



Photocatalytic decomposition of 4-chlorophenol over oxide catalysts

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Abstract

4-Chlorophenol in the presence of catalysts was decomposed in aqueous solution by a 125 W medium pressure mercury lamp in a thermostated quartz batch photoreactor, and the organic bound chlorine was catalytically converted into the environmentally less harmful inorganic chloride. Differences in the concentration of 4-chlorophenol and of the intermediates, such as hydroquinone and quinone, are followed by HPLC. The best catalyst among a homolog series for the photo-decomposition of 4-chlorophenol was selected as finely dispersed platinum oxide on a TiO₂ semiconductor support, and kinetic parameters of the Langmuir–Hinshelwood type decomposition reaction were reported for the selected catalyst. A simple mechanism of substrate degradation in accord with the chosen kinetic model was postulated. The developed process may serve photooxidative removal of chlorophenols in wastewater without using costly oxidants. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chlorinated organic compounds, especially chlorophenols, show low biodegradability, and therefore are persistent pollutants, posing serious risks to the environment once mixed into natural water [1]. Biological treatment procedures for the decomposition of chlorinated phenols usually proved to be inefficient due to their resistance to biodegradation. Direct photolysis of chlorophenols in aqueous solutions, uncatalyzed photooxida-

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tive treatment under UV light using ozone or hydrogen peroxide [2] or photooxidation using photocatalysts greatly enhance the low attenuation rate of chlorophenols.

Several catalysts such as CdS [3], α -Fe₂O₃ and ZnO and TiO₂ [4,5] were utilized in photocatalytic oxidations. The photocatalytic degradation of some organochlorine compounds on illuminated TiO₂ has been demonstrated [6]. The removal of organically bound chlorine in the presence of Ag loaded TiO₂, H₂O₂ and air was also achieved by Alberici and Jardim (1994). Photocatalytic decomposition using TiO₂ under UV light is cheap (i.e., does not require costly oxidants), non-toxic, and also TiO₂ shows almost no catalytic deactivation for considerable time on-stream.

In this study, a detailed investigation has been carried out on the photocatalytic removal of 4-chlorophenol in the presence of various catalysts prepared in our laboratory, namely, PtO₂/TiO₂, PtO₂/SiO₂, SiO₂, TiO₂, and the catalyzed conversions were compared with those obtained under UV irradiation only.

2. Experimental

2.1. Chemicals

Titanium oxide in Anatase form was supplied from Fluka. The 4-chlorophenol, hydroquinone, quinone, SiO₂, H₂PtCl₆ were all supplied from E. Merck. Acetonitrile and methanol were supplied by Riedel-de Haen.

2.2. Preparation of catalysts

The wet impregnation of the anatase TiO₂ powder (particle size 125–250 μ m by sieves) with hexachloroplatinic acid (H₂PtCl₆) solution of 147 ppm concentration was used in the preparation of the catalysts [7]. All the solutions were prepared with distilled and deionised water. After the impregnation of platinum, the slurry was stirred at ambient temperature for 1 day and the mother liquor decanted, and the precursor was first dried in a vacuum oven and then calcined under flowing air at 673 K for 12 h. During this calcination step, the platinum containing catalysts were assumed to be oxidized to produce finely dispersed platinum (IV) oxide on a TiO₂ semiconductor support [8]. The catalysts after calcination were ground into fine particles below 40 mesh. Several catalysts prepared in the above-described manner were utilised after grinding with no additional treatment.

2.3. Photooxidation and analysis

All photooxidation reactions were carried out in the thermostatic ($t = 25 \pm 0.1^\circ\text{C}$) and recirculated quartz-column photoreactor (immersion well-type quartz photoreactor) system supplied by ANSEROS (see Fig. 1). The UV source in these reactions was a 125 W-medium pressure Hg lamp (Philips HPK 125 W) of 3.4 cm in length, with a radius of 0.6 cm and a wavelength range of 240–570 nm, exhibiting maximum quantum efficiency at 250 nm.

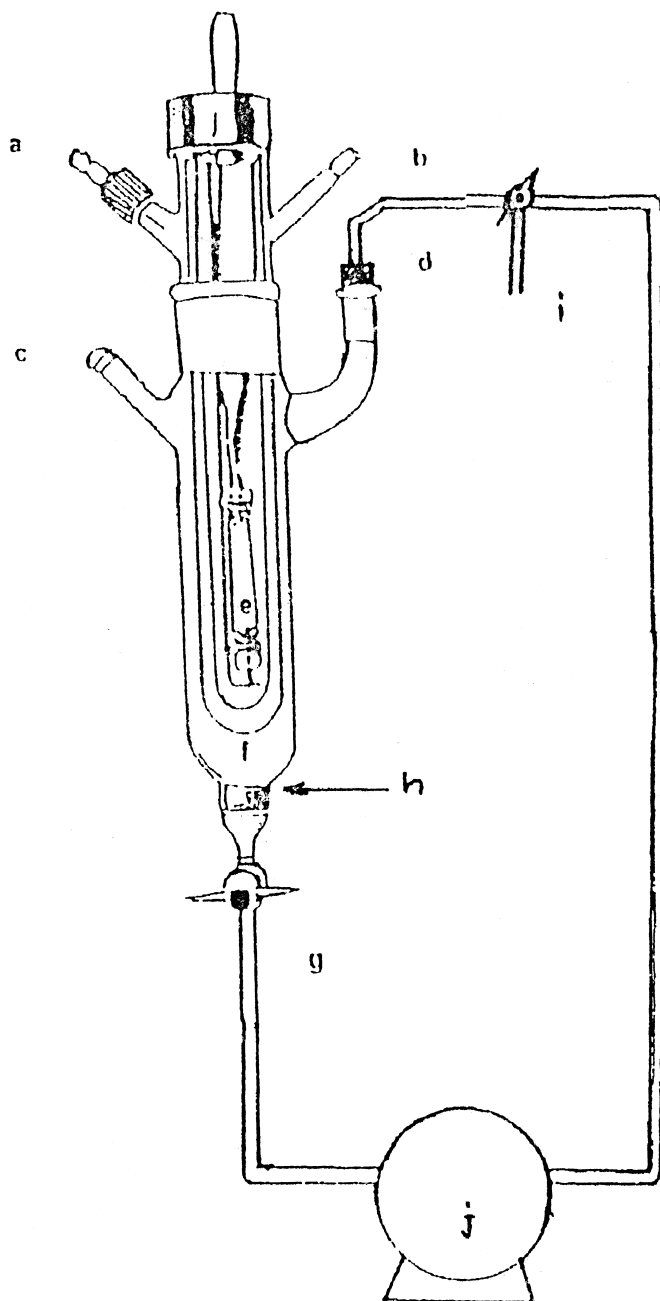


Fig. 1. Recirculated fix bed photoreactor. (a) cooling water inlet, (b) cooling water outlet, (c) gas inlet, (d) recirculated chlorophenol, (e) UV lamp, (f) sample solution, (g) safety stopcock, (h) fix-bed, (i) sampling stopcock, (j) recirculate pump.

Initially, 250 ml of the aqueous 4-chlorophenol solution (7.4×10^{-4} M) without any buffer was fed into the reactor by means of a circulation pump operating at a flow rate of 240 ml min^{-1} and N_2 purging as well as thermostatic water circulation were started. The addition of 100 mg catalyst (either SiO_2 or TiO_2 alone, or their platinized binary mixtures) and UV-illumination were simultaneously initiated, and the reaction progress was followed by the periodic measurement of the remaining chlorophenol concentration down to ppm level using HPLC analysis. The time schedule for sample drawing from the reaction mixture was six samples for the first hour, four samples for the second hour, and three samples for the next 2 h with equal time intervals for each hour. The HPLC instrument was a CECIL CE 1200, fitted with an ET 125/4 NUCLEOSIL 5 C₁₈ Phenol Column ($225 \text{ mm} \times 4.6 \text{ mm}$). Separation of different phenols were isocratic, and the mobile phase was a ternary mixture of acetonitrile:methanol:30 mM ammonium acetate solution (pH 5.0) in the volume ratio of 34:10:56. The eluent was delivered at a rate of 1.0 ml min^{-1} , and the wavelength for detection was 280 nm. The HPLC analysis under the described circumstances allowed a good separation of the interested compound (4-chlorophenol, hydroquinone or quinone) within 20 min. Silver nitrate was used for qualitatively confirming the liberation of inorganic chloride as the final photooxidation product of the organo-bound chlorine. The presence of chloride ions was also tested by means of an ion-selective electrode coupled to an Orion 801 A pH/mV meter.

3. Results and discussion

Experiments were conducted using a 7.4×10^{-4} M solution of 4-chlorophenol in the presence of SiO_2 , TiO_2 (anatase), $\text{PtO}_2/\text{TiO}_2$ and $\text{PtO}_2/\text{SiO}_2$ catalysts (the last two containing 1% (w/w) platinum) with UV illumination. The quartz reactor vessel was illuminated with a 125 W Hg lamp. The oxidation rate was followed by monitoring both the decrease in 4-chlorophenol concentration and also the changes in the concentrations of hydroquinone and quinone intermediates which are certainly less refractory than the parent compound. These results are shown in Figs. 2–6 for $\text{PtO}_2/\text{SiO}_2 + \text{UV}$, $\text{SiO}_2 +$

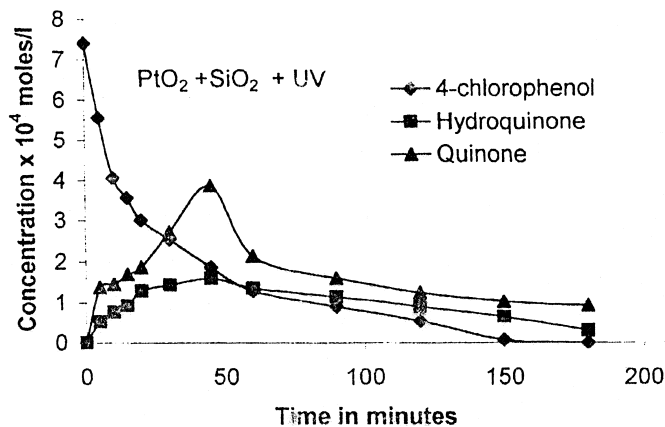


Fig. 2. Changes in 4-chlorophenol concentration in the presence of $\text{PtO}_2/\text{SiO}_2 + \text{UV}$ catalyst.

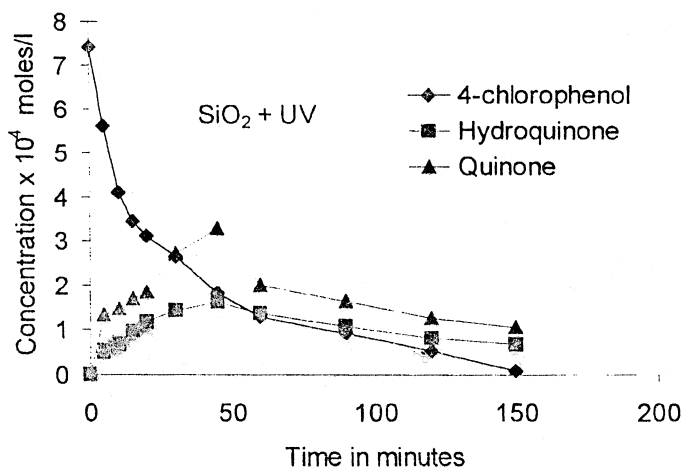


Fig. 3. Changes in 4-chlorophenol concentration in the presence of SiO₂ + UV catalyst.

UV, PtO₂/TiO₂ + UV, TiO₂ + UV, catalyst–irradiation combinations and only UV irradiation, respectively.

From the work of Ku and Hsieh [5], it was shown that the pH of contaminant solution had almost no effect on the initial reaction rate in the presence of TiO₂ and UV illumination. Similar observations were made in the photocatalytic decomposition of 3-chlorophenol by D'oliveria et al. [9]. The effect of pollutant solution pH was therefore not studied since the primary aim of this study was to find better photocatalysts producing photoreactants from water such as singlet oxygen, hydroxyl radicals, and hydrogen peroxide [10].

Ku and Hsieh [5] utilized a Langmuir–Hinshelwood type kinetic model for interpreting the decomposition of 2,4-dichlorophenol. The reaction rates observed in such surface-mediated reactions are proportional to the surface concentration of the adsorbed

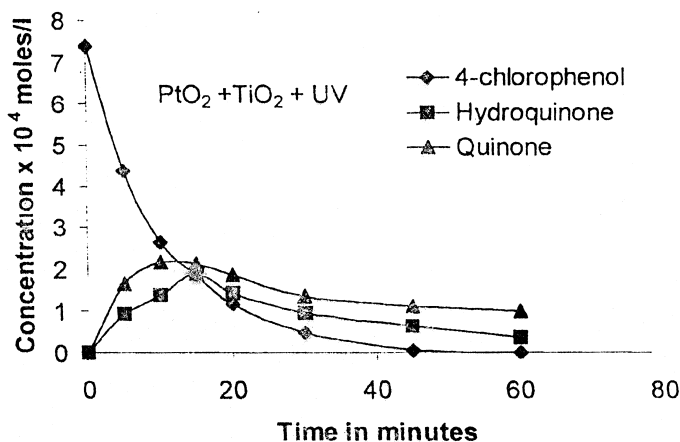


Fig. 4. Changes in 4-chlorophenol concentration in the presence of PtO₂/TiO₂ + UV catalyst.

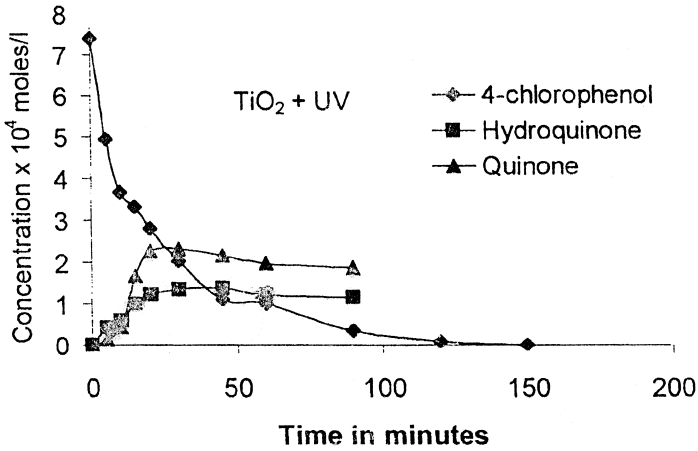
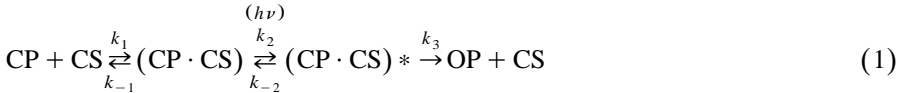


Fig. 5. Changes in 4-chlorophenol concentration in the presence of TiO₂ + UV catalyst.

reactant, which may in turn be expressed as a function of the solute concentration in bulk solution by the Langmuir equation [10].

A simple mechanism consistent with the Langmuir–Hinshelwood type kinetic model is one in which the reaction proceeds through adsorbed substrate and photoactivated intermediates:



CP: chlorophenol; CS: catalyst surface (free); (CP · CS): intermediary state of chlorophenol adsorbed to the catalyst surface; (CP · CS)*: photoactivated chlorophenol attached to the catalyst surface; OP: oxidation product of chlorophenol.

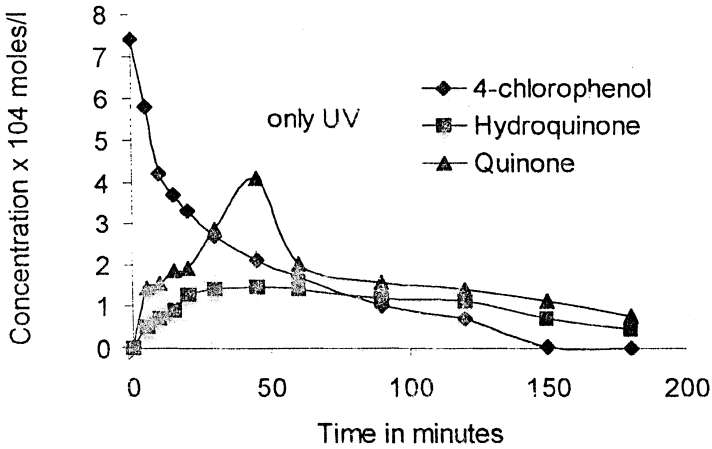


Fig. 6. Changes in 4-chlorophenol concentration in the presence of UV only.

For initial-velocity measurements, $[OP] = 0$, and hence the rate equations corresponding to Eq. (1) are

$$r_{CP} = -d[CP]/dt = k_1[CP][CS] - k_{-1}[(CP \cdot CS)] \quad (2)$$

and

$$d[(CP \cdot CS)]/dt = k_1[CP][CS] - k_{-1}[(CP \cdot CS)] - k_2[(CP \cdot CS)] + k_{-2}[(CP \cdot CS)^*] \quad (3)$$

$$d[(CP \cdot CS)^*]/dt = k_2[(CP \cdot CS)] - k_{-2}[(CP \cdot CS)^*] - k_3[(CP \cdot CS)^*] \quad (4)$$

At steady state, the rate of accumulation of both intermediates would be zero, i.e. the left-hand side of Eqs. (3) and (4) could be set to zero yielding

$$\frac{k_1[CP][CS]}{(k_{-1} + k_2) - [k_{-2} \cdot k_2 / (k_{-2} + k_3)]} = [(CP \cdot CS)] = k'[CP][CS] \quad (5)$$

by the simultaneous solution of Eqs. (3) and (4). Combining this with the conservation of the total surface sites of catalyst, i.e. $[(CP \cdot CS)] = [CS]_0 - [CS]$, and substituting into Eq. (2) gives Eq. (6) for the initial rate

$$r_{CP} = -dC_{CP}/dt = (k_1 - k_{-1}k')[CP][CS] = (k_1 - k_{-1}k')[CS]_0[CP]/(k'[CP] + 1) \quad (6)$$

one derives a Langmuir–Hinshelwood type kinetic equation of the type

$$-dC_{CP}/dt = r_{CP} = kKC_{CP}/(1 + KC_{CP}) \quad (7)$$

where k and K are constants associated with the photooxidation rate and adsorption equilibrium, respectively, and C_{CP} is the concentration of 4-chlorophenol in bulk solution. This model is especially useful when the intermediary oxidation products accumulate on the catalyst surface by adsorption at relatively high substrate concentrations, limiting the reaction rate. The K term of Eq. (7) is associated with the adsorption constant of the substrate on TiO_2 in aqueous suspension [11], and the interaction of the intermediary oxidation products (i.e. hydroquinone and quinone) with the titania surface may essentially follow a similar trend as of the parent substrate in terms of the preferential orientation of the molecule with the plane of the aromatic ring perpendicular to the surface [12], thereby rendering the K term to partly compensate for the adsorption of intermediates. In this model, the retardation of the photooxidation rate is obvious at significantly high concentrations of the substrate, i.e. where saturation of the catalyst surface is attained when unity is negligible with respect to the KC_{CP} term (Tahiri et al. [11]) in the denominator of the right hand side of Eq. (7).

K and k constants of Eq. (7) for the $TiO_2/PtO_2/UV$ catalytic system are calculated based on the experimental finding of this study from the linearized rate equation by the multiple least squares method using Eq. (8), which is a modification of the double reciprocal Lineweaver–Burke plot [13], obtained by inversion of Eq. (7).

$$1/r_{CP} = 1/(kKC_{CP}) + 1/k \quad (8)$$

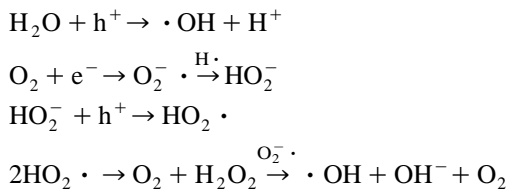
The k and K mean values obtained from multiple linear regression analysis were found to be 0.56 M min^{-1} and 0.24 M^{-1} for k and K , respectively. (Their reciprocals within

95% confidence interval [14] can be reported as $k^{-1} = 1.78 \pm 3.24$ and $K^{-1} = 4.16 \pm 1.87$). The square of the regression coefficient for this set of values was $R^2 = 0.96$. The acceptable fit between the calculated and observed decomposition rate of 4-chlorophenol confirms that decomposition could have taken place in accordance to the envisaged Langmuir–Hinshelwood type catalytic reaction over the above mentioned catalyst. The photooxidation reaction at the semiconductor (TiO_2)-electrolyte interface is facilitated if the substrate (CP) is adsorbed at the semiconductor surface [10].

Hence, the model Eq. (9) takes the following form for the $\text{TiO}_2/\text{PtO}_2$ catalytic system of UV photooxidation:

$$-dC_{\text{CP}}/dt = r_{\text{CP}} = 0.56 \times 0.24 \times C_{\text{CP}} / (1 + 0.24 \times C_{\text{CP}}) \quad (9)$$

The electrons and holes photo-generated on the semiconductor catalyst, i.e., $(\text{TiO}_2) + h\nu \rightarrow e^- + h^+$, cause the photolysis of water and the reduction of oxygen to yield hydroxyl radicals and other reactive oxygen species [15]:



In addition, the photoholes may react with the surface hydroxyl groups of titania to yield hydroxyl radicals [16]. Hydroxylated species arise at the early stages of hydrocarbon photooxidation by $\cdot\text{OH}$ or $\text{HO}_2 \cdot$ radical attack:



Since oxygen reduction on a platinumized anatase surface may occur at potentials more positive than either the onset photopotential or the reduction potential of O_2 on TiO_2 , platinumized TiO_2 may be more active in the photocatalytic sense and platinum may provide a site for the more efficient utilization of the photogenerated electrons in the reduction of O_2 [17].

The formation of intermediates was also followed by HPLC. Various quinones and organic acids were reported to be formed during the decomposition of chlorophenols, especially by Davis and Huang [3] and Turchi and Ollis [18]. The maximum levels of intermediates (i.e. hydroquinone and quinone) were reached between 20–60 min. The detection of hydroxylated intermediary oxidation products is in accord with the detection of salicylic acid in the photodecomposition of benzoic acid [15] as a result of $\cdot\text{OH}$ radical attack on the parent compound. Likewise, the detection of phenol for the case of benzene and of alcohols for the case of aliphatic hydrocarbons [17] suggest that attack by $\cdot\text{OH}$ or $\text{HO}_2 \cdot$ radicals is a likely first step in photooxidation. Observation of Figs. 2–6 reveals that both hydroquinone and quinone build up to a steady concentration—as in the case of salicylic acid in benzoic acid photodecomposition [15]—showing relative maxima at nearly the same time scale. This could be interpreted by assuming that some

parallel reactions of the substrate with $\cdot\text{OH}$, $\text{HO}_2\cdot$, holes, or other intermediates could have taken place to yield the more highly oxidation products together with the consecutive oxidation reactions deriving quinone from hydroquinone. Appearance of the maximum concentration levels of the intermediates was earlier than those found by Ku and Hsieh [5]. It was reported by Ku and Hsieh [5] that after 3–5 h, about 60–70% of 2,4-dichlorophenol was decomposed to organic intermediates. On the other hand, it took only 10–20 min to reach 60–70% of 4-chlorophenol decomposition over the $\text{PtO}_2/\text{TiO}_2$ catalyst.

As can be seen from Figs. 2–6, there is considerable decomposition of 4-chlorophenol with and without the catalyst, but it is noteworthy that there is a doubling in the initial decomposition rate when loaded with $\text{PtO}_2/\text{TiO}_2$ catalyst compared to the only TiO_2 containing system due to enhanced photocatalytic action of the platinumized semiconductor.

On the other hand, when the decomposition was achieved in the presence of only UV, $\text{TiO}_2 + \text{UV}$, and $\text{PtO}_2/\text{SiO}_2 + \text{UV}$ combinations, only small changes in initial reaction rates were achieved compared to the $\text{PtO}_2/\text{TiO}_2$ catalyst yielding almost a doubled removal rate attributable to a synergistic interaction between PtO_2 and TiO_2 .

In the literature, it was shown that the photodestruction of phenols and chlorophenols may follow pseudo first order kinetics [2,9], even in reactions where a mechanism of competitive adsorption–desorption between the intermediates produced by the partial oxidation of phenol could play an important role [16] enabling the definition of half-lives (see Table 1). In fact, a Langmuir–Hinshelwood kinetic equation as shown by Eq. (7) may comply with a pseudo-first order degradation when $KC \ll 1$, i.e. before saturation of the catalyst surface sites. The comparison of half-lives of degradation generated as a result of pseudo-first order approximation may be helpful in showing the overall effectivity and the possibility of synergistic combination of certain catalysts in wastewater treatment. Silica is not effective as a photocatalyst as the half-life with SiO_2 is almost the same as that with UV only, and their product distribution with respect to time (see Figs. 3 and 6) are almost identical. The half-life in the presence of $\text{PtO}_2/\text{TiO}_2$ catalyst was almost one-third of that of all other catalysts which did not contain TiO_2 . On the other hand, the half-life observed with the platinumized anatase was almost half of that without platinum. These data show the essential role of the semiconductor catalyst (TiO_2) similar to other n-type semiconductors which are known to promote the oxidation of substrates [19] and its synergically enhanced effectiveness by platinumization.

Table 1
Half-lives of 4-chlorophenol photodecomposition for different catalysts

| Catalysts used | Half-life (min) |
|--|-----------------|
| Only UV | 15.8 |
| $\text{SiO}_2 + \text{UV}$ catalyst | 15.4 |
| $\text{PtO}_2/\text{SiO}_2 + \text{UV}$ catalyst | 14.5 |
| $\text{TiO}_2 + \text{UV}$ catalyst | 12.0 |
| $\text{PtO}_2/\text{TiO}_2 + \text{UV}$ catalyst | 6.6 |

4. Conclusion

The photocatalytic decomposition of 4-chlorophenol over $\text{PtO}_2/\text{TiO}_2$ occurs faster than that obtained over any of $\text{PtO}_2/\text{SiO}_2$, SiO_2 , and TiO_2 catalytic systems. Reaction kinetics observed with the $\text{TiO}_2/\text{PtO}_2/\text{UV}$ catalytic system follow a Langmuir–Hinshelwood type rate expression envisaging a limiting rate with the saturation of the catalyst surface. The platinumized TiO_2 catalyst calcined under flowing air at 673 K proved to exhibit the shortest pseudo-first order half-life among the prepared catalysts. All these data point to the possible use of binary oxide heterogeneous photocatalysts such as finely dispersed platinum oxide on a TiO_2 semiconductor support for the faster photooxidative removal of chlorophenols. The developed process may serve photooxidative removal of chlorophenols in wastewater without using costly oxidants.

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