO_4^{-2}, and HPO_4^{-2} should be tested. Dissolved inorganic ions may compete for the active sites on the TiO_2 surface or deactivate the photocatalyst and, subsequently, decrease the degradation efficiency [38]. In the same approach, Chen et al. [39] found that the addition of H_2PO_4 and HCO_3 significantly inhibited the degradation of Acid Orange 7 in the TiO_2 system.

For IC photodegradation, the inhibition of decolorization is exhibited:

$$HCO_3^- < Cl^- < HPO_4^{-2} < SO_4^{-2} \qquad (6)$$

Inhibition effect of anions can be explained as the reaction of positive holes (h_{vb}^+) and resulting from the high reactivity and non-selectivity of $^\bullet OH$ toward non-target compounds present in the water matrix. The HCO_3^- and Cl^- ions were with less inhibition effect on IC decolorization. In TiO_2/UV system, HCO_3^- can trap $^\bullet OH$ to produce $CO_3^{\bullet -}$, which is less reactive [40]. This reaction appears to be of minor importance on the photodegradation of the IC. Additionally, in the case of Cl^- under neutral or alkaline conditions, the addition of Cl^- ion did not influence the reaction [41]. On the other hand, the SO_4^{-2} ions demonstrated more inhibition on the decolorization rate because it is possible for a high competitive adsorption of the dye on the TiO_2 surface, and they can trap both positive holes (h^+) and $^\bullet OH$ [41].

2.2.4. Effect of temperature

The IC photodegradation is temperature dependent, and it decreases with the rise of solution temperature.

It is known that an increase in temperature can affect the efficiency of e^-/h^+ recombination and adsorption/desorption processes of dye molecules on the TiO_2 photocatalyst surface [42]. Some of the most important surface phenomena are dye molecule aggregation, tautomerization, and geometric (*cis–trans*) isomerization, and all those processes can be affected by temperature variation. The increase in solution temperature causes disaggregation of the dye molecules [24].

Habib et al. [24] considered MW and anion site (sulfate and a carboxylic group), which can interact with molecules by ion–dipole interactions. According to these authors, the dye has low MW and less anionic showed a significant variation under different temperatures. Consequently, the change of the temperature of the solution has a significant effect on the effective collisions between dyes and the TiO_2 photocatalyst. In this case, the IC molecules possess a comparatively low MW (466.36 g mol^{-1}) and only two anion sites (sulfate groups). Therefore, the variation of the temperature should also affect its photodegradation.

2.2.5. Effect of hydrogen peroxide addition

The principal problem found in most photocatalysis processes using TiO_2 is the undesired electron/hole recombination, which represents the major energy-wasting step, thus restricting the feasible quantum yield of the photodegradation process. Hydrogen peroxide is an electron donor favoring the photocatalytic process inhibiting electron–hole recombination [43]. In this sense, the effect of H_2O_2 on the photocatalytic degradation of IC is examined. It was noted that when the hydrogen peroxide concentration increases, the photodegradation suffers an initial increase up to H_2O_2 0.022M and decrease at higher concentrations. Hydrogen peroxide at low concentration acts mainly as a source of $^\bullet OH$ and as an electron scavenger inhibiting the electron–hole recombination (Eq. 7) [44].

$$H_2O_2 + e^-_{CB} \rightarrow OH\bullet + OH^-$$
(7)

However, at higher concentrations, H_2O_2 reacts with $^\bullet OH$ and acts itself as a scavenger of the photoproduced holes. The H_2O_2 excess acts itself as a scavenger of the photoproduced holes. In this way, they behave like the self-quenching process of $^\bullet OH$ to form hydroperoxyl radicals ($OOH^\bullet$) (Eq. 8), where oxidation potential is much lower than that of $^\bullet OH$ [45], leading to a decrease in the photocatalytic efficiency.

$$H_2O_2 + {}^\bullet OH \rightarrow H_2O + {}^\bullet OOH$$
(8)
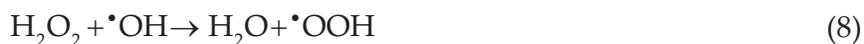
The optimum dosage of H_2O_2 is variable and has been reported that it was dependent on the initial dye concentration.

2.2.6. Effect of Initial pH

The effect of pH changes on the photodegradation rate is studied in the range of pH 2–11. The photocatalytic reaction occurs on the surface of the catalyst and is dependent on TiO_2 surface charge. In this way, the adsorptive properties of TiO_2 particles depended strongly on the solution pH [46]. The degradation of IC is faster in acid solutions (i.e., pH ranges from 2 to 5). At neutral and basic medium, the rate of dye degradation is slow, nevertheless in accumulated energy of Q_{uv} 70 kJ L^{-1}, all IC solutions are degraded. This effect can be explained by the surface charge density of TiO_2. The point of zero charge (pzc) of TiO_2 is at pH = 6.8. Thus, the TiO_2 surface is fully protonated in medium acidic solution and negatively charged under alkaline conditions (Eqs. 9 and 10) [47]:

$$pH \ < \ pzc : \Leftrightarrow TiOH + H^+ TiOH_2^+$$
(9)

$$pH \ < \ pzc : \Leftrightarrow TiOH + OH^-\ TiO^- + H_2O$$
(10)
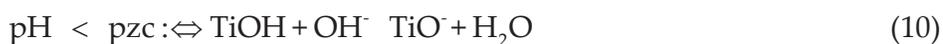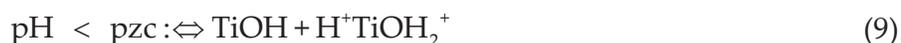
Considering the IC structure has sulfuric groups, which are negatively charged, at pH < 5.0, the positive charge through protonation (Eq. 9) on the photocatalyst surface promotes active interaction of a dye onto the catalyst surface and improves the photocatalytic degradation. On the other hand, for the basic solutions (pH > pzc), the surface of the catalyst is negatively charged through the proton abstraction by hydroxide ion (Eq. 10). Consequently, repulsions between a negative-charged surface of the catalyst and anionic dye fragments retard the surface adsorption, resulting in a low-photodegradation activity [48].

2.2.7. Effect of water matrix

In distilled water IC degradation is observed to be complete for an accumulated UV energy of 15 kJ L^{-1}, correspondingly ~12 minutes of irradiation time. However, for complex matrices of water like freshwater and simulated municipal wastewater treatment plant (MWWTP) secondary effluent, the degradation of the dye is slower. The freshwater and simulated MWWTP secondary effluent required ~25 kJ L^{-1} for complete photodegradation. When a real MWWTP secondary effluent was carried out, the complete IC photodegradation occurred at accumulated energy around 33 kJ L^{-1}. It is demonstrated that as the matrix more complex, the degradation rate of organic compounds is slower. This fact can be explained the presence of carbonate species on real wastewater that act as scavengers of the $^{\bullet}$OH generated on photocatalysis [49], as showed in Figure 7. Table 1 exhibited a high concentration of inorganic carbon in the real effluent, which is widely found in real wastewater [50].

Type of water	Inorg. Carbon (ppm)	TOC (ppm)	COD (ppm)	pH	Conduc. (µs cm^{-1})	Ionic species (mM)							
						Na$^+$	Ca^{+2}	Mg^{+2}	K$^+$	NH^{+4}	PO$_4$ $^{-3}$	Cl$^-$	SO$_4$ $^{-2}$
Fresh water	13.89	3.40	11.6	7.4	206	0.76	0.36	0.44	0.1	–	–	0.09	0.04
Synthetic MWWTP secondary effluent	9.98	17.76	57.59	8.0	261	1.27	0.36	0.45	0.17	0.35	0.01	0.04	0.93
Real MWWTP secondary effluent	69.92	26.9	81.2	8.3	1504	8.2	1.5	1.3	0.63	2.96	0.05	9.94	1.02

Table 1. Characteristics physical and chemical of different water matrices [29]

The total degradation of organic dyes leads to the conversion of organic carbon into gaseous CO$_2$, whereas nitrogen and sulfur heteroatoms are converted into inorganic ions, such as nitrate or ammonium and sulfate ions, respectively. In distilled water, the mineralization of the IC dye was completed around 90 kJ L^{-1} of accumulated energy. When complex matrices
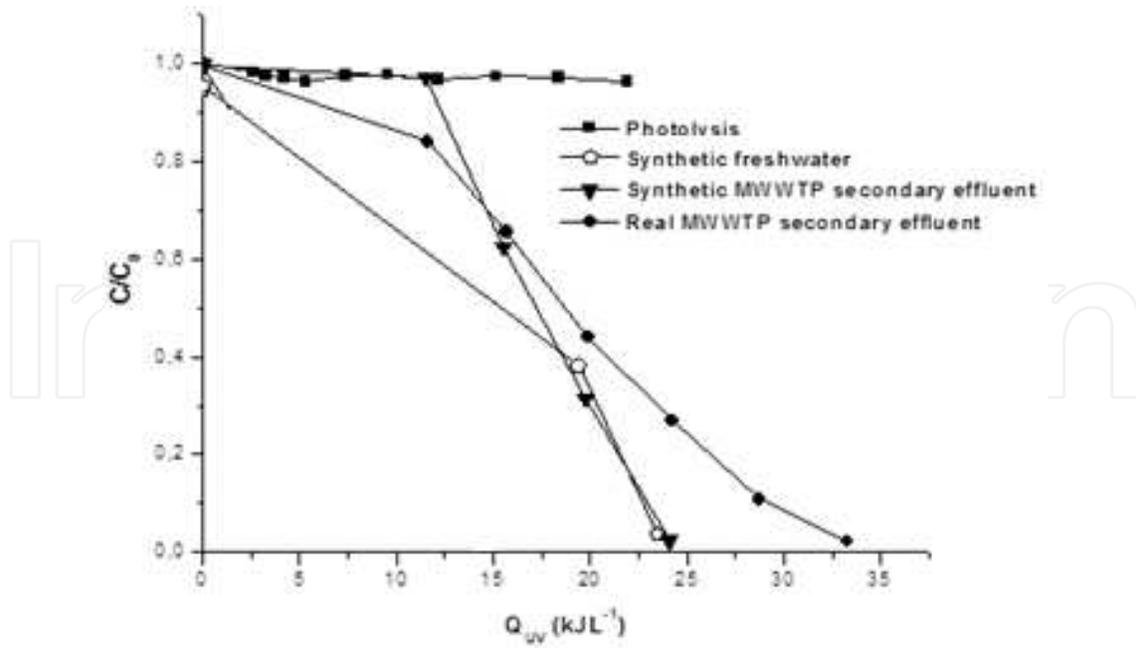
Figure 7. Photodegradation of Indigo carmine for different type of water mediated by 0.1 g L^{-1} of TiO$_2$ suspensions [29].

were tested, the mineralization was not complete. However, considering the theoretic TOC of the IC (12 mg L^{-1}) and initial TOC of the matrices (see Table 1), the dye was totally mineralized even in the presence of scavenger species [29].
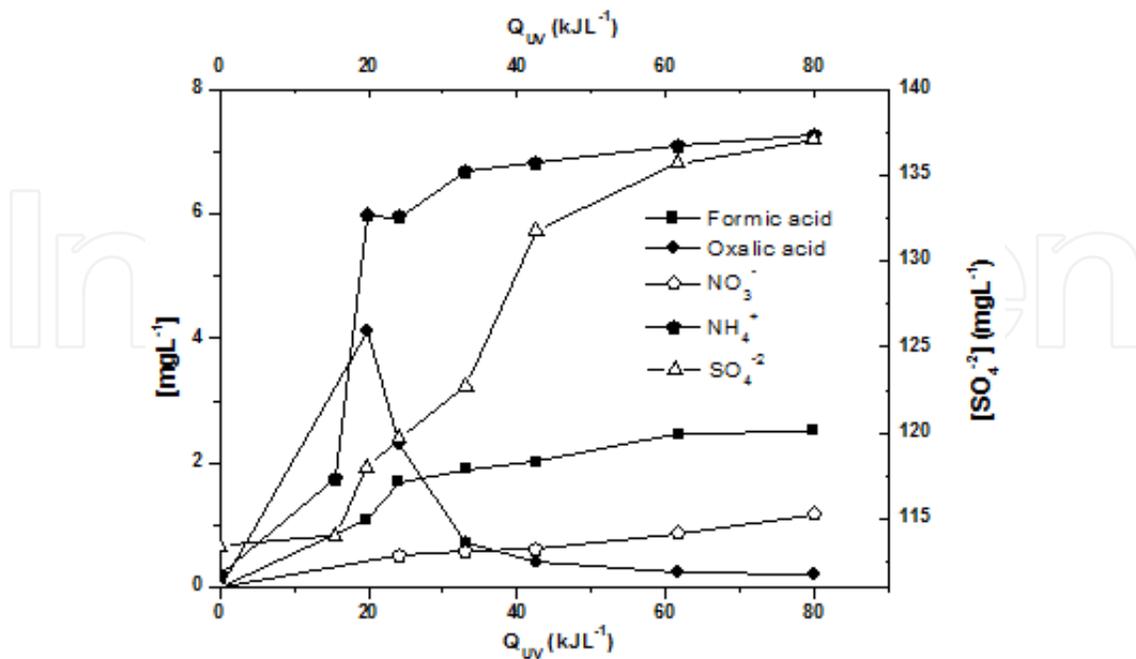

Figure 8. Ions and carboxylic acid concentrations formed during photodegradation of Indigo carmine [29].

The structure of IC dye has two sulfonic groups attached to two aromatic rings, and these results indicate that SO_4^{-2} ions are formed during the process. However, the sulfate ion concentration is lower than expected from theory stoichiometry, because by adsorption of SO_4^{-2} at the surface of titanium dioxide [51]. The evolution of NH_4^+ suggests that this ion is the primary N-containing mineralization product. It indicates its origin as first products resulted from the initial attack on the carbon-to-carbon double bond of IC. The formic and oxalic acids remain for the UV-accumulated energy of 80 kJ L^{-1} indicating the evaluation of ecotoxicology tests, according to Figure 8.

2.2.8. Recycling of TiO₂

One of today's main industrial wastewater treatment strategies is focused on the development of green technologies and management practices for environmental benefit. To attend this "new"concept, the recycling of the photocatalyst should be performed. In this study, the TiO_2 catalyst was recycled for consecutive reuse on this procedure up to eight times [34].

According to the results (Figure 9), the effectiveness of the TiO_2 decreased from 98% (first cycle) to 80% (fifth cycle) and subsequently to 50% (sixth cycle onward). However, the rate of degradation was kept significant even after eight cycles of TiO_2 reuse. The effectiveness of complete separation of photocatalysts from treated water is a critical step required to maintain a satisfactory degradation [52]. Moreover, agglomeration and sedimentation of IC around TiO_2 particles after each cycle of photocatalytic degradation are a possible cause of the observed decrease in its efficiency [53]. This study further shows that the reuse of the TiO_2 presents a promising photocatalytic performance with little variation of decay rate after eight consecutive usages and also high photochemical stability.
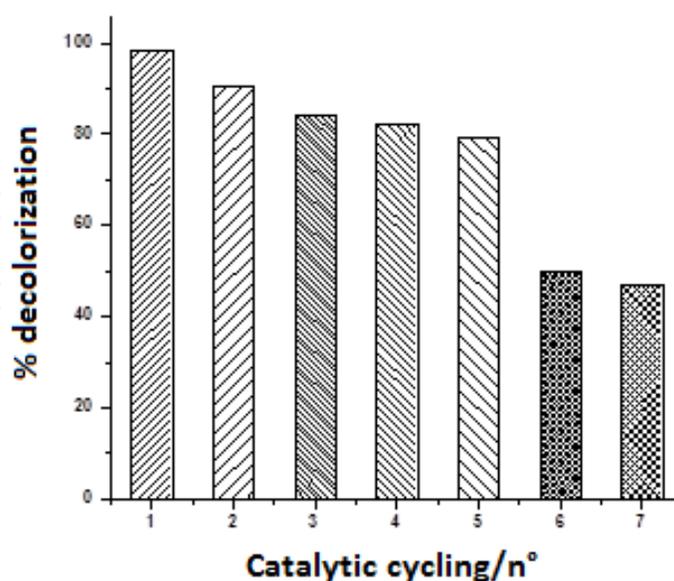

Figure 9. Recycling and reuse of TiO_2 on the photocatalytic degradation of Indigo carmine for an accumulated energy, Q_{uv}, of 15 kJ L^{-1} [34].

2.3. Supported TiO$_2$ on photodegradation of Indigo carmine dye

In the large-scale applications, the use of TiO$_2$ suspensions requires the separation and recycling of TiO$_2$ particles, mainly of nanometric dimension, from treated wastewater before discharge into the water bodies. This fact can be a great drawback for the application of this treatment once it is a time-consuming and an expensive process. Alternatively, the catalyst may be immobilized on a suitable solid inert material, which eliminates the need for catalyst removal step [1] and permits its reuse for several times.

On another study [29], the solar CPC photocatalytic degradation of IC using TiO$_2$ slurry for a treatment of real MWWTP secondary effluent demonstrated the greater efficiency of this procedure than with supported TiO$_2$. Probably, this indicates that the catalyst coated on glass spheres is not fully illuminated. Indeed, there are large amounts of TiO$_2$ particles inside the CPC tube, and a considerable amount of TiO$_2$ supported on glass spheres having some sites not activated for photocatalysis and lower surface area of the catalyst. However, supported TiO$_2$ has the enormous advantage of eliminating the catalyst removal step and thus reducing the costs of treatment considerably.

It should be emphasized that the decrease in the color of the IC solutions not provide complete data on the IC dye degradation. The TOC decrease suggests that during the irradiation processes of supported TiO$_2$, a large number of low MW compounds are formed. Furthermore, hydroxylation of aromatic reaction products leads to cleavage of the aromatic ring, resulting in the formation of oxygen-containing aliphatic compounds [31]. On the other hand, after the fading stage, a breakdown of carbon-to-carbon double bond of IC may form inorganic ions. Formate, acetate, and oxalate are detected during degradation in real MWWTP secondary effluent containing IC as shown in Figure 10.
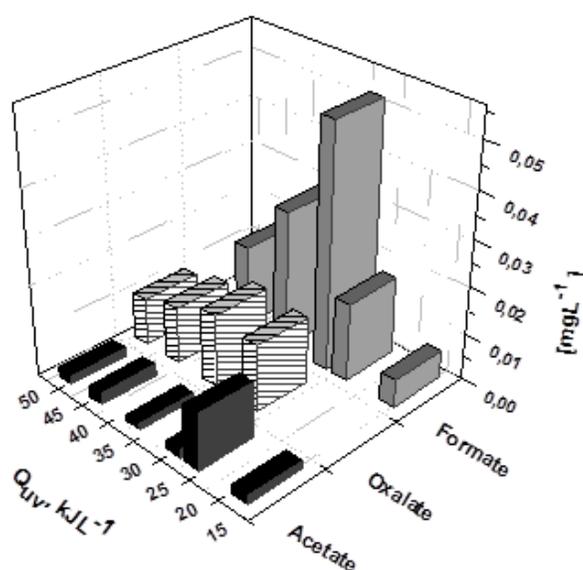

Figure 10. Evaluation of the concentrations of carboxylic acids followed by ion chromatography; formed during solar CPC photodegradation of Indigo carmine with supported TiO$_2$ in real MWWTP secondary effluent [34].

2.4. Decolorization of Indigo carmine dye using activated carbon/TiO$_2$/UV

First, the use of activated carbon (AC) is an efficient water and wastewater treatment; the treatment is based on the use of adsorbent substrates and has many applications on textile dye's wastewater treatments [54]. AC is probably the most versatile adsorbent because of its large surface area, polymodal porous structure, high adsorption capacity, and variable surface chemical composition. Furthermore, what makes ACs attractive to (textile) wastewater treatment is the possibility of tailoring their physical and/or chemical properties to optimize their performance on top of its, already powerful, strong hydrophobic and amorphous character [55]. The synergic role of AC with TiO$_2$ is also a parameter to investigate once it opens the opportunity to combine adsorption and photocatalytic remediation. In this way, the decolorization of the model effluent containing indigo dye is revised using AC in the dark and under irradiation and AC/TiO$_2$/UV.

The AC is used in two different situations. First, the AC in various concentrations is add in the solution of IC dye and kept in the dark. Furthermore, AC is submitted to the same conditions but kept under artificial irradiation during the all-time experiment. Similar decolorization rates are obtained when comparing experiments with different amounts of AC in the dark. Only in high concentrations, AC is able to remove the dye, but in this case, the determinant removal mechanism is adsorption of the dye in AC microporous structure. On the other hand, AC is not able to produce strong photocatalytic activity and had only adsorptive properties with an adsorption capacity of 28.5 mg IC per gram of carbon. The decolorization of AC/TiO$_2$/UV following the same profile of TiO$_2$/UV, but the constant K in TiO$_2$/UV was by itself more efficiency when compared with AC/TiO$_2$/UV. TiO$_2$ activity decreased in the presence of AC not only because AC can absorb light—i.e., by reducing the light flux in the sample—but also because AC can adsorb TiO$_2$, reducing the amount of photocatalyst available.

2.5. Ecotoxicological assessment

Photocatalytic degradation may generate toxic photoproducts. Thus, it is important to assess the toxicity of the solution after treatment. The ecotoxicological tests of IC and its photoproducts obtained by photocatalytic remediation treatment were evaluated. Two essays, two aquatic organisms, and one terrestrial organism were used. Aquatic organism represented by algae *Pseudokirchneriella subcapitata* (Chlorophyceae), a primary consumer *Daphnia similis* (Cladocera), and earthworm *Eisenia andrei* as terrestrial organism [29, 56, 57].

For all organisms, ecotoxicity tests are performed comparing the effects of solutions containing IC before and after photocatalytic treatment with TiO$_2$. Chronic toxicity tests with *P. subcapitata* indicated no significant toxic effect for any tested samples (Table 2), but sample containing IC, the sample with photoproducts in pH 7 and sample with TiO$_2$ filtered strongly stimulated algal growth indicating nutritional effects. Thus, the release of IC dye or its photoproducts into aquatic ecosystems may be expected to cause algal growth.

The species *D. similis* had a different response. Acute toxicity tests showed that IC dye caused a low toxicity, but photoproducts are highly toxic (Table 2). Photoproducts in pH 4 and 7, respectively, caused a mortality of 100%. According to Vautier et al. [7], photocatalysis of IC

Samples	*P. subcapitata* chronic test		*D. similis* acute test	
	Mean ± SD (#cells ml⁻¹)	Observed	Mortality (%)	pH
		Response		
Blank	119± 5	None	0	7.8
Indigo carmine only	315± 99	164% growth	20	7.1
Photoproducts generated by TiO₂ photocatalysis (pH 4)	113± 20	5% inhibition	100	4.2
Photoproducts generated by TiO₂ photocatalysis (pH 7)	395± 48	231% growth	100	7.0
Indigo carmine + TiO₂ ⁻ without photodegradation (time 0)	135± 15	13% growth	0	7.1
TiO₂ + ultrapure water	389± 37	227% growth	20	7.2

Table 2. Number of *Pseudokirchneriella subcapitata* cells per ml after 72h exposition, and percent immobilization of *Daphnia similis* after 48h exposition [29]

produces mainly aromatic metabolites such as 2-nitrobenzaldehyde and anthranilic. Moreover, carboxylic acids fragments are also present, such as malic and tartaric acids [29]. On the other hand, studies demonstrated that in the presence of TiO_2, absorption of some toxicants can be increased [29, 58]. In this approach, it a significant challenge to complete the removal of nano-TiO_2 after releasing treated effluents to prevent its contamination of aquatic ecosystems [29].

Furthermore, terrestrial acute ecotoxicological tests with *E. andrei* earthworms are performed. The earthworms are affected by various organic and inorganic compounds, which may cause bioaccumulation, and their preliminary results serve as a rapid indicator of the toxicity of the compounds. Moreover, it can be used as a complementary test for risk assessment of polluted areas [59]. Effects of different IC concentration and its photoproducts on earthworms are studied. In all cases, no mortality is observed. No significant difference ($p > 0.05$) of a reduction in mean weight earthworms is found from the paper treated with different concentrations of IC. Toxicity tests with earthworms are also carried out for the photodegradation products of IC, and no mortality is observed after 24 h exposure to different treatments. These results suggest that the presence of IC and its photoproducts do not demonstrate an effect on the earthworms for acute contact test (24 h). However, more tests must be performed for a better understanding of the IC toxicity for *E. andrei*.

3. Conclusions

Photodegradation of IC by TiO_2 was successful to remove colour from water; nevertheless, the degradation of IC in water with powdered TiO_2 depends on various parameters. Among the systems evaluated, the Reactor 1 (125 W mercury vapour lamp) was the most efficient. Solar

photocatalysis demonstrated better efficient in the summer but degraded the dye in the winter completely; then both seasons allow the solar photocatalysis efficient. CPC pilot plant photocatalysis simulated real situations of environmental remediation, reducing the duration and costs of the treatment. Moreover, a TiO_2 catalyst supported on glass spheres proved to have high efficiency to remove IC in different water matrices even in the presence of various ions that acted as scavengers. Ecotoxicological tests revealed that photoproducts generated on photocatalysis promoted different biological responses to both tested organisms as growth effect on the algae and toxicity higher for *D. similis*. These results show the importance of photoproducts toxicity evaluation and the need for a complete removal process for TiO_2 before its release in the environment.

Author details

Enrico Mendes Saggioro[1*], Anabela Sousa Oliveira[2,3] and Josino Costa Moreira[4]

*Address all correspondence to: enrico.saggioro@ensp.fiocruz.br

1 Department of Sanitation and Environmental Health, National School of Public Health, Oswaldo Cruz Foundation, Rio de Janeiro, Brazil

2 Interdisciplinary Centre for Research and Innovation, School of Technology and Management, Polytechnic Institute of Portalegre, Portalegre, Portugal

3 Molecular Physical Chemistry Center and Institute of Nanoscience and Nanotechnology, Instituto Superior Técnico, Technical University of Lisbon, Lisbon, Portugal

4 Studies Center of Occupational Health and Human Ecology, National School of Public Health, Oswaldo Cruz Foundation, Rio de Janeiro, Brazil

References

[1] Barka N, Assabbane A, Nounah A, Aîlchou Y. Photocatalytic degradation of Indigo carmine in aqueous solution by TiO_2-coated non-woven fibres. J Hazard Mater. 2008;152:1054–59. DOI: 10.1016/j.jhazmat.2007.07.080.

[2] Zainal Z, Hui LK, Hussein MZ, Taufiq-Yap YH, Abdullah AH, Ramli I. Removal of dyes using immobilized titanium dioxide illuminated by fluorescent lamps. J Hazard Mater. 2005;125:113–20. DOI: 10.1016/j.jhazmat.2005.05.013.

[3] Behnajaday MA, Modirhahla N, Daneshvar N, Rabban M. Photocatalytic degradation of an azo dye in a tubular continuous-flow photoreactor with immobilized TiO_2 on glass plates. Chem Eng J. 2007;127:167–76. DOI: 10.1016/j.cej.2006.09.013.

[4] Robinson T, McMullan G, Marchant R, Nigam P. Remediation of dyes in textile efflu-ent: a critical review on current treatment technologies with a proposed alternative. Bioresour Technol. 2001;77:247–55. DOI: 10.1016/S0960-8524(00)00080-8.

[5] Andreotti A, Bonaduce L, Colombini MP, Ribechini E. Characterisation of natural in-digo and shellfish purple by mass spectrometric techniques. Rapid Commun Mass Spectrom. 2004;18:1213–20. DOI: 10.1002/rcm.1464.

[6] Oliveira AS, Saggioro EM, Barbosa NR, Mazzei A, Ferreira LFV, Moreira JC. Surface photocatalysis: a study of the thickness of TiO_2 layers on the photocatalytic decompo-sition of soluble Indigo Blue dye. Rev Chim. 2011;62:462–68.

[7] Vautier M, Guillard C, Herrmann J. Photocatalytic degradation of dyes in water: case study of Indigo carmine. J Catal. 2001;201:46–59. DOI: 10.1006/jcat.2001.3232.

[8] Jenkins CL. Textile dyes are potential hazards. Arch Environ Health. 1978;40:7–12.

[9] Sanromán MA, Pazos M, Ricart MT, Cameselle C. Electrochemical decolourisation of structurally different dyes. Chemosphere. 2004;57:233–39. DOI: 10.1016/j.chemo-sphere.2004.06.019.

[10] Sano T, Puzenat E, Guillard C, Geantet C, Matsuzawa S. Degradation of C_2H_2 with modified-TiO_2 photocatalysts under visible light irradiation. Journal of Molecular Catalysis A: Chemical. 2008;284:127–133. DOI: 10.1016/j.molcata.2008.01.014.

[11] Khataee V, Vatanpour V, Amani AR. Decolorization of C.I. acid blue 9 solution by UV/nano-TiO_2, Fenton, Fenton-like, electro-Fenton and electrocoagulation processes: a comparative study. Journal of Hazardous Materials. 2009;161:1225–1233. DOI: 10.1016/j.jhazmat.2008.04.075.

[12] Eckenfelder WW. Industrial Water Pollution Control. 3rd ed. McGrawHill; 2000. 600 p. ISBN: 978-0070393646.

[13] Metcalf & Eddy. Wastewater Engineering – Treatment and Reuse. 4rd ed. McGraw-Hill; 2003. 1848 p. ISBN: 0-07-124140X.

[14] Linsebigler AL, Lu G, Yates JT. Photocatalysis on TiO_2 surfaces: principles, mecha-nisms and selected rules. Chemical Review. 1995;95:735–768.

[15] Zhao J, Wu T, Wu K, Oikawa K, Hidaka H, Serpone N. Photoassisted degradation of dye pollutants. 3. Degradation of the cationic dye rhodamine B in aqueous anionic surfactant/TiO_2 dispersions under visible light irradiation: evidence for the need of substrate adsorption on TiO_2 particles. Environmental Science & Technology. 1998;32:2394–2400. DOI: 10.1021/es9707926.

[16] Fujishima A, Rao TN, Tryk DA. Titanium dioxide photocatalysis. Journal of Photo-chemistry and Photobiology C: Photochemistry Reviews. 2000;1:1–21.

[17] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor elec-trode. Nature. 1972;238:37–8. DOI: 10.1038/238037a0.

[18] Mao K, Li Y, Zhang H, Zhang W, Yan W. Photocatalytical degradation of 17-ethiny-lestradiol and inactivation of *Escherichia coli* using Ag-modified TiO_2 nanotube ar-rays. Clean – Soil Air Water. 2013;41:455–462. DOI: 10.1002/clen.201100698.

[19] Ghosh JP, Achari G, Langford CP. Reductive dechlorination of PCBs using photoca-talyzed UV light. Clean – Soil Air Water. 2012;40:455–460. DOI: 10.1002/clen.201100186.

[20] Beduk F, Aydin ME, Ozcan S. Degradation of malathion and parathion by ozonation, photolytic ozonation and heterogeneous catalytic ozonation processes. Clean – Soil Air Water. 2012;40:179–187. DOI: 10.1002/clen.201100063.

[21] Martins AF, Mayer F, Confortin EC, Frank CS. a study of photocatalytical processes involving the degradation of the organic load and amoxicillin in hospital wastewater. Clean – Soil Air Water 2009;37:365–371. DOI: 10.1002/clen.200800022.

[22] Kist LT, Albrecht C, Machado EL. Hospital laundry wastewater disinfection with cat-alytic photoozonation. Clean – Soil Air Water. 2008;36:775–780. DOI: 10.1002/clen.200700175.

[23] Oliveira AS, Maia CG, Brito P, Boscencu R, Socoteanu R, Ilie M, Ferreira LFV. Photo-degradation of photodynamic therapy agents in aqueous TiO_2 suspensions. Sustaina-ble Develop Plan VI. 2013;173:359–369.

[24] Habibi MH, Hassanzadeh A, Mahdavi S. The effect of operational parameters on the photocatalytical degradation of three textile azo dyes in aqueous TiO_2 suspensions. J Photochem Photobiol A Chem. 2005;172:89–96. DOI: 10.1016/j.jphotochem.2004.11.009.

[25] Neamatu M, Simiriceanu I, Yediler A, Kettrup A. Kinetics of decolorization and min-eralization of reactive azo dyes in aquous solution by the UV/H_2O_2 oxidation. Dyes Pigm. 2002;53:93–99. DOI: 10.1016/S0143-7208(02)00012-8.

[26] Chen C, Wang Z, Ruan S, Zou B, Zhao M, Wu F. Photocatalytic degradation of C.I. Acid Orange 52 in the presence of Zn-doped TiO_2 prepared by a stearic acid gel method. Dyes and Pigments. 2008;77:204–209. DOI: 10.1016/j.dyepig.2007.05.003.

[27] Hoffman MR, Martin ST, Choi WY, Bahnemann DW. Environmental applications of semiconductor photocatalysis. Chemical Reviews. 1995;95:69–96. DOI: 10.1021/cr00033a004.

[28] Fujishima X, Zhang CR. Titanium dioxide photocatalysis: present situation and fu-ture approaches. Comptes Rendus Chimie. 2006;9:750–760. DOI: 10.1016/j.crci.2005.02.055.

[29] Saggioro EM, Oliveira AS, Buss DF, Magalhães DP, Pavesi T, Jimenéz M, Maldonado MI, Ferreira LFV, Moreira JC. Photo-decolorization and ecotoxicological effects of so-lar compound parabolic collector pilot plant and artificial light photocatalysis of In-

digo carmine dye. Dyes and Pigments. 2015;113:571–580. DOI: 10.1016/j.dyepig.2014.09.029.

[30] Gemeay AH, Mansour IA, El-Sharkawy RG, Zaki AB. Kinetics and mechanism of the heterogeneous catalyzed oxidative degradation of Indigo carmine. J Mol Catal A Chem. 2003;193:109–120. DOI: 10.1016/S1381-1169(02)00477-6.

[31] Al-Ekabi H, Serpone N. Photocatalytic degradation of chlorinated phenols in aerated aqueous solutions over TiO_2 supported on a glass matrix. J Phys Chem. 1998;92:5726–5731. DOI: 10.1021/j100331a036.

[32] Velmurugan R, Swaminathan M. An efficient nanostructured ZnO for dye sensitized degradation of Reactive Red 120 dye under solar light. Sol Energ Mat Sol C. 2011;95:942–950. DOI: 10.1016/j.solmat.2010.11.029.

[33] Saggioro EM, Oliveira AS, Pavesi T, Maia CG, Ferreira LFV, Moreira JC. Use of titanium dioxide photocatalysis on the remediation of model textile wastewaters containing azo dyes. Molecules. 2011;16:10370–10386. DOI: 10.3390/molecules161210370.

[34] Saggioro EM, Oliveira AS, Jimenéz M, Maldonado MI, Correia FV, Moreira JC. Solar CPC pilot plant photocatalytic degradation of Indigo carmine dye in waters and wastewaters using supported-TiO_2: influence of photodegradation parameters. International Journal of Photoenergy. 2015; 20:1-12. DOI: 10.1155/2015/656153.

[35] Wang C, Lee C, Lyu M, Juang L. Photocatalytic degradation of C.I. Basic Violet 10 using TiO_2 catalysts supported by Y zeolite: an investigation of the effects of operational parameters. Dyes and Pigments. 2008;76:817–824. DOI: 10.1016/j.dyepig.2007.02.004.

[36] Augugliaro V, Baiocchi C, Prevot AB, García-López E, Loddo V, Malato S, Marcí G, Palmisano L, Pazzi M, Pramauro E. Azo-dyes photocatalytic degrdation in aqueous suspension of TiO_2 under solar irradiation. Chemosphere. 2003;49:1223–1230. DOI: 10.1016/S0045-6535(02)00489-7.

[37] Tanaka K, Padermpole K, Hisanaga T. Photocatalytic degradation of commercial azo dyes. Water Research. 2000;34:327–333. DOI: 10.1016/S0043-1354(99)00093-7.

[38] Konstantinou IK, Albanis TA. TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations. A review. Applied Catalysis B: Environmental. 2004;49:1–14. DOI: 10.1016/j.apcatb.2003.11.010.

[39] Chen X, Wang W, Xiao H, Hong C, Zhu F, Yao Y, Xue Z. Accelerated TiO_2 photocatalytic degradation of Acid Orange 7 under visible light mediated by peroxymonosulfate. Chemical Engineering Journal. 2012;193–194:290–295. DOI: 10.1016/j.cej.2012.04.033.

[40] Galindo C, Jacques P, Kalt A. Photodegradation of the aminoazobenzene acid Orange 52 by three advanced oxidation processes: UV/H_2O_2, UV/TiO_2 and Vis/TiO_2:

comparative mechanistic and kinetic investigations. Journal of Photochemistry and Photobiology A: Chemistry. 2000;130:35–47. DOI: 10.1016/S1010-6030(99)00199-9.

[41] Wang K, Zhang J, Lou L, Yang S, Chen Y. UV or visible light induced photodegradation of AO7 on TiO_2 particles: the influence of inorganic anions. Journal of Photochemistry and Photobiology A: Chemistry. 2004;165:201–207. DOI: 10.1016/j.jphotochem.2004.03.025.

[42] Daneshvar N, Rabbani M, Modirshahla N, Behnajady MA. Kinetic modeling of photocatalytic degradation of Acid Red 27 in UV/TiO_2 process. Journal of Photochemistry and Photobiology A: Chemistry. 2004;198:39–45. DOI: 10.1016/j.jphotochem.2004.05.011.

[43] Tseng D, Juang L, Huang H. Effect of oxygen and hydrogen peroxide on the photocatalytic degradation of monochlorobenzene in TiO_2 aqueous suspension. International Journal of Photoenergy. Article ID 328526, 2012. DOI: 10.1155/2012/328526.

[44] Dostanic JM, Loncarevic DR, Bankovic PT, Cvetkovic OG, Jovanovic DM, Mijin DZ. Influence of process parameters on the photodegradation of synthesized azo pyridine dye in TiO_2 water suspensions under simulated sunlight. Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering. 2011;46:70–79. DOI: 10.1080/10934529.2011.526905.

[45] Haji S, Benstaali B, Al-Bastaki N. Degradation of methyl orange by UV/H_2O_2 advanced oxidation process. Chemical Engineering Journal. 2011;168:134–139. DOI: 10.1016/j.cej.2010.12.050.

[46] Senthilkumaar S, Porkodi K. Heterogeneous photocatalytic decomposition of Crystal Violet in UV-illuminated sol-gel derived nanocrystalline TiO_2 suspensions. Journal of Colloid and Interface Science. 2005;288:184–189. DOI: 10.1016/j.jcis.2005.02.066.

[47] Santiago DE, Dona-Rodríguez JM, Arana J, Fernández-Rodríguez C, González-Díaz O, Pérez-Pena J, Silva AMT. Optimization of the degradation of imazalil by photocatalysis: comparison between commercial and lab-made photocatalysts. Applied Catalysis B: Environmental. 2013;138–139:391–400. DOI: 10.1016/j.apcatb.2013.03.024.

[48] Mittal A, Mittal J, Kurup L. Batch and bulk removal of hazardous dye, Indigo carmine from wastewater through adsorption. Journal of Hazardous Materials. 2006;137:591–602. DOI: 10.1016/j.jhazmat.2006.02.047.

[49] Pelaez M, de la Cruz AA, O′Shea K, Falaras P, Dionysiou DD. Effects of water parameters on the degradation of microcystin-LR under visible light-activated TiO_2 photocatalyst. Water Research. 2011;45:3787–3796. DOI: 10.1016/j.watres.2011.04.036.

[50] Guohong X, Guoguang L, Dezhi S, Liqing Z. Kinetics of acetamiprid photolysis in solution. Bull Environ Contam Toxicol. 2009;82:129–132. DOI: 10.1007/s00128-008-9520-8.

[51] Herrmann JM, Guillard C, Arguello M, Agüera A, Tejedor A, Piedra L, Fernandez-Alba A. Photocatalytic degradation of pesticide pirimiphos-methyl – determination

of the reaction pathway and identification of intermediate products by various analytical methods. Catal Today. 1999;54:353–367. DOI: 10.1016/S0920-5861(99)00196-0.

[52] Peng Z, Tang H, Yao K. Recyclable TiO_2/carbon nanotube sponge nanocomposites: controllable synthesis, characterization and enhanced visible light photocatalytic property. Ceramics International. 2015;41:363–368. DOI: 10.1016/j.ceramint. 2014.08.079.

[53] Lv Y, Yu L, Zhang X, Yao J, Zou R, Dai Z. P-doped TiO_2 nanoparticles film coated on ground glass substrate and the repeated photodegradation of dye under solar light irradiation. Applied Surface Science. 2011;257:5715–5719. DOI: 10.1016/j.apsusc. 2011.01.082.

[54] Malik PK. Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36. Dyes and Pigments. 2003;56:239–249. DOI: 10.1016/S0143-7208(02)00159-6.

[55] Marsh H, Rodríguez-Reinoso F. Activated Carbon. 1st ed. Elsevier: Oxford; 2006. p. 322–327.

[56] Franciscon E, Zille A, Dias FG, Menezes CR, Durrant LR, Cavaco-Paulo A. Biodegradation of textile azo dyes by a facultative *Staphylococcus arlettae* strain VN-11 using a sequential microaerophilic/aerobic process. Int Biodeterior Biodegrad.2009;63:280–288. DOI: 10.1016/j.ibiod.2008.10.003.

[57] Bergsten-Torralba LR, Nishikawa MM, Baptista DF, Magalhães DP, da Silva M. Decolorization of different textile dyes by *Penicillium simplicissimum* and toxicity evaluation after fungal treatment. Braz J Microbiol. 2009;40:808–817.

[58] Zhang X, Sun H, Zhang Z, Niu Q, Chen Y, Crittenden JC. Enhanced bioaccumulation of cadmium in carp in the presence of titanium nanoparticles. Chemosphere. 2007;67:160–166. DOI: 10.1016/j.chemosphere.2006.09.003.

[59] Paoletti MG. The role of earthworms for assessment of sustainability and as bioindicators. Agriculture, Ecosystems & Environment. 1999;74:137–155. DOI: 10.1016/S0167-8809(99)00034-1.