EFFECTS OF pH, TEMPERATURE AND VARIOUS ANIONS ON THIOUREA DISAPPEARANCE IN AQUEOUS MEDIA WITH TITANIUM DIOXIDE UNDER UV-IRRADIATION. PHOTOMINERALIZATION KINETICS

Abdelghani BOUSSAOUD[a,*], Gerard DUC[b1], Jean Pierre MEILLE[b2] and Michelle PETIT-RAMEL[b3]

[a] *Laboratoire de Chimie-Physique, Faculté des Sciences, Agadir, Morocco; e-mail: boussaoud@hotmail.com*

[b] *Laboratoire d'Instrumentation et de Chimie Analytique II, Université Claude Bernard, Lyon I, France; e-mail:* [1] *duc@univ-lyon1.fr,* [2] *meille@univ-lyon1.fr,* [3] *mpetit-ramel@univ-lyon1.fr*

Disappearance of thiourea in aqueous suspensions of TiO_2 or ZnO occurs under near-UV irradiation. The effects of some parameters such as initial concentration of thiourea, temperature, pH and common inorganic anions were examined. The results indicate that the process follows the Langmuir–Hinshelwood type kinetics. In the presence of anions such as nitrates, chlorides and sulfates, the initial disappearance rate of thiourea at pH 6 drops. It is found that the initial rate of thiourea disappearance increases when temperatue of reaction mixture increases. Finally, kinetics of thiourea photomineralization to nitrite, nitrate, sulfite and sulfate are established.

Keywords: Thiourea; TiO_2; Kinetics; Photodegradation; Photooxidation; Photomineralization; Semiconductors.

Titanium dioxide (or other semiconductors) produces electrons and holes which subsequently initiate reduction and oxidation reactions[1], when illuminated with the light of energy higher than that of the semiconductor band gap. The model generally accepted for the oxidation of organics in oxygenated aqueous suspensions of UV-irradiated semiconductor is that at the surface of particles, both oxygen and an organic solute, are adsorbed. Oxygen reacts with photoelectrons to form the superoxide radical anion, $O_2^{\cdot-}$, and the organic reacts with the photoholes either directly or *via* an adsorbed hydroxyl radical intermediate, OH$^\cdot$ (refs[2–4]). The availability of both readily oxidizable and reducible species on the surface inhibits the recombination between photoelectrons and photoholes that would otherwise occur.

Thus the photocatalytic processes at the semiconductor–electrolyte interface has been successfully applied to eliminate toxic substances[5–7]. Using this method, some researchers[8,9] were interested in thiourea since it has been usual component of industrial wastes.

In the present work, the photocatalytic elimination of thiourea in UV-irradiated TiO_2 in aqueous suspensions is examined by varying initial concentration of thiourea, temperature, pH and the presence of common inorganic anions (Cl^-, SO_4^{2-} or NO_3^-). We also determined the formation kinetics of some inorganic anions due to the mineralization of thiourea.

EXPERIMENTAL

Photoreactions were performed in a photochemical immersion reactor which had a double wall of Pyrex for thermostatting reaction mixture and excluding light below 290 nm. The reaction compartment had inlet and outlet ports for bublling oxygen. A HPK125-W medium-pressure mercury lamp (Phillips) was used as an irradiation source. The intensity of the incident light inside the reactor was measured by uranyl oxalate actinometer according to Bard[10] and it was found to be $4.58 \cdot 10^{-6}$ einstein s^{-1}. The thiourea concentrations were determined by HPLC (Jasco 8800) using a Spherisorb ODS-2 column (25 cm × 4.6 mm) and a UV variable detector fixed at $\lambda = 240$ nm. Water (Solvachim) was used as mobile phase with a flow rate of 0.5 ml min^{-1}. Separate ion chromatographic system was used for the analysis of produced anions in the irradiated solution of thiourea. The system consisted of a Dionex Ionchrom Chromatograph equipped with a 100 µl injection valve and a conductivity detector, a Sarasep AN1 analytical column (25 cm × 4.6 mm) and a 3380A Hewlett–Packard integrator. A flow rate of 1 ml min^{-1} of carbonate buffer (1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$) used as mobile phase was maintained during the analysis.

The following materials were used as received: thiourea (>97%), ZnO (98%) were purchased from Fluka; NaCl (98%), Na_2SO_4 (99%), $NaNO_3$ (99%) and $NaNO_2$ were from Prolabo; NaOH (98%), Na_2SO_3 (98%) and HNO_3 (65%) were from Merck. Titanium dioxide was Degussa P-25 (80% anatase, 20% rutile), had a surface area of 50 m^2 g^{-1}.

Aqueous solutions (the sample volume was 1 000 ml) of thiourea alone or with dissolved salts, were added to catalyst (0.5 g l^{-1}) and stirred for 60 min in dark. The pH of solutions was adjusted by adding concentrated NaOH or HNO_3 solutions. During exposure, oxygen was bubbled in the stirred reaction mixture. At regular irradiation times, samples were immediately filtered through Millipore filters (0.45 µm) and subjected to HPLC analysis.

In order to quantify nitrite, nitrate, sulfite and sulfate anions, samples from the irradiated solutions were filtered through 0.22 µm Millipore disks, collected and analyzed by ion chromatography. Anion concentrations were determined by the comparing peak areas with those of calibration solutions.

RESULTS AND DISCUSSION

Effect of Catalyst

No decrease in the organic was observed after 60 min of UV irradiation of thiourea solutions ($\lambda \geq 290$ nm) without a semiconductor. In the dark, thiourea solution with semiconductor showed only a slight decrease in thiourea concentration attributed to adsorption. However, photodegradation was accelerated by adding TiO_2 or ZnO and bubbling the solution with oxygen. Under these conditions and at pH 6, the kinetics of thiourea consumption was apparently zero-order during the first 40 min at high starting concentrations (Fig. 1). Beside in terms of initial rate, ZnO is more photoactive than TiO_2 in photooxidation of thiourea, the initial rates with the former being higher. If the degradation rate is controlled by substrate adsorption as proposed[9,11], the photoactivity difference should be attributed to metal/ligand interaction of thiourea ZnO particle surface[12].

Effect of Initial Concentration of Solute (C_0)

As shown in Fig. 2, below $5 \cdot 10^{-4}$ mol l^{-1}, the initial rate of thiourea disappearance (r_0) on UV-irradiated Degussa P-25 TiO_2 increases with increasing C_0. This dependence approximately follows the Langmuir–Hinshelwood behaviour. This indicates that reaction occurs with adsorbate substrate.
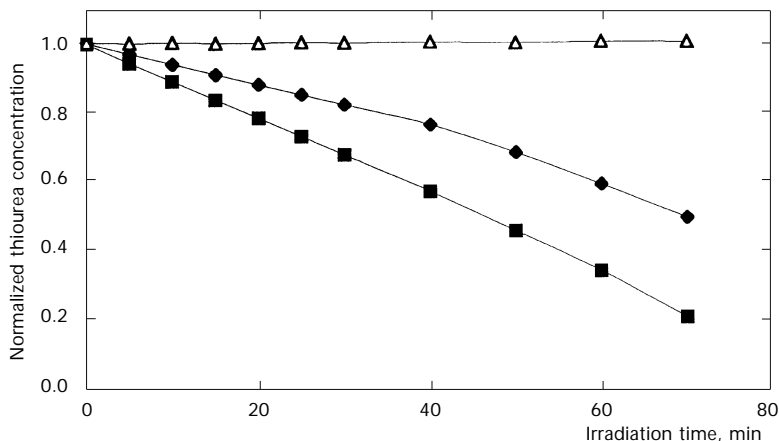

FIG. 1

Thiourea disappearance kinetics in the presence or absence of TiO_2 or ZnO *versus* the irradiation time; ● TiO_2, ■ ZnO, △ no catalyst

$$r_0 = \frac{kKC_0}{1 + KC_0} ,$$

where k and K are respectively the rate constant and adsorption equilibrium constant. Their values (k = 8.3 μmol min^{-1}, K = 8 698.2 l mol^{-1}) are obtained from the $1/r_0$ *versus* $1/C_0$ dependence (Fig. 3). The value of k has no absolute
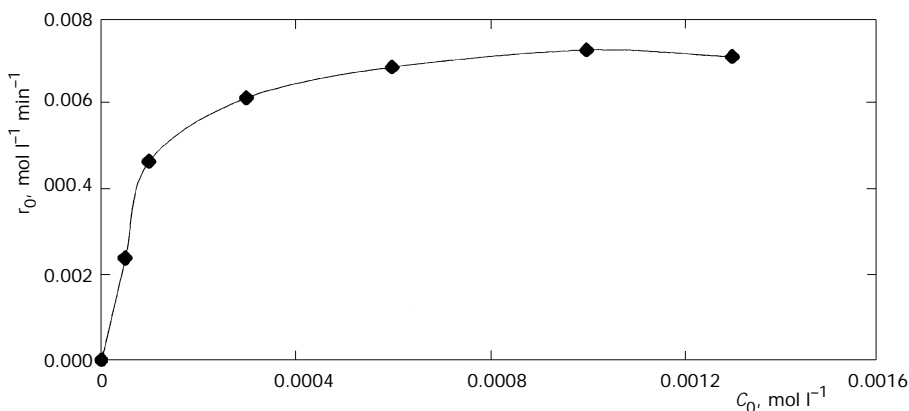

FIG. 2

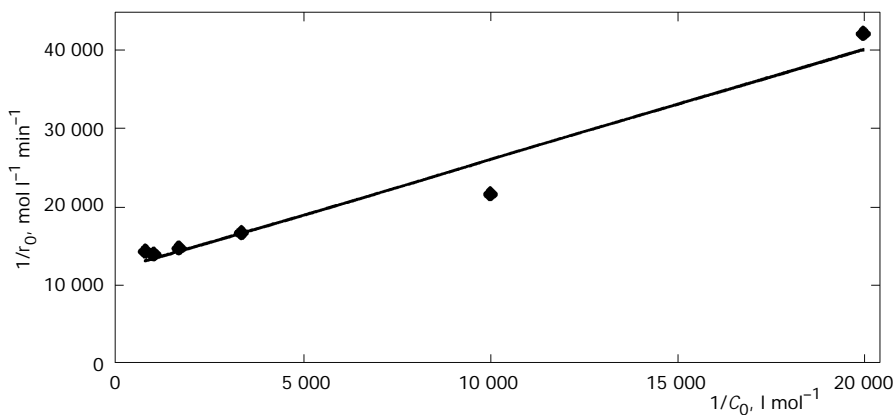Dependence of the initial thiourea disappearance rate *versus* its initial concentration

FIG. 3

The reciprocal initial thiourea concentration *versus* the reciprocal initial disappearance rate

meaning because it depends on the experimental conditions. According to Cunningham[13], the value of K measured in dark is lower than that determined by kinetics.

Effect of Temperature

The rate of thiourea disappearance was affected by temperature since an increase in temperature from 25 to 45 °C led to about 93% enhancement of the initial degradation rate. By plotting the log r_0 *versus* $1/T$ dependence (Fig. 4), apparent activation energy of 16.78 kJ mol^{-1} was obtained.

Effect of pH

The dependence of the initial rate of thiourea disappearance on pH of the mixture is illustrated in Fig. 5. Unlike in other previous works[14–16], the initial rate of thiourea degradation is high at very low pH and decreases to reach its lowest value at about pH 4. Then, the initial rate slightly increases with pH of the reaction mixture. For TiO_2 (Degussa P-25), the zero-point potential (pzp) is at about pH 6 (ref.[17]). Thus, at low pH, the semicoductor particle surface is positively charged, while at pH > 6, the surface is negatively charged. This brings about important consequences on adsorption/desorption properties of the catalyst particle surface.
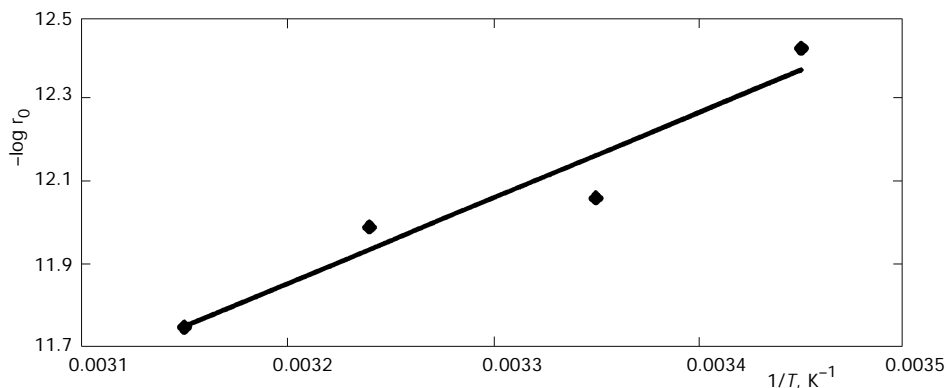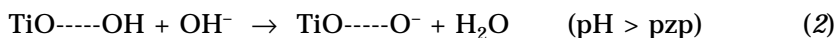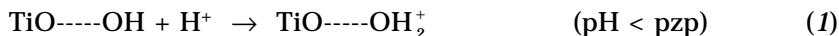

FIG. 4
The Arrhenius plot in the studied temperature range; $C_0 = 1 \cdot 10^{-3}$ mol l^{-1}, $R^2 = 0.9275$

$$TiO\text{-----}OH + H^+ \ \rightarrow \ TiO\text{-----}OH_2^+ \qquad (pH < pzp) \qquad (1)$$

$$TiO\text{-----}OH + OH^- \ \rightarrow \ TiO\text{-----}O^- + H_2O \qquad (pH > pzp) \qquad (2)$$

Thus, at very low pH, the protonation affinity of thiourea could be an important parameter for its adsorption on the charged surface of TiO_2 catalyst and, subsequently, for its reactivity. Another oxidation reaction type could be coupled to this process if we take into account the protonated species resulting from the protonation of sulfur[9].

When the mixture becomes alkaline, the abundance of hydroxyl ions (OH⁻) makes for additional OH• radicals capable of reacting with organic substrates.

Effect of Various Anions

As shown in Fig. 6, the presence of chloride, sulfate and nitrate ions in solution, caused a decrease in the initial photodegradation rate of thiourea. When the concentration of inorganic anions is around 10^{-4} mol l⁻¹, the thiourea disappearance rate is reduced by 21% for nitrates, 29% for chlorides and 39% for sulfates.

The behaviour of these anions can be attributed to blocking of active sites of TiO_2 and/or to their competition for oxidizing species. It has been reported that sulfates are strongly adsorbed on TiO_2 particles while chlorides easily react with oxidizing radicals[18–20] as follows :
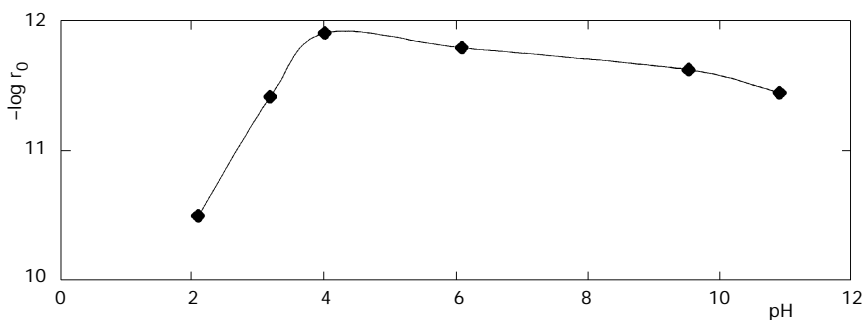

Fig. 5
The initial photodegradation rate *versus* pH for thiourea; $C_0 = 1 \cdot 10^{-3}$ mol l⁻¹

$$Cl^- + Ox^\bullet \rightarrow Cl^\bullet + Ox^- . \tag{3}$$

Photomineralization of Thiourea

Figure 7 shows the effect of UV-irradiation time on the thiourea photo-oxidation. Thus under TiO_2-mediated photocatalytic oxidation, the main
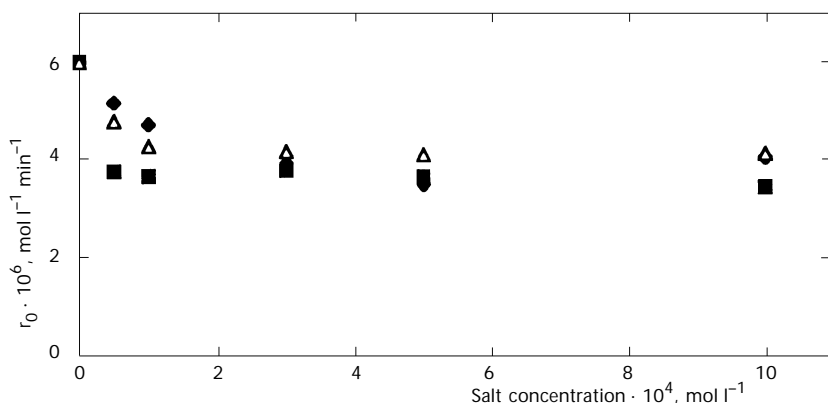

Fig. 6
Dependence of initial photodegradation rate on initial salt concentrations; $C_0 = 1 \cdot 10^{-3}$ mol l^{-1}; ◆ $NaNO_3$, ■ Na_2SO_4, △ $NaCl$
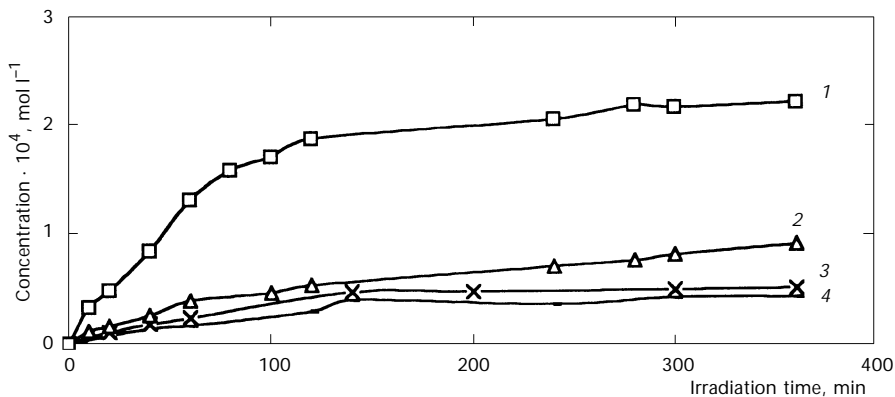

Fig. 7
Plots of the obtained anion concentrations *versus* the irradiation time; $C_0 = 1 \cdot 10^{-3}$ mol l^{-1}; 1 SO_4^{2-}, 2 SO_3^{2-}, 3 NO_3^-, 4 NO_2^-

elements are converted to their inorganic compounds with considerably different initial rates.

Under our experimental conditions, it seems that sulfur is mainly transformed to sulfite and sulfate ions. The laters appear with apparent initial rates of 0.6 µmol l^{-1} min^{-1} for sulfite and 2 µmol l^{-1} min^{-1} for sulfate. However, it is necessary to note that photogenerated holes photooxidize sulfite to sulfate[21,22] as follows:

$$SO_3^{2-} + H_2O + 2\ H^+ \rightarrow SO_4^{2-} + 2\ H^+ . \tag{4}$$
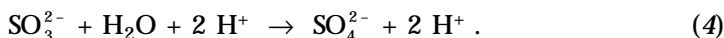
Thiourea nitrogen shows a very difficult conversion to nitrite and nitrate. Their initial rates of formation are respectively 0.28 and 0.44 µmol l^{-1} min^{-1}. According to Low[23], the relative concentrations of nitrate and ammonium depend largely on the nature of nitrogen atoms in the compound, and on the UV-irradiation time and initial concentration. Under our experimental conditions, thiourea probably produces more ammonium ions during photomineralization since it is well known that ammonium ions are not easily converted to nitrate *via* nitrite ions.

CONCLUSION

At high concentrations, the photocatalytic oxidation kinetics of thiourea exhibits a zero-order dependence rate with respect to substrate in the presence of TiO$_2$ or ZnO catalyst. Photooxidation of thiourea in the presence of TiO$_2$ follows the Langmuir–Hinshelwood kinetics. This kind of relation, which describes several photooxidative conversions, suggests a rate controlled by competitive adsorption of a OH$^•$ radical and the substrate.

Thiourea disappearance by photooxidative process shows a dependence on pH of the solution. High rates are observed at very low pH; this can be attributed to the sulfur affinity to its protonation. At alkaline pH, an abundance of hydroxyl ions is responsible for the enhanced oxidation rate.

In the presence of some common ions like nitrates, chlorides and sulfates at various concentrations, the thiourea photooxidative process is inhibited in the order NO$_3^-$ > Cl$^-$ > SO$_4^{2-}$. These ions compete on the surface of catalyst particles for blocking and/or reacting with oxidizing species such as OH$^•$.

Taking into consideration that increasing temperature increases the initial thiourea disappearance rate, the apparent activation energy was calculated as 16.78 kJ mol^{-1}.

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