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Photodegradation Kinetics of *o*-Nitroaniline (ONA), *m*-Nitroaniline (MNA), *p*-Nitroaniline (PNA), *p*-Bromoaniline (PBrA) and *o*-Chloroaniline (OClA) in Aqueous Suspension of Zinc Oxide

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Photodegradation of several aniline derivatives including *o*-nitroaniline (ONA), *m*-nitroaniline (MNA), *p*-nitroaniline (PNA), *p*-bromoaniline (PBrA) and *o*-chloroaniline (OClA) have been studied in aqueous solution using zinc oxide. Rate constants spane the range from 6.46×10^{-3} min^{-1} to 2.59×10^{-2} min^{-1}. The slower degradation rate of *p*-bromoaniline (PBrA), 6.46×10^{-3} min^{-1} could be related to oxidation potential of the corresponding aromatic rings. The Langmuir-Hinshelwood (L-H) rate constant k_r and adsorption constant, (K_A) for all five aniline derivatives are reported.

Key words: photodegradation, aniline derivatives, zinc oxide

Many agricultural pesticides of profuse use have molecular structure with a six-member nitrogen containing aromatic heterocycle [1,2], and significant amount of these compounds and contaminants of surface waters and soils. As a consequence, in the last decade both the thermal and the photochemical ways of the degradation of such contaminants have been topics of growing interest [3,4]. In particular, their photoinduced degradation under natural condition, *i.e.* in water solution and in the presence of air, has been tested with variable success, and the reactions involved have been studied in order to know more about the natural photochemical decay [5]. Aniline derivatives are toxic and classified as typical environmental pollutants [6]. About 300 chemical products and intermediates are currently manufactured from aniline. The major uses of aniline are in the polymer, rubber, agricultural, and dye industries [7–9]. The Colour Index lists 174 dyes made from aniline and over 700 dyes prepared from aniline derivatives [8]. Important agricultural uses for aniline derivatives include herbicides, fungicides, insecticides, animal repellents, and defoliants. Aniline and its N-alkyl derivatives have been utilized as antiknock compounds in leaded gasolines. Aniline salts are used as motor fuel additives to prevent carburator icing and as rust inhibitors. Diarylamines are of greatest industrial importance as rubber antioxidants and antiozonants, as stabilizers in rubber and explosives [9].

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Some diarylamines that retard the destructive effect of intense gamma or neutron irradiation have been termed antirads [10]. Diarylnitrosamines find use as vulcanization inhibitors with certain accelerators [11]. Aniline and its derivatives are frequently found in both effluents of waste water treatment plants and surface water. Owing to the interest in environmental protection, the photodegradation may play an important role in their elimination from aquatic environment. In Scheme 1, the structures of selected aniline derivatives are given.

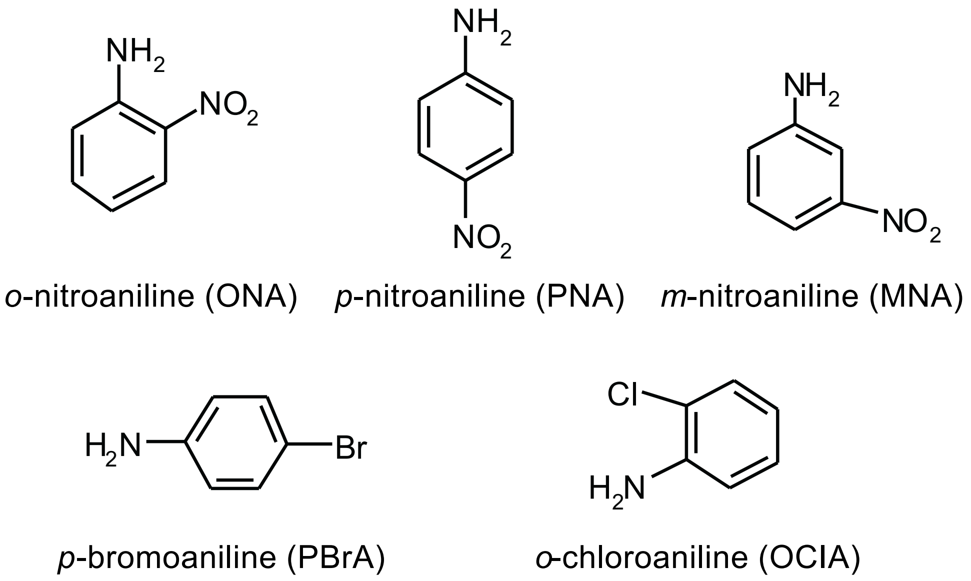
Photocatalytic reaction in aquatic environments is gaining increasing interest in the last few years. Marine and fresh waters are mixtures of dissolved inorganic and organic compounds, biological species and colloidal aggregates [12–15]. Whereas direct [16,17] or indirect [18] photolytic reaction have received large attention, only recently photoprocesses at the surface and interphases and, in particular, photocatalytic reaction [19] at semiconductor material have gained a relevant importance. Semiconductor mediated photocatalytic mineralization has gained much attention. Pramauro and co-workers have reported the photocatalytic degradation of several aniline derivatives in aqueous solution and its kinetics containing TiO_2 suspension [20,21]. Among semiconductors titanium dioxide is one of the most popular and promising materials as a photocatalyst [22], but studies on ZnO assisted photoreactions of organic pollutants are scanty. In continuation of our ongoing programme to develop photochemical reactions [23–26], we wish to report the photodegradation kinetics of *o*-nitroaniline (ONA), *m*-nitroaniline (MNA), *p*-nitroaniline (PNA), *p*-bromoaniline (PBrA) and *o*-chloroaniline (OClA) in aqueous suspension of zinc oxide under illumination from a 400W high pressure Hg lamp. The kinetics of the photodegradation of aniline 4-ethylaniline, and 4-chloroaniline in aqueous suspension of polycrystalline titanium dioxide has been studied, and the overall rate constants have been evaluated in water [27,28].

The aim of this work was to study the influence of the substitutions of aniline on the susceptibility of this compound to photodegradation, looking for the experimental conditions, that maximize the photodegradation of this family of contaminants. With this purpose we have evaluated the photodegradation rate constant of disubstitued anilines, (ONA), (MNA), (PNA), (PBrA) and (OClA) under different experimental conditions of medium pH.

EXPERIMENTAL

Reagents: (ONA), (MNA), (PNA), (PBrA) and (OClA) standards and all solvents were purchased from Merck (Darmstad FRG). ZnO used was of analytical grade. The surface area of ZnO was 8 m^2g^{-1}. The powders were suspended in a reactor and stirred for 3 min. before use. Triply distilled water was used throughout. Aniline derivatives were added to the pure water and adjusted to the known pH, using 2 mM NaOH or 8.5% (v/v) H_3PO_4, respectively.

Apparatus: UV-VIS spectrophotometer (Shimadzu 160) was used for spectrophotometric monitoring of aniline derivatives concentration. A centrifuge was used for separation of photocatalysts from solution.



Scheme 1. Structures of selected aniline derivatives.

Analytical determinations: The concentrations of unreacted anilines were determined by a Shimadzu 160 UV-VIS spectrophotometer at 411, 357, 382, 291, 285 nm for (ONA), (MNA), (PNA), (PBrA) and (OClA), respectively. To make sure, that contribution from other absorbing species (*e.g.* transient degradation products) has been excluded, total organic carbon (TOC) determination was used for measurement of mineralization of the title compounds.

Photooxidation experiments: The photooxidation experiments were carried out by exposing 15 ml of oxygenated, magnetically stirred, aqueous solution of aniline derivatives (25 ppm) and photocatalyst (40 mg) to the illumination from a 400 W high-pressure mercury lamp. The Pyrex photoreactor was uniformly illuminated and kept at constant temperature of 25°C regulated by a thermostat. In all cases, to ensure a lack of direct UV photolysis, blank experiments were carried out by irradiation of the test solution. The concentration of aniline derivatives was monitored by periodic sampling during the experiment, using a Shimadzu 160 UV-VIS spectrophotometer by the light absorption peaks at 411, 357, 382, 291, 285 nm for ONA, MNA, PNA, PBrA and OClA, respectively. The initial solution of aniline derivatives was used as standard. Concentration of ammonia was determined spectrophotometrically at $\lambda = 510$ nm with Nessler's reagent. The formation of CO_2 was detected as $BaCO_3(s)$, separated in the aqueous solution saturated with $Ba(OH)_2$, in which the gases exiting from the reactor were bubbled. In addition to spectrophotometric methods, total organic carbon (TOC) determination was used for measurement of mineralization of title compounds.

General experimental procedure: To a solution (25 ppm) of ONA, MNA, PNA, PBrA and OClA (15 cm^3) in a Pyrex reactor was added ZnO (40 mg). It was placed in Pyrex water bath at room temperature. The reaction cell aerated with oxygen during the progress of reaction (flux 1 ml/min). The mixture was stirred magnetically and irradiated with 400 W high-pressure Hg lamp for 5 h. After that the ZnO powder was separated by centrifugation and the photolyte was analysed by UV-VIS spectroscopy.

RESULTS AND DISCUSSION

The effect of the catalyst amount on the degradation of aniline derivatives is illustrated in Fig. 1, which compares the degradation (decrease of aniline derivatives concentration) obtained with different amount of ZnO, added to the aqueous solution of aniline derivatives under the same irradiation conditions (irradiation time, 2.5 h). Although degradation increased with increasing catalyst amount, the oxidations appeared to approach a constant value, suggesting an optimum catalyst amount of 40 mg ZnO. It is interesting to note, that this phenomenon has been observed previously in other photocatalytic reactions over TiO_2 [29–31]. The results illustrated in Fig. 2 show, that the degradation of aniline derivatives increases linearly with amount of catalyst up to 40 mg. Above this amount of ZnO or vigorous stirring increased the turbidity of solution thus, reduced the light transmission through the solution.

The results obtained from photocatalytic degradation experiments of aniline derivatives with varying pH from 3 to 12 are illustrated in Fig. 2. From the plot we can see, that the degradation of aniline derivatives in neutral medium is higher than in acidic or basic medium. pH can affect either the surface properties of the photocatalyst, the isoelectric point of the oxides in the range of 5–6, the yield of oxidizing radicals or the chemical form of the substrate. ZnO or TiO_2 has an amphoteric character and aniline derivatives can undergo acid-base equilibrium. Consequently, the adsorption of the substrate may be affected, influencing strongly the degradation [20,32–33].

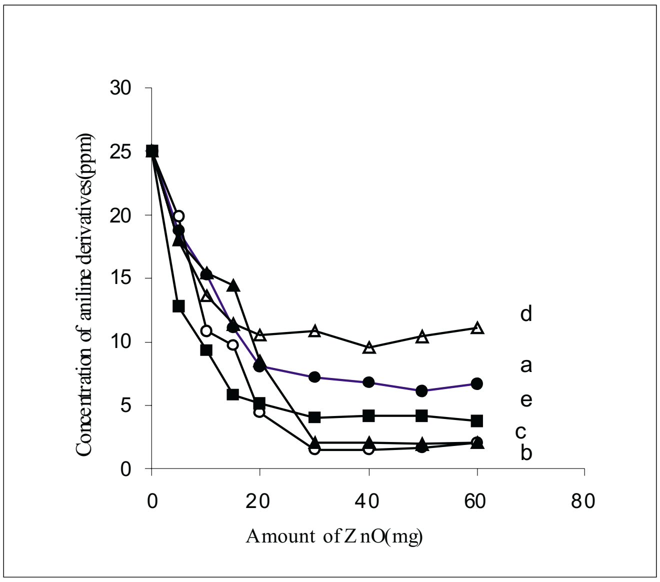


Figure 1. Aniline derivatives concentration (ppm) *vs*. the amount of ZnO for runs carried out by using Pyrex photoreactor (v = 15 ml); lamp 400 W high-pressure Hg; pH = 7; Flux of O_2 = 1 ml/min, irradiation time = 2.5 h and aniline derivatives (a) (ONA), (b) (MNA), (c) (PNA), (d) (PBrA), (e) (OClA).

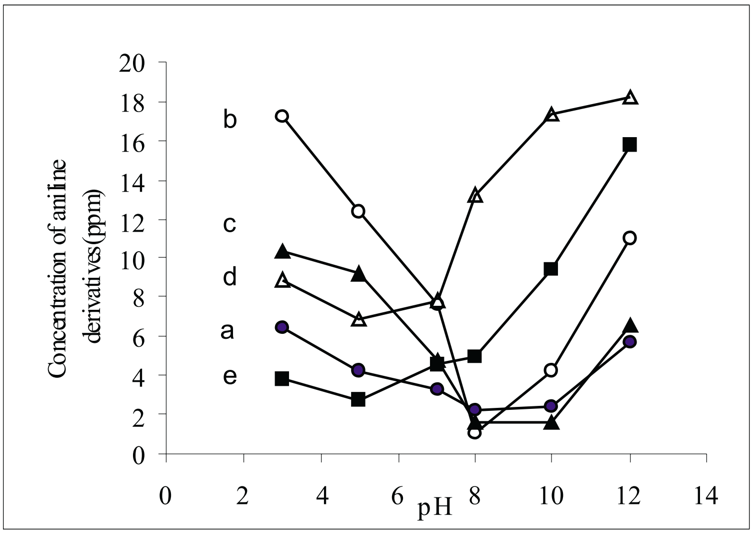


Figure 2. Aniline derivatives concentration (ppm) *vs.* pH. Initial pH of solution for runs carried out by using the Pyrex photoreactor (v = 15ml) amount of ZnO 40 mg; lamp 400 W high-pressure Hg; Flux of O_2 = 1ml/min; and aniline derivatives (irradiation time): (a) (ONA) (4 h), (b) (MNA) (4 h), (c) (PNA) (4 h), (d) (PBrA) (4 h) and (e) (OClA) (4 h).

The degradation of all the investigated aniline derivatives obeys the pseudo-first order kinetics.

$$-\frac{dc}{dt} = kc \qquad (1)$$

where *c* is the concentration of aniline derivatives and *k* is the experimental first-order rate constant. Linear plots of $\mathrm{Ln}(C_0/C_t)$ *versus* time were obtained (Fig. 3), from which *k* can be evaluated. Table 1 reports *k* and measured half-lifes of the (ONA), (MNA), (PNA), (PBrA) and (OClA) together with the corresponding correlation coefficient, *r*.

Table 1. Kinetics parameters of the degradation. Initial aniline derivatives concentration, 25 ppm, ZnO = 40 mg, initial pH = 8.

Compound	$t_{1/2}$ (min)	k (min^{-1})	r (corresponding correlation coefficient)
o-nitroaniline (ONA)	104	6.7×10^{-3}	0.9953
m-nitroaniline (MNA)	26	2.59×10^{-2}	0.9966
p-nitroaniline (PNA)	77	2.05×10^{-2}	0.9915
p-bromoaniline (PBrA)	96	6.46×10^{-3}	0.9985
o-chloroaniline (OClA)	58	1.33×10^{-2}	0.99885

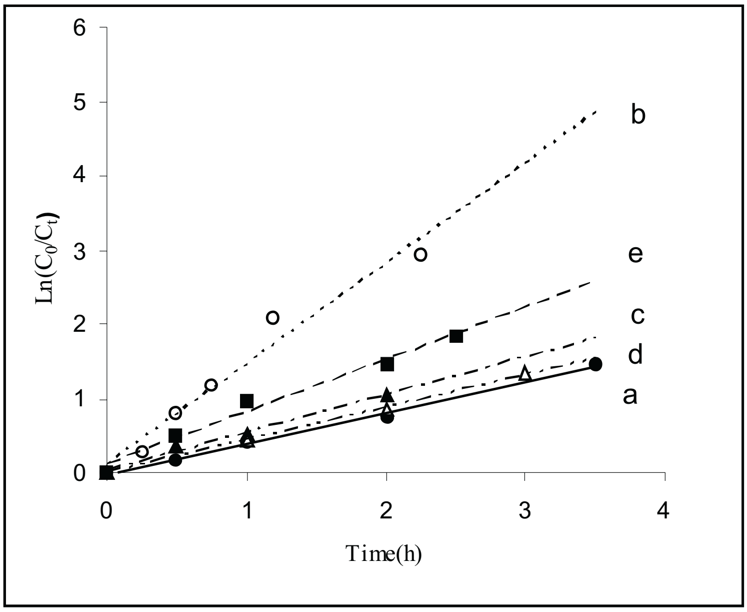


Figure 3. Kinetics of the degradation (a), (ONA), (b), (MNA), (c), (PNA), (d), (PBrA) and (e) (OClA). Substrate concentration, 25 ppm, ZnO = 40 mg, pH = 8.

It can be noted that the degradation kinetics vary, depending on the substituents present on the aniline. The slower degradation rate of *p*-bromoaniline (PBrA), 6.46×10^{-3} min^{-1} and *o*-nitroaniline (ONA), 6.70×10^{-3} min^{-1} could be related to the oxidation potential of the corresponding aromatic rings.

Increasing the aniline derivatives concentrations caused a decrease in rate. This effect can be explaind by assuming a competition between reaction intermediates and substrate for the active sites of zinc oxide [34]. The importance of aniline derivatives preadsorption on zinc oxide photocatalyst can be proved by a Langmuir-Hinshelwood (L-H) kinetic model [35–37], modified to accommodate the reaction occurring at a solid-liquid interface. The surface coverage θ is related to the initial concentration of the substrate C_0 and to the apparent adsorption equilibrium constant K_A (2).

$$\theta = \frac{KC_0}{1 + KC_0 + K_s C_s} \tag{2}$$

The rate of product formation can then be written as a single-component L-H kinetic rate expression (3–6), where k is the apparent reaction rate constant

$$Rate = R = \frac{-dc}{dt} = k_r \theta = k_r \frac{KC_0}{1 + KC_0 + K_s C_s} \tag{3}$$

$$K_A = \frac{K}{1 + K_s C_s} \tag{4}$$

$$Rate = R = -\frac{dc}{dt} = k_r \theta = k_r \frac{K_A C_0}{1 + K_A C_0} \tag{5}$$

$$\frac{1}{R} = \frac{1}{k_r K_A C_0} + \frac{1}{k_r} \tag{6}$$

occurring at the active site on the zinc oxide photocatalyst surface. The linear plots of $\frac{1}{R_{L-H}}$ *versus* $\frac{1}{C_0}$ for (ONA), (MNA), (PNA), (PBrA) and (OClA) are shown in Fig. 4, which tests the validity of the L-H model. Table 2 reports the L-H rate constant k_r and adsorption constant, (K_A) for all five aniline derivatives.

Table 2. Langmuir-Hinshelwood parameters of the degradation of aniline derivatives.

Compound	K_A (L·mg^{-1})	k_r (mg· min^{-1}· L^{-1})
o-nitroaniline (ONA)	7.5×10^{-3}	0.7228
m-nitroaniline (MNA)	4.4×10^{-3}	1.847
p-nitroaniline (PNA)	1.75×10^{-2}	0.7346
p-bromoaniline (PBrA)	1.5×10^{-2}	0.3349
o-chloroaniline (OClA)	7.0×10^{-4}	7.1890

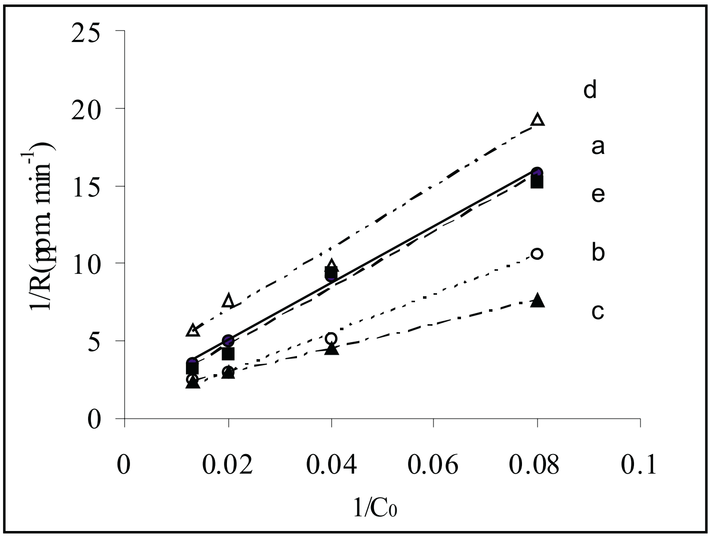


Figure 4. Langmuir-Hinshelwood kinetics degradation of (a), (ONA), (b), (MNA), (c), (PNA), (d), (PBrA) and (e) (OClA). Substrate concentration, 25 ppm, ZnO = 40 mg, pH = 8.

CONCLUSIONS

Under the reported conditions, all of the examined aniline derivatives, (ONA), (MNA), (PNA), (PBrA) and (OClA) were degraded in less than 3 h, using zinc oxide semiconductor photocatalyst. The degradation of aniline derivatives in neutral medium is higher than in acidic or basic medium. The linear plots of $\frac{1}{R_{L-H}}$ *versus* $\frac{1}{C_0}$ for (ONA), (MNA), (PNA), (PBrA) and (OClA), the L-H rate constant k_r and adsorption constant, (K_A) for all five aniline derivatives are reported.

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