



ORIGINAL ARTICLE

Photocatalytic degradation of paracetamol on TiO₂ nanoparticles and TiO₂/cellulosic fiber under UV and sunlight irradiation



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Received 15 August 2013; accepted 31 March 2014
Available online 12 April 2014

KEYWORDS

TiO₂ P25;
Photocatalysis;
TiO₂/cellulosic fiber;
Sunlight;
Paracetamol

Abstract In the present study, photocatalytic degradation of acetaminophen ((N-(4-hydroxyphenyl)acetamide)), an analgesic drug has been investigated in a batch reactor using TiO₂ P25 as a photocatalyst in slurry and under UV light. Using TiO₂ P25 nanoparticles, much faster photodegradation of paracetamol and effective mineralization occurred, more than 90% of 2.65×10^{-4} M paracetamol was degraded under UV irradiation. Changes in pH values affected the adsorption and the photodegradation of paracetamol. pH 9.0 is found to be the optimum for the photodegradation of paracetamol. HPLC detected hydroquinone, benzoquinone, p-nitrophenol, and 1,2,4-trihydroxybenzene during the TiO₂-assisted photodegradation of paracetamol among which some pathway products are disclosed for the first time. The results showed that TiO₂ suspension/UV system is more efficient than the TiO₂/cellulosic fiber mode combined to solar light for the photocatalytic degradation of paracetamol. Nevertheless the immobilization of TiO₂ showed many advantages over slurry system because it can enhance adsorption properties while allowing easy separation of the photocatalyst from the treated solution with improved reusable performance.

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1. Introduction

Heterogeneous photocatalysis using titania photocatalyst is a rapidly expanding technology for water treatment from

refractory and toxic organic pollutants such as dyes, pesticides and pharmaceuticals (Scott and Ollis, 1995; Hoffmann et al., 1995; Mills and Le Hunte, 1997; Konstantinou and Albanis 2004; Shemer et al., 2006). The effectiveness of these environmentally friendly photochemical methods for wastewater treatment is due to the in situ generation of the strongly oxidizing hydroxyl radicals ($\cdot\text{OH}$), which oxidize a broad range of organic pollutants that could be present in water and wastewaters (Cheng et al., 2007). Among the various organic pollutants that are considered to cause environmental hazard phenolic compounds occupy a prominent position. Many of the widely used drugs, pesticides contain a phenolic part. As a model compound we have chosen paracetamol, also known as acetaminophen.

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Peer review under responsibility of King Saud University.



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The presence of trace paracetamol and other xenobiotic compounds in drinking water is also of public concern since little is known about potential chronic health effects associated with long-term ingestion of these compounds through drinking water (Nikolaou et al., 2007; Ikehata et al., 2006). In a study conducted in 2000, paracetamol was ranked as one of the top three drugs prescribed in England, and the mass of paracetamol through prescription alone totaled more than 400 tons in that year (Sebastine and Wakeman, 2003). Paracetamol has been found with a concentration of up to $6 \mu\text{g L}^{-1}$ in European STP effluents (Ternes, 1998), up to $10 \mu\text{g L}^{-1}$ in natural waters in USA. To avoid this risk, several oxidation methods are required to be developed for the overall destruction of paracetamol from wastewaters. The oxidation of the paracetamol has been tested by using ozone and $\text{H}_2\text{O}_2/\text{UV}$ (Andreozzi et al., 2003); $\text{O}_3/\text{Fe}^{2+}/\text{UVA}$ (Skoumal et al., 2006), the sequential adsorption-batch CWAO process (Quesada-Penate et al., 2012), the anodic oxidation system using BDD anode (Brillas et al., 2005), and sonolysis (Quesada-Penate et al., 2009). Moctezuma et al. (2012) and Zhang et al. (2010) reported the use of titanium dioxide TiO_2 as photocatalyst for the degradation of paracetamol. In this study we attempt to identify the degradation mechanism of paracetamol in aqueous TiO_2 P25 suspension using both UV and solar irradiation. The efficiency of photocatalytic oxidation using semi-conductive photocatalysts such as TiO_2 was examined. To achieve this goal, the photodegradation of paracetamol should be compared using different irradiation processes such as TiO_2 P25/UV and TiO_2 -cellulosic fiber/solar. The effects of various experimental parameters, such as pH, and adsorption isotherms on the photocatalytic degradation of paracetamol as well as the identification of intermediates and reusability of TiO_2 -cellulosic fiber of were assessed.

2. Materials and methods

The artificial light photocatalytic activity test was conducted in a laboratory-scale photoreactor. It is a 120 cm^3 cylindrical photoreactor, operating in a closed recirculating circuit driven by a centrifugal pump and with a stirred reservoir tank equipped with a device for withdrawal of samples (Elghniji et al., 2012). The reactor was filled with 1.5 L of paracetamol solution ($2.65 \times 10^{-4} \text{ M}$), to which Evonik Degussa P25 titanium dioxide (TiO_2 -P25) was added at the concentration of 0.4 g L^{-1} . Illumination was carried out using a 11 W low-pressure mercury lamp, (Philips, Holland) with a wavelength in the range of 200–280 nm. The pH of solutions was adjusted by HCl (0.1 M) or NaOH (0.1 M). Before the photocatalytic degradation, the suspension was magnetically stirred in the dark for 30 min in order to establish a paracetamol adsorption/desorption equilibrium. All experiments were conducted at $298 \pm 1 \text{ K}$. To maintain an aerobic environment, pure oxygen was purged in the stirred reservoir tank and its concentration was maintained around $40 \pm 2 \text{ mg l}^{-1}$. At given time intervals, about 2 mL aliquots were sampled, diluted and filtered with a cellulose acetate membrane filter membrane ($0.45 \mu\text{m}$ pore size, 25 mm diameter) to remove all solid particles. In the degradation of paracetamol using sunlight instead of UV light, the photocatalytic device was adapted from a previous work of Atheba et al. (2009). Experiments using sunlight irradiation were carried out from 11 a.m. to 2:30 p.m. The reactor was

built in rectangular form (35 cm long, 24 cm wide and 8 cm depth) in a material based on polymethylmethacrylate (PMMA) with an angle of 26.8 degrees. A constant flow rate of paracetamol solution ($2.65 \times 10^{-4} \text{ M}$) through the reactor irradiated by sunlight thanks to a tube (Masterflex, IL, USA) connects by either side of the reactor. Paracetamol solution was pumped from a beaker by a peristaltic pump (Masterflex L/S) with a flow rate of 0.18 L min^{-1} . At least five repetitions with each film were performed to evaluate the reproducibility of the measurements. The film was washed with deionized water before starting a new experiment. The paracetamol concentration was estimated by measuring their absorbance at 204 and 246 nm using a UV-Vis Double Beam PC, Scanning spectrophotometer UVD-2950 and HPLC analysis. The column employed was the RP-C18 (eurosphere-100) column (220 mm length, 4.6 mm inner diameter). A UV detector was used with the wavelength set at $\lambda = 246 \text{ nm}$ for paracetamol, $\lambda = 290 \text{ nm}$ for hydroquinone, $\lambda = 245 \text{ nm}$ for benzoquinone, $\lambda = 317 \text{ nm}$ for p-nitrophenol, and $\lambda = 286 \text{ nm}$ for 1,2,4-trihydroxybenzene. Acetonitrile/water/ H_3PO_4 4 mM mobile phase in the ratio 70/30/0.3 was used in isocratic elution at flow rate of 1 mL min^{-1} .

3. Results and discussion

3.1. Effect of pH on paracetamol adsorption

The pH of the aqueous solution can affect the adsorption of pollutants on the photocatalyst surface. Fig. 1 shows that adsorption amount of paracetamol onto the TiO_2 P25 Degussa increased with increasing of pH up to 9.0. This can be attributed to the great amount of hydroxide ions available on TiO_2 surface at pH 5.5–9.0. In fact at neutral media, paracetamol is primarily in its nonionic form; water solubility is minimized and the adsorption onto the catalyst is maximized. On the other hand, the adsorption rate significantly decreased at pH 11.0, mainly due to surface ionization of TiO_2 . As the point of zero charge of the TiO_2 is 6.3, TiO_2 surface is positively charged in acidic media (pH \sim 6.3), whereas it is negatively

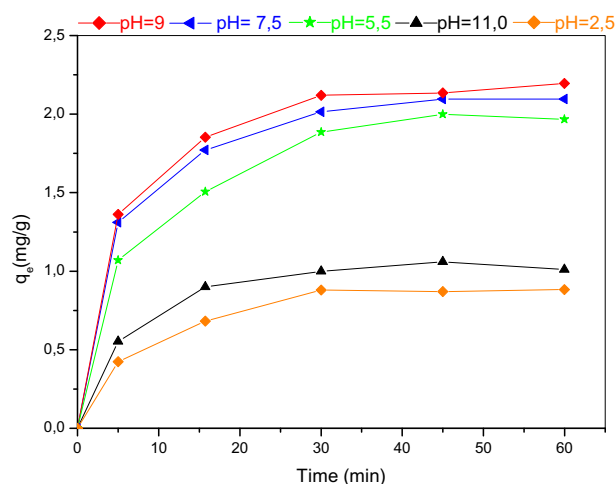


Figure 1 Adsorbed paracetamol in the dark by TiO_2 P25 for initial concentration of $2.65 \times 10^{-4} \text{ M}$.

charged at alkaline conditions ($\text{pH} > 6.3$). Thus, increasing pH (e.g., to 11.0) gradually increases the electrostatic repulsion between TiO_2 surface and paracetamol ($\text{pK}_a = 9.5$) (Brunner et al., 1998; yang et al., 2008), which is negatively charged at pH above 9.0 and further reduced already poor adsorption of paracetamol.

3.2. Effect of pH on paracetamol photodegradation

Fig. 2a shows the absorption spectra of paracetamol solution at different reaction times. The absorbance change at λ_{max} 246 nm of paracetamol is attributed to $n-\pi^*$ transition of the C=O group. Upon extended photocatalysis, this peak gradually diminished and another band appear to grow with a λ_{max} at 320 nm. The observed band is due to the red-shifted absorption of ρ band of the ring from the contribution of both the electron donating group -OH and the electron withdrawing group -NO₂ (Beildeck et al., 2005; Li et al., 1999). In the photocatalytic process, pH can influence the degradation rates. Generally, the pH of the solution determines the surface charge properties of TiO_2 P25, the size of aggregates formed, the charge of organic molecules, adsorption of molecules onto TiO_2 P25 surface and the concentration of hydroxyl radicals. Hence, the photodegradation of paracetamol on the TiO_2 P25 was studied in pH range from 2.5 to 11.0. Fig. 2b demonstrates that photodegradation of paracetamol is not favored in an acidic solution ($\text{pH} < 5.5$). It is well known that the photodegradation efficiency is bound to the distribution of the species of paracetamol and the state of TiO_2 P25 surface according to pH value and the presence of cations or anions in the solution. At acidic to neutral media, the paracetamol is primarily in its nonionic form; the water solubility is minimized and the adsorption onto the catalyst is maximized. An increase in the solution pH enhances the photodegradation, and reaches a maximum at pH 9.0. This can be attributed to enhanced formation of $\cdot\text{OH}$, because at high pH (e.g., 9.0) more hydroxide groups available on TiO_2 P25 surface can be easily oxidized and form more $\cdot\text{OH}$ (Zheng et al., 1997; Galindo et al., 2000), which consequently increases the effi-

ciency of paracetamol degradation. On the basis of detailed kinetic analysis and the time of evolution of the intermediates during the photocatalytic transformation of phenol, Minero et al. (2000) suggested that the oxidation of phenol proceeds 90% through the reaction with TiO_2 -bound hydroxyl radicals $\cdot\text{OH}$; the remaining 10% is via direct interaction with the holes. However, the photodegradation decreases when the pH further increases to 11. The charge attraction between negatively charged paracetamol molecules and positively charged TiO_2 particles enhances the coupling of paracetamol molecules with TiO_2 particles. On the other hand, paracetamol tends to exist as anions form at higher pH values ($\text{pH} > \text{pK}_a$). Such anions have extremely high solubility in solution and will not be adsorbed significantly. Thus, increasing pH (e.g., to 11) gradually increases the electrostatic repulsion between TiO_2 surface ($\text{pH}_{\text{PZC}} = 6.3$) and paracetamol ($\text{pK}_a = 9.5$) (Yang et al., 2008), which is negatively charged at pH above 9.5 and reduced already poor adsorption of paracetamol. Hence, it is not surprising that the degradation rate of paracetamol is decreased at a pH higher than 9.0. It is also confirmed in this work that paracetamol photodegradation using TiO_2/UV process follows the first-order kinetics. The apparent rate constants are 3.6×10^{-3} , 7.4×10^{-3} , 12.6×10^{-3} , 17.3×10^{-3} and 3×10^{-3} at pH ranging from 2.5 to 11, respectively. The high activity can be attributed to the synergetic effects of high adsorption activity and strong absorption in the UV light region of TiO_2 P25 sample. In addition, the high dispersibility and the well-developed crystallinity of TiO_2 P25 containing anatase and rutile phases in a ratio of 80:20, which meant a low density of recombination centers, were probably another reason (Colthup et al., 1975).

3.3. Analysis of intermediates using HPLC

In order to identify the intermediates and final products of the photochemical degradation of paracetamol, as well as to probe the degradation mechanism of the pharmaceutical product, a high-performance liquid chromatography (HPLC) was employed. Fig. 3 presents the HPLC separations obtained

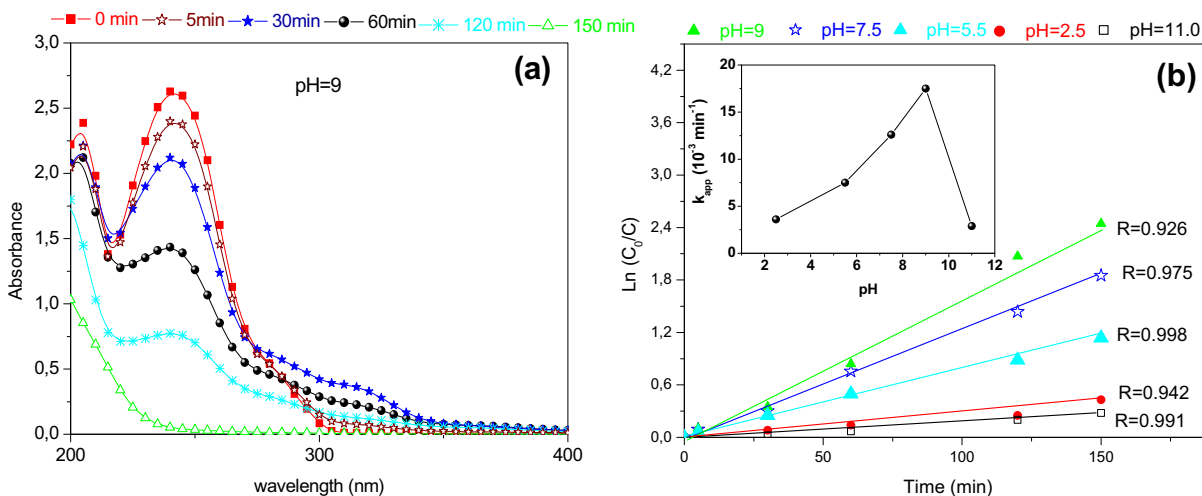


Figure 2 (a) UV-Vis absorption spectra depicting the degradation profile of paracetamol using TiO_2 P25 photocatalyst; (b) variations in $\ln(C_0/C)$ as a function of irradiation time and linear fits of TiO_2 P25 in paracetamol solution at different pHs, with inset of the apparent rate constant.

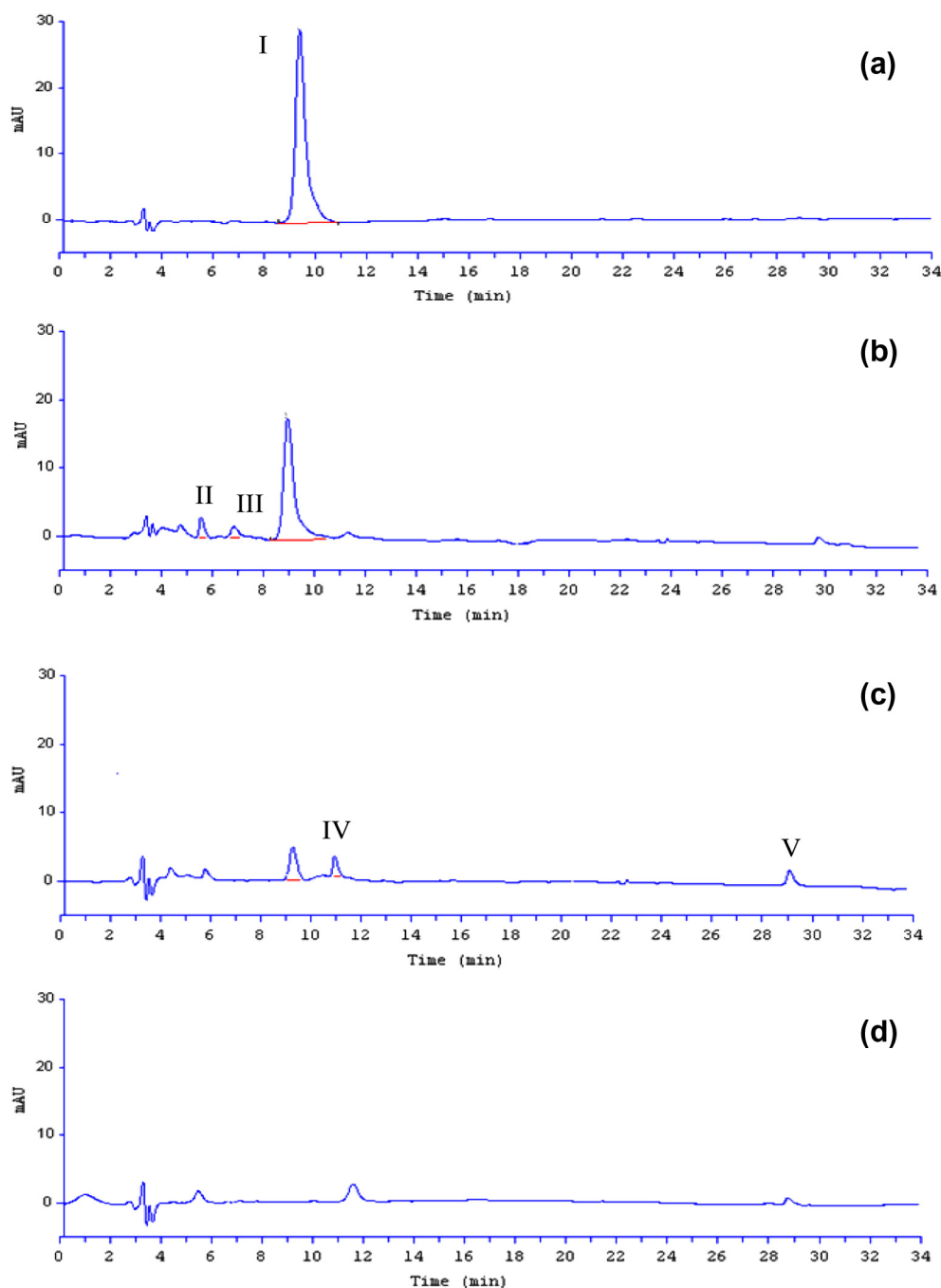


Figure 3 High-performance liquid chromatograms of paracetamol solution during photochemical degradation. Initial paracetamol concentration = 2.65×10^{-4} M, degradation time τ [min]: (a) 0, (b) 30, (c) 60, (d) 150. Peak numbers: (I) paracetamol, (II) hydroquinone, (III) benzoquinone, (IV) p-nitrophenol, and (V) 1,2,4-trihydroxybenzene.

for paracetamol solution samples taken during photochemical degradation experiments. It can be seen that the main peak at the retention time $t_R = 9.69$ min, due to paracetamol, decreases gradually and disappears after 150 min. There are several separation peaks appearing during the degradation experiment, which can be ascribed to the intermediates of the paracetamol degradation. They are most likely hydroquinone (II), benzoquinone (III), p-nitrophenol (IV), and 1,2,4-trihydroxybenzene (V). Further investigations of end products of paracetamol degradation are underway in this laboratory.

All species in the solution were identified by the comparison of the retention times of the observed peaks with the retention times of standard HPLC peaks. These aromatic intermediates were also determined for paracetamol degradation by means of other advanced oxidation processes (Almeida et al., 2011; Moctezuma et al., 2012). The concentration of 1,2,4-trihydroxybenzene initially increased linearly with the degradation of paracetamol (Fig. 3). After the disappearance of 76% of paracetamol, the concentration of 1,2,4-trihydroxybenzene reaches the maximum and the ratios of 1,2,4-trihydroxyben-

zene to the degraded paracetamol were kept about 12% within 60 min. Hence, we can suggest that the relatively high concentration of 1,2,4-trihydroxybenzene should be explained as originating from the free hydroxyl in the TiO₂ P25 system. After 150 min of irradiation, the concentration of these intermediates underwent a fast drop, indicating the mineralization of paracetamol.

3.4. Reusability of TiO₂ films for paracetamol solar photodegradation

Using solar energy to execute water purification processes is the direction of the scientific research on photocatalysis. A valuable feature of the TiO₂ films is their reusability without mechanical failure. After the initial 150 min of irradiation in paracetamol, the films were washed with deionized water in order to be cleansed of any adsorbed dye on the surface, which allows for more versatility in their use without worry of cross contamination. The films were then filled with new paracetamol solution. As anticipated, each attempt at degradation resulted in slightly higher final paracetamol concentrations, but after five attempts the TiO₂ films were performing only slightly worse than the original TiO₂ films (Fig. 4). Similar results were achieved after five attempts with the TiO₂ films in the degradation of malachite green (Sirès et al., 2006). As shown in Fig. 4, the first degradation ratio of paracetamol was 83%, and that of the fifth times was ca. 80%, indicating the TiO₂ film had a very good stability and could be reused several times. All degradation curves indicate first-order kinetics; therefore they were fitted as first order reactions regarding the decrease of absorbance at 286 nm. Fig. 5 shows the variations in $\ln(C_0/C)$ after repetitive experiments under sunlight irradiation. Obviously, the TiO₂ film could efficiently degrade paracetamol. The apparent-reaction-rate constants k_{app} for each run were 10.2×10^{-3} , 9.8×10^{-3} , 9.4×10^{-3} , 8.4×10^{-3} and 8.38×10^{-3} . Compared with the TiO₂ (Degussa P25), which is considered as excellent and standard photocatalysts, the enhancement in paracetamol degradation under visible light using the TiO₂ film is certainly significant. This could be simply accounted for by the increase in the number of active sites and in the amount of photons absorbed by TiO₂.

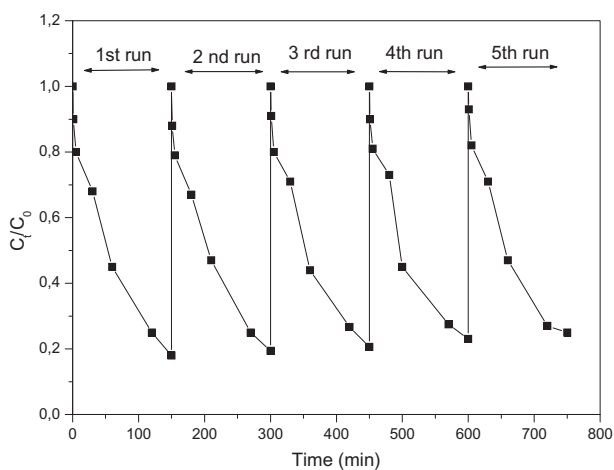


Figure 4 Cyclic photocatalytic degradation of paracetamol aqueous solution under TiO₂/cellulosic fibers.

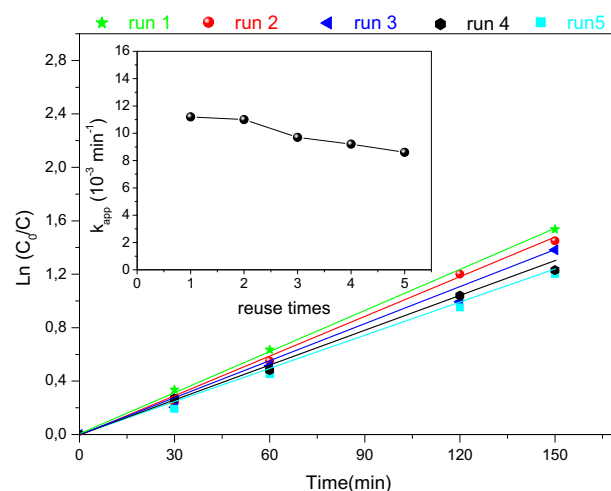


Figure 5 Variations in $\ln(C_0/C)$ as a function of irradiation time and linear fits in paracetamol photodegradation under TiO₂/cellulosic fibers, with inset of the apparent rate constant.

4. Conclusion

TiO₂ (P25 Degussa) /UV and TiO₂ films/solar light systems were applied to assess the suitability of these processes to promote the degradation and mineralization of paracetamol. The pH of a treated solution impacted the photodegradation kinetics of this compound. The optimum value of pH was found to be 9.0 under UV and solar light sources. Changes in photodegradation rate at different pH values could be partially attributed to the formation of high concentration of hydroxyl radicals at basic pH. However, at pH higher (than the point of zero charge (PZC), the semiconductor surface is negatively charged resulting in electrostatic repulsion between phenolate ion form of paracetamol and the semiconductor. This will result in a decrease in the rate of photocatalytic degradation of paracetamol. Reusability and mechanical integrity of the TiO₂/cellulosic fiber were also investigated. The decreased trend in final degradation efficiency was only 17% after five repetitive experiments under sunlight irradiation, indicating that the TiO₂ film had very good stability and could be reused several times. The main intermediate products generated during the photocatalytic reaction were found to be hydroquinone, benzoquinone, p-nitrophenol, and 1,2,4-trihydroxybenzene.

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