

Simultaneous recovery of metals and degradation of organic species:

Copper and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T)

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Abstract

In mixed wastewater streams, the presence of metal ions can retard the destruction of organic contaminants and the efficiency of recovery of the metal is reduced by the presence of organic species. The reduction in the efficiency of these methods is due to the formation of complexes between the organic species and the metal ions in solution. Results are presented for copper - 2,4,5-T system in which both effects occur. A photolytic cell alone can achieve the complete degradation of 2,4,5-T, in the presence of TiO₂ or H₂O₂, at pH 3.5. The addition of Cu(II) ions, however, retard the degradation of 2,4,5-T and complete mineralization of 2,4,5-T was not achieved and the system also leaves Cu(II) ions in solution. An electrolytic cell alone can be used to recover copper in pH range 1.5 – 4.5 but is not capable of achieving complete disappearance of 2,4,5-T by anodic oxidation. A combined photolytic – electrolytic system is capable of achieving simultaneous destruction of 2,4,5-T and recovery of copper from mixed wastewater streams at pH 3.5. The percentage destruction of 2,4,5-T and the recovery of copper can be increased further by using a combined photolytic and an activated carbon concentrator cell system. This system can achieve the simultaneous recovery of copper and the degradation of 2,4,5-T without the use of an additional oxidants or catalysts.

Keywords: 2,4,5-Trichlorophenoxyacetic acid; Copper; Photolytic; Electrolytic; Combined system.

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1. Introduction

2,4,5-trichlorophenoxyacetic acid (2,4,5-T), an organochlorine compound, was a widely used herbicide in the European Union and USA to control weeds and enhance crops yield. Although now banned in developed countries but it is still being used in most developing countries for weed control on cereal crops, grasslands and lawns. It is considered to be less readily biodegradable than the analogous herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) and, therefore, has potential toxicity towards humans and animals. The greater resistance to microbial metabolism likely stems from the additional chlorine constituent on the aromatic ring. However, in soil, biodegradation to form CO₂ can be accelerated significantly by the amendment of inorganic nutrients [1]. Herbicides can be washed away to the surface water bodies or reach water-bearing aquifers below ground from application onto crop fields. The control of organic pollutants in water is an important issue and the latest environmental regulations limit the discharge of these compounds into the environment.

Water contamination with organochlorine compounds can arise in various ways including runoff from cropland, effluent from industry, disinfection of drinking water supplies and treatment of wastewater with chlorine. This type of contamination can lead to the formation of mixed effluent containing both heavy metal ions and the toxic organic pollutants. Successful treatment of this type of effluent to achieve legislative compliance will depend upon whether the heavy metals affect the process of degradation of the organic species and whether the presence of organic pollutants hinders the process of removal of the heavy metal.

There are many possible methods which can be used to remove or destroy 2,4,5-T and other organochlorine compounds including adsorption [2], anodic oxidation [3], biological degradation [1,4], ozonisation [5], solar radiation [6] and treatment with ultraviolet radiation [7]. Most electrolytic, photolytic and photocatalytic treatments destroy organic compounds by reaction with hydroxyl radical ($\cdot\text{OH}$) which can be produced from different systems. The

efficiency of many of these methods is reduced in the presence of heavy metal ions and this is particularly true if the presence of organic species form strong complexes with the metal ions in solution [8,9].

Similarly there are many methods which can be used for the removal and recovery of copper ions from different solutions including chemical precipitation [10], biosorption [11], solvent extraction [12], cementation [13], electro dialysis [14] and electrolysis [15], but there are practical limitations in most of the methods arising from failure to remove organic pollutant. In our previous publications we have reported that a combined photolytic – electrolytic system is required for the successful treatment of mixed wastewater streams in order to comply with the discharge consent levels [8,16,17]. In one of our publications we reported the effects of Cu(II) ion on the photodegradation of 2,4-D [8] and the main aim of this study is to investigate whether the presence of an additional chloride group has any effect on the degradation of chlorophenoxy herbicide, 2,4,5-T. This manuscript describes the effects of Cu(II), which is frequently present in wastewater, on the photolytic degradation of 2,4,5-T and on the effects of 2,4,5-T on the electrolytic recovery of Cu(II) ions, and optimised a combined photolytic - electrolytic cell system for the simultaneous removal of copper and the degradation of 2,4,5-T as part of studies on the simultaneous recovery of metals and degradation of organic pollutants [8,16,17].

2. Materials and methods

2.1. Reagents and model solutions

The herbicide 2,4,5-T (97%) was obtained from Sigma-Aldrich and used as such without further purification. Other chemicals were of reagent grade or higher and obtained from Merck and Fluka. The photocatalyst (TiO₂) and hydrogen peroxide (30-31%) were obtained from BDH Chemicals Ltd., Poole, England. Model mixed solutions (10 L)

containing known concentrations of 2,4,5-T (50 mg L^{-1}) and copper (100 or 500 mg L^{-1}) were prepared by dissolving 2,4,5-T and reagent grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water. Reagent grade sulfuric acid and sodium hydroxide solution were used to study the effect of pH. The eluent used for HPLC analyses comprises a pH buffer and acetonitrile in the ratio 1:1. The acetonitrile, HPLC grade, was supplied by Fisher Chemicals and the buffer was prepared by dissolving 5.0 g of $\text{Na}_2\text{H}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$ in approximately 1 L of distilled water containing 1 g L^{-1} centramide, adjusting the pH with orthophosphoric acid, and making up the volume to 1 L with distilled water.

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 and the surface area ($56.8 \text{ m}^2 \text{ g}^{-1}$) was previously determined by Brunauer-Emmett-Teller (BET) method [16].

2.2. Analytical methods

The analysis of copper was carried out by flame atomic absorption spectroscopy (Perkin-Elmer 2380) and the degradation of the 2,4,5-T was followed by optical spectroscopy, total organic carbon (TOC), and by HPLC. The detection limit for copper using Perkin Elmer 2380 AAS is 0.02 mg L^{-1} and the recovery of copper was taken to be complete if the residual level was below this value. The degradation of 2,4,5-T was monitored by measuring the total organic carbon (TOC) content, after purging the acidified sample to remove inorganic carbon, with a TOC analyzer, Model 700, O.I. Corporation, Texas, USA, by directly injecting a centrifuge sample. For the characterization of intermediate products, reverse-phase chromatography was performed with Cecil HPLC liquid chromatography pump (CE 1100 Series), equipped with a mobile phase reservoir of 1 L capacity, a Rheodyne 7125 valve injection unit with a 0.2 ml loop, $25 \text{ cm} \times 3 \text{ mm}$ (i.d.) separation column packed with Pinnacle

ODS 5 μm particles, a Perkin-Elmer LC-75 spectrometric detector, and Kipp & Zonen chart recorder and using a UV-detector to monitor the 2,4,5-T 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 2,4,5-T degradation was determined from the HPLC peak area data and monitoring changes in total organic carbon (TOC) with time.

2.3. Photolytic cell system

The photolytic cell system used was described in detail in an earlier communication [16]. The cell consists of a UV probe surrounded by a reaction chamber of 3.5 L capacity. Model solutions containing a known concentration of 2,4,5-T (50 mg L^{-1}) and initial pH values ranging between 1.5, 2.5, 3.5, 4.5 and 5.5 were 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 was controlled by a valve. Compressed air was used as the oxidant in the photolysis and was supplied through an inlet and exits through an outlet. The temperature in the reaction chamber was monitored continuously with a digital thermocouple and maintained at 25-30 $^{\circ}\text{C}$ by passing tap water through a cooling jacket surrounding the UV-probe. The effects of pH, UV source, copper ions, titanium dioxide (TiO_2) and hydrogen peroxide (H_2O_2) on the degradation of 2,4,5-T were studied by carrying out duplicate experiments for 8 hours under identical conditions.

2.4. Electrolytic cell system

The electrolytic cell system used was described in detail in an earlier communication [16]. The cell consists of an electrolytic chamber of 1.5 L capacity through which the solution to be treated was pumped from a reservoir via inlet and back to the reservoir via outlet. The electrolyte flow rate was 5 L min^{-1} and the flow controlled by a valve. The cell

contains two anodes made from titanium mesh substrate coated with RuO₂ (total surface area of 0.1 m²) and a single stainless steel plate cathode (surface area of 0.025 m²). This system was used for the simultaneous deposition of copper on the cathode and destruction of 2,4,5-T on the anode surfaces. The effects of pH, H₂O₂ and 2,4,5-T (50 mg L⁻¹) on the recovery of copper and the effect of Cu(II) ions (100 mg L⁻¹) on the anodic oxidation of 2,4,5-T were studied. The electrolytic process was carried out for 8 hours at a current density of 10 A/m².

2.5. Combined photolytic – electrolytic cell system

The combined photolytic – electrolytic cell system was also described in detail, in our earlier communication [16]. This cell was used for the simultaneous destruction of 2,4,5-T and recovery of copper from model aqueous solutions. The electrolytic process was carried out at a current density of 10 A/m². Samples were collected periodically from the reservoir tank to determine the levels of metal ions and the concentration of 2,4,5-T in solution. The effects of hydrogen peroxide (H₂O₂) on the degradation of 2,4,5-T and on the simultaneous recovery of copper and degradation of 2,4,5-T were studied using the combined photolytic – electrolytic cell system. In the activated carbon concentrator system, the cathode is enclosed in the concentrator medium. This concentrator system alone and the combined photolytic – activated carbon concentrator system were also used for the simultaneous recovery of copper and the degradation of 2,4,5-T at pH 3.5.

3. Results and discussion

3.1. Photolytic/photocatalytic cell system

3.1.1. Effect of pH

The pH of the aqueous solution is an important parameter since it influences the surface charge properties and could, therefore, change the rate of mineralisation of the organic pollutant. The self-pH of the model solution containing 50 mg L⁻¹ of 2,4,5-T is \cong 4.1-4.3. A set

of experiments was carried out at pH 1.5, 2.5, 3.5, 4.5 and 5.5 to investigate the effect of pH on the photodegradation of 2,4,5-T using a 400 W UV-probe. The pH was adjusted at the beginning of the experiments by addition of aqueous solution of 0.1 M NaOH or 0.1 M H₂SO₄. The results show that the degradation rate increased by decreasing the solution pH from 4.5 to 3.5. However, no further increase in the degradation rate was achieved by further decreasing the pH from 3.5 to 2.5 and 1.5. Similarly, increasing the pH from 4.5 to 5.5 resulted in a small decrease in the initial rate of degradation but >70% mineralization was achieved after 8 h in the absence of photocatalyst (TiO₂) or oxidant (H₂O₂). Although the rate of degradation was increased at the initial stages of the reaction especially at pH 2.5 but pH 3.5 was found to be the optimum for the degradation of 2,4,5-T because >99% degradation, in the presence of photocatalyst (TiO₂), can be achieved with minimum time at this value (Table 1). The results also indicated that the complete mineralization of 2,4,5-T can only be achieved in the presence of TiO₂ or H₂O₂. Our results are in close agreement with the previous studies on the effect of reaction pH on the degradation of phenoxyacetic acid herbicides [7,8]. It has also been reported [6] that the higher concentration of intermediate products are usually produced at higher pH values, which means that the photocatalytic degradation of chlorophenoxy herbicides at lower pH favours rapid and direct ring cleavage. It is likely that a slight increase in acid concentration can affect the degradation of organic pollutants in two ways: (a) by increasing the rate of hydroxyl radical formation and hence the efficiency of photocatalytically 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. All subsequent studies were carried out at pH 3.5.

3.1.2. Effect of UV source

The concentration and the nature of photoproducts formed during the degradation of organic contaminants mainly depend on the pH of the solution and the UV source. The effect

of the UV-source on the degradation of 2,4,5-T was studied by carrying out duplicate experiments under identical conditions. The mineralisation of 2,4,5-T in the absence and presence of aqueous suspension of TiO₂ (0.1% w/v) was studied at pH 3.5, optimum pH for photodegradation, using 125 W and 400 W UV-probes. The main difference between the two UV sources is the intensity of the output but they do have slightly different output characteristics and the emission bands of 400 W UV source are narrower. The results in Fig. 1 show that in the absence of TiO₂ suspension only 3% degradation was achieved after 8 h when the solution was irradiated with the 125 W UV-probe but this value increased to 90% when the degradation was carried out in the presence of TiO₂ suspension. Although, the degradation rate was increased in the presence of TiO₂ suspension but complete mineralisation of 2,4,5-T was not achieved even after 8 h. On the other hand, the degradation of 2,4,5-T was considerably faster with the 400 W UV-probe even in the absence of TiO₂ suspension and 75.8% degradation was achieved after 8 h but the corresponding value in the presence of TiO₂ suspension was >99.9% (Fig. 1).

3.1.3. Intermediate products

It is well documented that the formation of intermediate products, during the photocatalytic degradation of organic contaminants, mainly depends on the UV source and most of these intermediates ultimately degrade to produce carbon dioxide and water under the optimum reaction conditions. Grimes and Ngwang [18] have reported that the photocatalytic degradation of phenol, a simple organic compound, proceeds through the formation of three intermediate products when a 125 W UV-probe was used as a light source. Our recent work, however, showed that phenol degradation proceeds through the formation of only two intermediate products when a 400 W UV-probe is used as a light source. These results confirmed that the UV source not only effect the concentrations of the intermediate products but also change the nature of these intermediate compounds particularly in the presence of

Degussa P25 TiO₂ suspension. We have identified that, in the case of 400 W UV-probe, the photocatalytic degradation of 2,4,5-T proceeds through the formation of phenol, 2,4,5-trichlorophenol and 2,4-dichlorophenol before complete mineralization to produce CO₂, H₂O and chloride ions. HPLC results show that much higher concentrations of these three intermediate products are present in the case of 125 W UV-probe compared to 400 W. Previous work carried out by Sing et al. [7] on the photocatalytic degradation of 2,4,5-T, in the presence of Degussa P25 TiO₂ and UV light (125 W), showed that the degradation also proceeds through the formation of three intermediate products namely, 2,4,5-trichlorophenol, 2,4-dichlorophenol and 1,2,4-trichloro-5-methoxy benzene. We could not find any evidence to support the formation of 1,2,4-trichloro-5-methoxy benzene as a photoproduct during the photodegradation of 2,4,5-T under the conditions studied in this work. Similarly, it has been reported that the photocatalytic degradation of phenoxyacetic acid (PAA) in the presence of Degussa P25 TiO₂ and UV light (125 W) and produced two intermediate products namely, phenol and 1,2-diphenoxyethane [7]. However, photodegradation of PAA in the presence of Degussa P25 TiO₂ and concentrated solar radiation produced five intermediate products namely, phenol, hydroquinone, pyrocatechol, resorcinol and benzoquinone [6]. Previous findings and our present work on the photodegradation of 2,4,5-T have highlighted the need to use a suitable UV source that produces few photoproducts with low concentrations and under these conditions the overall degradation rate will increase. All subsequent studies on the effects of TiO₂ as a photocatalyst, hydrogen peroxide as an oxidant and copper ions were, therefore, carried out at pH 3.5 and using the 400 W UV-probe.

3.1.4. Effect of TiO₂ and H₂O₂

The aim of this task was to investigate the effects of TiO₂ (0.05-0.15% w/v), as a photocatalyst, and H₂O₂ (0.5-1.5% v/v), as an oxidant, on the photodegradation of 2,4,5-T. The results indicated that the degradation of 2,4,5-T proceeded much more rapidly in the

presence of TiO_2 and H_2O_2 . The degradation increased with the increase in photocatalyst loading from 0.05 to 0.1% (w/v) whereas the degradation decreased on further increase in catalyst loading from 0.1 to 0.15% (w/v). Similarly, increasing the concentration of H_2O_2 from 0.5 to 1.0% (v/v) increased the degradation of 2,4,5-T and no further advantage in the overall degradation was achieved by increasing the oxidant concentration from 1.0 to 1.5% (v/v). We found that the addition of 0.1% (w/v) TiO_2 or 1.0% (v/v) H_2O_2 was the optimum value because complete disappearance of 2,4,5-T was achieved after 8 h. The degradation values presented in Table 1, calculated using TOC and HPLC data, showed that the addition of TiO_2 and H_2O_2 together also improved the reaction efficiency and higher degradation of 2,4,5-T was achieved especially at the initial stages of the reaction. It has been suggested that the hydroxyl radicals ($\cdot\text{OH}$), superoxide radical anion ($\text{O}_2^{\cdot-}$) and hydroperoxyl radical anion ($\text{HO}_2^{\cdot-}$) [7] are the primary oxidising species in the photolytic/photocatalytic oxidation processes and four possible mechanisms, all based on the attack of hydroxyl radical ($\cdot\text{OH}$), for the degradation of organic water contaminants have been proposed [6].

3.1.5. Effect of Cu(II) ions

It has been reported [8,9,19] that the presence of heavy metal ions can affect the photodegradation of organic pollutants in aqueous solution. The aim of this task was to investigate the effect of the presence of Cu(II) ions ($100\text{-}500\text{ mg L}^{-1}$) on the photodegradation of 2,4,5-T (50 mg L^{-1}). The results indicated that the presence of Cu(II) ions lead to a significant reduction in the efficiency of the degradation of 2,4,5T, specifically in the absence of TiO_2 or H_2O_2 , and the extent of degradation at pH 3.5 was 25.3% and 2.1% after 2 h in the absence and in the presence (100 mg L^{-1}) of copper ions respectively. The corresponding values after 8 h are 75.8 and 8.7% respectively. A further reduction in the degradation of 2,4,5-T was noticed when the concentration of Cu(II) ions increased from 100 to 500 mg L^{-1} . This decrease in the percentage degradation of 2,4,5-T is probably due to a complex

formation between Cu(II) ions and the organic species or some of the intermediate products. Optical absorption spectra of 2,4,5-T solutions (Fig. 2a) in the absence and presence of Cu(II) ions ($100\text{-}500\text{ mg L}^{-1}$) show that a complex is formed between the two species as would be expected because of the known interaction between copper and carboxylate groups [19,20]. It has also been confirmed that the degradation of 2,4,5-T in the presence of Fe(II) ions produced Fe(III)-oxalato complex [3] and the complex formation of this type must alter the susceptibility of the organic molecule to photolytic degradation.

The reduction in the extent of 2,4,5-T degradation in the presence of copper can be largely overcome by the addition of TiO_2 (0.1% w/v) as a heterogeneous photocatalyst or H_2O_2 (1.0% v/v) as an oxidant. The percentage degradation of 2,4,5-T, in the presence of 100 mg L^{-1} of copper, was 65.6 and 68.7% after 8 h in the presence of TiO_2 and H_2O_2 respectively. These values reduced to 55.3 and 57.8% when Cu(II) concentration increased from 100 to 500 mg L^{-1} (Table 1). The increase in the rate of degradation presumably arises because of the ease of radical formation in the presence of TiO_2 and H_2O_2 . Although the degradation of 2,4,5-T, in the presence of Cu(II) ions and TiO_2 suspension, was increased but complete mineralisation was not achieved even after 8 hours (Fig. 2b). It has been reported [19] that the recombination of electron/hole pairs, in the presence TiO_2 suspension, is an interfering reaction which, in the absence of appropriate electron acceptor or donor, is very efficient and will ultimately reduce the degradation of organic contaminant. To overcome the recombination of the electron/hole (e^-/h^+) pairs, the effect of H_2O_2 as an electron acceptor, in addition to air, in the presence of TiO_2 suspension was investigated. The results in Table 1 show the combined effect of $\text{TiO}_2+\text{H}_2\text{O}_2$ on the degradation of 2,4,5-T in the presence of Cu(II) ions. Although, we noticed some beneficial effect on the photocatalytic degradation of 2,4,5-T, especially at the initial stages of the reaction, but complete mineralization was not achieved even after 8 hour with the combined action of TiO_2 and H_2O_2 . The increase in

degradation of 2,4,5-T is probably due to the catalytic decomposition of H_2O_2 in the presence of Cu(II) ions to produce $\cdot\text{OH}$ radicals via homogeneous photo-Fenton type like reaction $\text{Cu(II)} + \text{e}^- \rightarrow \text{Cu(I)}$; $\text{Cu(I)} + \text{H}_2\text{O}_2 \rightarrow \text{Cu(II)} + \text{OH}^- + \cdot\text{OH}$. However, the presence of Cu(II) ions can also decrease the production of $\cdot\text{OH}$ radicals due to a cyclic reaction involving reduction and oxidation of Cu(II) ions ($\text{Cu(II)} + \text{e}^- \rightarrow \text{Cu(I)} + \text{h}^+ \rightarrow \text{Cu(II)}$). These two opposing reactions are responsible for not increasing the overall degradation of 2,4,5-T especially in the presence of TiO_2 and H_2O_2 .

3.2. Electrolytic cell system

An electrolytic cell system is normally used for the electrodeposition of metal ions from aqueous solutions but the system can also be used for the degradation of water organic contaminants. Electrolytic treatment of various organic contaminants, in the absence of metal ions, has been carried using different types of anode materials, for example, Pt, carbon, boron-doped, gas diffusion, Ti/IrO_2 and Ti/SnO_2 and the oxidation occurs at electrodes at the surface of which hydroxyl radicals ($\cdot\text{OH}$) can be accumulated [3]. In the present work, electrolytic recovery of copper (100 and 500 mg L^{-1}), in the absence and presence of 2,4,5-T (50 mg L^{-1}), was carried out at pH 1.5 and 3.5 and at a current density of 10 A m^{-2} . The aim of this task was to investigate whether the presence of 2,4,5-T hinders the recovery of copper or whether the presence of Cu(II) ions hampers the anodic oxidation of 2,4,5-T.

3.2.1. Effect of 2,4,5-T on the recovery of copper

An important parameter in the electrolytic recovery of metal ions is the reaction pH and in some cases the pH of the solution must be kept constant to achieve the highest percentage recovery of metal ions. Our results indicate that the electrodeposition of Cu(II) ions, in the absence of 2,4,5T, is almost independent of the pH in the range 1.5-4.5 and complete recovery of copper can be achieved at all pH values studies in this work. However, the recovery of copper at pH 1.5 is slightly lower compared to pH 3.5 and this decrease is

attributed to the competition between the reduction of Cu(II) ions and the evolution of hydrogen gas due to the reduction of H⁺ ions at the cathode surface. Complete recovery of copper, from solutions containing 100 mg L⁻¹ Cu(II), was achieved after 10 h. A 7% increase in the recovery of copper was obtained after 2 h when copper concentration was increased from 100 to 500 mg L⁻¹. In concentrated solution, the transport of ions takes place due to diffusion, migration and convection processes whereas in the case of dilute solution (100 mg L⁻¹) the ion transport is only due to diffusion, migration and convection do not take part in ion transportation, and this difference can lead to the formation of a barrier layer near the cathode surface which is depleted in Cu(II) ions and ultimately reduced the recovery of copper.

The recovery of copper was also reduced in the presence of 2,4,5-T and this could be due to the difference in the transport of hydrated Cu(II) ions and complexed Cu(II) ions under the influence of the electric field. A decrease of 13.5% (after 8 hours at Cu 500 mg L⁻¹ and at pH 3.5) in the electrolytic recovery of copper, in the presence of 2,4,5-T (50 mg L⁻¹), is a clear indication that the chemistry of the process has changed and the difference in ion transportation coupled with an increase in activation energy for cathodic deposition ultimately reduced the recovery of copper. The formation of a complex between Cu(II) and the carboxylate group in 2,4,5-T can be shown by changes in both the UV spectrum of 2,4,5-T containing different concentration of Cu(II) (Fig. 2a) and the ESR spectrum of 2,4,5-T on addition of copper [20]. Complete recovery of copper, in the presence of 2,4,5-T, was not achieved even after 10 h.

3.2.2. Effect of Cu(II) ions on the anodic oxidation of 2,4,5-T

A set of experiment was conducted using the electrolytic cell system to oxidise 2,4,5-T (50 mg L⁻¹) in the absence and presence of Cu(II) ions (100 mg L⁻¹) at pH 3.5, the optimum pH for the photocatalytic degradation of 2,4,5-T. The results indicated that the electrolytic

system can not be used to achieve complete mineralisation and only 46.8% degradation of 2,4,5-T was achieved after 8 hours in the absence of copper ions (Fig. 3a). It can be noticed that there is an increase in the absorbance values after 6 hours and this could be due to the formation of some stable photoproducts. The degradation of 2,4,5-T was increased from 46.8 to 54.5% after 8 hours in the absence and presence of H₂O₂ respectively. On the other hand, the addition of copper ions (100 mg L⁻¹) decreased the electrooxidation of 2,4,5-T and the degradation after 2 h was 10.5% in the absence of Cu(II) but this reduced to 7.3% in the presence of Cu(II) (Table 2). The corresponding values after 8 h are 46.8 and 22.6% respectively. The percentage recovery of copper after 2 and 8 h is 25.3 and 78.6% respectively. The changes in the UV spectra of 2,4,5-T solution containing copper as a function of time during the electrolytic recovery of copper and the degradation of 2,4,5-T are given in Fig. 3b. The data in Table 2 show that the addition of H₂O₂ as an oxidant increases both the degradation of 2,4,5-T (by combined chemical and electrooxidation) and the percentage recovery of copper (by reducing the amount of complexing ligand). The results indicated that the electrolytic cell system alone can not be used to achieve the complete recovery of copper and degradation of 2,4,5-T.

3.3. Combined photolytic - electrolytic cell system

The research work conducted on the simultaneous recovery of copper and the degradation of 2,4,5-T using model aqueous solutions containing 100 mg L⁻¹ Cu(II) and 50 mg L⁻¹ 2,4,5-T at pH 3.5 revealed that the photolytic cell system, in the presence of H₂O₂, is capable of achieving 68.7% degradation of 2,4,5-T with zero recovery of copper after 8 h whilst the electrolytic cell system, in the presence of H₂O₂, is capable of achieving 94.8% recovery of copper with only 25.3% degradation of 2,4,5-T. It is suggested that a combined photolytic and electrolytic cell system should achieve the simultaneous degradation of organic species and the recovery of metals in a total effluent clean up. The combined system can be

used to achieve complete mineralization of 2,4,5-T after 6 h in the absence of copper ions compared with 8 h in the photolytic cell system. The presence of 100 mg L⁻¹ of copper slightly decreases the degradation of 2,4,5-T but gives 93.7% degradation of 2,4,5-T and 79.5% recovery of copper in 8 h at pH 3.5. The addition of hydrogen peroxide (1.0% v/v) in the combined system increases the degradation of 2,4,5-T and also the percentage recovery of copper. The anodic oxidation of 2,4,5-T after 2 and 8 h is 35.7 and 99.9% respectively. Similarly, the percentage recovery of copper after 2 and 8 h is 49.1 and 88.5% respectively. This increased in 2,4,5-T degradation is attributed to (1) the continuous removal of copper at the cathode surface which ultimately reduces its effect on the photolytic oxidation and (2) the photooxidation and the electrooxidation processes occurring simultaneously in the combined system (Table 3).

3.4. Combined photolytic - activated carbon concentrator cell system

The simultaneous degradation of 2,4,5-T and the recovery of copper can also be achieved by using an activated carbon electrochemical concentrator system compared with a standard electrochemical cell system. Two nylon mesh pockets containing activated carbon granules (BDH, particle size 0.85-1.70 mm) were placed around the cathode surface. The basic concept of the concentrator cell is to achieve concentration of ions in electrolyte in an area close to the electrodes. This effectively creates a new cell with a concentrated electrolyte near the electrodes and this can lead to increase reaction efficiency. The data on the percentage degradation of 2,4,5-T and the recovery of copper from solution containing 100 mg L⁻¹ of Cu(II) and 50 mg L⁻¹ of 2,4,5-T using an activated carbon concentrator and combined photolytic - activated carbon concentrator cell systems are given in Table 4. The results show that the combined photolytic and activated carbon concentrator system is capable of destroying 2,4,5-T and at the same time recovering copper from mixed effluent streams. This system does not require the addition of H₂O₂ to achieve complete mineralisation of

2,4,5-T. The concentrator system is able to increase the concentration of ions near the electrodes which ultimately increases the reaction efficiency. Our results have also highlighted the importance of the configuration of the concentrator medium relative to the inter electrode gap. In order to achieve the maximum degradation of 2,4,5-T and the highest recovery of copper the gap between the concentrator medium and the electrodes must be kept to minimum and this arrangement would ultimately accelerate the effective ion transportation for maximum copper recovery. The concentrator system has three further advantages: (1) *in-situ* regeneration of activated carbon occurs in the system due to the production of H_3O^+ ions at the anode surface, (2) the effectiveness of activated carbon concentrator material is independent of pH of the solution and recovery of copper and the degradation 2,4,5-T can be achieved at any pH and (3) complete effluent clean-up can be achieved rapidly without the use of additional oxidants or catalysts. The additional initial cost incurred due to the incorporation of the concentrator material, granular activated carbon, in the electrolytic cell system is minimum compared to the benefits obtained due to the reduction in the treatment time from 8 h to 5 h. In addition, there is no need for additional oxidants or catalysts.

4. Conclusions

The conclusion of research on the simultaneous recovery of copper and the degradation of 2,4,5-T from model aqueous solutions using a photolytic, an electrolytic and a combined photolytic - electrolytic cell systems is summarised as follows:

- (1) An electrolytic cell system can be used to recover copper but is not capable of achieving the complete anodic oxidation of 2,4,5-T.
- (2) A photolytic cell system can achieve 2,4,5-T degradation but leaves copper ions in solution. The presence of Cu(II) reduces the degradation of 2,4,5-T and complete mineralisation can only be achieved in the presence of TiO_2 suspension or H_2O_2 .

- (3) The use of combined photolytic - electrolytic cell can, however, lead to the simultaneous recovery of copper and the degradation of 2,4,5-T. The addition of H₂O₂ is necessary to achieve the complete recovery of copper and the degradation of 2,4,5-T.
- (4) Similar results to that of the combined photolytic – electrolytic system can also be achieved by using an activated carbon electrochemical concentrator cell system.
- (5) The degradation of 2,4,5-T and the recovery of copper can be further improved by combining the photolytic and activated carbon concentrator cell systems. This system does not require the addition of H₂O₂ to achieve the complete recovery of copper and the degradation of 2,4,5-T.

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Figure Captions

Fig. 1 - Effect of UV-irradiation source on the degradation of 2,4,5-T in the absence and presence of TiO₂ suspension. Experimental conditions: [2,4,5-T]₀ 50 mg L⁻¹; [TiO₂] 0.1% w/v; pH 3.5; solution volume 10 L; irradiation time 8 h.

Fig. 2 - a) UV spectra of 2,4,5-T containing Cu(II) ions a) as a function of concentration between 2,4,5-T (constant concentration of 50 mg L⁻¹) and Cu(II) ions (variable concentration between 100-500 mg L⁻¹) and b) as a function of time using a photolytic cell system. Experimental conditions: [Cu(II)]₀ 100 mg L⁻¹; [2,4,5-T]₀ 50 mg L⁻¹; [TiO₂] 0.1% w/v; UV source 400 W; pH 3.5; solution volume 10 L; irradiation time 8 h.

Fig. 3 - UV spectra of 2,4,5-T as a function of time using an electrolytic cell system a) in the absence and b) in the presence of Cu(II) ions. Experimental conditions: [Cu(II)]₀ 100 mg L⁻¹; [2,4,5-T]₀ 50 mg L⁻¹; pH 3.5; solution volume 10 L; current density 10 A m⁻²; reaction time 8 h.

Fig. 4 – UV spectra of 2,4,5-T containing Cu(II) ions as a function of time using a) combined photolytic - electrolytic cell system and b) combined photolytic -activated carbon concentrator cell system. Experimental conditions: [Cu(II)]₀ 100 mg L⁻¹; [2,4,5-T]₀ 50 mg L⁻¹; pH 3.5; solution volume 10 L; current density 10 A m⁻²; UV source 400 W; absence of an oxidant (H₂O₂) or photocatalyst (TiO₂); reaction time 8 h.