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Heterogeneous photocatalyzed degradation of uracil and 5-bromouracil in aqueous suspensions of titanium dioxide

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Abstract

Photocatalyzed degradation of uracil (**1**) and 5-bromouracil (**2**) has been investigated in aqueous suspensions of titanium dioxide under a variety of conditions. The degradation was studied by monitoring the change in substrate concentration employing UV spectroscopic analysis technique and depletion in total organic carbon (TOC) content as a function of irradiation time. The degradation of the compounds under investigation was studied using various parameters such as, different types of TiO_2 powders, pH, catalyst concentration, substrate concentrations, and in the presence of electron acceptors like hydrogen peroxide (H_2O_2) and potassium bromate ($KBrO_3$) besides molecular oxygen. Photocatalyst Degussa P25 was found to be more efficient for the degradation of both compounds as compared with other TiO_2 powders such as UV100, PC500 and TTP.
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Keywords: Photocatalysis; Semiconductor; Titanium dioxide; Uracil; 5-Bromouracil

1. Introduction

The photocatalyzed reaction of organic molecules in the presence of semiconductor such as TiO_2 has become a subject of serious study as it shows promise in becoming a viable commercial technology for the wastewater treatment [1–5]. This process bears a close analogy to the charge separation developed in a photochemical cell, containing semiconductor electrodes and the principles governing photoelectrochemistry apply equally well to reactions occurring on the surface of irradiated particles [6]. On irradiation of the semiconductor at appropriate wavelengths, an electron is excited from the valance band to the conduction band, yielding an electron–hole pair. The reaction of this electron–hole pair with a variety of electron acceptors and donors, as well as the electron–hole recombination processes has been well studied [7,8]. The formation of cation radicals of organic substrates, following an electron transfer from it to

the excited semiconductor has been unambiguously characterized, both from product analysis [9] as well as by spectroscopic studies [10]. The trapped hole in TiO_2 can lead to the formation of hydroxyl radicals, which can abstract a hydrogen atom from weak C–H bonds and reacts with multiple bonds, including reactions with aromatic systems, leading to the formation of free radicals. In the presence of oxygen, these free radicals can be rapidly converted to unstable peroxy radicals. Subsequent reactions of the peroxy radicals and other intermediates formed can lead to the oxidation of the organic materials, dissolved in water. Of the two possible pathways for the initial oxidation reactions namely, the one involving direct oxidation of organic substrate and other proceeding through $OH^{\bullet}$ radical mediated reactions, the current prevailing view favours the latter [11].

The primidine base pesticide derivative uracil (**1**), which is extensively used as herbicide, may be utilized preferentially for nucleic acid biosynthesis in tumors [12]. Substitution at five-position of uracil by halogen atom results in the drastic changes in the biological properties of the compound [13].

Few studies related to the degradation of uracil (**1**) and its bromoderivatives have been reported earlier. Aliskandarani et al. [14] has studied the influence of pollutant concentration,

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1
Uracil
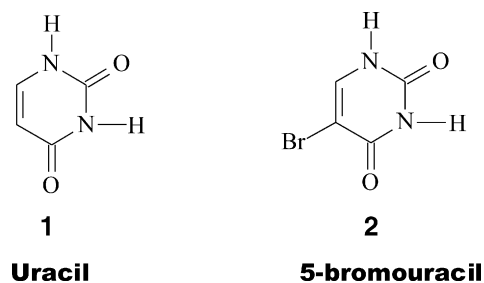
2
5-bromouracil

Fig. 1.

volume of solution and stirring speed on the photodegradation of uracil (**1**) and 5-halouracils in the presence of titanium dioxide. Vaz et al. [15] has studied the influence of pH and anion on the photomineralization of these systems. The photodegradation of water samples taken from a heavily polluted well containing various types of herbicides have been reported by Muszkat et al. [16]. In spite of these studies, no major efforts have been made to study the details of the degradation kinetics, the knowledge of which is essential for the proper design of the treatment plant. Therefore, we have undertaken the detailed kinetic study of uracil (**1**) and 5-bromouracil (**2**) (Fig. 1) under different parameters.
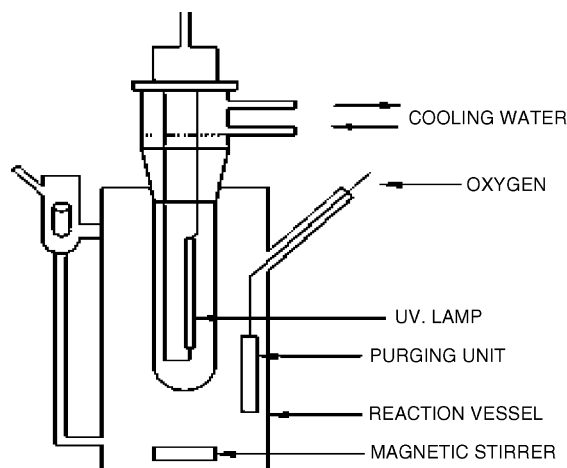
2. Experimental

2.1. Reagents and chemicals

Reagent grade uracil (**1**) was obtained from CDH Pvt. Ltd., India and 5-bromouracil (**2**) was purchased from Fluka and used as such without any further purification for the degradation study. The photocatalyst, titanium dioxide Degussa P25 (Degussa AG, $1 \, \text{g L}^{-1}$), was used in most of the experiment, whereas other catalyst powders namely Hombikat UV100 (Sachtleben chemie GmbH, $1 \, \text{g L}^{-1}$), PC500 (Millennium inorganic chemicals, $1 \, \text{g L}^{-1}$) and TTP (Travancore Titanium Products, India, $1 \, \text{g L}^{-1}$) were used for comparative studies. Degussa P25 consists of 75% anatase and 25% rutile with a specific BET-surface area of $50 \, \text{m}^2 \, \text{g}^{-1}$ and primary particle size of 20 nm [17]. Hombikat UV100 consist of 100% anatase with a specific BET-surface area $> 250 \, \text{m}^2 \, \text{g}^{-1}$ and primary particle size of 5 nm [18]. The photocatalyst PC500 has a BET-surface area of $287 \, \text{m}^2 \, \text{g}^{-1}$ with 100% anatase and primary particle size of 5–10 nm [19]. The other chemical used in this study such as NaOH, HNO_3, H_2O_2 and $KBrO_3$ were obtained from Merck.

2.2. Procedure

Solutions of uracil (**1**) and 5-bromouracil (**2**) of desired concentrations were prepared in double distilled water. An immersion well photochemical reactor made of Pyrex glass equipped with a magnetic stirring bar, water circulating jacket and an opening for supply of molecular oxygen was used. A schematic diagram of the reactor is shown below.

For the irradiation experiment, aqueous solution (250 mL) of the compound was taken into the photoreactor, required amount of photocatalyst was added and the solution was stirred and bubbled with molecular oxygen for at least 30 min in the dark to allow equilibration of the system so that the loss of compound due to adsorption could be taken into account. The zero time reading was obtained from blank solution kept in the dark but otherwise treated similarly to the irradiated solution. pH of the reaction mixture was adjusted by adding a dilute aqueous solution of HNO_3 or NaOH. The suspensions were continuously purged with molecular oxygen throughout each experiment. Irradiations were carried out using a 125 W medium pressure mercury lamp (Philips, radiant flux $\approx 4.890 \, \text{mW/cm}^2$) and. IR-radiations were eliminated by a water jacket. Samples (10 mL) were collected before and at regular intervals during the irradiation (5-bromouracil (1.0 mM, 240 min), uracil (0.5 mM, 120 min)) and analyzed after centrifugation.

2.3. Analysis

The degradation of uracil (**1**) and 5-bromouracil (**2**) was followed by measuring the decrease in absorption intensity at 259.5 and 277 nm respectively as a function of irradiation time after 75–80% dilution using Shimadzu UV–vis Spectrophotometer (1601). The mineralization of uracil (**1**) and 5-bromouracil (**2**) was monitored by measuring the depletion in TOC as a function of irradiation time using Shimadzu 5000A TOC Analyzer.

The degradation rate for the decomposition and mineralization of the pollutants were calculated using the expressions given below:

$$-\frac{d[A]}{dt} = kc \tag{1}$$

$$-\frac{d[TOC]}{dt} = kc \tag{2}$$

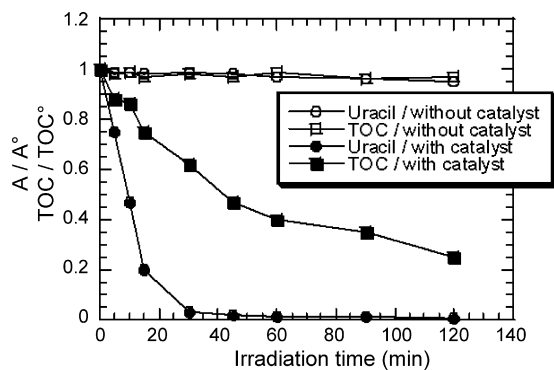where k is the rate constant and c is the concentration of the pollutant.

Fig. 2. Depletion in TOC and change in absorption intensity at 259.5 nm as a function of irradiation time for the photocatalyzed degradation of uracil (1) in the presence and absence of TiO_2 in aqueous suspensions.

3. Results and discussion

3.1. Irradiation of an aqueous suspension of uracil (1) and 5-bromouracil (2) containing TiO_2

Irradiation of an aqueous solution of uracil (1) and 5-bromouracil (2) in the presence of the photocatalyst (TiO_2, Degussa P25, $1 g L^{-1}$) by the pyrex filtered output of a 125 W medium pressure mercury lamp under oxygen lead to the decrease in the absorption intensity and depletion in TOC content as a function of time. Figs. 2 and 3 show the change in the absorption intensity and depletion in TOC as a function of irradiation time for the photocatalytic degradation of uracil (1) and 5-bromouracil (2) in the presence and absence of TiO_2. The compounds under investigation undergo decomposition when irradiated in the presence of TiO_2, whereas no observable loss of compound was seen in the absence of TiO_2. Control experiments were carried out in all cases, employing unirradiated blank solutions where no observable loss of the compound due to adsorption on the catalyst was found. The zero irradiation time readings were obtained from blank solutions kept in the dark, but otherwise treated similarly to the irradiated solutions. Both the degradation and the mineralization curves can be fitted reasonably well by an exponential decay curve suggesting

first order kinetics. The degradation rates for the mineralization and decomposition of 1 and 2 were calculated in terms of $M min^{-1}$. The zero irradiation time reading was obtained from blank solutions kept in the dark, but otherwise treated similarly to the irradiated solutions.

3.2. Comparison of different photocatalysts

The photodegradation of uracil (1) and 5-bromouracil (2) was tested with four different TiO_2 powders, namely, Degussa P25, Hombikat UV100, PC500 and TTP. The degradation rate for the decomposition and mineralization of uracil (1) and 5-bromouracil (2) is shown in Table 1.

It could be seen from the table that in the case of uracil (1), the degradation rate for the decomposition of the compound is much higher in the presence of Degussa P25 as compared with other TiO_2 powders. Whereas in the case of 5-bromouracil (2) the influence of Degussa P25 on the degradation rate for the decomposition of the compound was not as pronounced as observed in case of uracil (1). In contrast it is interesting to note that in the case of 5-bromouracil (2) the degradation rate for the mineralization of the compounds employing photocatalyst Degussa P25 and UV100 is more or less same. The photocatalyst obtained from TTP was found to be of lower efficiency for the degradation of the compounds under investigation.

The differences in the photocatalytic activity are likely to be due to differences in the BET-surface, impurities, lattice mismatches or density of hydroxyl groups on the catalyst's surface, since they will affect the adsorption behavior of a pollutant or intermediate molecule and the lifetime and recombination rate of electron–hole pairs. Earlier studies have also shown that Degussa P25 was found to show better activity for the photocatalytic degradation of a large number of organic compounds [20–22]. Also Linder et al. [23] showed that Hombikat UV100 was almost four times more effective than P25 when dichloroacetic acid was used as the model pollutant. On the other hand Hombikat UV100 was found to be better for the degradation of benzidine, 1,2-diphenyl hydrazine and remazol brilliant blue R as reported earlier [24,25]. The better efficiency of Degussa P25 photocatalyst could be explained by a quantum size effect [26,27] and references cited therein. When the particles become too small, there is a 'blue shift' with an increase of the band gap energy, detrimental to the near UV-photon absorption, and an increase of the electron–hole recombination. Too high specific area is not beneficial for an optimum efficiency. The reason for the better photocatalytic activity of Degussa P25, could be attributed to the fact that P25 being composed of small nano-crystallites of rutile being dispersed within an anatase matrix. The smaller band gap of rutile "catches" the photons, generating electron–hole pairs. The electron transfer, from the rutile conduction band to electron traps in anatase phase takes place. Recombination is thus inhibited allowing the hole to move to the surface of the particle and react [28].

In all following experiments, Degussa P25 was used as the photocatalyst, since this material exhibited highest overall activity for the degradation of the pollutants.
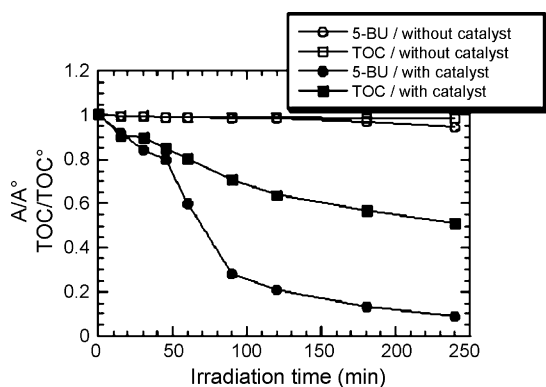

Fig. 3. Depletion in TOC and change in absorption intensity at 277 nm as a function of irradiation time for the photocatalyzed degradation of 5-bromouracil (2) in the presence and absence of TiO_2 in aqueous suspensions.

Table 1
Degradation rate for the decomposition of uracil (**1**) and 5-bromouracil (**2**) under different parameters

Parameters		Uracil (**1**) degradation rate (M min^{-1})		5-Bromouracil (**2**) degradation rate (M min^{-1})	
		Decomposition	Mineralization	Decomposition	Mineralization
Type of phortocatalyst (1 g L^{-1})	P25	0.59	0.0083	0.011	0.0028
	UV100	0.013	0.0033	0.0098	0.0026
	PC500	0.018	0.0046	0.008	0.0023
	TTP	0.0032	0.0010	0.0054	0.00037
pH	3	0.043	0.0056	0.0068	0.0013
	5	0.059	0.0083	0.011	0.0028
	7	0.061	0.0085	0.019	0.0036
	9	0.08	0.0089	0.023	0.0049
Substrate concentration (mM)	0.25	0.04	0.0071	–	–
	0.5	0.059	0.0083	0.010	0.0017
	0.75	0.072	0.0103	0.010	0.0027
	1.0	0.078	0.0108	0.011	0.0028
	1.5	–	–	0.012	0.0029
Catalyst concentration (g L^{-1})	0.25	0.038	0.0054	0.005	–
	0.5	0.049	0.0069	0.0097	0.0021
	1.0	0.059	0.0083	0.011	0.0028
	2.0	0.137	0.0116	0.013	0.0032
	3.0	0.180	–	0.019	0.0050
	4.0	0.075	–	0.012	–
	5.0	0.060	–	0.011	–

The adsorption of both the pollutants on the surface of the four different types of photocatalyst such as Degussa P25, UV100, PC500 and TTP was investigated by stirring the aqueous solution in the dark for 24 h in a round bottomed flask containing varying amounts of TiO$_2$ such as 0, 0.25, 0.5, 1, 2, 3, 4 and 5 g L^{-1}. Analysis of the solution showed no appreciable adsorption of the compounds on the surface of all the four types of photocatalysts.

3.3. Effect of pH

An important parameter in the heterogeneous photocatalysis is the reaction pH, since it determines the surface charge properties of the photocatalyst and therefore the adsorption behavior of the pollutant and also the size of aggregates it forms. The degradation rate for the decomposition and mineralization of uracil (**1**) and 5-bromouracil (**2**) has been investigated in the pH range between 3 and 9 in the presence of TiO$_2$.

The degradation rate for the decomposition and mineralization of uracil (**1**) and 5-bromouracil (**2**) as a function of reaction pH is shown in Table 1. It is interesting to note that the degradation rate for the decomposition of the compounds increases significantly with the increase in the reaction pH whereas its influence on the mineralization rate was not much pronounced. Similar results of the effect of reaction pH on the degradation of uracil and 5-halouracil derivatives have been reported earlier by Vaz et al. [15].

The interpretation of pH effect on the photocatalytic process is very difficult task because of its multiple roles such as electrostatic interactions between the semiconductor surface, solvent molecules, substrate and charged radicals formed during the reaction process. The ionization state of the surface of the photocatalyst can be protonated and deprotonated under acidic and alkaline conditions, respectively, as show in following equations:

$$TiOH + H^+ \rightarrow TiOH_2^+ \qquad (3)$$

$$TiOH + OH^- \rightarrow TiO^- + H_2O \qquad (4)$$
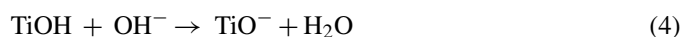
The point of zero charge (pzc) of the TiO$_2$ (Degussa P25) is widely reported at pH $\sim$ 6.25 [29]. Thus, the TiO$_2$ surface will remain positively charged in acidic medium (pH < 6.25) and negatively charged in alkaline medium (pH > 6.25). The better rate at higher pH may be attributed to more efficient generation of hydroxyl radicals by TiO$_2$ with increasing concentration of OH$^-$. At the alkaline pH values, the hydroxyl radicals have to diffuse away and degrade the dye in the bulk solution.

3.4. Influence of substrate concentration

It is important both from mechanistic and from application point of view to study the dependence of photocatalytic reaction rate on the initial substrate concentration. Hence, the effect of initial substrate concentration on the degradation of compounds **1** and **2** was studied at different initial substrate concentrations in the range between 0.12 and 1.5 mM. The degradation rate for the decomposition and mineralization of uracil (**1**) and 5-bromouracil (**2**) as a function of substrate concentration is shown in Table 1. The degradation rates were found to increase with the increase in the substrate concentrations. Interestingly the rate for the decomposition of the compound was found to increase markedly with the increase in substrate concentration in the case of uracil (**1**).

As oxidation proceeds less and less of the surface of the (TiO$_2$) particle is covered as the pollutant is decomposed. Evi-

dently, at total decomposition, the rate of degradation is zero and a decreased photocatalytic rate is to be expected with increasing illumination time. Our results on the effect of the initial concentration on the degradation rates of uracil (**1**) and 5-bromouracil (**2**) shown in the table are in agreement with the number of studies reported earlier.

3.5. Effect of catalyst concentration

Whether in static, slurry or dynamic flow reactors, the initial reaction rates were found to be directly proportional to catalyst concentration, indicating a heterogeneous regime. However, in some cases it was observed that above a certain concentration, the reaction rate even decreases and becomes independent of the catalyst concentration. This limit depends on the geometry and working conditions of the photoreactor and for a definite amount of TiO_2 in which all the particles, i.e., the entire surface exposed, are totally illuminated. When the catalyst concentration is very high, after traveling a certain distance on an optical path, turbidity impedes further penetration of light in the reactor. In any given application, this optimum catalyst concentration $[(TiO_2)_{OPT}]$ has to be found, in order to avoid excess catalyst and ensure total absorption of efficient photons.

The influence of the photocatalyst concentrations on the degradation rates were investigated in the range between 0.25 and $5\,g\,L^{-1}$. Degradation rate for the decomposition and mineralization of uracil (**1**) and 5-bromouracil (**2**) is shown in Table 1. As expected, the rates were found to enhance with the increase in concentration of the photocatalyst up to $3\,g\,L^{-1}$ and a further increase in catalyst loading lead to decrease in degradation rate.

3.6. Effect of electron acceptors

Since hydroxyl radicals appear to play an important role in the photocatalytic degradation of organic pollutants. The electron acceptors such as hydrogen peroxide and potassium bromate were added into the solution in order to enhance the formation of hydroxyl radicals and also to inhibit the electron–hole $(e^- - h^+)$ pair recombination. Figs. 4 and 5 show the degradation rate for
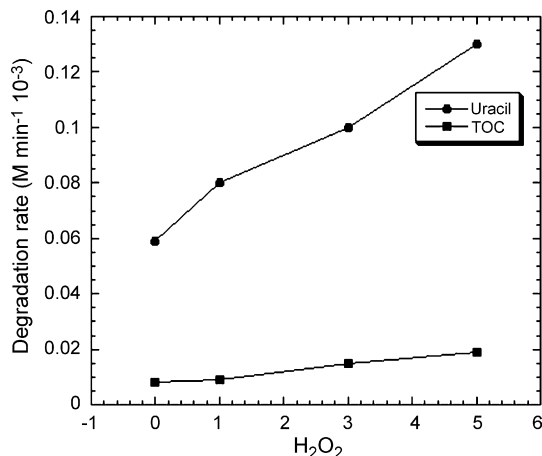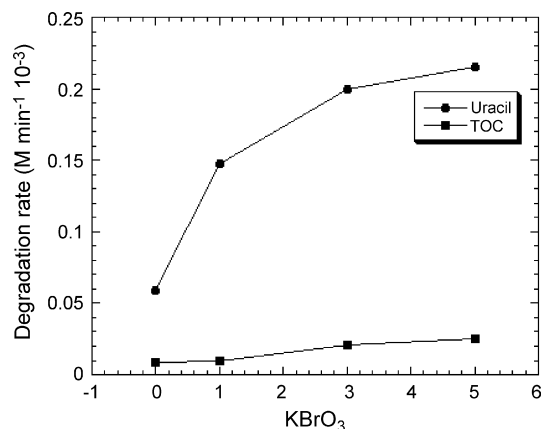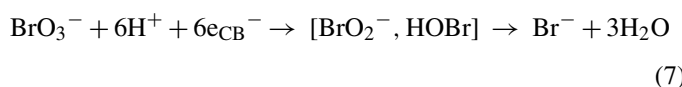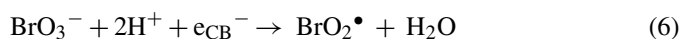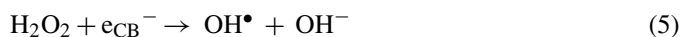
Fig. 5. Degradation rate for the degradation and mineralization of uracil (**1**) at different $KBrO_3$ concentrations.

the decomposition and mineralization of uracil (**1**) in the presence of hydrogen peroxide and potassium bromate at different concentrations. It could be seen from the figure that the rate for the decomposition of the compound increases with increase in the concentration of both H_2O_2 and $KBrO_3$ whereas it effects on the mineralization rate was not all that pronounced.

The degradation rate for the decomposition and mineralization of 5-bromouracil (**2**) in the presence of TiO_2 containing H_2O_2 and $KBrO_3$ is shown in Fig. 6. As expected both the additives showed beneficial effect on the degradation rate of the compounds under investigation.

The electron acceptors such as hydrogen peroxide and potassium bromate are known to generate hydroxyl radicals by the mechanisms shown in Eqs. (5)–(7):

$$H_2O_2 + e_{CB}{}^- \rightarrow OH^\bullet + OH^- \tag{5}$$

$$BrO_3{}^- + 2H^+ + e_{CB}{}^- \rightarrow BrO_2{}^\bullet + H_2O \tag{6}$$

$$BrO_3{}^- + 6H^+ + 6e_{CB}{}^- \rightarrow [BrO_2{}^-, HOBr] \rightarrow Br^- + 3H_2O \tag{7}$$

The respective one-electron reduction potentials of different species are: $E(O_2/O_2{}^{\bullet -}) = -155\,mV$, $E(H_2O_2/OH^\bullet) = 800\,mV$

Fig. 4. Degradation rate for the decomposition and mineralization of uracil (**1**) in the presence of TiO_2 containing H_2O_2 at varying concentration.
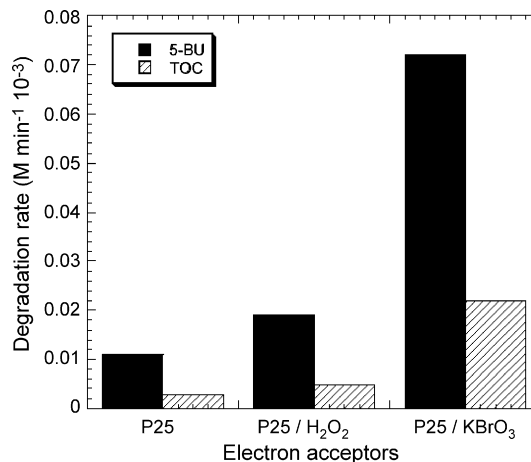
Fig. 6. Degradation rate for the degradation and mineralization of 5-bromouracil (**2**) in the presence of electron acceptors.

and $E(BrO_3{}^-/BrO_2{}^\bullet) = 1150\,mV$ [30]. From the thermodynamic point of view both employed additives should therefore be more efficient electron acceptors than molecular oxygen.

It was observed that bromate ions markedly enhanced the degradation rate of compounds uracil (**1**) and 5-bromouracil (**2**), as compared with H_2O_2. The remarkable effect of potassium bromate on the enhanced degradation rate of number of compounds has been reported earlier. The reason can be attributed to the maximum number of electrons it reacts as shown in Eqs. (5)–(7). Another possible explanation might be a change in the reaction mechanism of the photocatalytic degradation. Since the reduction of bromate ions by electrons does not lead directly to the formation of hydroxyl radicals, but rather to the formation of other reactive radicals or oxidizing agents, e.g. $BrO_2{}^-$ and HOBr. Furthermore, bromate ions by themselves can act as oxidizing agents. Linder has proposed a mechanism for the photocatalytic degradation of 4-chlorophenol in the presence of bromate ions considering direct oxidation of the substrate by bromate ions [31].

4. Conclusion

TiO_2 can efficiently catalyze the photomineralization of uracil (**1**) and 5-bromouracil (**2**) in the presence of light. The photocatalyst Degussa P25 showed better photocatalytic activity for the degradation of the model pollutants under investigation. The addition of electron acceptors such as hydrogen peroxide and potassium bromate can enhance the decomposition of model system. The observations of these investigations clearly demonstrate the importance of choosing the optimum degradation parameters to obtain high degradation rate, which is essential for any practical application of photocatalytic oxidation processes.

Acknowledgements

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