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Photodegradation of Aromatic Amines by Ag-TiO_2 Photocatalyst

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The photocatalytic degradation of *ortho*, *para* and *meta*-nitroanilines (ONA, PNA and MNA) was investigated by Ag-TiO_2 suspension. The effect of some parameters such as the amount of photocatalyst, irradiation time of UV light, flow rate of O_2, pH, and temperature for the Ag-TiO_2 photocatalyst was also examined. Degradation of amines was small when the reaction was carried out in the absence of photocatalyst, and negligible in the absence of the UV light. Degradation rate of aniline derivatives decreases with increasing O_2 in the system. The effect of pH indicated that effective degradation occurred in alkaline conditions. Degradation kinetics of these aromatic amines can be described by Langmuir-Hinshelwood equation and shows pseudo-first order law.

Keywords: Photodegradation, Aniline derivatives, Aromatic amines, Ag-TiO_2 Photocatalyst

INTRODUCTION

Aniline and its derivatives are well known as toxic and carcinogenic compounds [1]. These compounds are frequently found in both effluents of waste water treatment plants and surface water. Important agricultural uses of aniline derivatives include herbicides, fungicides, insecticides, animal repellents and defoliants. The color Index lists indicates that over 700 dyes were prepared from aniline derivatives [2]. Recently, increasing attention has been paid to removing these aromatic compounds from the environment [3,4].

Advanced oxidation processes (AOPs) are alternative methods for the complete degradation of pollutants [5,6]. AOPs include photocatalysis systems such as combination of a semiconductor (TiO_2, ZnO, *etc.*) and UV light. TiO_2 has been widely used because of its various merits such as low cost, high photocatalytic activity, chemical activity and non-toxicity. However, its applications have been limited for several reasons such as low photon utilization efficiency and need for a high power UV excitation source. One way to solve these problems is the modification of catalysts by doping them with various metals such as Ag, Pt, Fe, Au, *etc.* [7,8]. The metals deposited or doped on TiO_2 act as electron traps, facilitating electron-hole separation and promoting the interfacial electron transfer process [9]. The important active species are produced in photodegradation processes through well-known mechanism [10-11], as shown in Fig. 1. In photocatalytic degradation of organic pollutants, the substrate molecules react with hole or, more probably, with hydroxyl radicals, to give a number of hydroxylated reaction intermediates [12,13].

The aims of this work are investigation of photocatalytic degradation of aromatic amines and the study of the influence of various parameters on this photocatalytic system in the presence of Ag-TiO_2. The kinetics of the photodegradation of these compounds has been also studied.

EXPERIMENTAL

Reagents and Apparatus

Ortho, *para* and *meta*-Nitroaniline (ONA, PNA, MNA) standards were purchased from Merck (Darmstadt FRG).

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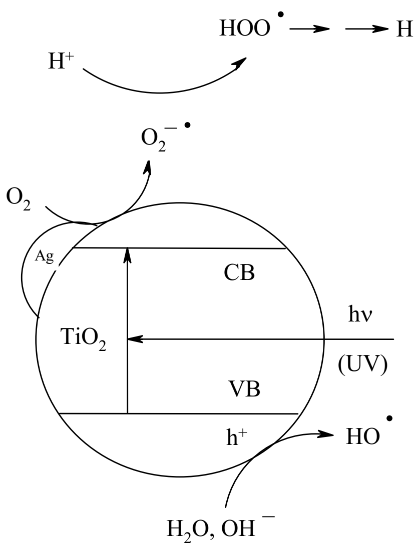

Fig. 1. TiO_2-photosentisition pathway under UV irradiation.

Amine solutions were prepared by dissolving the amines in double distilled water and dimethylformamide (DMF, 5% v/v). Solvents and other materials such as NaOH, HCl, KCl, HgI_2, KI, K_2HPO_4, KH_2PO_4, $Na_2B_4O_7.10H_2O$, $KHC_8H_4O_4$ and $Ba(OH)_2$ were purchased from Merck. The commercially available TiO_2 powder, which was in anatase crystalline form, and has a surface area about 50 m^2 g^{-1} and primary particle size of 30 nm was obtained from Merck.

A 400 W high-pressure mercury lamp provided irradiation. Shimadzu 160 UV-Vis spectrophotometer was used for spectrophotometer monitoring of aniline derivatives. Separation of photocatalyst from suspension was carried out with centrifuge. pH measurements were made using Testo 230 pH meter.

Preparation of Photocatalyst

Ag loaded-TiO_2 containing 1% (w/w) silver was prepared by reported procedure [14]. Initially, 9.2 ml of $AgNO_3$ solution (0.1 M) was added to a TiO_2 slurry containing 10 g of TiO_2 followed by *ca.* 10 ml of a 1% (w/v) Na_2CO_3 solution. The aqueous suspension was dried at room temperature and then backed for 6 h at 400 °C. No useful information was obtained by XRD, but the amount of Ag loading was determined by ICP method. The XRD patterns showed that the TiO_2 phase did not change during the catalyst preparation (Fig. 2).

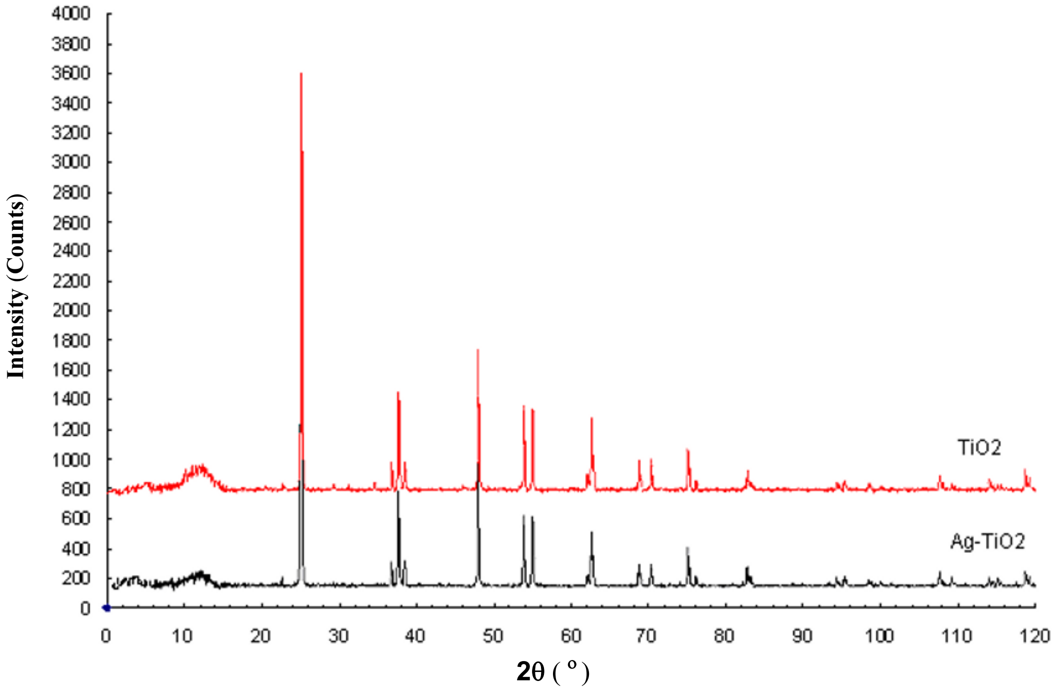

Fig. 2. The XRD pattern of TiO_2 and Ag-TiO_2.

Procedures

A suspension contaning 15 ml of aniline derivatives (30 mg l^{-1}) and photocatalyst was poured into a Pyrex photoreactor having dimensions 1.5 × 15 cm (diameter × height). It was then placed in Pyrex water bath at room temperature. Water circulating jacket was used for cooling Pyrex photoreactor, elimination of IR-radiation and short-wavelength UV-radiation. The mixture was stirred magnetically and irradiated with a 400 W high-pressure mercury lamp. The set up of the Photodegradation experiments is shown in Fig. 3. After that, the photocatalyst was filtered, the photolyte was analysed by UV-Vis spectrophotometer at λ_{max} = 412, 382 and 375 nm for *ortho*, *para* and *meta*-nitroanilines, respectively.

The formation of CO$_2$ was detected as BaCO$_3$(s) separated in aqueous solution saturated with Ba(OH)$_2$ in which the gases exiting from the reactor were bubbled. Ammonia concentration was determined spectrophotometrically at λ = 410 nm with Nessler's reagent.

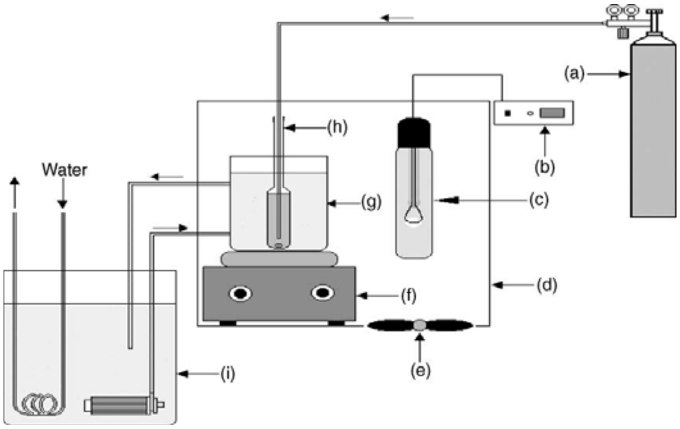

Fig. 3. Photocatalytic degradation set up: (a) oxygen cylinder; (b) power supply; (c) 400 W high-pressure Hg lamp; (d) photoreactor with aluminum foil as reflector for a full irradiation of catalyst; (e) fan; (f) magnetic stirrer; (g) 2 L Pyrex beaker; (h) photocatalytic degradation cell; (i) water thermostat hake model f-122.

RESULTS AND DISCUSSION

The photoactivity of the catalysts depends on their electronic properties, particle size distribution, the texture, the type of pores present, the different hydroxylation of the surfaces, the acid-base properties, the amount of adsorbed reactant species, *etc*. [15]. The position of workfunction of metal will be critical for the effective transfer of electrons on the conduction bond of titanium dioxide toward adsorbed electrolytes [16]. The Photocatalytic degradation of PNA (20 ppm) was investigated over a heterogeneous photocatalyst of Ag-TiO$_2$ (1%, w/w) and TiO$_2$ for 2 h. The degradation percentage of this compound in the presence of Ag-TiO$_2$ (40 mg) and TiO$_2$ (40 mg) powders was 81 and 10, respectively.

Photodegradation of target compounds was carried out in the presence of Ag-TiO$_2$ (30 mg) with UV irradiation (Fig. 4). These compounds are not degraded with the Ag-TiO$_2$ suspension in the dark or UV light in the absence of photocatalyst for 2 h period.

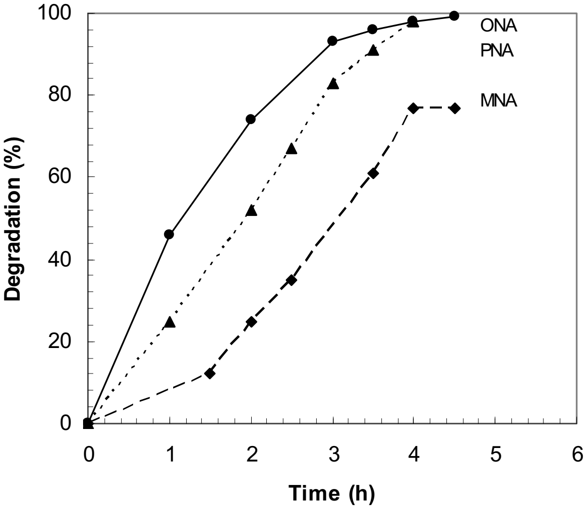

Fig. 4. Influence of irradiation time on photodegradation of aniline derivatives. Concentration of amines (30 ppm); Ag-TiO$_2$ (30 mg).

The effect of photocatalyst amount on the degradation of aniline derivatives is shown in Fig. 5. Experiments performed with different amounts of Ag-TiO$_2$ showed that although degradation percentage increases with an increase in photocatalyst amount, this process appears to approach a constant value and then decreases. This observation can be explained in terms of availability of active sites on the catalyst surface and the penetration of UV light into the suspension. Above the constant value of Ag-TiO$_2$ increases turbidity of

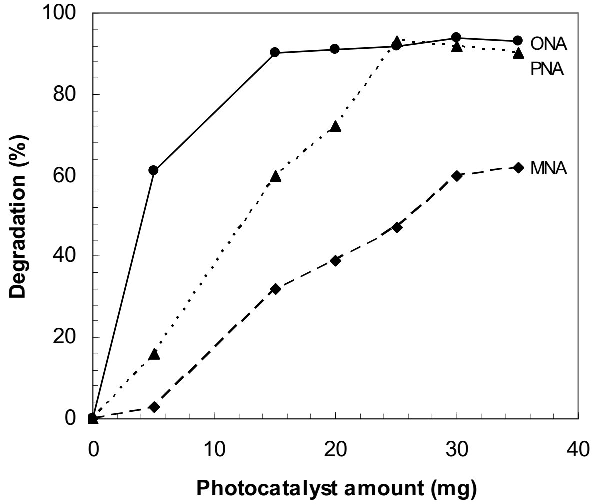

Fig. 5. Degradation of aniline derivatives *vs*. the amount of Ag-TiO_2. Concentration of amines (30 ppm); Ag-TiO_2 (30 mg); irradiation time: ONA (3 h), PNA (3.5 h) and MNA (3.5 h).

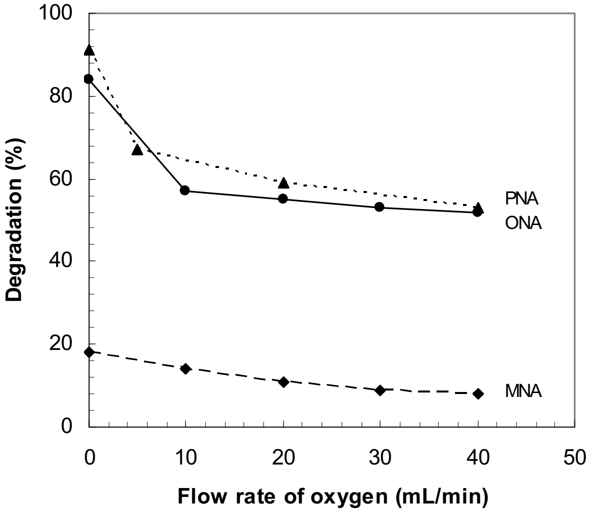

Fig. 6. Effect of oxygen flow rate on degradation of aniline derivatives. Concentration of amines (30 ppm); Ag-TiO_2 (25 mg); irradiation time: ONA (1.5 h), PNA (2 h) and MNA (1.5 h).

suspension, but reduces the light transmission through the suspension [17].

As shown in Fig. 6, degradation of target compounds decreases with increasing oxygen flow rate. The degradation percentage for argon bubbled suspensions (with 30 ppm of amine and 30 mg of catalyst) were 91, 97 and 53 for ONA, PNA and MNA, respectively. It seems that the reduction of nitro group to amino group by the scavenging of conduction bond electrons is an efficient process [18]. Adsorptive oxygen at the surface of photocatalyst competes with amine for trapping of electrons.

The photodegradation of ONA, PNA and MNA in the presence of Ag-TiO_2 was studied in the pH range between 5-11 (Fig. 7). The increasing of degradation percentage with increasing pH can be attributed to the increase in the number of OH^- ions at the surface of TiO_2, since hydroxyl radicals can be formed by trapping photo-produced holes [3]. Hence, at acidic pH values, the particle surface is positively charged, R-NH_3^+ (due to reaction of aromatic amine with H^+) may not be absorbed onto the positive surface of photocatalyst effectively, thus, photodegradation decreases.

The observed rates are slightly affected by temperature in the range 25-60 ºC, and photocatalytic process can be carried out effectively at laboratory temperature.

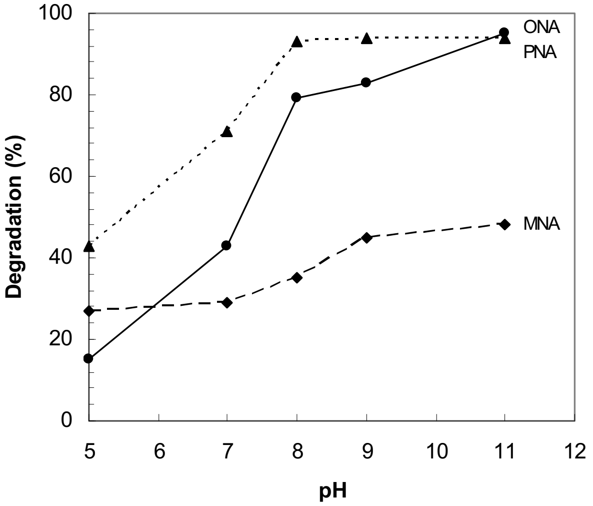

Fig. 7. Effect of pH on photodegradation of aniline derivatives. Concentration of amines (30 ppm); Ag-TiO_2 (25 mg); irradiation time: ONA (120 min), PNA (165 min) and MNA (180 min).

Many studies [19-21] have applied the Langmuir-Hinshelwood (L-H) expression to the analysis of heterogeneous photocatalytic reaction, where the reaction rate R is proportional to the surface coverage θ.

$$R = -dC/dt = k_r \theta = k_r KC/(1 + KC) \qquad (1)$$

where k_r is the reaction rate constant, K is the absorption coefficient of the reactant, and C is the reactant concentration. When C is very small, the KC product is negligible with respect to unity so that Eq. (1) describes pseudo-first order kinetics. The values of k_r and K are used to explain the coefficients defining the rate determining reaction events and pre-equilibrium adsorption within an adsorbed monolayer at the oxide surface and the aqueous solution interface. The effect of light intensity is also incorporated in k_r and K which accounts for the equilibrium constant for fast adsorption-desorption processes between surface monolayer and bulk solution [22]. The integration of Eq. (1) with the limit condition at the start of irradiation, t = 0, the concentration is the initial one, $C = C_0$, gives:

$$\ln(C_0/C) = k't \qquad (2)$$

where k' is the apparent pseudo-first-order reaction constant. Plot of $\ln(C_0/C_t)$ *vs*. irradiation time gave a straight line (Fig. 8). The pseudo-first order rate constants of the reactions in the presence of Ag-TiO$_2$ ($k_{Ag\text{-}TiO2}$), TiO$_2$ (k_{TiO2}) and ratio of these values are listed in Table 1. Discrepancy between the pseudo-first-order reaction rate constants may be due to different photocatalytic degradation mechanisms and/or to a competition for degradation between the reactant and the intermediate products.

Table 2 shows the advantage of this catalytic system in comparison with previously reported systems for degradation of organics.

CONCLUSIONS

The photocatalytic activity of Ag-TiO$_2$ catalysts in photodegradation of ONA, PNA and MNA has been investigated and compared with that of pure TiO$_2$. The results of this research indicated that photodegradation of aniline derivatives was obviously affected by irradiation time, the amount of photocatalyst, pH and oxygen. Degradation

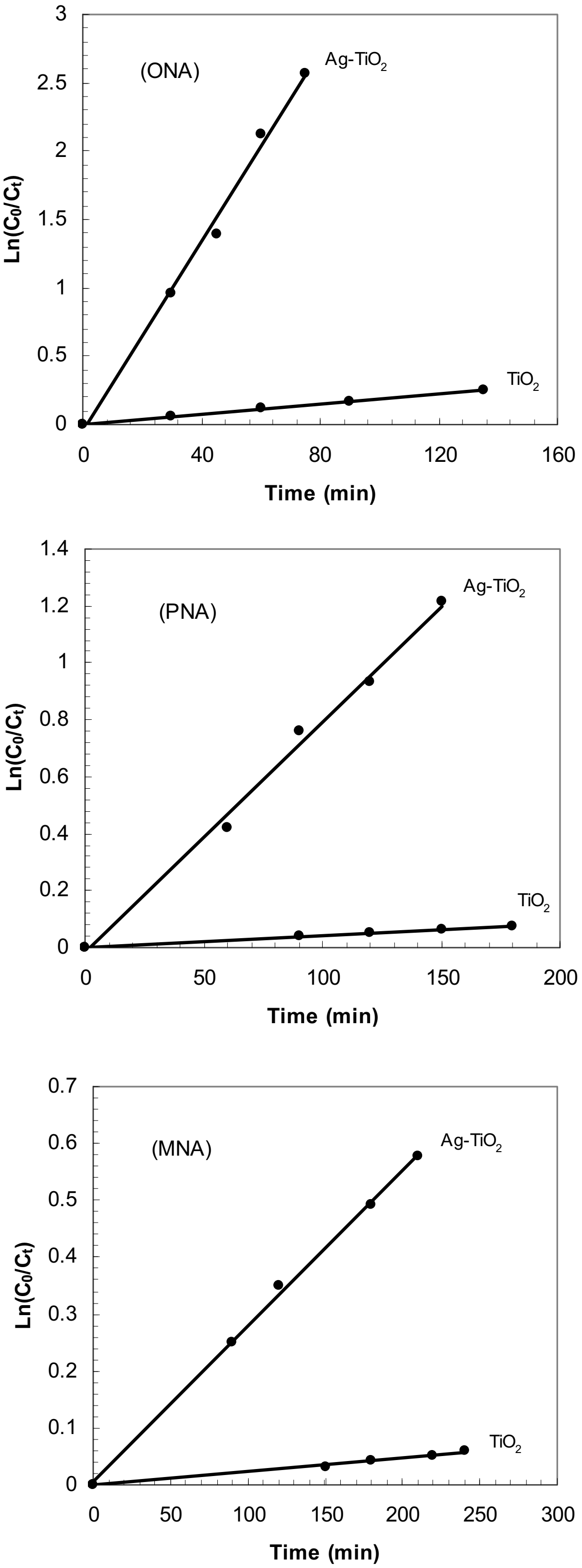

Fig. 8. Plots $\ln(C_0/C_t)$ *vs*. irradiation time. Concentration of amines (30 ppm); Ag-TiO$_2$ (25 mg), solution pH =11.

Table 1. Rate Constant Values of the Photoreactions in the Presence of TiO_2 and Ag-TiO_2 Particles

	k_{TiO2} (min^{-1})	$k_{Ag\text{-}TiO2}$ (min^{-1})	$k_{Ag\text{-}TiO2}$ / k_{TiO2}
ortho-Nitroaniline	1.83×10^{-3}	3.47×10^{-2}	19.0
para-Nitroaniline	4.14×10^{-4}	8.11×10^{-3}	19.6
meta-Nitroaniline	1.32×10^{-4}	2.74×10^{-3}	20.8

percentage was negligible when the reaction was carried out in the absence of photocatalyst and also in the absence of UV light. We observed that the optimum amount of photocatalyst was about 30 mg. Degradation of selected compounds is higher at basic medium and in deaerated suspension. The linear plots of $\ln(C_0/C_t)$ *vs*. irradiation time and rate constants (k) in the presence of Ag-TiO_2 and TiO_2 are reported. Degradation kinetics of amine derivatives can be described by Langmuir-Hinshelwood equation. The photocatalytic

Table 2. Summary of the Literature on the Effects of Silver on the Photocatalytic Degradation of Organics

Compound	Effect	Conditions				
		TiO_2	Ag loading (%)	Substrate (mg l^{-1})	pH	
p-Nitroaniline	Enhanced 8.1 times	Merck	1	20	11	-
Chloroform	Enhanced 1.25 times	Aldrich	0.75	200	3	[14]
Urea	Enhanced 5.2 times	Aldrich	0.75	100	3	[14]
1,4-Dichlorobenzene	Enhanced by 35%	Degussa P25	1.50	-	-	[23]
Methyl orange	Enhanced	Merck	-	-	8.75	[24]
Malic acid	Enhanced by 12%	Quartz supported TiO_2	6	50	-	[25]
Methyl violet dye	Enhanced 2 times	Aldrich	0.75	20	7	[26]
2-Propanol	Enhancement	Rutile	0.5	30000	-	[27]
E. coli	Enhancement	Aldrich	0.75		7	[28]
Sucrose	Enhanced 4 times	Degussa P25	2	100	3.5	[10]
Oxalic acid	Enhanced 5 times	Degussa P25, 1 g/l	2×10^{-4} M Ag	450	3 ± 0.3	[29]
Methylene blue	Enhanced 2.2 times	Rutile TiO_2	-			[30]
Phenol	Enhanced 3.6 times	Aldrich	0.4	16.7		[31,32]
Methyl orange	Enhanced 2 times	Degussa P25, thin films	10^{-3} M Ag	6.12	9.2	[33]
Rhodamine B	Enhanced by 30%	Degussa P25	2	4.79	4.5	[34]
2-Chlorophenol	Enhanced 1.5 times	Degussa P25	4.5×10^{-4}	111	4.5	[35]
Sirius Gelb GC (Azo dye)	Enhanced 2.5 times	Aldrich	0.75	20	3.5	[7]
2-Propanol	Retarded	Anatase	0.5	30000		[27]
Salicyclic acid	No effect	Degussa P25	2	100	3.5	[9]
Phenol	No effect (2 at %), Retarded (20 at %)	Degussa P25	2,20	100	3.5	[36]
Resorcinol	No effect	Degussa P25	0.1-20	9.7	3 ± 0.5	[37]
4-Chlorophenol	Enhanced	Degussa P25 (sol/gel)	0.5	64.3	5.5	[38]

degradation of aniline by Ag-TiO_2 photocatalyst can be used as a practical and useful way for the removal of environmental pollutants that contribute to industrial wastewater treatment plants.

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REFERENCES

[1] N. Irving Sax, Dangerous Properties of Industrial Materials, 4th, Van Nostrand Reinholds Co., New York, 1975, pp. 16, 408.

[2] C.D. Stevenson, Queens. J. Agric. Sci. 19 (1962) 179.

[3] L. Wenhua, L. Hong, C. Sao'an, Z. Jianqing, C. Chunan, J. Photochem. Photobiol. A: Chem. 131 (2000) 125.

[4] M.H. Habibi, M. Khaledisardashti, M. Montazerozohori, Annal. di Chim. 94 (2004) 421.

[5] V. Augugliaro, A.B. Prevot, V. Loddo, G. Maric, L. Palmisano, M. Schiavello, Res. Chem. Intermed. 26 (2000) 413.

[6] M. Canle L., J.A. Santaballa, E. Vulliet, J. Photochem. Photobiol A: Chem 175 (2005) 192.

[7] A. Ozkan, M.H. Ozkan, R. Gurkan, M. Akcay, M. Sokmen, J. Photochem. Photobiol. A: Chem. 163 (2004) 29.

[8] S. Matsuo, N. Sakaguchi, K. Yamada, T. Matsuo, H. Wakita, Appl. Surf. Sci. 228 (2004) 233.

[9] J. Herrmann, J. Disdier, P. Pichat, J. Phys. Chem. 90 (1986) 6028.

[10] V. Vamathevan, R. Amal, D. Beydoun, G. Low, S. McEvoy, J. Photochem. Photobiol. A: Chem. 148 (2002) 233.

[11] N. Sobana, M. Muruganadham, M. Swaminathan, J. Mol. Catal. A: Chem. 258 (2006) 124.

[12] A. Di Paola, V. Augugliaro, L. palmisano, G. Pantaleo, E. Savinov, J. Photochem. Photobiol. A: Chem. 155 (2003) 207.

[13] A. Sobczynski, L. Duczmal, W. Zmudzinski, J. Mol. Catal. A: Chem. 213 (2004) 225.

[14] M. Kondo, W. Jardim, Water Res. 25 (1991) 823.

[15] A. Di Paola, G. Marci, L. Palmisano, M. Schiavello, K. Uosaki, S. Ikeda, B. Ohtani, J. Phys. Chem. B 106 (2002) 637.

[16] K.Y. Song, Y.T. Kwon, G.J. Choi, W.I. Lee, Bull. Korean Chem. Soc. 20 (1999) 957.

[17] I.K. Konstantinou, T.A. Albanis, Appl. Catal. B: Environ. 49 (2004) 1.

[18] M.S. Vohra, K. Tanaka, Water Res. 36 (2002) 59.

[19] M.H. Habibi, S. Tangestaninejad, M. Khaledisardashti, Polish J. Chem. 78 (2004) 851.

[20] L. Hong, C. Sao'an, Z. Jiangqing, C. Chunan, Chemosphere 38 (1999) 283.

[21] H. Al-Ekabi, N.Serpone, J. Phys. Chem. 92 (1988) 5726.

[22] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.-M. Herrmann, Appl. Catal. B: Environ. 31 (2001) 145.

[23] W. Lee, H.-S. Shen, K. Dwight, A. Wold, J. Solid State Chem. 106 (1994) 288.

[24] L.-C. Chen, T.-C. Chou, Ind. Eng. Chem. Res. 33 (1994) 1436.

[25] J.-M. Herrmann, H. Tahiri, Y. Ait-Ichou, G. Lassaletta, A.R. Conzalez-Elipe, A. Fernandez, Appl. Catal. B: Environ. 13 (1997) 219.

[26] M. Sokmen, D.W. Allen, F. Akkas, N. Kartal, F. Acar, Water Air Soil Pollut. 132 (2001) 153.

[27] A. Sclafani, M.-N. Mozzanega, P. Pichat, J. Photochem. Photobiol. A: 59 (1991) 181.

[28] M. Sokmen, F. Candan, Z. Sumer, J. Photochem. Photobiol. A: 143 (2001) 241.

[29] E. Szabo-Bardos, H. Czili, A. Horvath, J. Photochem. Photobiol. A 154 (2003) 195.

[30] H. Tsuji, H. Sugahara, Y. Gotoh, J. Ishikawa, Nucl. Instrum. Meth. B 206 (2003) 249.

[31] H. Tsuji, T. Sagimori, K. Kurita, Y. Gotoh, J. Ishikawa, Surf. Coat. Technol. 158 (2002) 208.

[32] A. Dobosz, A. Sobczynski, Water Res. 37 (2003) 1489.

[33] I.M. Arabatzis, T.S. Stergiopoulos, M.C. Bernard, D. Labou, S.G. Neophytides, P. Falaras, Appl. Catal. B: Environ. 42 (2003) 187.

[34] H.M. Sung-Suh, J.R. Choi, H.J. Hah, S.M. Koo, Y.C. Bae, J. Photochem. Photobiol. A: Chem. 163 (2004) 37.

[35] D. Shchukin, E. Ustinovich, D. Sviridov, P. Pichat, Photochem. Photobiol. Sci. 3 (2004) 142.

[36] V. Vamathevan, R. Amal, D. Beydoun, G. Low, S. McEvoy, Chem. Eng. J. 98 (2004) 127.

[37] S.W. Lam, R. Amal, K. Chiang, T.M. Lim, G.K.-C. Low, Proceedings of the 1st Asia Regional Conference on Ultraviolet Technologies for Water, Wastewater and Environmental Application, Singapore, 2002.

[38] M. Moonsiri, P. Rangsunvigit, S. Chavadej, E. Gulari, Chem. Eng. J. 97 (2004) 241.