

Available online at www.sciencedirect.com

Applied Catalysis B: Environmental 57 (2004) 23–30

www.elsevier.com/locate/apcatb

Photocatalytic degradation of 2-chlorophenol by Co-doped TiO₂ nanoparticles

M.A. Barakat^{a,c}, H. Schaeffer^a, G. Hayes^a, S. Ismat-Shah^{a,b,*}^aDepartment of Materials Science and Engineering, University of Delaware, Newark, DE 19716, USA^bDepartment of Physics and Astronomy, University of Delaware, Newark, DE 19716, USA^cCentral Metallurgical R&D Institute (CMRDI), P.O. Box 87, Helwan, Cairo 11421, Egypt

Received 31 August 2004; received in revised form 5 October 2004; accepted 8 October 2004

Abstract

The photocatalytic degradation of 2-chlorophenol (2-CP) in aqueous solution was studied using Co-doped TiO₂ nanoparticles catalyst. The catalyst samples were synthesized by a sol–gel technique from TiCl₄ with different concentrations of Co(III) dopant and calcination temperatures. The typical composition of the prepared Co-doped TiO₂ was Ti_{1-x}Co_xO₂, where x values ranged from 0.004 to 0.14. Several analytical tools, such as X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area measurement, X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray analysis (EDAX), were used to investigate the nanoparticles structure, size distribution, and composition. The catalytic activity of the prepared nanoparticles was measured in a batch photoreactor containing appropriate solutions of 2-CP with UV irradiation of 100 W. High performance liquid chromatography (HPLC) was used for analyzing the concentration of 2-CP in solution at different time intervals during the photodegradation experiment. Parameters affecting the photocatalytic process such as catalyst crystallinity, light absorption efficiency, concentration of the catalyst and the dopant, solution pH, and 2-CP concentration have been investigated.

Results obtained revealed that Co-doped TiO₂ showed high activity for UV-photocatalytic degradation of 2-CP. The surface area of the catalyst was measured to be 39.7 m² g⁻¹. The photodegradation process was optimized by using 10 mg/L Co-doped TiO₂ with Co doping concentration of 0.036, after 3 h irradiation. The efficiency values of the 2-CP photodegradation were 93.4% and 96.4% at solution pH of 9 and 12, respectively. The photodegradation follows a pseudo-first-order reaction and the observed rate constant values change with the 2-CP concentration. The optical absorption properties of the samples were also measured. The presence of Co ions in the TiO₂ structure caused a significant absorption shift towards the visible region. The photodegradation efficiency matched the maximum light absorption efficiency. © 2004 Elsevier B.V. All rights reserved.

Keywords: 2-Chlorophenol; Photocatalytic degradation; Nanoparticle

1. Introduction

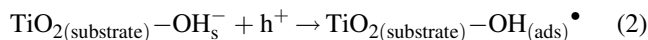
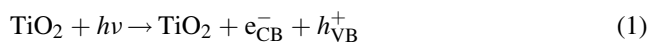
The presence of chlorinated compounds in aquatic environments has caused several environmental pollution problems. A representative of this class of compounds is 2-chlorophenol (2-CP). Photocatalytic degradation of such organic pollutants with semiconducting oxides holds promise for the purification and treatment of both drinking and industrial wastewater [1–4]. Among the semiconductors

being studied, TiO₂ is one of the most efficient photocatalysts as it is a stable and inexpensive photosensitive material [5]. The effective photoexcitation of TiO₂ semiconductor particles requires the application of light with energy equal to or higher than its band gap energy. It is generally reported that anatase with a band gap (E_g) of 3.2 eV is more efficient as a photocatalyst than rutile [6–8]. However, the overall photoreactivity of TiO₂ is also determined by various other factors such as electron/hole generation rate and formation of OH• radicals. The concept of the photocatalytic process using semiconducting TiO₂ particles has previously been reported [3,9,10]. TiO₂ acts as

* Corresponding author.

E-mail address: ismat@udel.edu (S. Ismat-Shah).

a photocatalytic reductant or oxidant (RO-type). Augugliaro et al. [10] reported that in a photocatalytic process electron–hole pairs generated must be trapped in order to avoid recombination and extend carrier life-time. The hydroxyl ions (OH^-) are the likely traps for holes, leading to the formation of hydroxyl radicals which are strong oxidant agents, while the traps for electrons are adsorbed oxygen species, leading to the formation of superoxide species (O_2^-) which are unstable, reactive and may evolve in several ways.



Several investigators have studied the photocatalytic decomposition of phenol and chlorinated phenolic compounds in aerated aqueous suspensions of TiO_2 upon illumination with near-UV light [11–15]. Different kinetic models were proposed in order to characterize the reaction [16–20]. In most of the above studies, Langmuir–Hinshelwood model [16] was used to describe the degradation rate expressions in terms of the disappearance of compounds or the formation of CO_2 . It has been demonstrated that catalyst dosage, initial concentration of pollutants, pH [21], UV light intensity [22,23], and concentration of charge trapping species [24,25] are the main parameters affecting the degradation rate of 2-CP in TiO_2 suspension. Mogyorosi et al. [26] investigated an organophilized clay mineral as adsorbent, combined with Degussa P25 TiO_2 photocatalyst, to improve the efficiency of 2-CP degradation. The photodegradation process with TiO_2 suspensions was also investigated in the presence of metal ions as electron scavengers [27–30]. The reaction rates in presence of the metal ions were higher than that obtained when only oxygen was used.

The preparation methods of TiO_2 catalysts have a great effect on the photocatalytic properties. Bickley et al. [31] prepared TiO_2 catalysts by ultrasonic nebulization with flame hydrolysis or furnace pyrolysis. They reported that the products had photocatalytic activities similar to that of the TiO_2 P25. Immobilization of the catalyst in the form of a thin film increases the photoreactivity [31,32]. Sol–gel methods have also been used for the synthesis of metal oxides thin films or powders [33–35]. The synthesis of metal oxides by sol–gel method generally involves hydrolyzing metal alkoxide dissolved in an organic solvent with controlled amounts of water. Acids or bases (HCl , NH_4OH , etc.) catalyze the hydrolysis reaction. The metal oxides are synthesized in both powder and thin film forms as free-standing particles or on substrates, respectively. It was reported that TiO_2 prepared by sol–gel method showed higher activity than TiO_2 suspension [33,34].

Several groups have recently investigated the effects of metal ion doping on the photocatalytic properties of TiO_2 . The incorporation of transition metal ions into the TiO_2 crystal lattice may alter the photoreactivity by shifting the

band gap of the catalysts into the visible region [36–38]. However, the photoactivity of the doped TiO_2 photocatalysts depends substantially on the nature of the dopant ion and its concentration, in addition to the method of preparation of the catalyst [39,40]. The reflectance spectra of TiO_2 -containing Fe showed increased absorption dependence on Fe concentration and firing temperature [39]. Iwasaki et al. [41] reported that TiO_2 doped with a small amount of Co(II) ions has highly photocatalytic activity under UV–vis light irradiation at Co doping concentration of 0.03 mol%. Fu et al. [42] and Moonsiri et al. [43] demonstrated the catalytic activity of precious metals-doped TiO_2 on 4-CP degradation under UV irradiation. They reported that the addition of a small amount of either Pt or Ag to sol–gel synthesized TiO_2 improved the catalytic activity compared to Degussa P25. Burns et al. [44] investigated the photocatalytic degradation of 2-CP using sol–gel synthesized Nd-doped TiO_2 under UV irradiation. They reported that doping TiO_2 with Nd(III) reduced the photodegradation time due to the difference in the ionic radii of Nd(III) and Ti(IV). Much larger substitutional Nd caused localized charge perturbation and formation of oxygen vacancies which act as electron traps. Jung and coworkers [45,46] investigated the doping of transition metals such as Pd(II), Pt(IV), Nd(III), and Fe(III) in TiO_2 thin film synthesized by metallorganic chemical vapor deposition method. They also demonstrated that Nd(III) doping improved the photodegradation of 2-CP under UV irradiation.

Previously, we reported the results of the synthesis of Co-doped TiO_2 nanoparticles via a sol–gel technique with various Co(III) doping concentrations and annealing temperatures [47]. In this work, the photocatalytic activity of the prepared samples has been evaluated via the degradation of 2-CP in aqueous solution under UV irradiation. Parameters affecting the photodegradation process such as the catalyst crystallinity, optical absorption, concentration of the catalyst and dopant, solution pH, and 2-CP concentration have been studied.

2. Experimental

2.1. Materials

Co-doped TiO_2 nanoparticles containing 0.004–0.14 mol% Co(III) ion dopant were synthesized via a sol–gel technique and calcined at different temperatures, as described in our previous work [47]. Briefly, doped TiO_2 nanoparticles were synthesized from titanium tetrachloride: TiCl_4 (Fluka 98%), and cobalt(III) 2, 4-pentanedionate: $\text{Co}[\text{CH}_3\text{COCH}=\text{C}(\text{O}-)\text{CH}_3]_3$ (Alfa Aesar). The dopant stoichiometry was controlled by dissolving the Co(III) precursor in ethanol (Pharmco, 200 proof) prior to the drop wise addition of TiCl_4 . The reaction was performed at room temperature while stirring in a fume hood to avoid exposure to the Cl_2 and HCl gases that evolve during the reaction. The

solution was allowed to rest and cool back to room temperature for settling the powder precipitate. The powder samples were dried in a dessicator and then annealed for 1 h in a box furnace operating between 200 and 900 °C in ambient atmosphere, during which the anatase to rutile phase transformation took place. The calcined samples were pulverized using a mortar and pestle.

The standard grade 2-CP was purchased from Merck with 99.5% purity. All other chemicals used in this work were of reagent-grade quality. The water used was deionized water. The light source was a water-cooled 100 W high-pressure mercury lamp (Hanovia 608A36, ACE Glass, NJ, USA), the spectral irradiance for the UV lamp (260 W/m²) ranges from 228 to 420 nm at a distance of 1 m from the light source, according to information provided by the manufacturer. The light intensity of the UV lamp used for the photodegradation experiments was recorded with a diode array spectrophotometer (HP 8452A).

2.2. Characterization

Specific surface area of Co-doped TiO₂ samples was 39.7 m² g⁻¹, as measured by physical adsorption of N₂ using BET method. The BET measurements were performed in a NOVA2000 gas sorption analyzer (Quantachrome Corporation). The change in the values of BET surface area for different samples was very small as the samples have a similar particle sizes. The average particle size of the prepared samples was 25 nm [47]. XRD analysis was performed to determine the effects of the Co doping on the rutile and anatase concentrations. The dopant concentration was verified by energy dispersive X-ray analysis (EDAX) and X-ray photoelectron spectroscopy (XPS). The band gap of the Co-doped TiO₂ samples was measured by ultraviolet–visible (UV–vis) light absorption experiments in a spectrophotometer (Hewlett-Packard, HP8452A Diode-array). The samples were diluted in methanol solutions and sonicated before the measurements.

2.3. Catalytic activity

Photodegradation experiments were performed with a photocatalytic reactor system. This bench-scale system consisted of a cylindrical Pyrex-glass cell with 1.5 L capacity (of 12 cm inside diameter and 15 cm height and a reflective interior surface). A 100 W mercury lamp was placed in a 5 cm diameter quartz tube with one end tightly sealed by a Teflon stopper. The lamp and the tube were then immersed in the photoreactor cell with a light path of 3.5 cm. The photoreactor was filled with 1 L of 12.5–75 mg/L aqueous 2-CP solution with 10–50 mg/L of Co-doped TiO₂ nanoparticles. The whole reactor was cooled with a water-cooled jacket on its outside and the temperature was kept at 22 °C. Compressed air was purged into the solution by bubbling compressed air from the bottom to maintain an aerobic condition magnetic stirrer was also used to keep the

solution chemically uniform. The pH values of the solutions were adjusted by adding NaOH (1 M) and HClO₄ (1 M) using an Orion Model 801A pH meter. The pH was kept at a specific value during experiments using a pH controller (New Brunswick Scientific, Edison, NJ). Solutions were radiated by UV light for specific time intervals. A 5 mL sample was drawn every 30 min. The experiments were carried out for 180 min. The liquid samples were filtered for analysis through 0.2 μm syringe filters (Gelman Acrodisc syringe filter with 25 mm diameter, and Nylon membrane of 0.2 μm pore size, PN4436T, Pall Gelman Laboratory, Ann Arbor, MI). Samples were analyzed for the residual concentrations of 2-CP by high performance liquid chromatograph (HPLC).

3. Results and discussion

XRD was used to determine the effect of Co doping concentrations on the anatase to rutile phase transformation at different calcination temperatures. The mass fraction of rutile (X_r) in the samples was calculated based on the relationship between the integrated intensities of anatase(1 0 1) and rutile(1 1 0) peaks. Fig. 1 shows selected XRD patterns obtained from samples with 0.072 mol% Co. The samples were calcined at temperatures of 400, 600, and 800 °C. The XRD patterns show that the samples annealed up to 400 °C are amorphous. Upon annealing at 600 °C, the samples become crystalline with predominantly anatase structure. The annealed samples at 800 °C have 100% rutile structure. Additionally, small peaks related to the CoTiO₃ phase start to appear with the formation of rutile. Fig. 2 plots X_r as a function of Co doping concentrations at different calcination temperatures. It can be seen that X_r for the samples calcined at 600 °C is almost zero for all the Co concentrations studied in this research. X_r increases with the increase in the annealing temperature beyond 600 °C and with the increase in cobalt doping concentration, reaching

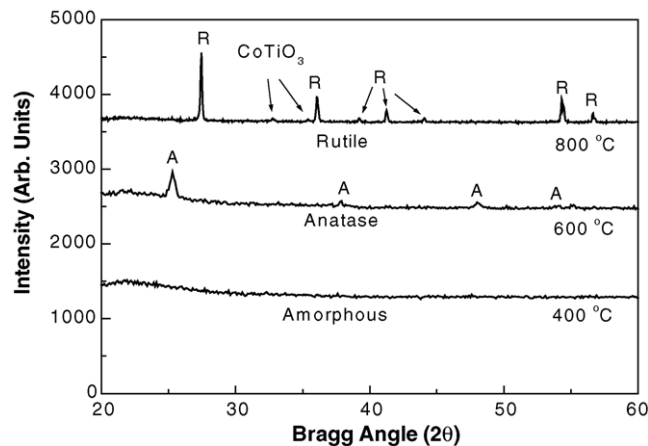


Fig. 1. XRD patterns for 0.072 mol% Co-doped TiO₂ samples at different calcination temperatures.

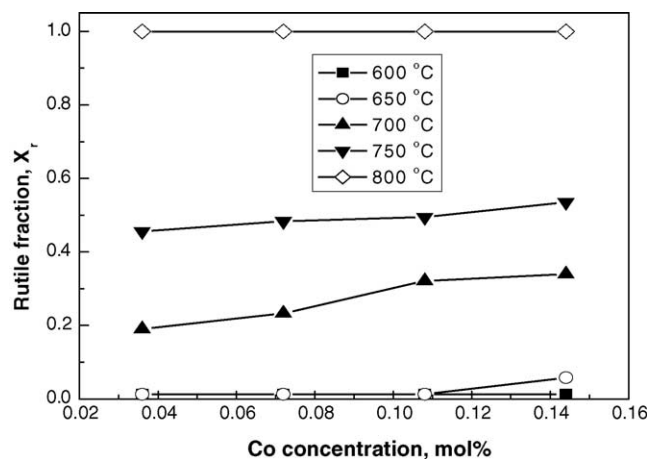


Fig. 2. Effect of Co doping concentrations on the anatase to rutile phase transformation at different calcination temperatures.

a maximum value of 1.0 for the samples calcined at 800 °C.

The efficiency of photodegradation of 2-CP as a function of different experimental parameters is demonstrated in Figs. 3–8. To study the effect of the catalyst crystal structure on the 2-CP photodegradation, samples annealed at different temperatures showing different crystal structures were used. Fig. 3 summarizes the results of these experiments. The highest degradation of 2-CP was achieved with samples that were annealed at 600 °C. The crystalline nature of the anatase structure is primarily responsible for the photocatalytic activity of the nanoparticles. Particles with anatase structure are known to have a better photocatalytic activity [6–7]. Additionally, the small particle size of TiO_2 (about 25 nm [47]) provides a large surface area where the catalytic reactions could occur and the photoreactivity is enhanced. The band gap energy measured for this anatase sample by UV–vis spectrophotometry was 3.2 eV, which is identical to that of the bulk TiO_2 . The annealed samples at 800 °C

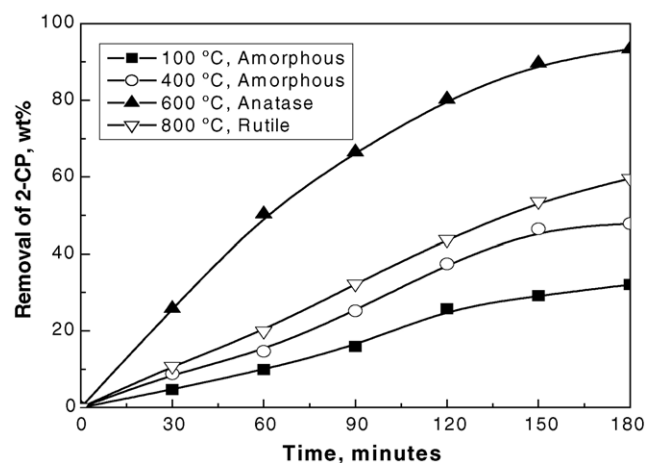


Fig. 3. Catalytic effect of the Co-doped TiO_2 crystal structure on the 2-CP photodegradation. Co = 0.036 mol%, catalyst dosage = 10 mg/L, 2-CP = 50 ppm, pH = 9.

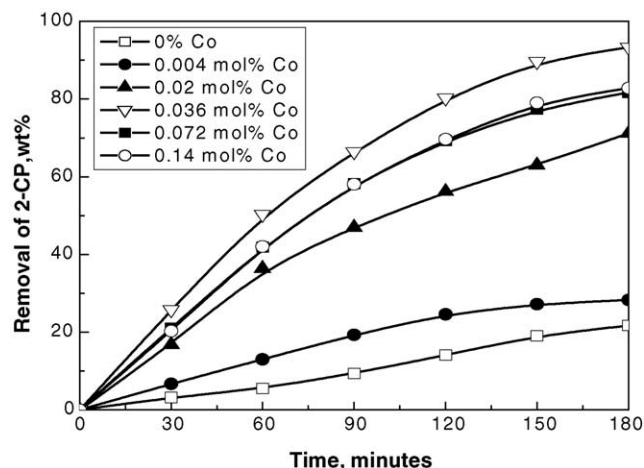


Fig. 4. Effect of Co doping concentration on the 2-CP photodegradation. Catalyst dosage = 10 mg/L, 2-CP = 50 ppm, pH = 9.

have rutile structure and gave lower degradation efficiency compared with that of 600 °C annealed anatase samples. The effect of crystalline structure on the photodegradation was also observed by Tsai and Cheng [8]. They reported that between the lab-made anatase and rutile TiO_2 , the anatase showed better photocatalytic activities in decomposition of phenolic contaminants. The activities strongly depended on the calcination temperature of the catalysts. Iwasaki et al. [41] confirmed that the catalytic activity of Co-doped TiO_2 declines above 600 °C where rutile structure and a new compound, CoTiO_3 , are formed. This is in agreement with our data.

Fig. 4 shows the effect of the concentration of Co-dopant on photodegradation of 2-CP. Samples with the Co concentration ranging from 0.004 to 0.14 mol% were studied. It can be seen that with the undoped sample (0% Co), about 18% of 2-CP was removed at pH 9 after 3 h of irradiation of UV. The photodegradation efficiency of 2-CP increased with increasing Co concentration, reaching a

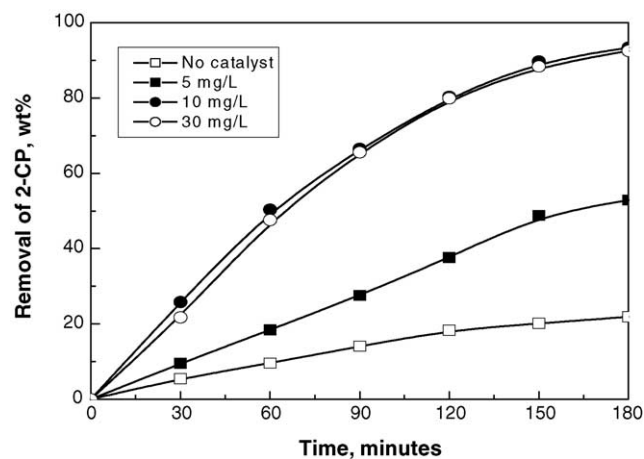


Fig. 5. Effect of the Co-doped TiO_2 dosage on the 2-CP photodegradation. Co = 0.036 mol%, 2-CP = 50 ppm, pH = 9.

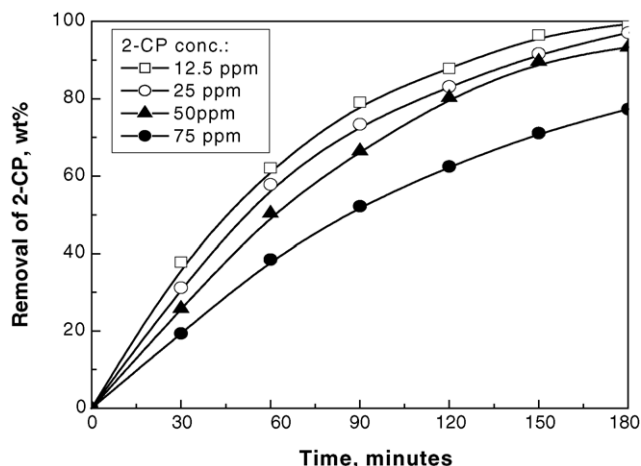
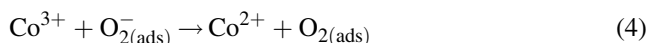


Fig. 6. Effect of 2-CP concentration on its photodegradation rate. Co = 0.036 mol%, catalyst dosage = 10 mg/L, pH = 9.

maximum value of 93.4% with sample containing 0.036 mol% Co that was annealed at 600 °C. A further increase in Co concentration to 0.14 mol% resulted in a decrease in the photodegradation efficiency to 83%. One possible mechanism of this change in the photodegradation efficiency is as follows; by irradiation of the Co-doped TiO₂, Co(III) ions work as electrons scavengers which may react with the superoxide species and prevent the holes–electrons (h⁺/e⁻) recombination and consequently increase the efficiency of the photo-oxidation. The possible reaction is shown below:



Additionally, a higher Co concentration leads to a decrease in the anatase to rutile phase transformation temperature and the formation of CoTiO₃ compound, as mentioned above. This also resulted in a decrease in the photodegradation rate. Iwasaki et al. [41] and Choi et al. [48,49] also confirmed the

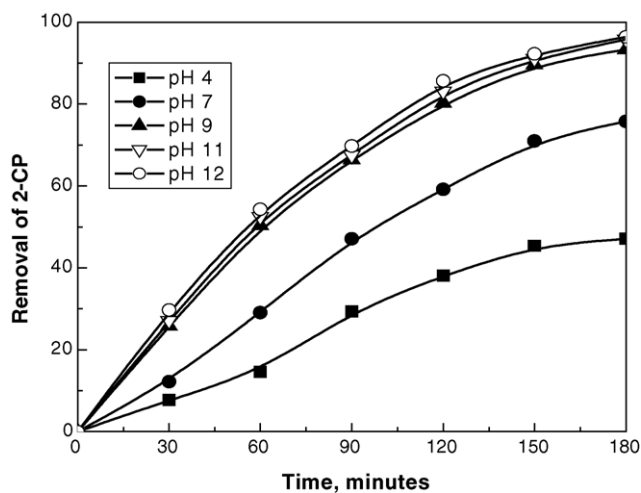


Fig. 7. The effect of solution pH on the 2-CP photodegradation. Co = 0.036 mol%, catalyst dosage = 10 mg/L, 2-CP = 50 ppm.

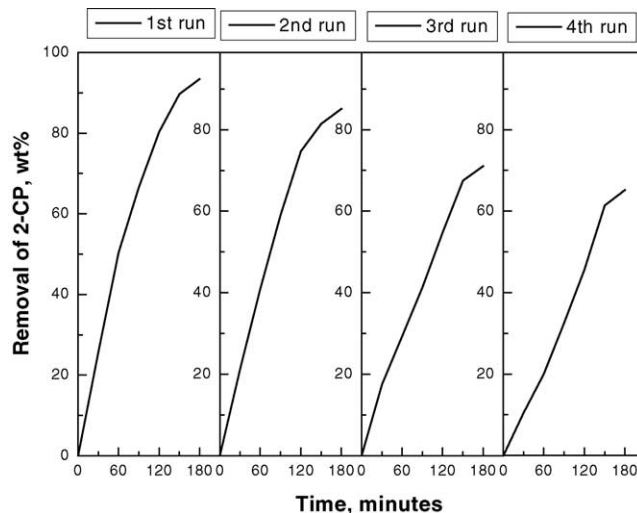


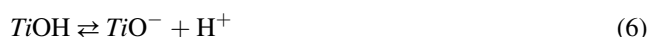
Fig. 8. The reproducibility of the Co-doped TiO₂ catalyst for 2-CP photodegradation at comparable rates for four cycles. Co = 0.036 mol%, catalyst dosage = 10 mg/L, 2-CP = 50 ppm.

retarding effect of increasing Co(III) ion doping on the photocatalytic activity of TiO₂ under UV light irradiation.

Fig. 5 shows the effect of the Co-doped TiO₂ dosage on the 2-CP degradation. It can be seen that in the absence of the catalyst about 18% of 2-CP was removed at pH 9 after 3 h of irradiation of UV. This is mainly a photolysis process. This also confirmed that the rate of 2-CP photolysis is almost the same as the rate of photocatalytic decomposition of 2-CP with the undoped sample (lowest curve of Fig. 4). The 2-CP degradation increased by adding Co-doped TiO₂ with Co concentration of 0.036 mol%. The degradation reached a maximum value of 93.4% with catalyst dosage of 10 mg/L. However, a further increase in the catalyst dosage slightly decreased the degradation efficiency. The photodecomposition rates of pollutants are influenced by the active site and the photoabsorption of the catalyst used. Adequate loading of the catalyst increases the generation rate of electron/hole pairs for enhancing the degradation of pollutants. However, addition of a high dose of the semiconductor decreases the light penetration by the photocatalyst suspension [50] and reduces the degradation rate.

The effect of varying 2-CP concentration on its degradation rate is shown in Fig. 6. The lower the 2-CP concentration, the higher the efficiency of 2-CP decomposition. A Langmuir–Hinshelwood type [16] of relationship can be used to describe the effect of 2-CP concentration on its degradation. The limitation of surface sites for the reaction may control the 2-CP decomposition. At a concentration of 12.5 ppm, 2-CP can be totally decomposed (complete oxidation) within 3 h. The results clearly demonstrate that the photocatalytic oxidation process is promising at low concentrations of the pollutant. This is also true for heterogeneous catalytic systems where the reaction occurs at the interface between two phases. The reactivity of the reaction is generally high at low pollutants concentrations.

The pH of the solution has a strong effect on the photodegradation process, as shown in Fig. 7. Degradation efficiency of 2-CP has not been found to be significant at low pH values but increased rapidly with increase of the pH, attaining a maximum value of 93.4% for pH of 9. Further increase in pH showed only a small increase in the photodegradation efficiency. Since the protons are potential-determining ions for TiO_2 , the surface charge development is affected by the pH [13]. Upon hydration, surface hydroxyl groups (TiOH) are formed on TiO_2 . These surface hydroxyl groups can undergo proton association or dissociation reactions, thereby bringing about surface charge which is pH-dependent:



where TiOH_2^+ , TiOH , TiO^- are positive, neutral and negative surface hydroxyl groups, respectively. A low pH is associated with a positively charged surface which cannot provide hydroxyl groups which are needed for hydroxyl radical formation. Consequently, the rate of 2-CP degradation may decrease. On the other hand, higher pH value can provide higher concentration of hydroxyl ions (OH^-) to react with the holes to form hydroxyl radicals (OH^*), thereby enhancing the photodegradation of 2-CP [21]. The pH decreases during the photodegradation runs and was adjusted by using 0.1 M NaOH. The change in the pH is due to the liberation of HCl during the degradation reaction. The reaction can be represented mechanistically [23] and stoichiometrically [27] as follows:

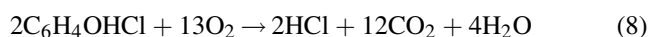
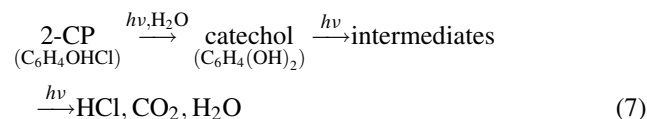


Fig. 8 shows the reproducibility of the catalyst for 2-CP degradation during a four cycles experiment. Each experiment was carried out under identical conditions of 50 ppm 2-CP initial concentration, 10 mg/L Co-doped TiO_2 with Co concentration of 0.036 mol%, and 3 h irradiation time. After each degradation experiment, the concentration of 2-CP was adjusted back to its initial value of 50 ppm. A small and gradual decrease in the activity of the catalyst was observed after the first two cycles, after which the activity remained essentially unchanged. The photodegradation efficiency values were 93.4%, 85.1%, 77.8%, and 76.6% for the first to fourth runs, respectively. The reason of the initial decrease in the photodegradation efficiency is still unknown but the repeatability of oxidative reduction of 2-CP indicates that this is indeed a photocatalytic reaction and no catalyst was reduced in the process. The rate of the reaction was calculated by plotting $\ln[2\text{-CP}]/[2\text{-CP}]_0$, at pH of 9, as a function of time, as shown in Fig. 9. Here $[2\text{-CP}]_0$ and $[2\text{-CP}]$ are the initial and remaining 2-CP concentrations in the solution, respec-

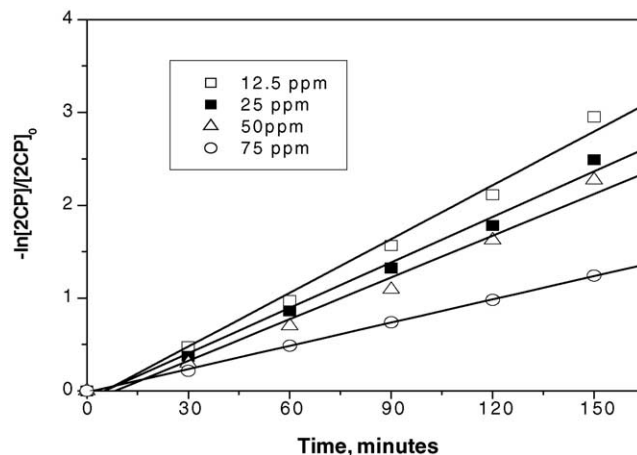


Fig. 9. The reaction rate of the 2-CP photodegradation.

tively. The plot gave different straight lines which confirmed that the degradation process follows a pseudo-first-order reaction. The observed rate constant values were calculated to be 0.020, 0.015, 0.012, and 0.008 min^{-1} with 2-CP concentration of 12.5, 25, 50, and 75 mg/L, respectively.

Optical properties of Co-doped TiO_2 directly affect the photoreactivity, based on light absorption efficiency and functioning wavelength range. High absorption efficiency and wide range of light absorption greatly improves the photoreactivity of Co-doped TiO_2 by increasing photogeneration rates of the charge carriers. The comparison of light absorption as a function of the wavelength for Co-doped TiO_2 with different Co concentrations is presented in Fig. 10. The absorption spectrum of the Co-doped TiO_2 shows absorption in the region 350–500 nm, with shifts in the absorption curve to a longer wavelength compared to

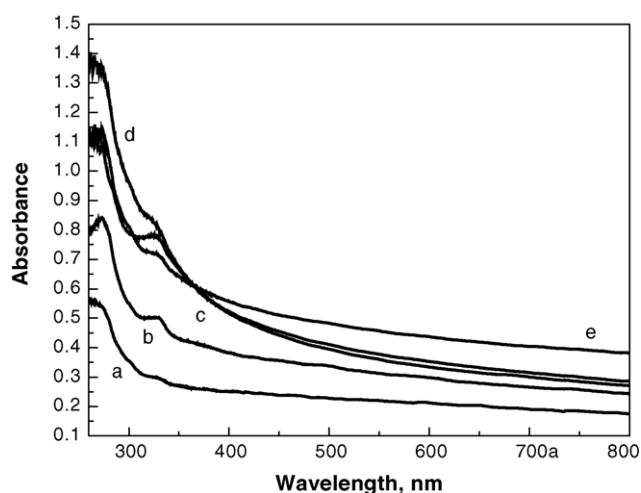


Fig. 10. Effect of Co doping concentrations on the optical absorption of TiO_2 : (a) 0% Co; (b) 0.143 mol% Co; (c) 0.072 mol% Co; (d) 0.02 mol% Co; (e) 0.036 mol% Co.

that of undoped TiO₂. The absorption reaches a maximum value for samples with 0.036 mol% Co. Further increase in the Co concentration resulted in the movement of the absorption curves back to lower wavelength. This would further explain the enhancement of 2-CP degradation in samples with 0.036 mol% Co. Indeed Fig. 4 shows that the photodegradation efficiency parallels the light absorption efficiency. As the Co dopant concentration increases, the light absorption increases to a maximum value and the photodegradation efficiency matches this light absorption maxima. The light absorption and photodegradation efficiency decrease simultaneously. The effect of higher dopant concentration on charge carrier life-time has been discussed in [40,41,51]. Dopant concentrations above an optimal value result in forming recombination centers or trapping the charges for a very long time thereby reducing the photodegradation efficiency.

4. Conclusion

The study revealed that Co-doped TiO₂ sol–gel nanoparticles showed a high activity for UV-photocatalytic degradation of 2-CP. The typical composition of the prepared Co-doped TiO₂ was Ti_{1-x}Co_xO₂ with the value of *x* ranging from 0.004 to 0.14. The surface area of the catalyst (anatase, annealed at 600 °C) was 39.7 m² g⁻¹. The photocatalytic activity strongly depends on Co doping concentration. The photodegradation process was optimized by using 10 mg/L Co-doped TiO₂ with Co doping concentration of 0.036, after 3 h irradiation. The efficiency values of the 2-CP photodegradation were 93.4% and 96.4% at solution pH of 9 and 12, respectively. The photodegradation follows a pseudo-first-order reaction with observed rate constants of 0.020, 0.015, 0.012, and 0.008 min⁻¹ with 2-CP concentration of 12.5, 25, 50, and 75 mg/L, respectively. The light absorption measurements confirmed that the presence of 0.036 mol% Co doping ions in the TiO₂ structure caused significant absorption shift into the visible region compared to the pure TiO₂ powder. The photodegradation efficiency matches this light absorption maxima.

Acknowledgement

The authors acknowledge NSF-NIRT (Grant No. DMR-0210284) for financial support of this project.

References

- [1] P.C. Calza, C. Minero, E. Pelizzetti, *Environ. Sci. Technol.* 31 (1997) 2198.
- [2] D.C. Schmelling, K.A. Gray, P.V. Kamat, *Water Res.* 31 (1997) 1439.
- [3] A.P. Davis, D.L. Green, *Environ. Sci. Technol.* 33 (1999) 609.
- [4] A. Topalov, D. Molnar-Gabor, J. Csanadi, *Water Res.* 33 (1999) 1371.
- [5] A. Braun, in: E. Pelizzetti, M. Schiavello (Eds.), *Photochemical Conversion and Storage of Solar Energy*, Kluwer, Dordrecht, 1991, p. 551.
- [6] K. Tanaka, T. Hisanaga, A.P. Rivera, in: D.F. Ollis, H. Al-Ekabi (Eds.), *Photocatalytic Purification and Treatment of Water and Air*, Elsevier, Amsterdam, 1993, p. 169.
- [7] M.A. Fox, M.T. Dulay, *Chem. Rev.* 93 (1993) 541.
- [8] S.J. Tsai, S. Cheng, *Catal. Today* 33 (1997) 227.
- [9] M.A. Barakat, Y.T. Chen, C.P. Huang, *Appl. Catal. B: Environ.* 53 (2004) 13.
- [10] V. Augugliaro, V. Loddo, G. Marci, L. Palmisano, M.J. LopezMunoz, *J. Catal.* 166 (1997) 272.
- [11] J.C. D'Ollveira, G. Al-Sayyed, P. Pichat, *Environ. Sci. Technol.* 24 (1990) 990.
- [12] M. Ralph, *Water Res.* 24 (1990) 653.
- [13] J.M. Tseng, C.P. Huang, *Water Sci. Technol.* 23 (1991) 377.
- [14] C.D. Dong, C.P. Huang, *Trace Met. Environ.* 3 (1993) 701.
- [15] C. Dong, C.P. Huang, *Am. Chem. Soc., Aquat. Chem.* 244 (1995) 291.
- [16] D. Chen, A.K. Ray, *Appl. Catal. B: Environ.* 23 (1999) 143.
- [17] A.M. Peiro, J.A. Ayllon, J. Peral, X. Domenech, *Appl. Catal. B: Environ.* 30 (2001) 359.
- [18] J. Theurich, M. Lindner, D.W. Bajnemann, *Langmuir* 12 (1996) 6368.
- [19] L. Rideh, A. Wehrer, D. Ronze, A. Zoulalian, *Catal. Today* 48 (1999) 357.
- [20] H. Mehmet, E. Erol, A. Resat, *J. Environ. Sci. Health A: Toxic/Hazar. Subs. Environ. Eng.* A37 (2002) 365.
- [21] R.A. Doong, C.H. Chen, R.A. Maitheepala, S.M. Chang, *Water Res.* 35 (2001) 2873.
- [22] G.L. Puma, P.L. Yue, *Ind. Eng. Chem. Res.* 38 (1999) 3238.
- [23] G.L. Puma, P.L. Yue, *Ind. Eng. Chem. Res.* 41 (2002) 5594.
- [24] I. Ilisz, Z. Laszlo, A. Dombi, *App. Catal. A: Gen.* 180 (1999) 25.
- [25] I. Ilisz, A. Dombi, *App. Catal. A: Gen.* 180 (1999) 35.
- [26] K. Mogyorosi, A. Farkas, I. Dekany, *Environ. Sci. Technol.* 36 (2002) 3618.
- [27] L. Rideh, A. Wehrer, D. Ronze, A. Zoulalian, *Ind. Eng. Chem. Res.* 36 (1997) 4712.
- [28] J.N. Chen, Y.C. Chan, M.C. Lu, *Water Sci. Technol.* 39 (10–11) (1999) 225.
- [29] M.C. Lu, J.N. Chen, H.D. Lin, *J. Environ. Sci. Health B: Pest. Food Contam. Agric. Wast.* B 34 (1999) 17.
- [30] R.A. Doong, R.A. Maitheepala, S.M. Chang, *Water Sci. Technol.* 42 (2000) 253.
- [31] R.I. Bickley, T. Gonzalez-Carreno, L. Palmisano, in: B. Delmon, P. Grange, P.A. Jacobs, G. Poncelet (Eds.), *Preparation of Catalysts IV*, vol. 31, Elsevier, Amsterdam, The Netherlands, 1987, p. 297.
- [32] I.M. Arabatzis, S. Antonarakis, T. Stergiopoulos, A. Hiskia, E. Papaconstantinou, M.C. Bernard, P. Falaras, *J. Photochem. Photobiol. A: Chem.* 149 (2002) 237.
- [33] G. Pecchi, P. Reyes, P. Sanhueza, J. Villaseñor, *Chemosphere* 43 (2001) 141.
- [34] S.S. Hong, C.S. Ju, C.G. Lim, B.H. Ahn, K.T. Lim, G.D. Lee, *J. Ind. Eng. Chem.* 7 (2001) 99.
- [35] S. Yamazaki, T. Hayashi, *J. Chem. Res. Synopses* 7 (2003) 423.
- [36] V. Brezová, A. Blažková, L. Karpinský, J. Grošková, B. Havl'ýnová, V. Jor'ýk, M.J. Ceppan, *J. Photochem. Photobiol. A: Chem.* 109 (1997) 177.
- [37] M.I. Litter, *Appl. Catal. B: Environ.* 23 (1999) 89.
- [38] K. Wilke, H.D. Breuer, *J. Photochem. Photobiol. A: Chem.* 121 (1999) 49.
- [39] W. Lee, W.-M. Gao, K. Dwight, A. Wold, *Mater. Res. Bull.* 27 (1992) 685.
- [40] D. Dvoranova, V. Brezova, M. Mazur, M.A. Malati, *Appl. Catal. B: Environ.* 37 (2002) 91.
- [41] M. Iwasaki, M. Hara, H. Kawada, H. Tada, S. Ito, *J. Colloid Interface Sci.* 224 (2000) 202.

- [42] X. Fu, X. Zhang, S. Song, X. Wang, H. Tan, M. Tao, *Chin. Acad. Sci., Yingyong Huaxue* 14 (1997) 77.
- [43] M. Moonsiri, P. Rangsunvigit, S. Chabadej, E. Gulari, *Chem. Eng. J.* 97 (2004) 241.
- [44] A. Burns, W. Li, C. Baker, S.I. Shah, *Mater. Res. Soc. Symp. Proc.* 703 (2002) 193.
- [45] O.J. Jung, *Bull. Korean Chem. Soc.* 22 (2001) 1183.
- [46] O.J. Jung, S.H. Kim, K.H. Cheong, W. Li, S.I. Shah, *Bull. Korean Chem. Soc.* 24 (2003) 49.
- [47] M.A. Barakat, G. Hayes, S. Ismat-Shah, *J. Nanosci. Nanotechnol.*, in press.
- [48] W. Choi, A. Termin, M.R. Hofmann, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 1091.
- [49] W. Choi, A. Termin, M.R. Hofmann, *J. Phys. Chem.* 98 (1994) 1369.
- [50] A. Doongr, W.H. Chang, *J. Photochem. Photobiol. A: Chem.* 116 (1998) 221.
- [51] E. Pelizzetti, C. Minero, *Langmuir* 9 (1993) 2995.