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RELATIONSHIP BETWEEN STRUCTURE OF SOME NITROAROMATIC POLLUTANTS AND THEIR DEGRADATION KINETIC PARAMETERS IN UV-VIS./TiO_2 SYSTEM

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Abstract. The degradation of dinitrobenzene (DNB) and dinitrotoluene (DNT) from aqueous solution under UV-vis. irradiation using heavy metal (0.5 wt.% Fe, 1 wt.% Co, 1 wt.% Ni)-doped titania was investigated. Dopant type, structure and initial pollutant concentration influence on the degradation efficiency were evaluated in order to set up the optimal working conditions which assure substrate advanced degradation. The kinetics of nitroaromatics degradation and organic nitrogen mineralisation was assessed and pseudo-first order rate constants were calculated. Fe doped photocatalyst with lowest metal content (0.5 wt.%) showed a considerable better behaviour in respect to pollutant degradation than Co and Ni (1 wt.%)-doped titania catalysts. Degradation rate constant was higher for DNT than DNB, due to the presence of alkyl group substituted to aromatic ring in the case of toluene derivative. This has a determinative effect on pollutant adsorption on catalyst surface and degradation pathway. For highest pollutant concentration tested (3×10^{-4} M), optimum working conditions (0.5 wt.% Fe-doped – TiO_2 loading of 200 mg/l, pH 7 and 240 min irradiation time) assure advanced nitroaromatics degradation ($\eta_{DNB} = 89\%$, $\eta_{DNT} = 94\%$) and organic nitrogen mineralisation ($\eta_{DNB} = 44\%$, $\eta_{DNT} = 47\%$).

Keywords: nitroaromatic compounds, photocatalysis, heavy metal doped TiO_2, kinetic parameters.

AIMS AND BACKGROUND

Hazardous organic compounds like nitroaromatics are frequently found in chemical and petroleum industries discharged effluents. Due to their bio-refractory character[1] and high chemical stability can not be efficiently removed by classical biological

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or physicochemical treatment processes. In the past decades, many papers have presented degradation of toxic pollutants in wastewater by advanced oxidation processes[2,3]. Several researchers studied the mineralisation of nitroaromatic compounds using UV/Fenton's reagent[4,5] or UV/H_2O_2 technique[6,7]. Li et al.[8] investigated the conversion of 2,4,6-TNT by the Fenton 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[9,10]. Beside these photoinduced techniques, UV/semiconductor photocatalysis has been proved to be effective in degradation of nitroaromatics[11]. Among various semiconductors, titania was a widely studied photocatalyst, due to its chemical inertness, low cost, photostability and nontoxicity[12,13]. In order to improve optical absorption and photocatalytic activity of TiO_2, many attempts have been made, one feasible approach consisting in doping oxide semiconductor with non-metal, metal or both for composite catalysts[14]. In the case of metals doping, various dopants induced different changes on catalyst photoactivity according to ionic radii and redox potential of $M^{n+}/M^{(n+1)+}$. In the present paper the dopant type (Fe, Co, Ni) influence on nitroaromatics degradation kinetic parameters was studied. The selected pollutants were1,3-dinitrobenzene (DNB) and 2,4-dinitrotoluene (DNT), the last one being the most toxic between nitroderivatives which are commonly founded in wastewater. This approach allowed assessing the relationship between pollutant structure and degradation rate in UV/doped-TiO_2 system. The substrate initial concentration influence on degradation efficiency was also evaluated in order to set up the optimal working conditions which assure advanced pollutants degradation.

EXPERIMENTAL

The following reagents were used: 1,3-dinitrobenzene and 2,4-dinitrotoluene of 99% purity (Sigma-Aldrich), n-hexane GC grade (Fluka), NaOH 1N, HCl 1N (Merck). The Fe, Co and Ni doped TiO_2 catalysts nanopowder containing 0.5 wt.% (Fe) and 1 wt.% (Co, Ni) metal load and more than 85% anatase content were used. These have been synthesised by alkoxide route of sol-gel method, using TiO_2 as precursor titanium ethoxide, $Ti(OC_2H_5)_4$, and metal nitrate as dopant source. The resulting sol has been converted to xerogel by drying at 80°C, and then calcinated at 400°C. The photodegradation experiments were carried out using a Heraeus laboratory scale UV-vis. reactor (V = 400 ml) equipped with a medium-pressure mercury lamp which emits in the range: 320–500 nm, with a photons flow I_0 = 3.9×10^{-6} einstein s^{-1}. Solutions with $(0.34–3.14) \times 10^{-4}$ M pollutant content were photo-oxidised in the following working conditions: pH 7; photocatalyst dose = 200 mg/l; irradiation time = 30–240 min. Prior to irradiation, the photocatalyst nanopowder was added to the samples, and solutions were bubbled with air

(50 l/h), in the dark, for 30 min in order to attain pollutant adsorption equilibrium. In order to evaluate the efficiencies of pollutant degradation and organic nitrogen mineralisation, the initial and irradiated samples were analysed for nitroaromatics, NH_4^+ and NO_3^- concentrations. DNB and DNT concentrations were determined via gas chromatography coupled with flame ionisation detector (GC-FID) using an Agilent 6890N equipment. Mineralisation products (NH_4^+, NO_3^-) were determined using a Dionex ICS-3000 Ion Chromatograph, with separate anions and cations columns and suppressed conductivity detectors. All experiments were duplicated to assure data quality.

RESULTS AND DISCUSION

Photocatalytic activity. Titanium dioxide is a photoactive semiconductor. When it is illuminated with UV light, an electron from its valence band is promoted to its conduction band, generating an electron deficiency or a hole in its valence band, thus overloading its conduction band. The holes react with water molecules or with the hydroxyl ions and hydroxyl ($^{\bullet}OH$) radicals are formed, which are strong oxidants of the organic molecules. Since the depositing or incorporating metal ion dopants into the titanium dioxide particles can change photocatalytic activity, the dependence of photocatalytic activity versus the type and concentration of metal ions doping has been assessed. It was found that each metal dopant presents an optimum concentration for the best photocatalytic performance of the doped-TiO_2 material. The photocatalytic activity of Fe, Co, Ni doped TiO_2 reported to DNT degradation from aqueous solution (3.14×10^{-4} M) was investigated. The dopant concentrations, reported to TiO_2 were 0.5 wt.% (Fe) and 1 wt.% (Co, Ni). It was selected a low Fe concentration because our previous study regarding nitrobenzene degradation on Fe-doped TiO_2 with 0.5–5 wt.% metal content showed that above 0.5% Fe level, metal acts as electron–hole recombination centres decreasing photocatalytic activity[15]. All experiments were performed at pH 7, with 200 mg/l catalyst dose and irradiation time between 30 and 240 min. The efficiency of pollutant degradation was assessed by determination of DNT concentration versus irradiation time in treated samples. Kinetic curves obtained for the three catalysts tested, linearised by a first order reaction kinetic, are presented in Fig. 1. From the slope of each line the pseudo-first order rate constants, k_1, were calculated. Various dopants induced different modification on catalyst photoactivity. As is presented in Fig. 1 values of DNT degradation rate constants obtained for the three tested doped catalysts decreasing in order 0.5 wt.% Fe > 1 wt.% Co > 1 wt.% Ni-TiO_2, from 1.94×10^{-4} to 0.95×10^{-4} s^{-1}. Best photocatalytic activity of Fe-doped titania reported to DNT degradation can be assigned to its electronic configuration. Thus, among dopants, Fe^{3+} ion presents only five electrons on *d* orbitals and therefore is more accessible to electron trapping than Co^{3+} or Ni^{3+} ions (with six and seven electrons) which have less available half-occupied *d* orbitals.

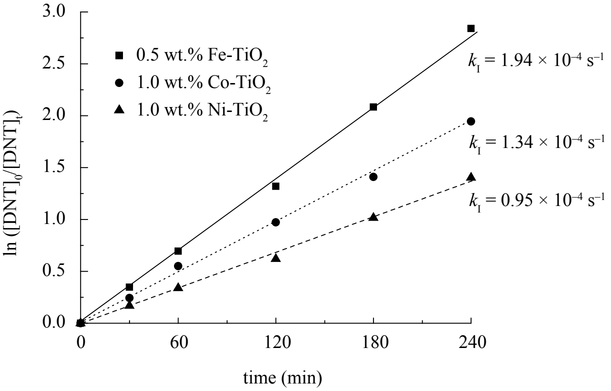

Fig. 1. DNT degradation rate constants of 0.5 wt.% (Fe) and 1 wt.% (Co, Ni) doped TiO_2 pH 7, photocatalyst dose – 200 mg/l, $[DNT]_0 = 3.14 \times 10^{-4}$ M

This behaviour is responsible for the increase of electron-hole pairs lifetime, which assures improved photocatalytic activity of Fe-doped TiO_2 compared with Co- and Ni-doped catalysts. This results are in accordance with those of other authors which showed drastically increases of charges lifetime from tens ns to minutes for 0.5 wt.% Fe-TiO_2 (Ref. 16).

Pollutant structure effect. In order to assess if any relationship exists between pollutant structure and its photocatalytic degradation, two nitroaromatic derivatives, DNB and DNT, have been studied comparatively the last one having an additionally alkyl group substituted to aromatic ring. Experiments were performed using 0.5 wt.% Fe-TiO_2 catalyst with improved photocatalytic activity, in the same working conditions with those presented in the case of nitrotoluene derivative degradation. In Table1 experimental results are presented.

Under the same working conditions, various nitroaromatics degradation efficiencies have been obtained, depending on pollutant structure. For similar number of nitro group, as the case of DNT and DNB, toluene nitroderivative is faster degraded (94.15%) than nitrobenzene derivative (87.61%) for 240 min irradiation time. This behaviour can be assigned to the effect of alkyl group substituted to aromatic ring. Due to its electron-donating nature (inductive effect, +I) alkyl group polarised σ covalent bound between aromatic ring and side-chain. As result a side-chain attack of photogenerated hydroxyl radicals takes place and alkyl group is oxidised to carboxyl group in subsequent steps. The formation of corresponding nitrobenzoic acid was also observed by Vohra and Tanaka for photocatalytic degradation of nitrotoluene[11]. In the case of DNB, the attack of electrophile hydroxyl radicals is burdened due to the electrons withdrawing character (mesomeric effect,

–M) of substituted nitro groups which reduce electric density of the aromatic ring. Consequently, benzene nitroderivatives will be harder degraded by photocatalysis than corresponding toluene nitroderivatives and $k_I^{DNB} < k_I^{DNT}$, as experimental results showed. The same behaviour was also registered in respect to organic nitrogen mineralisation, but the efficiency was permanently lower than pollutant degradation efficiency, due to nitroaromatics conversion to by-products with nitrogen content in their structure.

Table 1. Influence of nitroaromatic structure on the pollutant degradation and organic nitrogen mineralisation, pH 7, catalyst dose – 200 mg/l, $[Ar–NO_2]_0 \cong 3 \times 10^{-4}$ M

$Ar–NO_2$	Time (min)	$\eta_{Ar–NO_2}$ (%)	$\eta_{inorg\ N}$ (%)	$k_I^{Ar–NO_2}$ (s^{-1})	$k_I^{inorg\ N}$ (s^{-1})
DNT	30	29.35	10.15	1.94×10^{-4}	0.37×10^{-4}
	60	50.68	13.50		
	120	73.29	29.18		
	180	87.56	36.12		
	240	94.15	47.38		
DNB	30	22.97	7.78	1.45×10^{-4}	0.31×10^{-4}
	60	46.21	12.37		
	120	64.80	26.07		
	180	77.01	32.05		
	240	87.61	43.79		

$k_I^{Ar–NO_2}$ is the pseudo-first order rate constant for pollutant degradation, s^{-1}; $k_I^{inorg\ N}$ – pseudo-first order rate constant for conversion of organic to inorganic nitrogen by mineralisation, s^{-1}.

Pollutant initial concentration effect. It is known that performance of any surface process, as in the case of photocalysis is highly affected by the interaction between pollutant and catalyst reflected by the level of pollutant adsorption, expressed as equilibrium adsorption constant, K_{ads}. The Langmuir–Hinshelwood (L–H) kinetic model is the most commonly expression used to describe the heterogeneous catalytic processes. The Langmuir adsorption model has been applied to organic compounds in aqueous suspension according to the following expression:

$$r_0 = -\frac{dC}{dt} = \frac{k_r K_{ads} C_0}{1 + K_{ads} C_0} \qquad (1)$$

where r_0 is the degradation initial pollutant rate, M s^{-1}; C_0 – initial polutant concentration, M; k_r – reaction rate constant, M s^{-1}.

Experiments on 0.5 wt.% Fe–TiO_2 at 200 mg/l catalyst dose and pH 7, for both studied nitroderivatives were performed. The initial pollutant concentration was varied between $(0.34–3.14) \times 10^{-4}$ M, in order to determine the values of k_r and K_{ads}. Equation (1) was linearised by its reciprocal expression:

$$\frac{1}{v_0} = -\frac{1}{k_r} + \frac{1}{k_r K_{ads} C_0} \tag{2}$$

The v_0 values were independently obtained from kinetic curves by the linear feet, using only the experimental points during the first 30 min irradiation. The $1/v_0 = f(1/C_0)$ plot shown in Fig. 2 attests that the Langmuir–Hinshelwood model describes nitroderivatives photodegradation which occurs at the catalyst surface.

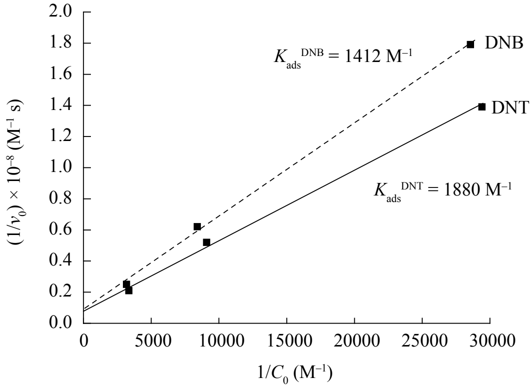

Fig. 2. Linearisation of the Langmuir–Hinshelwood equation in respect to DNT and DNB

The $1/k_r$ value has been obtained from the intersection of the straight line with the ordinate. Thus, the reaction rates for the two nitroderivatives were calculated and obtained values are $k_r^{DNT} = 11.92 \times 10^{-8}$ M s^{-1} and $k_r^{DNB} = 11.82 \times 10^{-8}$ M s^{-1}. The adsorption equilibrium constants calculated from the slope of the line are $K_{ads}^{DNT} = 1880$ M^{-1} and $K_{ads}^{DNB} = 1412$ M^{-1}. Experimental obtained values of K_{ads} revealed that nitrotoluene derivative is better adsorbed on photocatalyst surface than nitrobenzene derivative, due to polarisable molecules such nitrotoluenes easily generate hydrogen bonding interactions with Ti–OH groups on the catalyst surface, which assure enhanced DNT degradation compared with DNB. This is in accordance with values of rate constants and degradation efficiencies for the two studied pollutants (Table 1).

CONCLUSIONS

Doping of TiO_2 with heavy metal like Fe, Co, Ni can assure efficient nitroaromatics degradation, the best photoactivity in respect to DNT degradation being registered for 0.5 wt.% Fe-TiO_2 catalyst. Pollutant degradation and organic nitrogen mineralisation follow a pseudo-first order kinetics. In the same working conditions, nitrotoluene derivative (DNT) is faster photocatalytic oxidised than nitrobenzene derivative (DNB), due to determinative role of pollutant structure on its interactions with catalyst surface and degradation pathway. Under optimum working conditions (pH 7, initial nitroaromatics concentration = 3×10^{-4} M, photocatalyst dose = 200 mg/l, 240 min irradiation) pollutants degradation and organic nitrogen mineralization efficiencies are situated between 89–94% and 44–47%, respectively. This recommended photocatalytic process, using Fe-doped TiO_2, as a promising method for the treatment of wastewater with nitroaromatics content, especially taking into account that UV-vis. artificial source can be replaced with solar light, which assures costs saving.

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