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Effect of temperature on kraft black liquor degradation by ZnO-photoassisted catalysis

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Abstract

The ZnO-photocatalysed reaction of kraft black liquor, obtained from *P. radiata* pulping, was studied to determine the kinetic parameters that govern CO_2 evolution. The mineralization reaction exhibits a first-order dependence on the dissolved oxygen concentration and a half-order dependence on the concentration of the substrate at 25 °C. The catalysed reaction accounts for more than 95% of the CO_2 production, at all temperatures studied, and the uncatalysed reaction accounts for 5%. The apparent activation energy of the catalysed process was estimated to be 43.1 kJ mol^{-1}.

Keywords: Cellulose pulping effluent; ZnO photocatalysis; Kraft black liquor; Activation energy; Photodegradation kinetic; Zinc oxide

1. Introduction

In recent years, photocatalysis using semiconductor oxides has been studied extensively for the partial or total mineralization of organic compounds [1,2] and the reduction of inorganic compounds [3,4]. Considerable attention has been paid to the destruction of chemicals in contaminated waters and industrial effluents [5–9]. A recent study [10] has focused on the treatment of effluent from the pulp and paper industry, which contains large amounts of phenolic and polyphenolic compounds. This study combined photochemical and biological treatments to destroy the lignin derivatives, formed during the kraft processing of wood, which are considered to be dangerous to aquatic environments and human health [11].

The intermediates and mechanisms of the reactions involved have been discussed extensively, in particular using anatase TiO_2 as catalyst, which presents the highest activity [12–15], although a number of studies have used ZnO as catalyst [16–18]. In Ref. [18], it was concluded that ZnO is more effective, or at least presents the same activity, as anatase TiO_2 in the removal of chemicals in waters contaminated with lignin-related compounds [18].

It has been established that the photocatalysed degradation of organic matter in solution is initiated by photoexcitation of the semiconductor, followed by the formation of an "electron–hole pair" on the surface of the catalyst (Eq. (1)). The high oxidative potential of the holes in the catalyst permits the direct oxidation of organic matter (OM) to reactive intermediates (Eq. (2)). Very reactive hydroxyl radicals can also be formed either by the decomposition of water (Eq. (3)) or by the reaction of the hole with OH^- (Eq. (4)). The hydroxyl radical is an extremely strong, non-selective oxidant ($E° = +3.06$ V) which leads to the partial or complete mineralization of several organic chemicals.

$$ZnO + h\nu \longrightarrow ZnO(e^- + h^+) \tag{1}$$

$$OM + ZnO(h^+) \longrightarrow OM^{\bullet +} + ZnO \tag{2}$$

$$H_2O + ZnO(h^+) \longrightarrow OH^\bullet + H^+ + ZnO \tag{3}$$

$$OH^- + ZnO(h^+) \longrightarrow OH^\bullet + ZnO \tag{4}$$

Hidaka et al. [19], using electron spin resonance (ESR) experiments, have shown that electrons in the conduction band on the catalyst surface can reduce molecular oxygen to superoxide anion (Eq. (5)). This radical, in the presence of organic scavengers, may form organic peroxides (Eq. (6)) or hydrogen peroxide (Eq. (7)).

$$O_2 + ZnO(e^-) \longrightarrow O_2^{\bullet -} \tag{5}$$

$$O_2^{\bullet -} + OM \longrightarrow OM\text{–}OO^\bullet \tag{6}$$

$$O_2^{\bullet -} + HO_2^\bullet + H^+ \longrightarrow H_2O_2 + O_2 \tag{7}$$

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The electrons in the conduction band are also responsible for the production of hydroxyl radicals, species which have been indicated as the primary cause of organic matter mineralization [20].

Recently, we reported the photocatalysed mineralization of the phenolic compounds present in kraft black liquor and the discolouration of the solution [21]. This liquor, generated during the prehydrolysis of wood, has been classified as cytotoxic and probably mutagenic [22]. In our study, it was noted that the rate of carbon dioxide released from the reaction vessel was dependent on the amount of dissolved oxygen. The total elimination of the colour was achieved after 1 h of irradiation over platinum-impregnated ZnO.

This paper presents a kinetic analysis of the mineralization process of kraft black liquor irradiated by UV light ($\lambda > 254$ nm) in solution in the presence and absence of ZnO. The effect of temperature was evaluated and it was demonstrated that the photocatalytic process using ZnO is energetically favourable for the decomposition of phenolic compounds.

2. Experimental details

Diluted samples of kraft black liquor were irradiated with a General Electric UV mercury lamp (HR 250 DX 37/40, $\lambda > 254$ nm) in a vessel with a quartz window (Fig. 1). The experiments were carried out with 50 ml of black liquor (120 mg l^{-1}), which was prepared by dissolving 1 ml of the concentrated liquor in 1 l of distilled water with 1 g of ZnO (Merck GR).

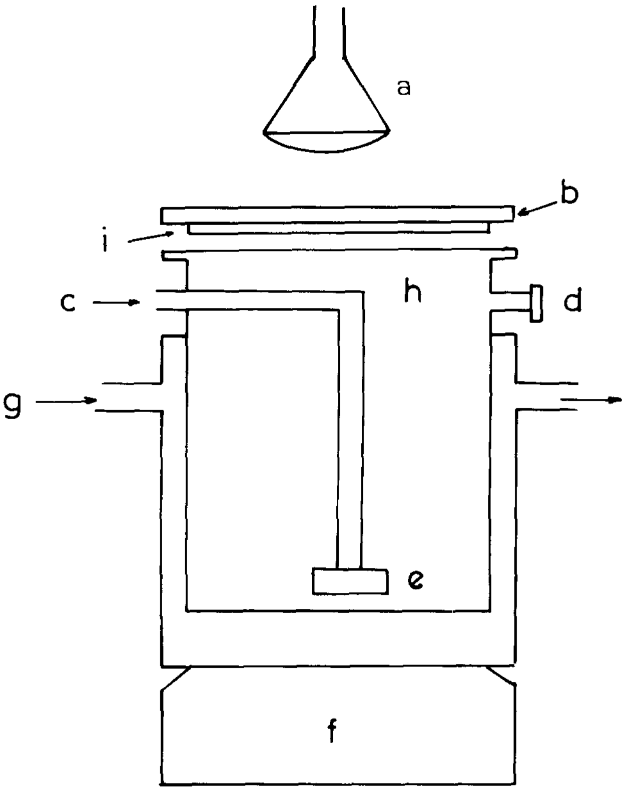

Fig. 1. Schematic diagram of the photochemical reaction system: (a) UV lamp; (b) quartz window; (c) oxygen inlet; (d) connection to gas chromatograph; (e) fritted end; (f) magnetic stirrer; (g) recirculating thermoregulated water bath; (h) 100 ml reaction vessel; (i) rubber ring.

The dependence of the oxygen concentration on the reaction rate was determined at 25 °C, controlling, in all runs, the different ratios of N_2/O_2 by flow meters with the same dilution of liquor (120 mg l^{-1}). The amount of dissolved oxygen at different temperatures was calculated using Henry's law.

The effect of the liquor concentration on the rate of CO_2 evolution was estimated using oxygen-saturated conditions and variable liquor concentrations (12, 25, 60 and 120 mg l^{-1}) at 25 °C.

The carbon dioxide released at different times of irradiation was determined by gas chromatography, using the conditions described previously [21].

The influence of temperature was studied with the reactor immersed in a thermoregulated bath.

3. Results and discussion

Fig. 2 shows the effect of the concentration of dissolved oxygen on the release of carbon dioxide from the reactor vs. the time of irradiation; the concentration of the liquor (120 mg l^{-1}) was maintained constant at 25 °C. The amount of dissolved oxygen was calculated from the partial pressures of oxygen at 25 °C by Henry's law. A clear dependence of the reaction rate on the oxygen concentration is observed in all runs, with the same profile of CO_2 released. Using the initial rate procedure, a first-order dependence on the dissolved oxygen concentration was determined. This is in agreement with a previous report where a first-order dependence was observed at higher temperature (35 °C) [21].

The profiles of carbon dioxide released from the reaction vessel using different dilutions of liquor at 25 °C, in oxygen-saturated conditions, are shown in Fig. 3. Initially, the CO_2 released from the system rises rapidly and, after approximately 5 min, it remains constant. After 30 min of irradiation

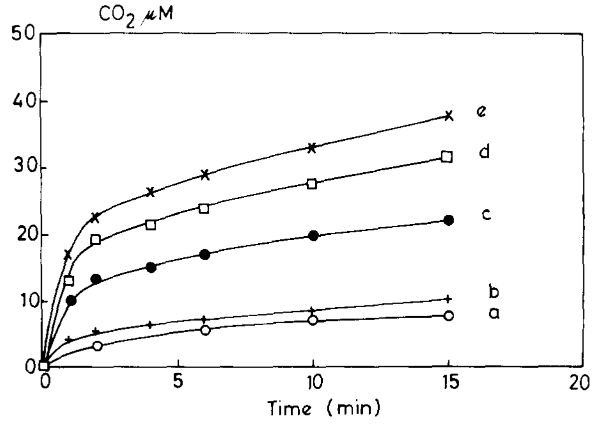

Fig. 2. Effect of oxygen concentration on CO_2 evolution during black liquor (120 ppm) photomineralization at 25 °C: (a) 0.1 mM; (b) 0.2 mM; (c) 0.4 mM; (d) 0.8 mM; (e) 1.3 mM.

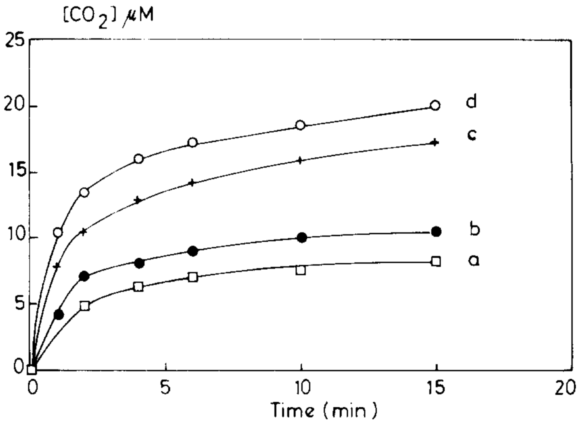

Fig. 3. Effect of liquor concentration on CO_2 release in oxygen-saturated conditions at 25 °C: (a) 12 mg l^{-1}; (b) 24 mg l^{-1}; (c) 60 mg l^{-1}; (d) 120 mg l^{-1}.

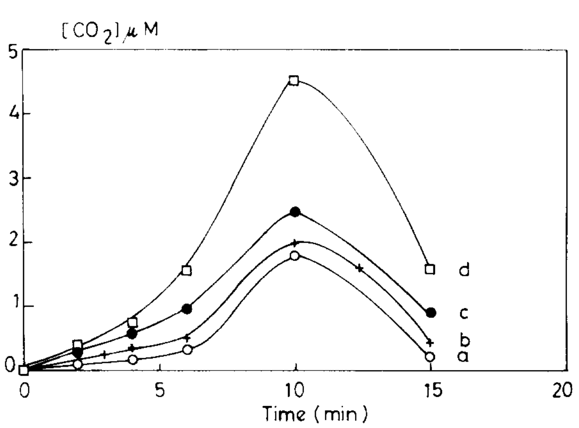

Fig. 4. Effect of temperature on the release of CO_2 in the uncatalysed photomineralization process of 50 ml (120 mg l^{-1}) black liquor: (a) 5 °C; (b) 15 °C; (c) 30 °C; (d) 40 °C.

(not shown), the rate of CO_2 evolution decreases linearly with time.

The dependence of CO_2 evolution on the reactant concentration during the mineralization of kraft black liquor is shown in Fig. 3. A half-order dependence (0.56) on the substrate concentration was calculated. Recently, Mathews and McEvoy [15] have pointed out that the order of photomineralization for simple molecules with TiO_2 varies from unity at low concentrations of the substrate to zero in concentrated solutions. However, for more complex substrates, the reaction occurs through several intermediates before the production of CO_2 (such as in our conditions with black liquor), and the dependence is difficult to predict. According to our results, the initial rate of production of CO_2 during kraft black liquor photomineralization by ZnO can be described by Eq. (8)

$$V_o = \delta CO_2/\delta t = k[O_2]^1[S]^{1/2} \quad (8)$$

where [S] and $[O_2]$ are the concentrations of black liquor (mg l^{-1}) and dissolved oxygen (mg l^{-1}) respectively.

During the irradiation of the substrate in the presence of the catalyst (ZnO), two reactions occur simultaneously: (i) the homogeneous reaction, which occurs when the substrate is directly converted to CO_2 by the absorption of light in the presence of dissolved oxygen; (ii) the heterogeneous catalysed reaction, which occurs when the catalyst absorbs light and, in its excited form, oxidizes the substrate according to the mechanisms indicated in Eqs. (1)–(7).

In order to determine the extent of the homogeneous process, photochemical reactions were carried out in the absence of ZnO at different temperatures. For identical times of irradiation and liquor concentrations (120 mg l^{-1}), the homogeneous mineralization of kraft black liquor in oxygen-saturated conditions shows a temperature dependence (Fig. 4). The amount of carbon dioxide released during photolysis in the absence of ZnO increases with temperature as a consequence of the internal energy increment of the system. After 10 min of irradiation in the absence of ZnO, the release of CO_2 decreases rapidly. The profile of CO_2 evolution is very different for catalysed photolysis. Fig. 5 shows the effect of temperature on the initial rate of CO_2 released during irradiation in the presence of catalyst (heterogeneous catalysed reaction).

The rates of mineralization for uncatalysed and catalysed reactions, at different temperatures, were calculated using the initial rate procedure and are depicted in Table 1. The amount of CO_2 produced during the uncatalysed reaction is very low at all temperatures. In the heterogeneous reaction, UV irradiation is the primary source of the electron–hole pairs because the band gap is too high to be overcome by thermal excitation. In spite of the fact that an increase in temperature leads to a decrease in the amount of dissolved oxygen, to the detriment of organic matter oxidation, the mineralization rate increases due to an increase in the collisional frequency between the catalyst and substrate. The dependence of the amount of dissolved oxygen on temperature is moderate. This means that the major percentage of mineralization (higher than 96% at all temperatures) occurs through the photocatalysed reaction, as shown in Table 1. The homogeneous reaction is weak compared with heterogeneous mineralization, indicating that catalyst addition is favourable and indeed nec-

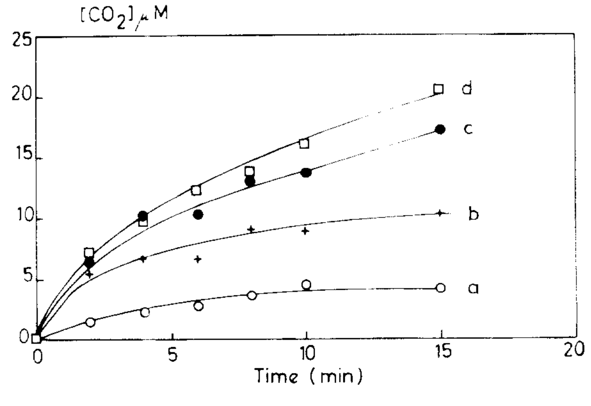

Fig. 5. Effect of temperature on the CO_2 released during the photocatalysed (1 g ZnO) reaction of 50 ml (120 mg l^{-1}) black liquor: (a) 5 °C; (b) 20 °C; (c) 30 °C; (d) 40 °C.

Table 1

Calculated rates (V) of black liquor mineralization during homogeneous and heterogeneous catalysis at different temperatures. The conditions of the catalysed reaction are described in the text

Temperature (°C)	$V(O_2+UV)$ (mol l^{-1} min^{-1})	$V(O_2+UV+ZnO)$ (mol l^{-1} min^{-1})	DO [a] (mol l^{-1})	Mineralization [b] (%)
5	2.87×10^{-8}	0.64×10^{-6}	1.91×10^{-3}	96
15	5.81×10^{-8}	1.30×10^{-6}	1.53×10^{-3}	96
30	11.11×10^{-8}	3.33×10^{-6}	1.17×10^{-3}	97
40	18.06×10^{-8}	5.33×10^{-6}	1.02×10^{-3}	97

[a] DO, dissolved oxygen, calculated by Henry's law [16].

[b] Percentage of mineralization via the catalysed reaction

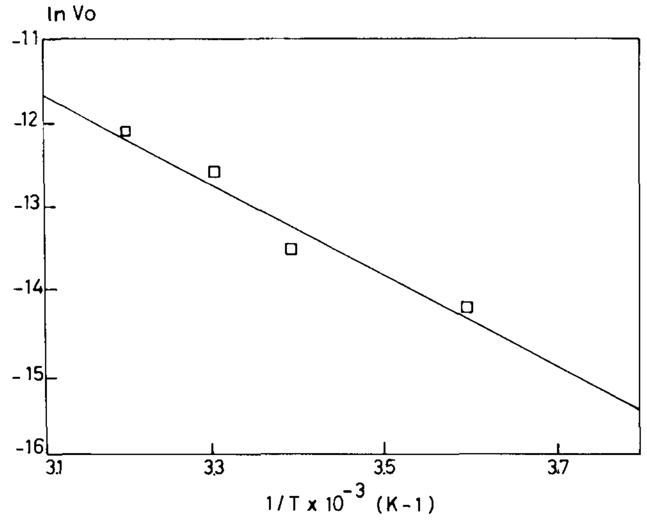

Fig. 6. Arrhenius plot of the photocatalytic degradation of kraft black liquor.

essary for the destruction of the organic matter present in the liquor.

Both reactions present a linear dependence on temperature. This means that the potentially temperature-dependent steps, such as adsorption, desorption, surface migration and rearrangements, appear to be rate determining. The apparent activation energy for the heterogeneous photochemical reaction was calculated from Fig. 6 using the Arrhenius equation. The value of 43.1 kJ mol^{-1} is slightly higher than the activation energies (3–30 kJ mol^{-1}) reported in Refs. [23–26]. The value calculated for our system must be considered as an average of the apparent activation energies of the compounds present in the liquor, and the difference between our E_a value and those of simple systems may be attributed to the complexity and diversity of the compounds dissolved.

The apparent activation energy of the uncatalysed reaction was not calculated because the low amount of CO_2 released does not permit a reliable value to be obtained. This value would not be comparable with that of the catalysed reaction due to the different reaction mechanisms involved. This is confirmed by the different profiles of CO_2 evolution shown in Figs. 4 and 5. An exponential liberation of CO_2 from the system during the first 10 min was observed in the homogeneous photochemical reaction. This was followed by a decrease in CO_2 evolution and the solution remained coloured after irradiation. In the catalysed reaction, a logarithmic profile of CO_2 liberation was observed (Fig. 5). After 15 min, the evolution of CO_2 continued and the solution became colourless after 20 min [21].

4. Conclusions

The mineralization reactions of kraft black liquor are temperature dependent and follow an Arrhenius behaviour. The degradation of organic matter, i.e. CO_2 evolution, occurs mainly by heterogeneous catalysis (more than 95%). At 25 °C, the reaction exhibits a first-order dependence on the oxygen concentration and a half-order dependence on the substrate concentration.

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