A Combined Photolytic – Electrolytic System for the Simultaneous Recovery of Copper and Degradation of Phenol or 4-Chlorophenol in Mixed Solutions

Abdul J. Chaudhary [a,*], Susan M. Grimes[b]

[a]*Institute for the Environment, Brunel University, Kingston Lane, Uxbridge, Middlesex, UB8 3PH, UK*

[b]*Centre for Environmental Control and Waste Management, Department of Civil & Environmental Engineering Imperial College, South Kensington London SW7 2AZ, UK*

Abstract

The effects of the presence of copper on the photooxidation of phenol and 4-chlorophenol and of the presence of the phenols on the recovery of copper by electrodeposition are studied in three systems: a photolytic cell in the presence and absence of TiO_2 as a catalyst or H_2O_2 as an oxidant; an electrolytic cell and a combined photolytic – electrolytic system. The optimum system for the simultaneous removal of copper and destruction of the phenols which overcomes the effects of copper-phenol reactions is a combined system with concentrator electrode technology incorporated into the electrolytic cell. This combined system achieves > 99% removal of copper and destruction of phenol or 4-chlorophenol in an 8 h period.

Keywords: Copper recovery; Degradation of phenols; Electrolytic cell; Photolytic cell; Combined photolytic-electrolytic cell; Wastewater treatment

[*]Corresponding author. Tel.: +44 (0)1895 266112; fax: +44 (0)1895 269761
E-mail address: abdul.chaudhary@brunel.ac.uk   (A.J. Chaudhary)

1. Introduction

In mixed industrial effluent, the presence of metal ions can retard the destruction of organic contaminants and the efficiency of the recovery of metal can be reduced because of complex formation between the metal ions present and the organic species. Aqueous effluent streams originating from many industries contain organic pollutants and metal ions too low to make their recovery easy but too high to be discharged to the environment without prior treatment. Phenol and its derivatives are considered to be primary pollutant components in wastewater due to their high toxicity, high oxygen demand and low biodegradability (Santos et al., 2001). Successful treatment of effluents containing phenols and heavy metal ions to achieve legislative compliance will depend upon whether the heavy metal ions affect the process of degradation of the phenols, and whether the presence of organic contaminants hinders the process of heavy metal removal. We now report on the effects of copper ions on the degradation of phenols (phenol and 4-chlorophenol) and on the effect of phenols on the electrolytic recovery of copper, and describe a combined photolytic - electrolytic system for the simultaneous recovery of copper and the degradation of phenols as part of studies on the simultaneous removal of heavy metals and destruction of organic contaminants (Chaudhary et al., 2000a; Chaudhary et al., 2000b; Chaudhary et al., 2001).

The efficiencies of processes designed to recover phenols from, or to mineralise phenols in aqueous media have been described (Kulkarni and Dixit, 1991; Garcia-Mendieta et al., 2003; Lazarova and Boyadzhieva, 2004). Activated carbon adsorption and solvent extraction processes have been used in processes of phenol recovery, while biological and chemical oxidation treatment methods have been conventionally preferred for the destruction of this type of organic compound. The methods of phenol mineralization considered in the present work are photolytic oxidation and anodic oxidation in the presence and absence of

titanium dioxide as a catalyst and hydrogen peroxide as a chemical oxidant. There have been reports (Brezová et al., 1995; Yawalkar et al., 2001; Esplugas et al., 2002) on the comparison of different advanced oxidation processes for phenols, the effects of the presence of metal contaminants on the efficiencies of some of these processes and here the effects of the presence of copper ions on phenols destruction are reported.

Electrochemical processes are usually used for the recovery of dissolved metal ions from industrial effluent streams but electrochemical oxidation of organic compounds is an alternative for wastewater treatment, replacing traditional chemical oxidation processes. The efficient electrolytic treatment of organic compounds depends upon the nature of the anode materials, and the effects of different anode materials have been described (Awad and Abuzaid, 2000; Pelegrini et al., 2001). The electrochemical oxidation of phenol-containing wastewater in sodium chloride solution has been described but this process produces intermediates that are chlorine-substituted organic compounds that can be even more toxic than the original phenols (Zareie et al., 2001).

2. Materials and methods

The effects of the presence of copper ions in phenol-containing solutions are studied for two systems designed to mineralise phenol and 4-chlorophenol, namely a photolytic cell for photolytic oxidation and an electrolytic cell for anodic oxidation of the phenols. The results of these studies are used to optimise the simultaneous recovery of copper and the destruction of the phenols in a novel combined photolytic-electrolytic system.

2.1. Photolytic cell system

The photolytic system used is described in detail in an earlier communication (Chaudhary et al., 2001). The cell consists of a UV probe surrounded by a reaction chamber of 3.5 L capacity, through which the fluid to be treated is pumped from a reservoir via an inlet, and back to the reservoir via an outlet. The flow rate (5 L min^{-1}) of the solution is controlled by a valve. Compressed air is used as the oxidant in the photolysis and is supplied through an inlet and exists through an outlet. The temperature in the system is measured by a digital thermocouple probe. The temperature in the reaction chamber is maintained at 25-30 ^{o}C by passing water through a cooling jacket surrounding the UV probe. The effects of UV source, acid concentration, copper ions, hydrogen peroxide and TiO_2 on the degradation of phenols was studied by carrying out duplicate experiments under identical conditions using 125 W and 400 W UV-probes.

The photocatalyst, used as supplied by BDH Chemicals Ltd, Poole, England, was TiO_2 (Degussa P-25) which is predominantly anatase, as shown by X-ray diffraction, with average particle size 30 nm. The BET surface area of the TiO_2, determined from nitrogen adsorption at –196 ^{o}C (ASAP 2000 Micromeritics) was 56.8 m^2 g^{-1}. The effect of TiO_2 was investigated by using the semiconductor particles suspended in solution. The effect of an oxidant on the photodegradation of phenol was investigated by using a hydrogen peroxide solution (30-31%) supplied by BDH Chemicals Ltd, Poole, England.

To optimise the conditions for achieving the photolytic degradation of phenols the effects of the output of the UV probe and of the acidity of the solution were studied. The effect of the UV probe was studied by carrying out replicate experiments under identical conditions using 125 and 400 W UV-probes. The results show that both UV probes are capable of destroying phenols, although degradation proceeds faster with 400 W compared to

a 125 W probe. The results show that 89% degradation of phenol is achieved after 8 h with a 400 W probe compared to only 45% degradation with a 125 W probe. The main intermediates formed in the photodegradation of phenol have been identified by the methods described earlier by us (Grimes and Ngwang, 2000) as 1,2-dihydroxybenzene (X), 1,4-dihydroxybenzene (Y) and 1,3,5-trihydroxybenzene (Z) using the 125 W probe. The concentrations of the intermediates (X) and (Y) formed when the 400 W probe is used are much lower and no evidence is found for the intermediate (Z). The UV- absorbance spectra for the degradation of 4-chlorophenol show that after 8 h using the 125 W probe there is still evidence for the presence of intermediates, in contrast to the spectra obtained using the 400 W probe that show no evidence for intermediates remaining after 8 h. In all subsequent experiments the 400 W probe was used.

Experiments were carried out to investigate the effects of sulphuric acid concentration (0.01-0.5 M) on the photodegradation of phenol and 4-chlorophenol (50 mg L^{-1}) using a 400 W probe. The results show that an increase in acid concentration decreases the time for degradation of the phenols but that no further advantage is achieved by increasing the acid concentration above 0.5 M. It is likely that an increase in acid concentration can affect the degradation of phenols in two ways: (a) by increasing the ease of hydroxyl radical formation and hence the efficiency of photolytically induced free radical decomposition at higher acid concentration and (b) by the formation of protonated organic species that may increase the efficiency of the degradation reaction. In all subsequent experiments the acid strength used was 0.5 M.

2.2. Electrochemical cell system

The electrolytic cell system used is described in detail in an earlier communication (Chaudhary et al., 2001). The cell consists of an electrolytic chamber of 1.5 L capacity through which the fluid to be treated is pumped from a reservoir via inlet and back to the reservoir via outlet. The electrolyte flow rate is 5 L min^{-1} and the flow controlled by a valve. The cell contains two anodes made from titanium mesh substrate coated with RuO_2 (total surface area of 0.1 m^2) and a single stainless plate cathode (surface area of 0.025 m^2). The effects of the presence of phenol and 4-chlorophenol (50 mg L^{-1}) on the recovery of copper (500 mg L^{-1}) were also studied. The electrolytic process was carried out at a constant current of 1.0 A.

2.3. Combined photolytic – electrolytic cell system

The combined photolytic – electrolytic cell system is also described in detail, in our earlier communication (Chaudhary et al., 2001). This cell was used for the simultaneous destruction of phenol and recovery of copper. In the combined photolytic – activated carbon concentrator system, the cathode is enclosed in the concentrator medium. The electrolytic process was carried out at a constant current of 1.0 A. Samples were collected periodically from the reservoir tank to determine the levels of metal ions and the concentration of phenols in solution.

Model mixed solutions (10 L) containing known concentrations of copper (500 mg L^{-1}) and organic species (50 mg L^{-1}) were prepared by dissolving reagent grade $CuSO_4 \cdot 5H_2O$ and phenol or 4-chlorophenol in distilled water. Reagent grade sulphuric acid was used to study the effect of acid concentration. The analysis of copper was carried out by flame atomic absorption spectroscopy (Perkin-Elmer Analyst 100) and the degradation of the organic

species was followed by optical spectroscopy, total organic carbon (TOC), and by HPLC to identify the intermediate species formed during the photodegradation of phenol and 4-chlorophenol. The degradation of phenol and 4-chlorophenol was followed by a HPLC system equipped with a mobile phase reservoir of 1 L capacity, a Rheodyne 7125 valve injection unit with a 0.2 ml loop, 25 cm × 4.6 mm (i.d.) separation column packed with Hypersil ODS 5 μm particles, a Perkin-Elmer LC-75 spectrometric detector, and Kipp & Zonen chart recorder for HPLC analysis. The eluent comprises a pH buffer and methanol in the ratio 3:7. The methanol, HPLC grade, was supplied by Rhône-Poulence Ltd. and the buffer was prepared by dissolving 5.0 g of $Na_2H_2PO_4\cdot12H_2O$ in approximately 1 L of distilled water, adjusting the pH with orthophosphoric acid, and making up the volume to 1 L with distilled water. The UV-detector was used to monitor the absorbance at 240 nm. The percentage recovery of copper was calculated from the weight of copper recovered and the amount of copper remaining in solution analysed by FAAS. The percentage of phenol and 4-chlorophenol degradation was determined from the HPLC peak area data and monitoring changes in total organic carbon with time.

3. Results and discussion

We show that the presence of copper ions in solution can retard the destruction of phenol and 4-chlorophenol by both photolytic and anodic oxidation systems. We have developed a combined photolytic-electrolytic cell system to achieve the simultaneous recovery of copper and the destruction of phenols from aqueous solutions.
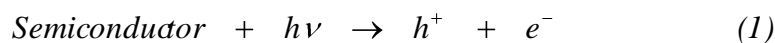
3.1. Photolytic/photocatalytic cell system

3.1.1 Photodegradation of phenol and 4-chlorophenol

The photodegradation of phenol and 4-chlorophenol is studied in the presence and absence of a heterogeneous catalyst or an oxidant and the factors influencing the degradation described.
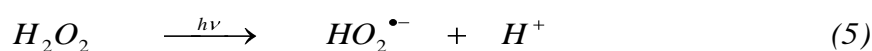
Both the HPLC and UV spectroscopic data along with the results from the total organic carbon analysis have been used to follow the photolytic degradation of phenol and 4-chlorophenol. The results (Table 1) show that, although the oxidation of phenol and 4-chlorophenol does occur in aqueous solutions in the absence of a catalyst (TiO_2) or an oxidant (H_2O_2), the degradation is quicker in the presence of both the catalyst and the oxidant. The degradation of 4-chlorophenol is shown to be slow compared to that of phenol especially in the initial stages of the reaction although both are eventually completely mineralised. The increase in the photodegradation in the presence of a catalyst or an oxidant is consistent with an increase in hydroxyl free radical formation.

The mechanism of photocatalytic degradation of phenol in the presence of TiO_2 suspension is well documented in the literature (Kartal et al., 2001). In the presence of TiO_2 suspension hydroxyl radicals are formed via the following reactions.

$$Semiconductor \;\; + \;\; h\nu \;\; \rightarrow \;\; h^+ \;\; + \;\; e^- \qquad\qquad (1)$$
$$H_2O_{(ads)} \;\; + \;\; h^+ \;\; \rightarrow \;\; {}^{\bullet}OH \;\; + \;\; H^+ \qquad\qquad (2)$$
$$OH^-{}_{(surface)} \;\; + \;\; h^+ \;\; \rightarrow \;\; {}^{\bullet}OH \qquad\qquad (3)$$

The addition of H_2O_2 to a reaction solution has the effect of increasing the degradation rate. An important step in the formation of a radical species is the cleavage of H_2O_2 in the presence of UV-light. The addition of H_2O_2 increases the rate of radical formation (both

hydroxyl ($^{\bullet}$OH) and hydroperoxyl (HO$_2{}^{\bullet}$) radicals) and ultimately the degradation of phenol. In the presence of H$_2$O$_2$, hydroxyl radicals are formed by the following reactions (Esplugas et al., 2002).

$$H_2O_2 \quad \xrightarrow{h\nu} \quad 2^{\bullet}OH \qquad\qquad\qquad (4)$$

$$H_2O_2 \quad \xrightarrow{h\nu} \quad HO_2^{\bullet-} \quad + \quad H^+ \qquad\qquad (5)$$

3.1.2 Effect of copper ions

A set of experiments was carried out to investigate the effects of the presence of 500 mg L^{-1} of Cu(II) ions on the photolytic degradation of phenol and 4-chlorophenol, alone and in the presence of TiO$_2$ or H$_2$O$_2$, in an 0.5 M acid solution using a 400 W probe. The data in Table 1 show that the presence of copper ions significantly reduces the degradation of the phenols. The presence of copper ions in a control aqueous solution reduces the percentage degradation of phenol from 89 to 19% and 4-chlorophenol from 85 to 21% after 8 h. The addition of H$_2$O$_2$ as an oxidant or TiO$_2$ as a catalyst however does not improve the efficiency of the degradation in the presence of copper ions.

There are two possible reasons for the significant reduction in the degradation of phenol and 4-chlorophenol in the presence of copper ions, namely metal - organic complex formation and reduction and oxidation of Cu(II) arising from reactions at photogenerated electrons and holes (Brezová et al., 1995). The results in Fig. 1 show that the UV spectrum of 4-chlorophenol changes with time in the presence of copper ions indicating the formation of Cu(II)-phenol complexes and this is likely to be the major factor affecting the photodegradation of the phenols.

3.2. Electrolytic cell system

Because electrochemical methods are normally the most efficient way to recover copper from aqueous solution, the possible use of anodic oxidation for the destruction of phenols and the effects of phenols in the recovery of copper were studied. The UV spectra of both phenol and 4-chlorophenol and the HPLC data for the products after 8 h show very little change with time both in the presence and absence of copper ions confirming that anodic oxidation does not result in efficient mineralisation of the phenols. The maximum degradation of phenols achieved by anodic oxidation was 8% and no advantage was achieved by the presence of TiO_2 as a catalyst or H_2O_2 as an oxidant.

The presence of phenols, however, has a major effect on the recovery of copper from mixed solutions by electrodeposition. The results in Table 2 show that > 99% recovery of copper is achieved in the electrolytic cell used after 8 h in the absence of phenols but that the percentage recoveries are reduced to less than 80% in the presence of phenol and 4-chlorophenol. Interestingly these recoveries increase slightly to about 85% in the presence of the H_2O_2 oxidant. The reduction in the efficiency of the removal of copper is consistent with the formation of strong Cu(II)-phenol complexes.

3.3. Combined photolytic – electrolytic cell system

The results obtained from the photolytic and electrolytic cell systems on Cu(II)-phenol solutions confirm that both the presence of copper ions in solution reduces the efficiency of the photolytic degradation of the phenols and that the presence of the phenols has a major effect in reducing the efficiency of copper recovery by electrodeposition. The combined photolytic – electrolytic cell system was designed to maximise the benefits of both parts of the system to optimise the simultaneous recovery of copper and the degradation of phenols.

Results of Table 3 show (a) that much improved phenol degradations and copper recoveries are achieved in the absence of a catalyst; (b) that copper recoveries of > 99% and phenol degradation (> 99%) or 4-chlorophenol degradation (> 90%) can be achieved simultaneously in the presence of H_2O_2 as oxidant and (c) improved phenol degradations but poor copper recoveries are obtained when TiO_2 is present as a catalyst – the poor copper recoveries must be due to adsorption or ion-exchange of Cu(II) ions on the TiO_2. The UV/Visible spectra of 4-chlorophenol, in the presence of copper ions, also indicated that the complete mineralisation (> 99%) of organic species can be achieved after 8 h during the combined processes of photooxidation and anodic oxidation.

The improved achievement in the combined system in which the aqueous copper phenol solution is simultaneously circulated through both parts of the system arises because the degradation of phenol in the photolytic cell immediately improves the efficiency of copper deposition and conversely any removal of copper on the cathode of the electrolytic cell immediately improves the efficiency of phenol photooxidation.

The data in Table 4 show that the combined cell system can be further improved with the use of concentrator cathode technology (Chaudhary et al., 2001) using activated carbon as the concentrator medium in the electrolytic cell of the combined system. The results show that the combined system with activated carbon concentrator cathode is capable of achieving a total degradation of phenols and at the same time achieving > 99% recovery of copper. The purpose of the concentrator cathode is to increase the concentration of copper ions near the electrode, which leads to an increase in the efficiency of metal recovery. The changes in the UV spectra of 4-chorophenol provide a comparison of the extent of phenol degradation from a copper-containing solution using an electrolytic system with a concentrator cathode alone

(Fig. 2a) and the improvements that are achieved using this cell in the combined system (Fig. 2b).

3.4. Comparison of different systems

The total organic carbon data was used to compare the efficiencies of the photodegradation of 4-chlorophenol in the presence of copper ions for all of the systems studied in this work. The results showed that complete mineralization of phenols is achieved by the use of a combined photolytic- electrolytic cell system in which concentrator cell technology is incorporated in the electrolytic cell. The plots of $\ln[C_t/C_o]$ *vs* time for various cell systems show that the phenols degradation follows first order kinetics. The slopes of these plots give phenols kinetic constants (k) which can be used to calculate the half-life ($t_{1/2}$) of phenols. The results in Table 5 also confirm that the combined photolytic − activated carbon concentrator cathode system is the most efficient.

4. Conclusions

The results of this work show that an electrolytic cell system alone can be used to recover copper but is not capable of achieving the anodic oxidation of phenol or 4-chlorophenol. On the other hand, use of a photolytic cell system alone can achieve phenols degradation but leaves copper ions in solution. The use of a combined photolytic and electrolytic system can, however, lead to the simultaneous recovery of copper and the destruction of phenols in aqueous solutions. The combined photolytic − electrolytic system in combination with the use of activated carbon concentrator cathode is an ideal system for the treatment of mixed effluent streams containing heavy metal ions and organic contaminants.

Acknowledgements

References

Awad, Y.M., Abuzaid, N.S., 2000. The influence of residence time on the anodic oxidation of phenol. Sep. Purif. Technol. 18, 227-236.

Brezová, V., Blazžková, A., Borošová, E., Čeppan, M., Fiala, R., 1995. The influence of dissolved metal ions on the photocatalytic degradation of phenol in aqueous TiO_2 suspensions. J. Mol. Catal. A-Chem. 98, 109-116.

Chaudhary, A.J., Donaldson, J.D., Grimes, S.M., Hassan, M., 2000a. Simultaneous recovery of metals and destruction of organic species: Cobalt and phthalic acid. Environ. Sci. Technol. 34, 4128-4132.

Chaudhary, A.J., Donaldson, J.D., Grimes, S.M., Hassan, M., Spencer, R.J., 2000b. Simultaneous recovery of heavy metals and degradation of organic species - copper and ethylenediaminetetra-acetic acid (EDTA). J. Chem. Tech. Biot. 75, 353-358.

Chaudhary, A.J., Donaldson, J.D., Grimes, S.M., Hassan, M., 2001. Simultaneous recovery of copper and degradation of 2,4-dichlorophenoxyacetic acid in aqueous systems by a combination of electrolytic and photolytic processes. Chemosphere 44, 1223-1230.

Esplugas, S., Gimenez, J., Contreras, S., Pascual, E., Rodriguez, M., 2002. Comparison of different advanced oxidation processes for phenol degradation. Water Res. 36, 1034-1042.

Garcia-Mendieta, A., Solache-Rios, M., Olguin, M.T., 2003. Comparison of phenol and 4-chlorophenol adsorption in activated carbon with different physical properties. Separ. Sci. Technol. 38, 2549-2564.

Grimes, S.M., Ngwang, H.C., 2000. Methodology for studying oxidation of organic species in solution. J. AOAC Int. 83, 584-587.

Kartal, O.E., Erol, M., Oguz, H., 2001. Photocatalytic destruction of phenol by TiO_2 powders. Chem. Eng. Technol. 24, 645-649.

Kulkarni, U.S., Dixit, S.G., 1991. Destruction of phenol from wastewater by oxidation with sulfite-oxygen. Ind. Eng. Chem. Res. 30, 1916-1920.

Lazarova, Z., Boyadzhieva, S., 2004. Treatment of phenol-containing aqueous solutions by membrane-based solvent extraction in coupled ultrafiltration modules. Chem. Eng. J. 100, 129-138.

Pelegrini, R.T., Freire, R.S., Duran, N., Bertazzoli, R., 2001. Photo assisted electrochemical degradation of organic pollutants on a DSA type oxide electrode: Process test for a phenol synthetic solution and its application for the E1 Bleach Kraft Mill effluent. Environ. Sci. Technol. 35, 2849-2853.

Santos, A., Yustos, P., Durban, B., Garcia-Ochoa, F., 2001. Oxidation of phenol in aqueous solution with copper catalysts. Catal. Today 66, 511-517.

Yawalkar, A.A., Bhatkhande, D.S., Pangarkar, V.G., Beenackers, A.A.C.M., 2001. Solar-assisted photochemical and photocatalytic degradation of phenol. J. Chem. Technol. Biot. 76, 363-370.

Zareie, M.H., Korbahti, B.K., Tanyolac, A., 2001. Non-passivating polymeric structures in electrochemical conversion of phenol in the presence of NaCl. J. Hazard. Mater. 87, 199-212.
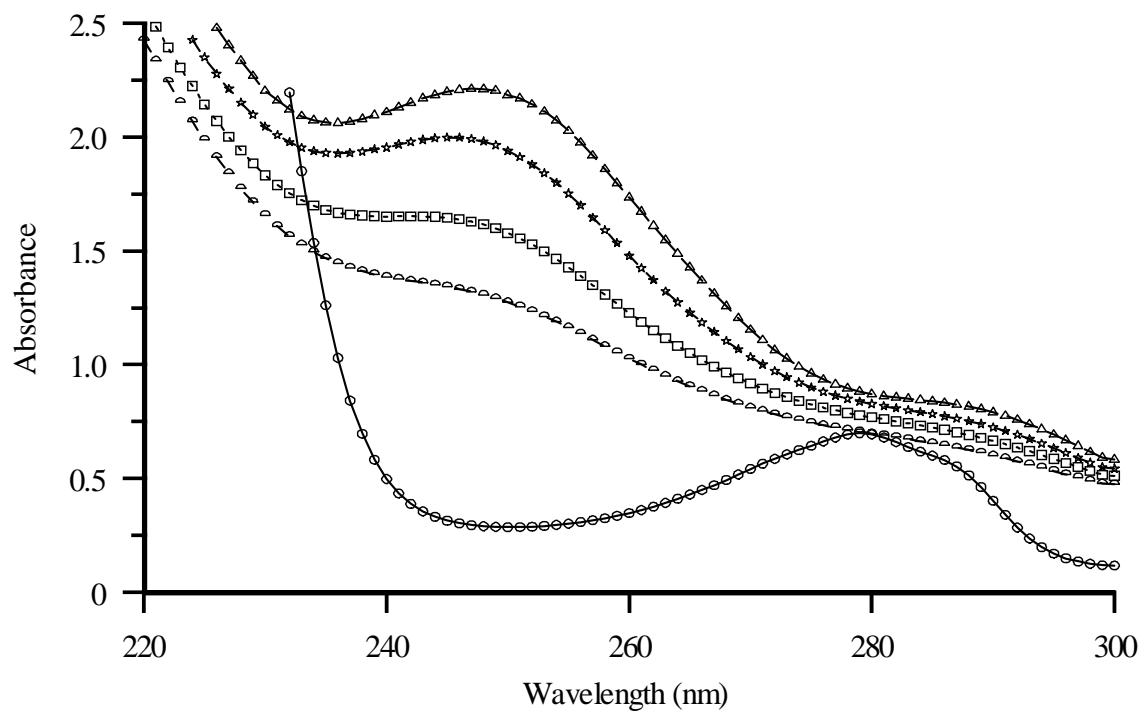
Fig. 1. UV-absorbance of 4-chlorophenol and its intermediates with time using a photolytic cell system. ○ 0 h; △ 2 h; ☆ 4 h; □ 6 h; ○ 8 h.

(Copper concentration 500 mg L^{-1}; 4-chlorophenol concentration 50 mg L^{-1}; Absence of an oxidant (H_2O_2) or a photocatalyst (TiO_2).
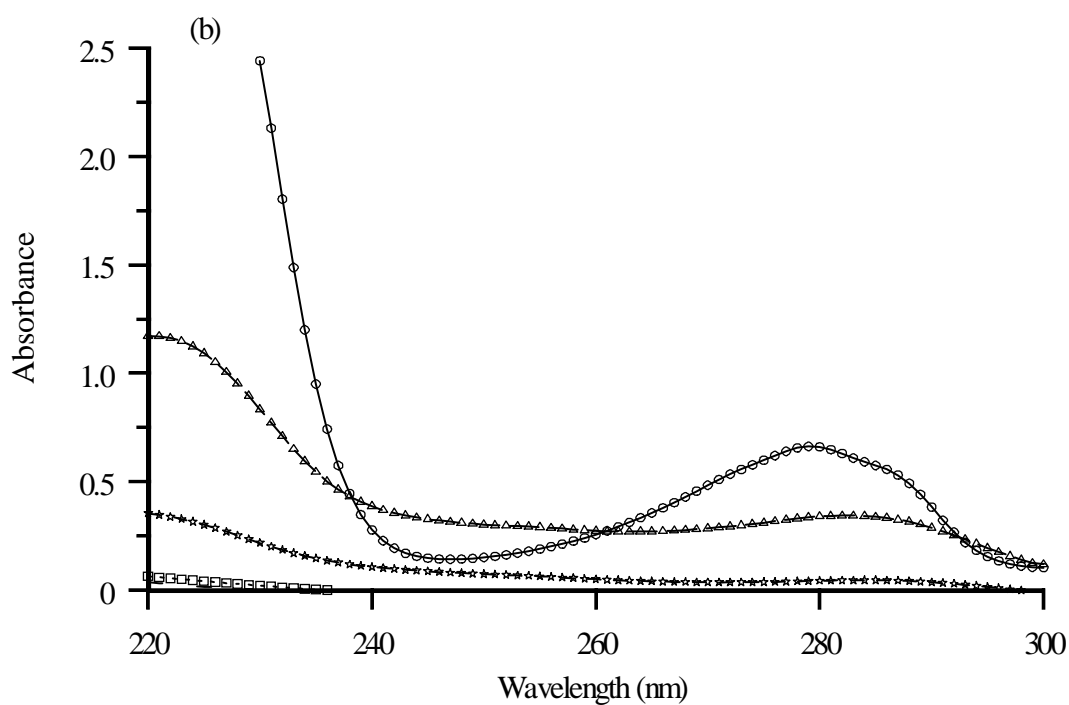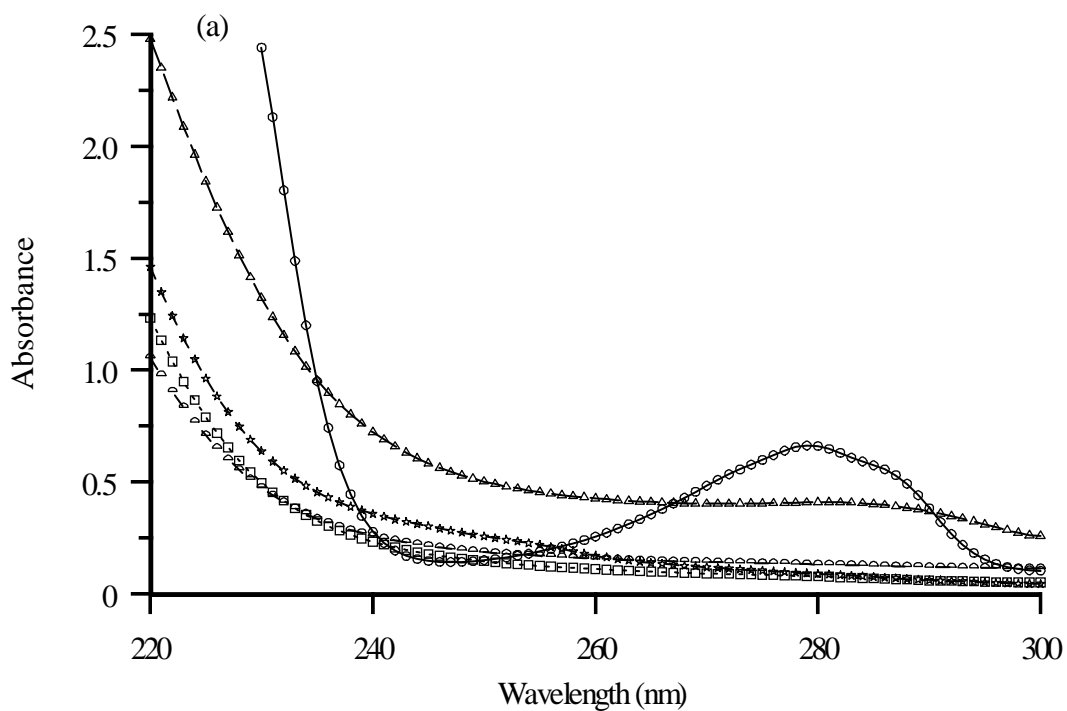
Fig. 2. UV-absorbance of 4-chlorophenol and its intermediates with time using (a) activated carbon concentrator cathode and (b) combined photolytic-activated carbon concentrator cathode. ○ 0 h; △ 2 h; ☆ 4 h; □ 6 h; ◠ 8 h.
(Copper concentration 500 mg L^{-1}; 4-chlorophenol concentration 50 mg L^{-1}; Absence of an oxidant (H_2O_2) or a photocatalyst (TiO_2).

Table1: Effect of TiO_2, H_2O_2 and Cu(II) ions on the photodegradation of phenol and 4-chlorophenol using a photolytic cell system[a]

	Photodegradation of phenol and 4-chlorophenol (%)											
	Control		Presence of TiO_2 (1 g L^{-1})		Presence of H_2O_2 (10 ml L^{-1})		Presence of Cu(II) (500 mg L^{-1})		Cu(II) in the presence of TiO_2		Cu(II) in the presence of H_2O_2	
Time (h)	Phenol	Chloro-phenol	Phenol	Chloro-phenol	Phenol	Chloro-phenol	Phenol	Chloro-phenol	Phenol	Chloro-phenol	Phenol	Chloro-phenol
2	28	18	36	33	37	34	18	15	19	18	20	18
4	50	33	57	51	60	54	18	17	20	20	21	19
6	68	61	79	73	81	78	18	19	21	22	21	20
8	89	85	97	96	97	96	19	21	21	23	22	22

[a]Phenol/4-chlorophenol concentration 50 mg L^{-1}; UV-probe 400 W.

Table 2: Effect of phenol/4-chlorophenol on the recovery of copper using an electrolytic cell system[a]

Time (h)	Recovery of Copper (%)				
	Absence of Phenol/Chlorophenol	Presence of		In the presence of H_2O_2	
		Phenol	Chlorophenol	Phenol	Chlorophenol
2	66	28	33	52	41
4	82	57	56	70	69
6	95	67	71	77	78
8	> 99	75	79	85	87

[a]Copper concentration 500 mg L^{-1}; Phenol/4-chlorophenol concentration 50 mg L^{-1}; Current 1 A.

Table 3: Effect of H_2O_2 and TiO_2 on the degradation of phenol, 4-chlorophenol and recovery of Cu(II) using a combined photolytic – electrolytic cell system[a]

	Degradation of phenol, 4-chlorophenol and the recovery of copper (%)											
					Presence of an oxidant or a catalyst							
Time	Absence of an oxidant or a catalyst				H_2O_2 (10 ml L^{-1})				TiO_2 (1 g L^{-1})			
(h)	Phenol	Cu(II)	Chlorophenol	Cu(II)	Phenol	Cu(II)	Chlorophenol	Cu(II)	Phenol	Cu(II)	Chlorophenol	Cu(II)
2	36	22	31	43	38	47	31	41	44	21	43	24
4	56	65	46	74	80	80	77	77	67	37	76	41
6	70	89	79	90	97	90	88	98	83	45	83	47
8	90	> 99	89	92	> 99	> 99	91	> 99	> 99	48	91	52

[a]Copper concentration 500 mg L^{-1}; Phenol/4-chlorophenol concentration 50 mg L^{-1}; UV-probe 400 W; Current 1 A.

Table 4: Degradation of phenol, 4-chlorophenol and recovery of copper, in the absence of an oxidant or a catalyst, using an activated carbon concentrator cathode alone and a combined photolytic – activated carbon concentrator cathode[a]

| Time (h) | Degradation of phenol, 4-chlorophenol and the recovery of copper (%) | | | | | | | |
| | Activated carbon concentrator cathode Electrolytic cell only | | | | Activated carbon concentrator cathode Combined system | | | |
	Phenol	Cu(II)	Chlorophenol	Cu(II)	Phenol	Cu(II)	Chlorophenol	Cu(II)
2	28	34	23	32	76	50	70	44
4	47	57	40	53	90	81	84	79
6	62	72	60	69	99	97	93	90
8	75	82	71	78	> 99	> 99	> 99	> 99

[a]Copper concentration 500 mg L^{-1}; Phenol/4-chlorophenol concentration 50 mg L^{-1}; UV-probe 400 W; Current 1 A.

Table 5: Kinetic constants and half-life of phenol and 4-chlorophenol for various cell systems[a]

Cell system	Presence of Cu(II) and absence of a catalyst or an oxidant			
	Phenol		4-Chlorophenol	
	k (h^{-1})	t$_{1/2}$ (h^{-1})	k (h^{-1})	t$_{1/2}$ (h^{-1})
Electrolytic	7.1×10^{-3}	97.6	6.7×10^{-3}	103.4
Photolytic	7.1×10^{-2}	9.7	6.2×10^{-2}	11.2
Combined photolytic – electrolytic	2.1×10^{-1}	3.3	1.9×10^{-1}	3.6
Combined photolytic – activated carbon concentrator	6.0×10^{-1}	1.2	5.8×10^{-1}	1.2

[a]Copper concentration 500 mg L^{-1}; Phenol/4-chlorophenol concentration 50 mg L^{-1}; UV-probe 400 W; Current 1 A.