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KINETIC AND MECHANISM OF TNT DEGRADATION BY UV-VIS PHOTOCATALYSIS ON IRON DOPED TiO_2

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Abstract

2,4,6-Trinitrotoluene(TNT) is one of most common toxic pollutant identified in wastewater generated from ammunitions plants, due to its potential carcinogenic characteristics. Various treatment methods were investigated in order to remove such toxic pollutants and among them, photocatalysis was successfully applied. From various semiconductors, titanium was a widely studied photocatalyst, due to its chemical inertness, low cost, photo stability and nontoxic character. Since, TiO_2 is only photoactive under UV irradiation, modification of semiconductor by metal doping, aimed to reduce photocatalyst band gape and increase its quantum efficiency in visible domain represents an important issue. Fe-TiO_2 assisted photocatalytic degradation of TNT in aqueous media, under UV-VIS irradiation was studied. The effects of operating parameters such as catalyst loading and pollutant concentration were assessed. TNT degradation was found to follow a pseudo-first order kinetic. The main oxidative species responsible for pollutant degradation are the surface adsorbed hydroxyl radicals.

Keywords: *Fe doped TiO_2, kinetic, mechanism, photocatalysis, 2-4-6-Trinitrotoluene*

Introduction

2,4,6-Trinitrotoluene(TNT) is one of most common toxic pollutant identified in wastewater generated from ammunitions plants. Due to its potential carcinogenic characteristics, TNT presence in water bodies presents risk for human health and aquatic life (Won et al. 1976). These reasons, imposed including of TNT on the list of priority pollutants which are strictly regulated in EU countries.

Although, the major route of natural TNT degradation in aquatic environment is photolysis, with a half-time about 70 days (Nahem et al. 1997), partial aromatic ring cleavage and pure mineralization imposed implementation of powerful treatment methods in order to assure an adequate pollutant removal. In the last decade, advanced oxidation processes (AOPs) have been proved to be effective for destruction of refractory toxic pollutants (Zaharia & Suteu 2014). Several researchers studied the mineralization of nitro aromatic compounds using UV/Fenton's reagent (Li et al. 1998; Liou et al. 2003) or UV/H_2O_2 technique (Ho 1986; Hwang et al. 2004). Li et al. (1997) investigated the conversion of 2,4,6-TNT by Fenton's reagent, in which higher oxidation efficiency was obtained at pH 3.0. Some other publications have been issued on the decomposition of 2,6-DNT through ozonation, H_2O_2/O_3 or UV/O_3 methods (Beltran, et al., 1998) (Beltran, et al., 1998). Beside these photoinduced techniques, semiconductor photocatalysis has been proved to be effective in degradation of nitroaromatics (Vohra & Tanaka 2002). Among various semiconductors, titania was a widely studied photocatalyst, due to its chemical inertness, low cost, photostability and nontoxicity (Ribeiro et al., 2015; Petrov et al. 2007). However, TiO_2 is only photoactive under UV light irradiation due to its wide band gap energy (3.2eV: anatase). Therefore, the modification of semiconductor aimed to reducing the photocatalyst band gape and increase its quantum efficiency in visible domain represents an important issue. One feasible approach consists in doping oxide semiconductor with metal, which allows to extend the light absorption of photocatalyst in visible region (Feng et al. 2014). Also, it is experimentally found that the presence of iron in Fe–TiO_2 catalysts enhances the photocatalytic activity of TiO_2 by acting both as hole and electron traps (Zhu et al. 2004).

0.5%Fe-TiO_2 assisted photocatalytic degradation of TNT in aqueous media, under UV-VIS irradiation was studied. The effects of operating parameters such as catalyst loading, pollutant concentration and irradiation time were assessed. The kinetic and mechanism of pollutant degradation were also investigated.

Experimental

The photodegradation experiments were performed in a batch reactor equipped with cooling system and a medium pressure Hg lamp as UV-VIS light source (λ = 320-550 nm). Thin film catalyst supported on glass plate 4 pieces placed at equal distances from central positioned UV-VIS lamp were immersed into reactor filled with (nitrobenzene) NB aqueous solution with pH=7 and 2.51×10^{-4}M content . During photocatalysis experiment air was bubbled into solution at 50L/h flow. TiO_2 and TiO_2 doped with various Fe concentration (0.5-5%wt.) catalysts were tested in order to assess the influence of metal dopant presence and its concentration on NB degradation efficiency at various irradiation times (30 -240 min). In order to evaluate the effect of the main active species involved in Fe-TiO_2 assisted photocatalytic degradation of NB we suppressed the free $\bullet OH$ radicals mediated process by addition of 14.63×10^{-3} M iso-propanol (i-PrOH) scavenger. Lock of $\bullet OH_{ads}$radicals production on the catalyst surface was assured by addition of 14.63×10^{-3}M sodium iodide (NaI). The initial and irradiated samples were analysed for NT and inorganic nitrogen (N_{inorg}= $N\text{-}NO_3^-$+ $N\text{-}NO_2^-$ + $N\text{-}NH_4^+$) concentrations by Gas Chromatography (GC), and Ion Chromatography respectively.

Results and Discussion

Effect of photocatalyst loading

A series of experiments were carried out on TNT solution with 2.72×10^{-4} M content at pH=7, by varying the 0.5%Fe-TiO_2 photocatalyst dose between 50-500 mg/L. For each photocatalyst dose, TNT initial degradation rates (r_0) were calculated at 30 min irradiation times.

The results presented in Fig. 1 show that r_0 values increases up to $0.64 \times 10^{-7} Ms^{-1}$ by increasing the catalyst dose from 50 to 200 mg/L. Increase of catalyst loading above 200 mg/L leads to degradation rate decrease. Thus, a value of $r_0 = 0.41 \times 10^{-7} Ms^{-1}$ was calculated at 500 mg/L dose. The enhancement of TNT initial degradation rate with catalyst loading was due to the increases in the surface area of the catalyst available for pollutant adsorption and degradation. Higher values than optimum catalyst dose (200 mg/L) increase the solution turbidity leading to decreases in the penetration depth of light into suspension and in the degradation rate (Robert et al.

2003; Daneshvar et al. 2004). In all subsequent experiments the optimum catalyst loading of 200 mg/L was applied.

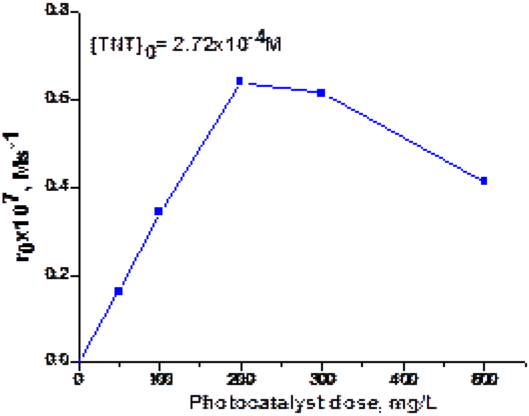

Figure 3. Evolution of TNT initial degradation rate (r_0) *vs.* photocatalyst dose

Effects of TNT initial concentration and irradiation time

Since TNT concentration in real aqueous systems varies, it was necessary to assess the influence of these parameters on pollutant conversion efficiency in order to set up the optimum working conditions which assure TNT advanced degradation. The experiments were carried out on four different initial TNT concentration, situated between (0.27-2.72) x 10^{-4} M, using established photocatalyst optimum dose, at pH=7 and various irradiation times (30-240 min). Experimental results are presented in the Table 1.

Under the same working conditions remanent pollutant concentration in irradiated samples increase with TNT initial concentration due to the competition between the organic degradation by-products and parent pollutant for the photo-generated species resulted by UV-VIS excitation of 0.5%Fe-TiO_2catalyst. This species, like •OH radicals and electrons are involved in oxidation and reduction reactions leading to organic pollutants conversion down to their mineralization. As result, at 60 min irradiation, ten times increasing of initial TNT concentration from 0.27 x 10^{-4}M to 2.72 x 10^{-4} M leads to decrease of TNT degradation efficiencies (η_{TNT}) from 91 to 67%. A similar behavior is observed in respect to organic nitrogen mineralization efficiencies (η_{Ninorg}) which decrease from 35 to 20%. The lower level of nitrogen mineralization compared with pollutant degradation is related to generation of nitrogen containing organic by-products during TNT degradation.

The negative effect of initial pollutant concentration increase on its degradation efficiency can be diminished by prolonging irradiation time, due to increasing of photonic energy absorbed by catalyst which assures higher concentrations of photo-generated •OH radicals and electrons, enhancing pollutant degradation efficiency. Thus, in the case of 0.27x10^{-4}M TNT initial concentration, prolonged irradiation time of 180 min assures the increase of pollutant degradation and organic nitrogen mineralization up to 99 and 71%, respectively. Comparable pollutant degradation efficiency was registered for 2.72 x 10^{-4} M TNT initial concentration, but only for 240 irradiation time, while organic nitrogen mineralization efficiency does not exceed 60%.

Table 5. Influence of initial TNT concentration and irradiation time on pollutant degradation and organic nitrogen mineralization by photocatalysis using 200 mg/L 0.5%Fe-TiO_2 catalyst

Irradiation time (min)	**TNTx10^{-4} (M)**	**N_{inorg}x10^{-4} (M)**	**η_{TNT} (%)**	**η $_{Ninorg}$ (%)**
0	0.270	0.816^{*}	0	0
30	0.107	0.149	60.37	18.39
60	0.025	0.282	90.74	34.81
120	0.003	0.463	98.89	57.16
180	0.0003	0.576	99.89	71.11
0	0.780	2.340*	0	0
30	0.368	0.750	52.82	13.85
60	0.168	1.532	78.46	25.00
120	0.032	3.200	95.89	42.87
180	0.008	4.536	98.97	59.19
240	0.002	6.048	99.76	69.10
0	1.500	4.500*	0	0
30	0.776	0.659	48.27	12.27
60	0.424	1.264	71.73	20.39
120	0.100	2.700	93.33	40.56
180	0.026	4.061	98.27	54.53
240	0.007	5.414	99.53	65.04
0	2.72	8.160*	0	0
30	1.566	0.553	42.43	12.80
60	0.901	1.105	66.87	19.70
120	0.298	2.210	89.04	37.69
180	0.089	3.415	96.72	40.55
240	0.019	4.960	99.3	59.33

**Organic nitrogen concentration corresponding to TNT initial concentration*

Kinetics and mechanism of TNT photocatalytic degradation

Using experimental data presented in Table 1, the kinetic curves in respect with pollutant degradation and organic nitrogen mineralization were draw. These curves were linearized by a kinetic equation of pseudo-first order. The Fig. 2 illustrates the kinetic equations for an initial TNT concentration of 2.72x10^{-4} M.

The rate constants for each pollutant initial concentration were calculated from the slops of linear plots. The k^{I}_{TNT} and k^{I}_{Ninorg} values decreased from 6.13 x 10^{-4} to 3.4 x 10^{-4} $s^{-1}$and from 1.16 x 10^{-4} to 0.59 x $10^{-4}s^{-1}$ respectively, for TNT initial concentration increasing between 0.27 x 10^{-4} and 2.72 x 10^{-4} M.

It is well known that understand the mechanism of the oxidizing species generated at the irradiated catalyst interface, is essential for understanding the mechanism of pollutant photocatalysis. Alcohols like iso-propanol (i-PrOH) are usually used as a diagnostic tool of •OH radicals mediated mechanism. To confirm the role of surface bound or free •OH radicals in the degradation mechanism, the photocatalytic experiments were carried out in the presence of NaI, a well-known surface •OH radical scavenger, as well as i-PrOH, a free •OH radical scavenger (Devi & Kavitha 2014). Besides, iodide ion is an excellent scavenger of hole which is easily captured by I^- and pathways due to oxidation by surface •OH radical are hindered (Yoon & Lee 2005).

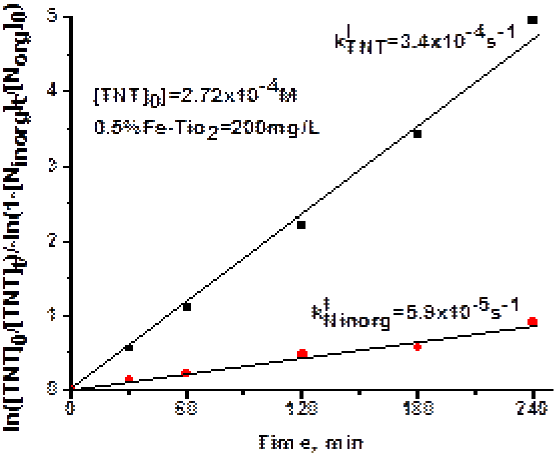

Figure 4. The pseudo-first order kinetics of TNT degradation and organic nitrogen mineralization

As is presented in Fig. 3 the rate of TNT degradation significantly decreased with NaI addition, indicating the crucial role of surface •OH radicals pathways. It should be emphasized that addition of NaI to the system allows TNT to react with $O_2^{\bullet-}$ radicals, resulted from reaction of electrons with dissolved O_2 (the experiments were performed under air bubbling), in the absence of surface •OH radicals which is a minor reaction pathway. However, it can be seen from Fig. 3 that adding of i-PrOH had smaller inhibitory effect on pollutant degradation rate than NaI, implying that free •OH radicals were not majorly involved in the TNT photodegradation process. The results showed that the surface •OH_{ads} radicals probably were responsible for the degradation of TNT rather than •OH_{free} radicals. Our findings are supported by the fact that presence of O_2 (electron scavenger) inhibited, reductive TNT degradation and pollutant direct photolysis occurs with much lower reaction rate than •OH radicals mediated process.

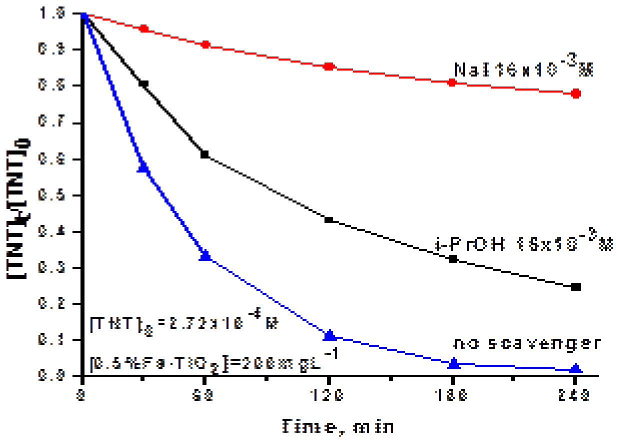

Figure 5. Effect of NaI and iso-propanol on efficiency of TNT photocatalytic degradation

Conclusions

TNT degradation and organic nitrogen mineralization was found to follow a pseudo-first order kinetics.

The main oxidative species responsible for pollutant degradation are the surface adsorbed hydroxyl radicals.

Application of UV-VIS photocatalysis, using 200 mg/L 0.5%Fe-TiO_2 catalyst, at pH=7 and 180-240 min irradiation time assures TNT advanced degradation (>99%) from initial concentrations situated between (0.27-2.72) x 10^{-4} M.

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