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Visible Light Active Fe-N Codoped TiO_2 Synthesized through Sol Gel Method: Influence of Operating Conditions on Photocatalytic Performances

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Acid Orange 7 (AO7) is an azo dye present in the effluents coming from the textile industry. It is a coloring agent consisting of an azo group bonded to aromatic rings. This azo dye can react with other chemical substances producing aromatic amines which cause toxic and carcinogenic effects in the environment. For this reason, it is necessary to eliminate this compound from aqueous discharges. Recently, the scientific research has focused the attention on heterogeneous photocatalysis based on semiconductor oxides because it is a technology able to completely degrade many organic pollutants to carbon dioxide and water at ambient temperature under UV/visible light irradiation. In photocatalysis, the most used semiconductor is titanium dioxide (TiO_2). TiO_2 presents various crystalline phase and a wide band gap (3.2 eV for anatase), therefore, it can be activated only under UV light irradiation. In order to make TiO_2 active under visible light, in this work TiO_2 doped with metallic (Fe) and non-metallic element (N) was synthetized through sol-gel method. The photocatalytic tests on discoloration of AO7 aqueous solution were carried in a photoreactor surrounded by visible-LEDs strip. To determine the optimum conditions for the photodegradation, the influence of photocatalyst dosage (1.5 - 6 g L^{-1}), initial AO7 concentration (5 - 20 mg L^{-1}), initial pH of the solution (3-8) and the incident visible light intensity (3.25 to 13 mW cm^{-2}) was investigated. It was observed that the Fe-N-TiO_2 photocatalyst reached about 90% of AO7 discoloration and 83% of mineralization efficiency under the optimized working conditions, in a very short time (60 min) using a photocatalyst dosage of 3 g L^{-1} and AO7 initial concentration of 10 mg L^{-1}.

1. Introduction

Contamination of the aquatic environment is progressively becoming a serious problem. As a result of the intense development of the chemical, pharmaceutical and agricultural industries, many chemical compounds such as pesticides, steroid hormones, antibiotics or dyes reach the aquatic environment (Zuccato et al., 2016). Among the different contaminants, the azo dyes for their recalcitrant and inhibitory nature cannot normally be degraded by the conventional biological wastewater treatments (Pagga & Brown, 1986). In this way, the research focused on the development of the eco-friendly alternative to obtain the transformation of the refractory molecules into non-noxious chemical products. The heterogeneous photocatalysis is a promising technique for wastewater treatment containing refractory organic pollutants (Ho et al., 2020). The photocatalytic process can be conducted under ambient conditions using TiO_2 semiconductor as photocatalyst (Hoffmann et al., 1995). Additionally, TiO_2 is non-toxic, highly active, cheap and stable under a wide range of chemical conditions, making it an ideal photocatalyst for environmental remediation applications (Konstantinoue & Albanis, 2004). Although TiO_2 has been used to degrade a large variety of organic and inorganic contaminants (Hoffmann et al., 1995), it is limited by its wide band gap (3.2 eV), which requires ultraviolet light irradiation for photocatalytic activation (Sima et al., 2013). Since UV light represents only a little fraction (~5%) of the solar light compared to visible light (45%), any shift in the optical response of TiO_2 from the UV to the visible spectral range could have an increased photocatalytic efficiency of the material (Sauer &

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Ollis, 2007). Therefore, it is necessary to extend the photo-response of TiO_2 to the visible spectrum by modification of its structure. Another problem is the high recombination rate of photo-generated electron–hole pairs. The recombination can be reduced by introducing charge traps for electrons and/or holes, thus raising their life time (Ni et al., 2007). A possible strategy to solve these TiO_2 limitations and to increase the efficiency of the photocatalytic activity could be the doping process with metal and non-metal elements (Fujishima et al., 2008). TiO_2 doped with transition metals, such as Fe, Cr, V, Mn, and Cu have been already used to improve the visible light absorption (Choi et al., 1994). Indeed, they form energy levels below the conduction band edge of the photocatalyst reducing the value of the band gap (Zhu et al., 2006,). However, these dopant metals have to be used in small quantity to avoid recombination of photogenerated pairs, which is enhanced by the large amount of these dopant species (Dholam et al., 2009). But the low content of metal doping implies only a small shift in the absorption edge of TiO_2 towards visible region. Doping TiO_2 with non-metallic anion such as N, P, F and C replaces O in the TiO_2 lattice generating energy levels just above the top of the valence band of TiO_2 to effectively narrow the band gap (Cong et al., 2007). Thus, an appropriate concentration of cations and anions should be able to both enhance the visible light absorption efficiency and reduce the recombination of the photogenerated charges. In this work the Fe–N codoped TiO_2 photocatalyst (Fe-N-TiO_2), synthesized in a previous study (Mancuso et al., 2020), was used to photodegrade the azo dye AO7 solution, with the aim of optimizing the operating conditions for photocatalytic process. The influence of the following operating parameters on the photocatalytic activity was analyzed: photocatalyst dosage, initial concentration of AO7 contaminant, initial pH of the solution and incident light intensity.

2. Materials and Methods

2.1 Chemicals

Titanium tetraisopropoxide (TTIP, $C_{12}H_{28}O_4Ti$>97%, Sigma Aldrich), urea (CH_4N_2O, Sigma Aldrich), iron(II) acetylacetonate ($[CH_3COCH{=}C(O)CH_3]_2Fe$, Sigma Aldrich), Acid Orange 7 ($C_{16}H_{11}N_2NaO_4S$, Sigma Aldrich) and distilled water were purchased. Molecular structure of AO7 is shown in Figure 1a.

2.2 Synthesis of photocatalyst

Fe-N codoped TiO_2 photocatalyst (Fe-N–TiO_2) was prepared via sol–gel method using urea as nitrogen precursor, iron(II) acetylacetonate as iron precursor and TTIP as TiO_2 precursor.

In the optimized formulation, 1.2 g of urea was added into 50 mL of distilled water and the resultant mixture was stirred for 5 min (solution A). For the next step, 25 mg of iron(II) acetylacetonate was dissolved in 12.5 mL of TTIP (solution B).Then, the solution B was added dropwise into the solution A. The mixture was maintained at room temperature under continuous stirring. The obtained suspension was centrifuged and washed with distilled water three times, finally placed in a muffle furnace at 450 °C for 30 min in static air.

2.3 Photocatalytic tests

Photocatalytic tests were performed in a cylindrical pyrex photoreactor (ID = 2.6 cm, L_{TOT} = 41 cm and V_{TOT} = 200 mL). Visible-LEDs strip (nominal power: 10 W; emission in the range 400 – 800 nm) was positioned in contact to the external surface of the photoreactor (Figure 1b). The experiments were conducted at room temperature with a total volume of solution equal to 100 mL. The suspension was left in dark conditions for 120 min to achieve the adsorption/desorption equilibrium of AO7 dye on the photocatalyst surface and then 60 min under visible light was performed. At regular time intervals, about 3.5 mL of the suspension was withdrawn from the photoreactor and centrifuged to remove the catalyst particles. The aqueous solution was then analyzed by UV-Vis spectrophotometer (Thermo Scientific Evolution 201) to monitor the reaction progress. In details, the discoloration of the chosen dye was monitored by measuring the maximum absorbance value at 485 nm (Rodríguez et al., 2019). The mineralization of the target pollutant was assessed by the measure of the total organic carbon (TOC) content of the solutions during the irradiation time. The TOC of solution was measured from CO_2 obtained by the high temperature (680 °C) catalytic combustion (Franco et al., 2019, Bahadori et al., 2018)

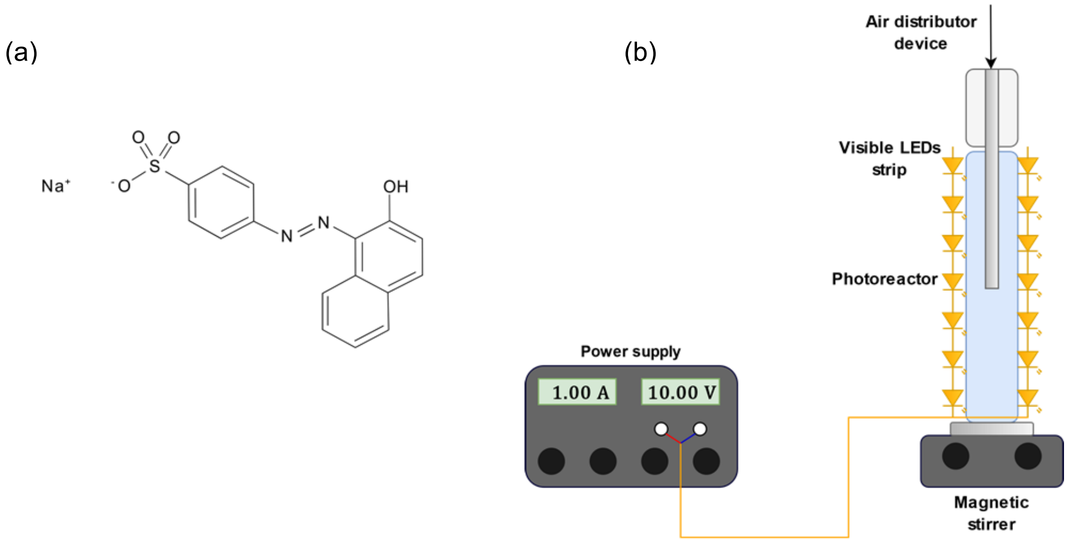

Figure 1: (a) molecular structure of AO7, (b) schematic picture of experimental setup.

A kinetic analysis of the photocatalytic discoloration of AO7 was carried out. The Langmuir–Hinshelwood model is usually used to describe the kinetics of photocatalytic process (Li et al., 2016). The derivation is based on the degradation rate (*r*), which is expressed as follows:

$$r = -\frac{dc}{dt} = \frac{k_r\, K_{ad}\, c}{1 + K_{ad}\, c} \quad (1)$$

where k_r, K_{ad} and *c* are the intrinsic kinetic constant (mg L^{-1} min^{-1}), adsorption equilibrium constant (L mg^{-1}) and concentration of dye (mg L^{-1}), respectively.

Since the adsorption can be neglected and the concentration of compounds is low, the equation above can be simplified to the first order kinetics expression with an apparent discoloration kinetic constant (k_{app}):

$$\ln\left(\frac{c_0}{c}\right) = k_r\, K_{ad}\, t = k_{app}\, t \quad (2)$$

The value of apparent discoloration kinetic constant (k_{app} min^{-1}) can be calculated by the slope of the straight line obtained from plotting $ln(c_0/c)$ vs irradiation time *t*.

The TOC removal (mineralization) and AO7 removal (discoloration) efficiency at the generic irradiation time were evaluated using the following relationship:

$$TOC\ removal\ efficiency\ (t) = \left(1 - \frac{TOC(t)}{TOC_0}\right) 100 \quad (3)$$

$$AO7\ removal\ efficiency\ (t) = \left(1 - \frac{c(t)}{c_0}\right) 100 \quad (4)$$

Where *TOC(t)* is the total organic carbon at the generic irradiation time (mg L^{-1}), TOC_0 is the initial total organic carbon (mg L^{-1}), *c(t)* is the AO7 concentration at the generic irradiation time (mg L^{-1}), c_0 is the initial AO7 concentration (mg L^{-1}).

3. Results and discussion

The effect of photocatalyst dosage on the photocatalytic AO7 degradation has been widely studied because the optimum photocatalyst dosage could maximize the photocatalytic performance and minimize the cost and energy (Vaiano et al., 2019). In fact, it is an important factor in the photocatalysis, because the photodegradation efficiency could be strongly affected by the number of available active sites of the selected photocatalyst. Therefore, a Fe-N-TiO_2 dosage ranging from 1.5 to 6.0 g L^{-1} was used to investigate to find out the optimal loading value (Figure 2a).

When the loading of Fe-N-TiO_2 photocatalyst increased from 1.5 to 3.0 g L^{-1}, the apparent kinetic constant for discoloration of AO7 increased from 0.009 min^{-1} to 0.035 min^{-1}. In fact, the adequate increase of photocatalyst dosage enhanced the quantity of photons absorbed and consequently increased the photodegradation rates (Wang et al., 2008). A further increase in catalyst dosage decreased slightly the photocatalytic degradation of AO7. The main cause of the photocatalytic activity decrease could be associated to the screening effect of the suspended particles (Viraraghavan & de Maria Alfaro, 1998).

In effect, the overloading of photocatalyst increased the solution turbidity and led to a decrease in the penetration of the photon flux in the reactor and thereby decreased the photocatalytic degradation rate, although the major presence of available active sites.

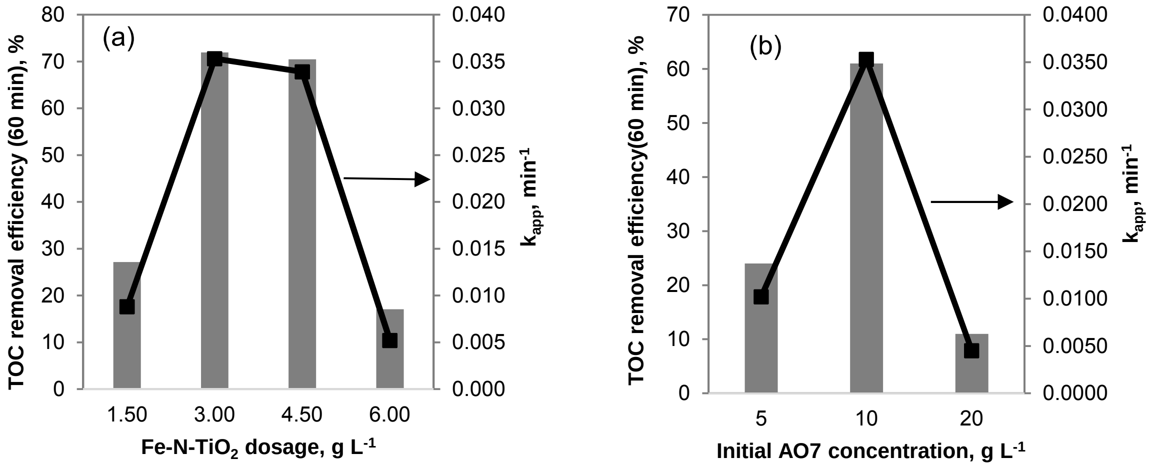

Figure 2: (a) effect of Fe-N-TiO$_2$ dosage on TOC removal efficiency and k_{app}, (b) effect of initial AO7 concentration on TOC removal efficiency and k_{app}; initial pH of solution: 5.5.

The photodegradation of AO7 at different initial concentrations (c_0 = 5, 10, 20 mg L^{-1}) were also investigated using the obtained optimal Fe-N-TiO$_2$ dosage (3 g L^{-1}) (Figure 2b). The mineralization efficiency of about 61% was achieved considering an initial AO7 concentration of 10 mg L^{-1}.On the other hand, at initial concentrations of 5 and 20 mg L^{-1}, the mineralization efficiency after 60 min of visible light irradiation were 24% and 11%, respectively. The probable formation of reactive oxygen species (ROS), such as hydroxyl radicals, superoxide and positive holes under visible light and their subsequent interaction with dye molecules determine the degradation mechanism (Stylidi et al., 2004). The possible explanation of the obtained results is that, as the initial concentration increases, more dye molecules in aqueous solution are present (Avasarala et al., 2010), therefore the photocatalytic activity enhances. However, when the initial concentration of the dye increases too, the photogenerated ROS are not enough for the degradation of the target dye (Grzechulska & Morawski, 2002). On the other hand, if the concentration of dye solution is excessively high, a fraction of emitted photons is absorbed by the dye molecules rather than the photocatalyst particles, and consequently the photocatalytic activity is reduced (Liu et al., 2006).

It was also reported that the pH value is another parameter which influences the surface charge of photocatalyst and degree of AO7 ionization in the solution (Cheng et al., 2018). Its effect was examined changing the initial pH solution in the range 3-8. In each photocatalytic test, the initial AO7 concentration and catalyst dosage were fixed at 10 mg L^{-1} and 3 g L^{-1}, respectively. The spontaneous pH of the solution was equal to 5.50 (at 10 mg L^{-1} AO7 initial concentration). The values of pH were modified with HCl or NaOH aqueous solution. The relative concentrations of AO7 dye (C/C_0) as a function of run time are illustrated and compared in Figure 3a. It was noted that the relative concentrations of AO7 dye decreased in dark conditions with the increase of the solution pH until the 8 value probably because the amount of AO7 adsorbed on the photocatalyst surface became quite negligible. The point of zero charge (PZC), corresponding to the condition where no net charge is present on the surface, is an important factor that controls the adsorption of pollutant and photocatalytic activity (Di Paola et al., 2002). The PZC of Fe-N codoped was 5.02 (Mancuso et al., 2020), for pH values lower than the PZC of photocatalyst, the surface of photocatalyst would be positively charged due to protonation of surface hydroxyl groups. Along with the increase of pH, deprotonation became dominant gradually. When pH was higher than PZC, surface of photocatalyst became negatively charged (Wang & Ku, 2007).

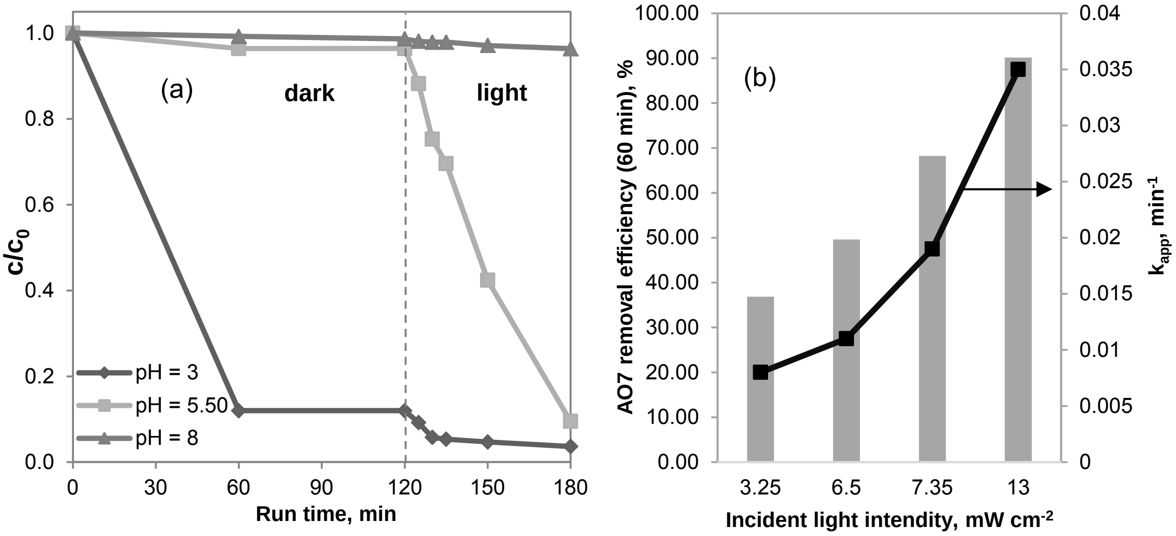

Figure 3: (a) effect of initial pH of the solution on the discoloration; (b) effect of incident light intensity on AO7 removal efficiency and k_{app}.

AO7 is normally an anionic dye. When pH < PZC of photocatalyst, the sulfonate –φ–SO_3– function in AO7 is still deprotonated, causing it to be negatively charged. Therefore, under acidic conditions, electrostatic attraction could facilitate adsorption of AO7 on the positively charged photocatalyst surface. On the contrary, when pH > PZC, less electrostatic force was available at the photocatalyst surface resulting in a less intense absorption of AO7. Figure 3a shows that the high adsorption of the dye on the photocatalyst material leads to a fast decrease of the dye concentration at acid pH. These results suggest that the influence of the initial pH of the solution on kinetics of photocatalytic process is due to the amount of the dye adsorbed on Fe-N-TiO_2.

Finally, the influence of incident light intensity on the degradation efficiency was analyzed in the range from 3.25 to 13 mW cm^{-2}, at optimal values of dye concentration (10 mg L^{-1}) and photocatalyst dosage (3 g L^{-1}) at the spontaneous pH of AO7 solution (pH=5.5). It is evident that the photodegradation of AO7 enhanced with increasing the light intensity as shown in Figure 3b. In fact, the excitation of Fe-N codoped TiO_2 particles and the consequent formation of ROS were favored with increasing the number of photons incident on the surface of the photocatalyst. Therefore, the increase of the incident light intensity produces an improvement of photocatalytic activity (Herrmann, 2005).

4. Conclusions

In this work, the photocatalytic degradation of AO7 was studied in aqueous Fe-N-TiO_2 suspensions. The AO7 degradation process was optimized with respect to four main parameters including photocatalyst dosage, AO7 initial concentration, initial pH of the solution, and incident light intensity. The experimental results revealed that the optimal photocatalytic loading and the optimal initial AO7 concentration were 3 g L^{-1} and 10 mg L^{-1} respectively, in the batch slurry photoreactor. Furthermore, the degradation efficiency of AO7 increased as the pH decreased, with a maximum efficiency at pH 3 due to the high amount of AO7 molecules adsorbed on the catalyst surface in dark conditions. Additionally, AO7 degradation efficiency was substantially improved by increasing the incident light intensity from 3.25 to 13 mW cm^{-2}.

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