

Effect of copper(II) on the photocatalytic degradation of sucrose

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Abstract

The photocatalytic mineralisation of sucrose, used here as a model organic compound, was investigated in the presence of dissolved copper(II) ions using Degussa P25 titanium dioxide as the photocatalyst. The copper ions were found to substantially enhance the photocatalytic mineralisation rates. The photocatalytic activity increased until an optimum metal concentration was reached. Beyond which, the activity first dropped slightly and then remained constant for the range of Cu(II) ion concentrations studied. At pH 3.5, with the optimum Cu(II) concentration of 2 at.%, a three-fold increase was observed in the maximum mineralisation rate. At pH 1.5, an approximately eight-fold increase was found in the mineralisation rate of sucrose, although the overall reaction rate was found to be lower than at pH 3.5. The copper ions showed little adsorption onto the TiO₂ surface. This is strong evidence to suggest that the enhancement of the photocatalytic mineralisation rate had occurred through a homogeneous pathway mechanism.

The findings of this study are important when considering the effects which inorganic ions commonly found in contaminated waters, such as copper(II), have on the photocatalytic degradation of organics. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many studies have been carried out to investigate the effect of metal ions in solution on the photoactivity of titanium dioxide. Copper ion in particular has been reported to be one of the more interesting, owing to the possibility of the photoreduction of copper(II) ions with the simultaneous enhancement of the TiO₂

photoactivity [3]. While most of these studies have been attempts at improving the performance of TiO₂ as a photocatalyst, such studies are also useful from a practical point of view.

Natural and waste waters invariably contain both organics and metal ions, and as such the rate of photocatalytic degradation can be very different from solutions that contain organic pollutants alone. Interestingly, copper(II) ions are commonly found in waste waters of developed nations, for example, waste waters in Australia have been found to contain copper ions which have leached from copper water pipes. It is, therefore, of practical interest to know how the inclusion of these metal ions will affect the treatment of water TiO₂ mediated photocatalytic oxidation.

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Studies on aqueous systems containing Cu(II) and TiO₂ under illumination [1–19] can be divided into two categories. Those in which the interest was focussed on the removal or recovery of the Cu(II) ions from solution through photodeposition [7,8,10–12] and those in which the interest was focussed on studying the effect the copper ions on the photocatalytic degradation of organic contaminants [1,3–6,9,13–19]. From the second group of studies, the presence of the dissolved transition metal ions in solution has been found to profoundly influence the rate of TiO₂ photocatalytic oxidation, either enhancing or retarding the photoactivity of the catalyst depending on parameters such as the concentration of the copper(II) ions, the solution pH, and the organic being degraded [1,3–19].

The effects of copper(II) ions have been studied on the photodegradation of the insecticide monocrofos [6] formic acid [1] acetic acid [4], propionic acid [5], toluene [13], phenol [14,16–18], EDTA [9] and methyl orange [12]. A number of postulations have been put forward with regards to the role the copper ions play in the mechanism of the photocatalytic degradation of these organics. Some studies have suggested that observed enhancement of the photocatalytic degradation rates was due to electron trapping by the copper ions leading to the prevention of electron hole-recombination [1,3,11,14,15,19–21]. Other studies have suggested the occurrence of a homogeneous, Fenton-type reaction mechanism induced by the presence of the dissolved transition metal ions [3,13,14,15]. Finally, the formation of a reactive ternary complex involving the dissolved metal ion has also been suggested to occur in TiO₂–copper(II) systems [3,20,22–25].

Despite the large number of studies carried out on these TiO₂–copper(II) systems, many aspects with regards to the role of the metal ions in the photocatalytic reactions remain unclear. In this work, the effect of copper(II) ions in solution on the photocatalytic oxidation of sucrose was studied.

2. Experimental

All the chemicals used in the experiments were of analytical reagent grade. The stock solutions were

prepared with water from a Millipore Water Milli-Q water purification system.

The titanium dioxide catalyst used was Degussa P25 (80% anatase and 20% rutile) with a BET surface area of 50 m²/g and an average aggregate size of 200 nm, made up of 30 nm primary particle.

An aliquot of a Cu(NO₃)₂ solution was added to 30 ml, 0.2 g/l suspensions of the photocatalyst Degussa P25. The suspensions were circulated through a slurry-type, spiral photoreactor. The light source employed was a 20 W blacklight blue fluorescent tube (maximum emission at ~350 nm). Matthews et al. [26] have given a thorough description of the system.

Sucrose was chosen as the model organic compound. The amount of sucrose mineralised was equivalent to 2000 μg of carbon. The volume of the reaction mixture was 30 ml, giving a final sucrose concentration of 67 mg/ml. This concentration was chosen since preliminary tests showed that at this substrate concentration the photocatalyst surface was saturated.

Information regarding the rate of carbon dioxide generation was obtained from conductivity measurements of a solution in which the generated CO₂ gas was bubbled [20]. By monitoring the rate of formation of carbon dioxide, the rate of mineralisation of the sucrose was determined. Calculations of the mineralisation rates involved converting the conductivity measurements to a carbon value using a previously obtained calibration curve.

The effect of the dissolved metal ion on sucrose mineralisation was investigated by varying initial metal ion concentration in the slurry. The experiments were carried out under two different acidic conditions. The two pH values for the reaction mixture tested were 1.5 and 3.5. The pH was adjusted by the addition of perchloric acid.

Atomic absorption spectroscopy (AAS, Varian[®] spectrAA 20 Plus) was used to determine the quantity of metal ions adsorbed or deposited onto the surface of the photocatalyst. This involved analysing the supernatant of the Degussa suspension before and after the reaction to quantify the copper ions present. The Degussa particles were also collected after the photoreaction, washed once with water, followed by a weak acid wash to remove any copper ions which had physically attached to the surface of the particles.

3. Results and discussion

In order to obtain information regarding the effect of copper(II) ions in solution on the photooxidation rate of sucrose, the copper ion concentration in the reaction mixture was initially varied from 0 to 7 at.% (1 at.% is equivalent to 2.5 mM of Cu^{2+} ions in solution). The reaction was carried out at pH 3.5. Fig. 1 shows the behaviour of these photocatalytic systems, presented as the rate of carbon dioxide generated (in terms of carbon mass per second) as the photoreaction proceeded.

As can be seen from Fig. 1, the rate of photocatalytic mineralisation of sucrose was significantly enhanced in the presence of copper. The maximum rates achieved for solution cupric ion doped photocatalyst were approximately three times faster than the maximum rate achieved when no copper ions were present (indicated by R_0 in Fig. 1).

A closer examination of these results involved inspecting the rates at 10 and 90% mineralisation of sucrose as well as maximum sucrose mineralisation rate as a function of atomic percent of copper. These are presented graphically in Fig. 2. This figure confirmed the existence of an optimum Cu(II) concentra-

tion (2 at.%) at which maximum enhancement of the photocatalytic mineralisation of sucrose was achieved. Further increases in the cupric ion concentration beyond the optimum point decreased the mineralisation rate slightly. Interestingly, past the optimum copper concentration, the reaction rate remained steady despite a further increase of the copper ion concentration up to 7 at.%.

Another set of experiments was performed at pH 1.5 for copper ion concentrations ranging from 7 to 20 at.%. The results are shown in Fig. 3. Due to the very slow mineralisation rates of sucrose using the undoped TiO_2 catalyst, the 90% mineralisation rate was not measured at pH 1.5.

As can be seen from Fig. 3, the presence of cupric ions also led to an enhancement in the sucrose mineralisation at pH 1.5. No optimum concentration was observed for this set of experiments. This is thought to be due to the fact that the optimum concentration (expected to be close to 2 at.% from the experiments at pH 3.5) was lower than the range of cupric ion concentrations investigated.

Interestingly, again, as was observed from the experiments carried out at pH 3.5, a further increase in the concentration of cupric ions from 7 to 20 at.% did

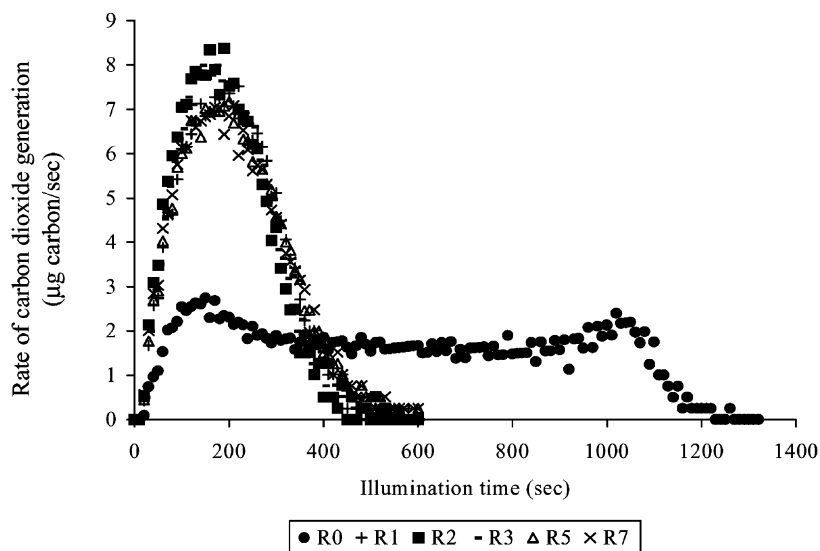


Fig. 1. The effect of Cu(II) ion concentration on the mineralisation rate of sucrose (first derivative) in terms of carbon mass per second calculated from the formation of carbon dioxide at an initial pH of 3.5. R_x is the rate of mineralisation, where x is the atomic percent of Cu^{2+} with respect to Ti^{4+} (R_1 is the rate of mineralisation for system with 1 at.% of Cu^{2+} with respect to Ti^{4+}).

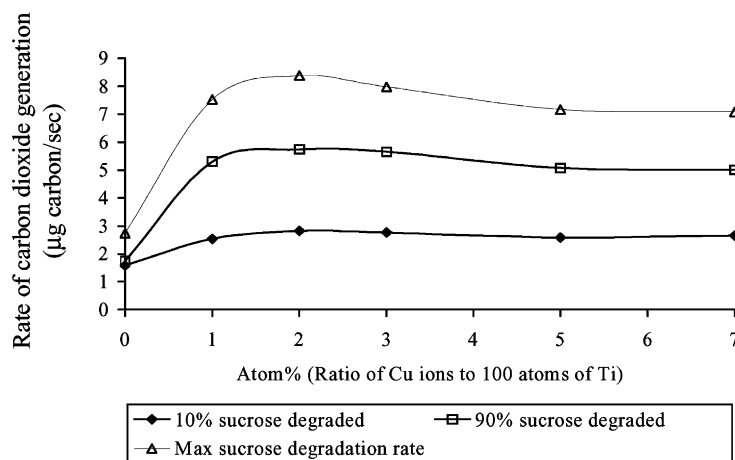


Fig. 2. The relationship between the initial copper ion concentration and the mineralisation rate of sucrose (after 10, 90 and 100% (max) photodegradation) in terms of carbon mass from the formation of carbon dioxide at an initial pH of 3.5.

not affect the sucrose mineralisation rate. This is not in agreement with what has been reported in the literature, where higher ion concentrations (beyond the optimum) were found to lead to lower rates due to UV absorbance by the metal species [3,20]. While the highest copper ion concentration tested in previous studies was lower than the Cu(II) concentrations investigated in our system, the catalyst loading used in those systems was 10 times higher at 2 g/l [3,20].

We postulate that under our experimental conditions, given the lower catalyst loading, the photons available for the photoreaction were in excess, hence, the presence of increased concentrations of UV absorbing species such as copper ions, did not significantly reduce the photons available for the photoreaction. Thus, a detrimental effect on the photocatalytic degradation rate of sucrose was not observed beyond optimum Cu(II) ion concentrations.

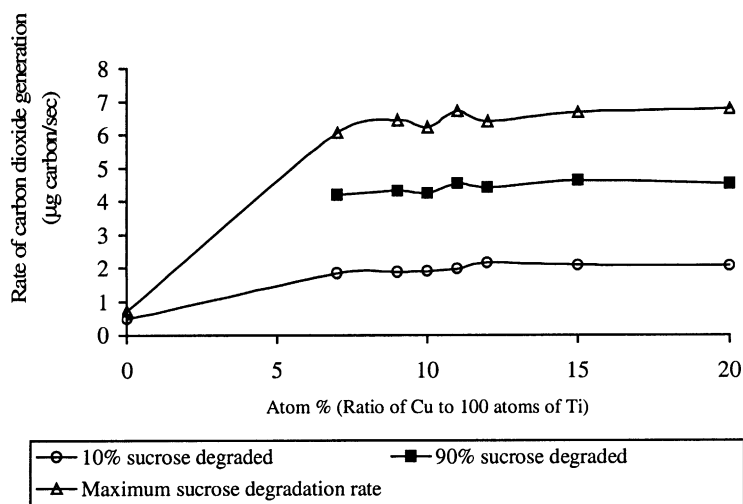


Fig. 3. The relationship between the initial copper ions concentration and the sucrose mineralisation rate in terms of carbon mass from the formation of carbon dioxide at an initial pH of 1.5.

Table 1
Analysis of the extent of adsorption of copper ions onto the TiO₂ surface^a

Sample	Cu(II) recovered from the supernatant (mg/l)	Cu(II) recovered after water wash of the collected TiO ₂ particles (mg/l)	Cu(II) recovered after acid wash of the collected TiO ₂ particles (mg/l)
Suspension of TiO ₂ + Cu(II) ions before the addition of sucrose ^b	30 ± 1	0.4 ± 0.1	1.6 ± 0.8
Suspension of TiO ₂ + Cu(II) ions after the mineralisation of sucrose ^c	31 ± 1	0.6 ± 0.2	0.7 ± 0.1

^a AAS initial cupric ion concentration present in solution was 2 at.%, which is equivalent to 31.8 mg/l. The initial pH was 3.5.

^b After UV illumination for 10 min.

^c After UV illumination for 20 min.

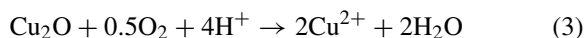
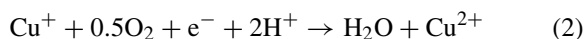
While Bideau et al. [4] observed a plateau in the photocatalytic oxidation rate of acetic acid, similar to that observed in our system, this was attributed to the formation of a neutral salt (diacetato complex) acting as a poison to the catalyst. From our studies, the formation of an intermediary poison can be ruled out since complete mineralisation of the sucrose molecule was achieved.

In order to understand the role of the copper ions during the photocatalytic oxidation of sucrose, AAS measurements were used to analyse the fate of the added copper ions after illumination both in the presence and the absence of sucrose. The objective of these tests was to find out the extent of adsorption of the copper ions onto the TiO₂ photocatalyst surface, and to deduce whether copper photodeposition had taken place as the reaction proceeded. The results of the AAS analysis are given in Table 1.

As can be seen from Table 1, the elemental analysis indicated that the copper ions were neither photodeposited nor adsorbed onto the TiO₂. In fact almost all of the copper ions added to the solution remained in the aqueous phase, as they were almost completely recovered in the supernatant. Our observations are in agreement with those reported by Butler and Davis [20] and Bleam and McBride [27] who also observed little adsorption of copper ions. The minimal adsorption by the Cu(II) onto the TiO₂ surface may be explained by the fact that for the pH values investigated, the TiO₂ surface itself is highly positively charged since the pH of the solution is well below the p*H*_{zpc} (zero point of charge) for TiO₂, thus hindering the adsorption of positively charged ions [20].

The fact that the Cu(II) ions in solution did not undergo photodeposition, as reported to occur in

previous studies [1,10,11] may be explained by a number of possibilities. Firstly, any photoreduced copper(II) ions (from reaction (1)) may have been regenerated in the presence of oxygen under acidic conditions as suggested by Foster et al. [11], as in reaction (2). Secondly, the presence of acid in the system may have led to the re-oxidisation of any reduced forms such as in reaction (3) [1]. In our study, the photoreaction was carried out at either pH 3.5 or 1.5, thus reaction (3) is likely to occur



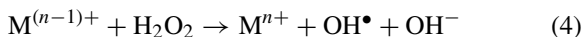
Another possibility which may also explain the absence of photodeposition of copper in our system, is the formation of a Cu(II)–organic complex in the presence of the sucrose molecule. The formation of Cu(II)–organic complexes in photocatalytic systems has been observed by Foster et al. [10].

The role of copper ions in solution in enhancing the photoactivity of titanium dioxide is generally believed to be via electron capturing at the semiconductor surface by the Cu(II) ions, as shown in reaction (1) [1,3,11,14,15,19]. This has been said to prevent electron–hole recombination resulting in an increased rate of hydroxyl radicals formation. Bideau and coworkers on the other hand have suggested the photocatalytic enhancement to occur through a redox cycle between adsorbed Cu(II) and Cu(I) on the surface of TiO₂ [1,5].

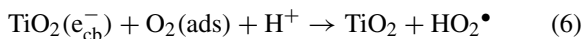
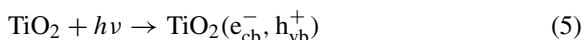
Since both of these mechanisms involve electron capturing by the copper ions, this means that both require significant adsorption of the metal ions onto the

TiO₂ surface [20]. We have shown that for our system little adsorption of Cu²⁺ had occurred (Table 1), hence, we can conclude that direct electron capturing by the Cu²⁺ ions on the TiO₂ surface is not the main mechanism by which the photooxidation of sucrose was enhanced.

For copper(II)–TiO₂ systems in which minimal Cu(II) adsorption was observed, Butler and Davis [20] and Sykora [3] suggested that the increase in the reaction rates occurred via a homogeneous catalysis pathway involving the Cu(II) ions rather than occurring at the TiO₂ surface (heterogeneous pathway). The homogeneous pathway has been said to involve Fenton-type reactions (as shown in reaction (4)) [3,13,14,15,23] in which metal ions catalyse the decomposition of H₂O₂



The source of H₂O₂ in the system is shown in the sequence of reactions given below (reactions (5)–(7)) in which the dissolved dioxygen is involved upon the photocatalytic activation of TiO₂.



Evidence for the occurrence of a Fenton-type reaction in TiO₂ photocatalytic systems containing dissolved Cu(II) ions was given by Fujishira et al. [13]. Fujishira et al. found that the distribution of the products resulting from the oxidation processes in TiO₂–dissolved Cu(II) systems was very similar to that observed in the Fenton reactions in acidic conditions of H₂O₂, Fe²⁺ and Cu²⁺. However, the postulation regarding the inducement of a Fenton-type reaction has been questioned by Wei et al. [16] and Bideau et al. [4]. They argued that the formation of hydroxyl radicals via the generated H₂O₂ (reaction (4)) was negligible compared with the formation of hydroxyl radicals generated by holes from the TiO₂ activation. They pointed to the difficulty in reducing oxygen to form H₂O₂ on illuminated TiO₂ (reaction (7)). This was later proven by Butler and Davis [20] who showed that O₂ or TiO₂ alone were insufficient to generate H₂O₂, O₂^{•-} and HO₂^{•-}. In our study, we did not attempt to follow the formation of H₂O₂

in solution as the reaction proceeded. However, based on the above studies [1,16,20], we postulate that the significant enhancements (three- and eight-fold enhancement of the photocatalytic reaction rate at pH 3.5 and 1.5 respectively), cannot be solely attributed to the Cu(II) ions taking part in Fenton-type reactions.

The final postulation to consider with regards to the role of Cu(II) ions in the enhancement of the photocatalytic degradation rates, is the involvement of a ternary reactive complex. This has been suggested by a number of studies [3,20,22–25]. Copper(II) ions readily form coordinated compounds. Such ternary complexes have been said to form between the copper ion, the organic or its oxidation intermediate, and an oxygen-containing species such as H₂O₂, O₂ or O₂^{•-} [3,20,22–25]. The ability of these compounds to take part in redox reactions, together with their photoreactivity have been said to be important for the photodegradation of organic pollutants in the environment [3]. A catalytic effect of the Cu(II) ion was said to occur either through redox Cu(II)–Cu(I) coupling reactions with the simultaneous the photodegradation of the pollutant present as a ligand in the coordination sphere of the copper central atom and/or be based on the secondary reactions of the active species produced photochemically from the copper complex [3].

The existence of copper sucrate complexes [28] and the poor adsorption of cupric ions observed in our study point to the feasibility of such ternary complexes forming in the system studied under investigation. Evidence regarding the involvement of a ternary complex emerges when the photocatalytic rates at pH 3.5 are compared with those at pH 1.5 (comparing Fig. 2 with Fig. 3).

It is clear that the photodegradation rates are faster at the higher pH. At first glance this does not seem to support the ternary-complex mechanism proposed above, since the formation of the complex is favoured at low pH [3,20] (according to our postulation, this in turn is expected to lead to increased oxidation rates). However, when Figs. 2 and 3 are analysed more closely, it is apparent that the overall extent of enhancement at pH 1.5 is in fact higher than that achieved at pH 3.5. For example, a 7 at.% doping level at pH 3.5 results in an increase in the maximum oxidation rate from 2.8 μg carbon/s for the undoped TiO₂ system to 7 μg carbon/s, which is a 2.5-fold enhancement. From Fig. 3, a 7 at.% doping level at pH 1.5 results in an increase in

the maximum oxidation rate from 0.8 for the undoped TiO₂ system to 6 μg carbon/s, which is a 7.5-fold enhancement. Thus, the presence of copper ions in solution at pH 1.5 in fact leads to a larger improvement in the photocatalytic reaction rate than at pH 3.5. With regards to the stability of the copper complexes at pH 1.5, it is important to note that the existence of monoacetato-copper complexes at pH values as low as pH ~ 1.8 [4] has been reported. Hence, the existence of ternary complexes involving sucrose is still feasible at pH 1.5.

Hence, our results may provide support for the postulation regarding the involvement of a ternary organo-copper complex as part of a homogeneous reaction mechanism. The overall lower oxidation rates observed at the low pH are believed to be due to factors such as the TiO₂ surface being abundant with H⁺ which interfere with the transfer of holes to the surface hydroxyl groups (OH⁻) [12].

The results provided in this study are preliminary, and hence, further experiments are required. Firstly, in order to clarify the role of the dissolved copper(II) ions in solution, the photodegradation of sucrose in homogeneous systems containing copper(II) ions only (i.e. in the absence of titanium dioxide) need to be undertaken. While some studies have reported that illuminated copper(II) ions led to a significant removal of toluene in the absence of TiO₂ [20], Bideau et al. showed that Cu(II) had no activity for the photodegradation of formic acid [1]. Thus, it is important to carry these experiment when sucrose is the organic being degraded. If indeed Cu(II) ions are capable of photodegrading sucrose, studies are also needed to verify whether the accelerating catalytic effect of the copper(II) ions is additive or synergetic when combined with TiO₂ photocatalysis. Varied substrate concentrations and a broader range of solution pH's will also provide further information with regard to the formation of the ternary complex.

4. Conclusions

In this study, the performance of the commercial photocatalyst Degussa P25 was investigated in the presence of dissolved copper(II) ions. A significant three-fold enhancement of the photocatalytic perfor-

mance was attainable by adding copper(II) ions to the photoreaction mixture. The optimum dopant concentration was found to be 2 at.%. Beyond the optimum concentration, the activity was found to drop slightly and then remained unchanged for the range of copper(II) ions concentration studied.

The absence of copper adsorption on the TiO₂ surface provides evidence to suggest a homogeneous reaction pathway leading to an enhancement of the reaction kinetics of the photooxidation of organics in the presence of copper(II) ions. The results also provide evidence to suggest the involvement of a ternary-organo-copper complex in this reaction mechanism.

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