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Influence of some aromatic and aliphatic compounds on the rate of photodegradation of phenol in aqueous suspensions of TiO_2

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Abstract

The influence of 3-nitrophenol, 4-nitrophenol, pentachlorophenol, ethanol, 2-propanol, ethanoic acid and ethanedioic acid on the photodegradation rate of phenol in an aqueous suspension of TiO_2 (anatase) irradiated in the near-UV region was investigated. Binary mixtures of organic compound and phenol in molar ratios of 1:1 and 10:1 were used for the photoreactivity experiments performed in a batch reactor. The mineralization rate of all the mixtures was also monitored by measuring the total organic carbon (TOC) concentration. The reactivity results indicate that the photodegradation rate of phenol is mainly determined by the total amount of aromatic substrates present in the reacting medium independently of their nature, while it is scarcely affected by the presence of aliphatic compounds. The TOC results indicate that the mineralization rate of aromatic compound–phenol mixtures is sensitive to the mixture composition, and the simultaneous presence of phenol and aliphatic compounds negatively affects the mineralization rate. A tentative explanation of the above behaviour is proposed by taking into account (i) the similar manner of photoadsorption of phenol molecules and of the other aromatic compounds on the active surface site(s), (ii) the different sites of photoadsorption for aromatic and aliphatic substrates and (iii) the possible formation of stable intermediate compounds from the degradation products of phenol and aliphatic compounds.

Keywords: Organic mixture photodegradation; Phenol photodegradation TiO_2; Heterogeneous photocatalysis

1. Introduction

The utilization of aqueous suspensions of TiO_2 illuminated by light of suitable energy to photodegrade several organic pollutants is well known in the literature [1,2]. The primary oxidant species have been reported to be OH radicals obtained by the reaction of photoproduced holes with surface hydroxyls or water [3]. OH radicals react very fast with a wide range of compounds, producing intermediate species which subsequently undergo easier photo-oxidation. Complete mineralization can be achieved after a time depending on the structural characteristics of the molecules under investigation and on the experimental conditions used. To date, very few papers have reported results on the degradation of mixtures of pollutants using the photocatalytic method [4–7], although these studies are essential in view of application purposes. Indeed, waste waters and industrial effluents contain in most cases several types of organic and/or inorganic pollutants.

This paper reports the study of the influence of 3-nitrophenol, 4-nitrophenol, pentachlorophenol, ethanol, 2-propanol, ethanoic acid and ethanedioic acid on the photodegradation rate of phenol in aqueous TiO_2 (anatase) suspension. Moreover, the total organic carbon (TOC) concentration was monitored and selected experiments lasting several hours were carried out in order to verify the complete mineralization of the binary mixtures of pollutants.

2. Experimental details

Phenol (Merck, pro analysi), 3-nitrophenol (BDH), 4-nitrophenol (BDH), pentachlorophenol (Fluka), 2-propanol (Carlo Erba, RPE), ethanol (Fluka), ethanoic acid (Merck), ethanedioic acid (Merck), NaOH (Merck) and TiO_2 Degussa P25 (crystalline phase, about 80% anatase and about 20% rutile; BET (Brunauer–Emmett–Teller) specific surface area 44 $m^2\ g^{-1}$) were used as received. The amount of TiO_2 for all the runs was 0.40 $g\ l^{-1}$. Phenol concentrations were 7×10^{-5}, 14×10^{-5}, 70×10^{-5} and 77×10^{-5} mol l^{-1}. The concentration of the other organic compounds was 7×10^{-5} or 7×10^{-4} mol l^{-1} according to whether the molar ratio between the organic compound and phenol was 1:1 or 10:1, except for the case of pentachlorophenol

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for which only the concentration of 7×10^{-5} mol l^{-1} was used because of its solubility limit. The initial pH was equal to 6.4, very close to the reported point zero change (p.z.c.) of TiO_2 Degussa P25 [8,9], and was adjusted by using NaOH. The choice of a pH value close to p.z.c. is a compromise in order to guarantee the existence on the catalyst surface of similar amounts of acid and basic sites, since both sites could be important for the occurrence of the adsorption processes and thus of the photoreactivity. The reactivity experiments were carried out in a batch cylindrical Pyrex photoreactor of volume 1.5 l. The reacting mixtures were saturated with oxygen at atmospheric pressure by bubbling O_2 before and during the irradiation. The photoreactor was provided with ports in its upper section for the passage of gases, for sampling and for pH and temperature measurements. A 500 W medium pressure Hg lamp (Helios Italquartz, Italy) was positioned within the inner part of the photoreactor and cooling water was circulated through a Pyrex jacket surrounding the lamp. The Pyrex thimble together with the water circulation allowed us to avoid lamp overheating and to eliminate from the reacting medium the IR component of the incident beams as well as any radiation below 300 nm. Samples for analyses ($V=10$ cm^3) were withdrawn at intervals of 2, 5 or 15 min. The catalyst was separated from the solution by filtration through 0.45 μm cellulose acetate membranes (HA, Millipore). The quantitative analysis of phenol was performed by a standard colorimetric method [10] and no interference by the other compounds was found under the experimental conditions used. The mineralization of the pollutants was monitored by a TOC analyser (Carlo Erba TCM 480) using samples of about 6 cm^3 volume. Selected reactivity experiments were carried out in order to verify the complete mineralization of the pollutants and they lasted about 4–8 h depending on the mixture investigated.

3. Results and discussion

Figs. 1 and 2 show semilogarithmic plots of typical reactivity results obtained with the 4-nitrophenol–phenol and ethanoic acid–phenol systems respectively. As may be observed from the data reported in the figures, the degradation process exhibits pseudo-first-order kinetics with respect to phenol concentration, expressed by the equation

$$-\frac{dC}{dt}=k_{obs}C \qquad (1)$$

the integration of which gives, for $C=C_0$ at $t=0$,

$$C=C_0\exp(-k_{obs}t) \qquad (2)$$

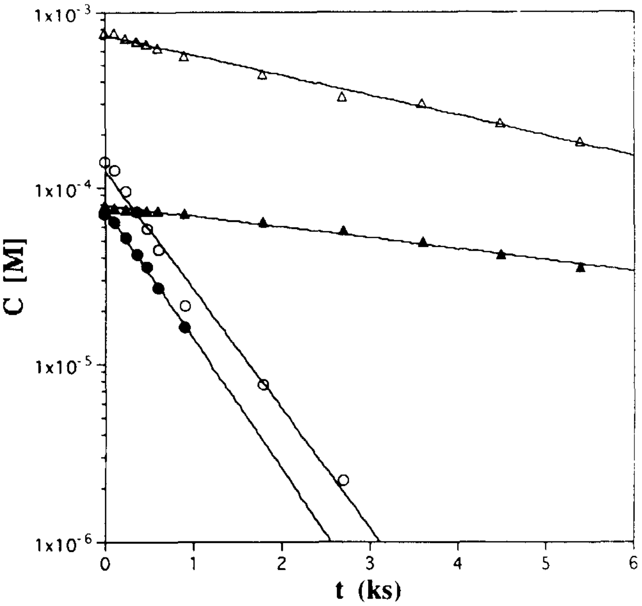

Fig. 1. Typical reactivity results as phenol concentration vs. reaction time. Initial 4-nitrophenol–phenol molar ratio: ●, 1:1; ▲, 10:1. Initial phenol concentration: ●,▲, 7×10^{-5} mol l^{-1}; ○, 14×10^{-5} mol l^{-1}; △, 77×10^{-5} mol l^{-1}.

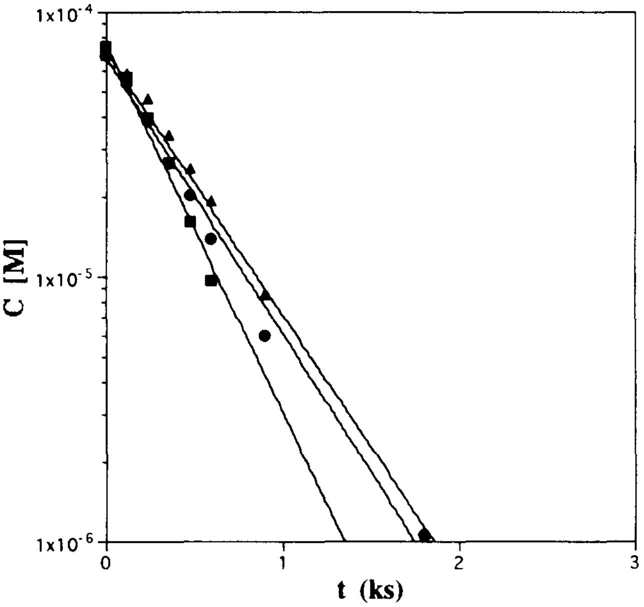

Fig. 2. Typical reactivity results as phenol concentration vs. reaction time. Initial ethanoic acid–phenol molar ratio: ●, 1:1; ▲, 10:1. Initial phenol concentration: ●, ▲, ■, 7×10^{-5} mol l^{-1}.

in which C is the phenol concentration at time t, C_0 is the initial phenol concentration and k_{obs} is the pseudo-first-order rate constant. Pseudo-first-order kinetics with respect to phenol concentration was shown by all the mixtures. By applying a least-squares best-fitting procedure to the C–t data, the values of k_{obs} have been obtained.

Table 1 reports the values of pseudo-first-order rate constant (k_{obs}) of phenol in the presence of the other

Table 1
Pseudo-first-order rate constants (k_{obs}) of phenol and of phenol in the presence of other organic compounds in two different molar ratios

	Molar ratio	Phenol $k_{obs} \times 10^3$ (s^{-1})	Molar ratio	Phenol $k_{obs} \times 10^3$ (s^{-1})
Phenol	–	2.98	–	–
Phenol:phenol	1:1	1.55	10:1	0.26
3-Nitrophenol:phenol	1:1	2.05	10:1	0.17
4-Nitrophenol:phenol	1:1	1.68	10:1	0.14
Pentachlorophenol:phenol	1:1	1.45	–	–
Ethanol:phenol	1:1	1.64	10:1	1.20
2-Propanol:phenol	1:1	2.17	10:1	1.50
Ethanoic acid:phenol	1:1	2.40	10:1	2.30
Ethanedioic acid:phenol	1:1	2.88	10:1	2.87

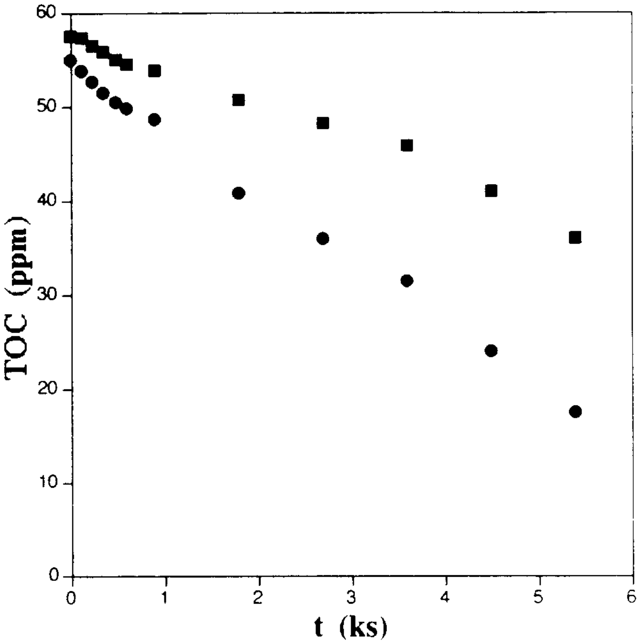

Fig. 3. Typical mineralization results as TOC concentration vs. reaction time. Initial 4-nitrophenol–phenol molar ratio: ●, 1:10; ■, 10:1.

organic compounds in molar ratios of 1:1 and 10:1. This table also reports the values of k_{obs} for three runs performed using solutions containing only phenol at concentrations of 7×10^{-5}, 14×10^{-5} and 77×10^{-5} mol l^{-1}; these runs are indicated in the table as "phenol", "phenol:phenol 1:1" and "phenol:phenol 10:1". In such a way the comparison of reactivity results among the various experiments can be done at equal phenol concentration or at equal concentration of organic molecules.

In Fig. 3. the TOC concentration vs. reaction time is reported for the case of mixtures of 4-nitrophenol and phenol. In Fig. 4 the TOC concentration vs. reaction time is reported for the case of mixtures of ethanoic acid and phenol. Fig. 5 reports a similar plot in the case of a longer experiment for a mixture of 4-nitrophenol and phenol in a molar ratio of 10:1.

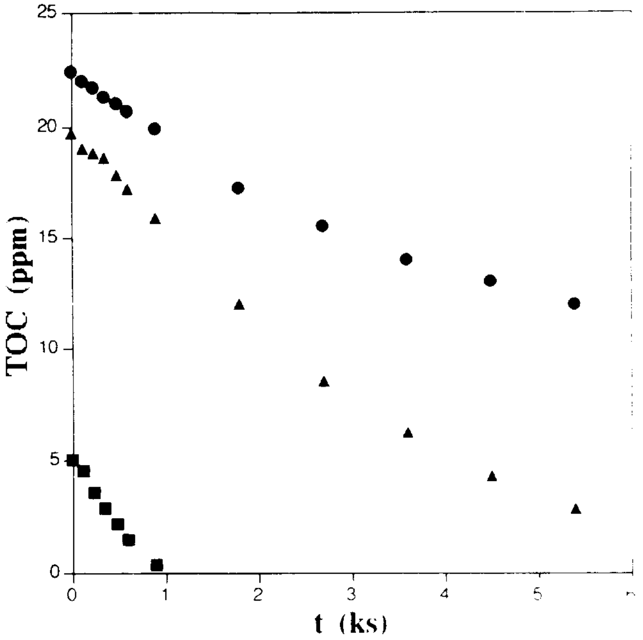

Fig. 4. Typical mineralization results as TOC concentration vs. reaction time: ●, initial ethanoic acid concentration 70×10^{-5} mol l^{-1} and initial phenol concentration 7×10^{-5} mol l^{-1}; ▲, initial ethanoic acid concentration 70×10^{-5} mol l^{-1}; ■, initial phenol concentration 7×10^{-5} mol l^{-1}.

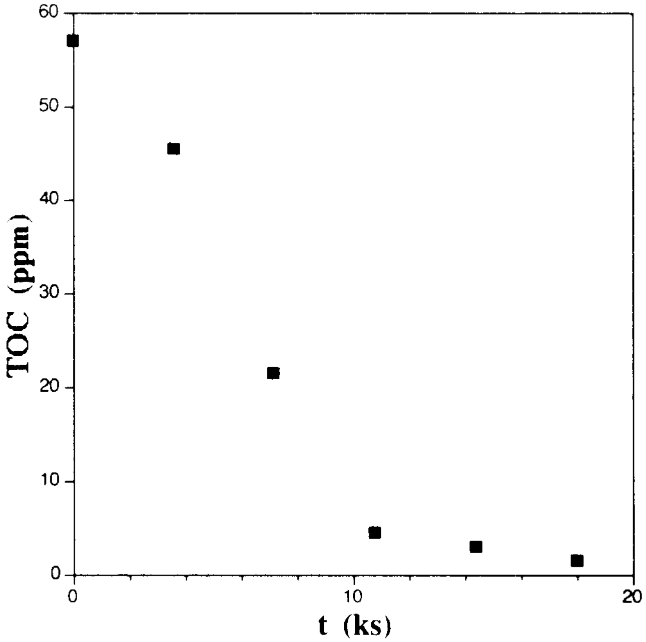

Fig. 5. Typical mineralization results as TOC concentration vs. reaction time. Initial 4-nitrophenol–phenol molar ratio 10:1.

From observation of the data reported in Table 1, the following statements may be made about aromatic compound–phenol mixtures:

(a) The k_{obs} values are not much different from mixtures with the same molar ratio;

(b) The k_{obs} values for mixtures with a 10:1 molar ratio are an order of magnitude smaller than those obtained for mixtures with a 1:1 molar ratio.

For all the aromatic compound–phenol mixtures the values of the kinetic constant are very similar to those obtained for solutions with a phenol molar concentration equal to the total molar concentration of the mixtures. The above results suggest that in these mixtures the primary degradation rate of phenol molecules is mainly determined by the total concentration of aromatic molecules.

For aliphatic compound–phenol mixtures the data reported in Table 1 indicate different behaviours for carboxylic acids and alcohols. In the first case the k_{obs} values are almost the same for all the mixtures independently of the molar ratio used and the values of k_{obs} are very close to those obtained for the solutions containing phenol concentrations corresponding to those of the mixtures. This finding suggests that the primary step of phenol oxidation is not significantly affected by the presence of the aliphatic carboxylic acids under investigation in the present work.

For mixtures containing an alcohol the values of k_{obs} indicate that the phenol photodegradation is negatively affected by the presence of the alcohol molecules, although in a less significant way that when some aromatic molecule is present. In this last case, when the concentration increases by one order of magnitude, the corresponding k_{obs} value decreases by about one order of magnitude. In the presence of either of the alcohols the kinetic constant value of the 10:1 molar ratio mixture is smaller by about 30% than that of the 1:1 mixture. This behaviour was confirmed by a run carried out using a molar ratio between 2-propanol and phenol of 400:1; in this case the k_{obs} value (6.17×10^{-4} s^{-1}) was smaller than those obtained with the ratios of 1:1 and 10:1 but higher than that obtained with aromatic compound–phenol 10:1 molar ratio mixtures.

The photoreactivity results clearly indicate that the photo-oxidation rate of phenol depends strongly on the concentration of the other organic compound only when the latter belongs to the same aromatic family. The presence of species belonging to different families, such as ethanedioic acid, ethanoic acid, ethanol and 2-propanol, has a negligible or less significant influence, also for high concentrations.

To explain the different reactivities exhibited by heterogeneous photocatalytic systems towards organic molecules, various hypotheses have been put forward. Among them, a different reactivity between the OH radicals and the substrates has been invoked. The very weak influence that the presence of ethanoic or ethanedioic acid has on the rate of photodegradation of phenol may be attributed to the rather small values of their rate constants for the reaction with $OH^{\bullet}$ in homogeneous medium (about 100 and 1000 times smaller respectively than the corresponding rate constants of several aromatic compounds) [11,12].

The more significant influence of alcohols can be justified by similar reasoning, since the values of their rate constants for the reaction with $OH^{\bullet}$ are larger than those reported for the acids but about one order of magnitude smaller than those reported for aromatic compounds [12].

Moreover, the alcohols (mainly ethanol) have relatively more influence at a molar ratio of 1:1 than at 10:1 compared with aromatic substrates and this can be tentatively explained by considering that ethanol is not much adsorbed and consequently the competition with phenol for the $OH^{\bullet}$ radicals produced on the catalyst surface does not significantly increase at the molar ratio of 10:1.

The possibility of interaction between species photoactivated on the surface of TiO_2 and organic molecules at the solid–liquid interface has also been hypothesized in the literature [3,13,14], although the occurrence of surface reactions between adsorbed photoactivated species must also be considered. In this last case the adsorption process on photoactive sites of the catalyst particles could be a determining step for the reaction rate, depending on the experimental conditions used.

By taking into account the heterogeneous process, it can be hypothesized for the systems studied in the present work that all the investigated molecules can adsorb on the catalyst surface for the occurrence of the photo-oxidation process, but only the aromatic compounds exercise a strong influence on the rate of primary degradation of phenol as they compete for the adsorption on some particular surface site(s) by the involvement of their π electrons. Although it cannot be excluded that several variously adsorbed phenol-like and/or phenate-like species are involved in the primary oxidative mechanism, the species adsorbed by interaction between the π electrons and some acidic site(s) on the catalyst surface are probably more destabilized than the others and consequently more easily photo-oxidized.

Preliminary results obtained by Fourier transform IR (FTIR) spectroscopic investigation in the gas–solid regime for phenol adsorbed on highly hydroxylated TiO_2 (anatase) surfaces showed the existence of different adsorbed species and in one case the aromatic ring was involved in the adsorption process [15]. The involvement of the aromatic ring of phenol in the adsorption process on TiO_2 (anatase) surfaces has been found in the gas–solid regime, but the experimental conditions chosen for the FTIR investigation, in particular the high surface hydroxylation, have been proven to be a good simulation of the real situation, i.e. the aqueous suspension where the photoreaction has been studied [16]. Indeed, for instance, the same intermediates [16–19] are produced under illumination in gas–solid and liquid–solid systems.

Turchi and Ollis [4] report that the photo-oxidation rate of benzene, carried out in an aqueous suspension of TiO_2, is hardly influenced by the presence of perchloroethylene, a non-aromatic compound. In order to explain this result, they hypothesize that benzene adsorbs on all sites of the TiO_2 surface, thus primarily reacting with surface hydroxyls, whereas perchloroethylene adsorbs only on specific site(s), primarily reacting with solution phase radicals. Adsorbed benzene and its intermediates would react with the radical species generated on the catalyst surface before they could react with the perchloroethylene in the solution phase and consequently the presence of perchloroethylene has a negligible influence on the photodegradation of benzene. The above explanation could be invoked also in the case of the mixtures of phenol and aliphatic compounds investigated in this work.

It has been observed moreover by Tunesi and Anderson [20] that the efficiency of the photodegradation process for 2-hydroxybenzoic acid (salicylic acid) and related aromatics depends upon the chemistry of their adsorption.

The mineralization data, some of which are reported in Figs. 3–5 as TOC concentration vs. reaction time, indicate that stable organic intermediates were produced in the course of the photodegradation process; however, the total mineralization of the organic molecules was always achieved after about 4–8 h of irradiation, depending on the type and initial concentration of the substrates. When only phenol molecules were present in the solution, the complete mineralization was achieved after shorter periods of time than when phenol was in the presence of another compound.

The mineralization rate of the mixtures was affected by the nature of the mixture components. For aromatic compound–phenol mixtures the TOC data indicate that the mineralization rate depends on the mixture composition. Fig. 3 reports the mineralization data of 4-nitrophenol–phenol mixtures in molar ratios of 10:1 and 1:10. It may be noted that these mixtures, even if they have the same molar concentration of organic compounds, exhibit different mineralization rates; the mixture with the higher content of 4-nitrophenol shows a mineralization rate lower than that of the phenol-rich mixture. The mineralization data of solutions of phenol or 4-nitrophenol with a concentration value equal to the highest one used in the mixtures are not reported for the sake of brevity. They show a pattern very similar to that of the mixture in which that compound is in excess. In other words, the mineralization rate of the aromatic compound mixtures is mainly determined by the mineralization rate of the most stable compound.

Fig. 4 reports the TOC data obtained with solutions of phenol and ethanoic acid alone and in mixture. The results indicate that these two compounds alone are easily mineralized and that when the ethanoic acid–phenol mixture is photodegraded, the mineralization rate is lowered with respect to those of the pure components. This finding suggests that during the photodegradation of this mixture, some stable intermediates are produced by the reaction of species deriving from the partial oxidation of the individual substrates. Moreover, a mechanism of competitive adsorption–desorption between the intermediates produced by the partial oxidation of phenol and the aliphatic molecules could also play a relevant role. Finally, it is worth noticing that although the mineralization rates of the mixtures are always lower than those of the pure components, the photocatalytic method is able to completely mineralize all the organic molecules. From observation of Fig. 5, indeed, it can be noticed that global photomineralization is eventually achieved.

Additional mechanistic studies are in progress in order to clarify better the above-described experimental results.

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