

Decolorization Treatment of Copper Phthalocyanine Textile Dye Wastewater by Electrochemical Methods

K. Dermentzis ^{*,1}, E. Valsamidou ², C. Chatzichristou ¹ and S. Mitkidou ¹

¹Dpt of Science, Laboratory of Chemical Technology - Electrochemistry, Kavala Institute of Technology,

²Dpt of Petroleum and Natural Gas Technology, Laboratory of Environment Protection, Kavala Institute of Technology, 65404 Agios Loukas, Kavala, Greece,

Received 25 June 2012; Accepted 15 January 2013

Abstract

Electrochemical decolorization and degradation treatment of aqueous copper phthalocyanine reactive dye solutions was comparatively studied by electrocoagulation, electrooxidation and electro-Fenton processes. In the electrocoagulation process with aluminum electrodes the colored aqueous solutions of initial pH 6.4 containing 50 mg L⁻¹ copper phthalocyanine and 6 g L⁻¹ NaCl were treated at applied current densities of 2.5 and 5 mA cm⁻². Fast and 100% decolorization was achieved in 4 and 2 minutes of electroprocessing respectively. The indirect electrooxidation process was conducted in acidic electrolyte solutions containing 50 mg L⁻¹ copper phthalocyanine and 6 g L⁻¹ NaCl with Ti/Pt and graphite plate electrodes at the applied current density of 10 mA cm⁻². Even after 90 minutes of electrolysis time the dye remained by 23 and 18.8 % respectively undegradable. By the direct and indirect electrooxidation with the same amount of Na₂SO₄ electrolyte and added H₂O₂ respectively and using the same electrodes, the copper phthalocyanine dye was not or was only barely degraded respectively. In the electro-Fenton process with Fe electrodes and added amounts of H₂O₂ at pH 3 and an applied current density of 5 mA/cm² complete degradation of copper phthalocyanine occurred in 15 minutes.

Keywords: Dye decolorization, electrocoagulation, electro-Fenton, electrooxidation, phthalocyanine

1. Introduction

The textile industry consumes enormous amounts of water during dyeing and finishing operations. Typical medium-scale textile factories produce approximately 1000 m³ of wastewater per day. Dye bearing wastewaters are toxic for the environment since dyes are stable compounds with low biodegradability and may cause carcinogenesis. Even 1-2 mg L⁻¹ of dye in water is highly visible affecting the water transparency and the gas solubility of water bodies.

The water soluble sulfonated phthalocyanine reactive dyes yield brilliant turquoise and green colors not available from any other dye category [1]. The most important reactive phthalocyanine dyes are anionic aromatic compounds which contain copper or nickel as their central atoms. Sulfonated phthalocyanines are synthesized by heating phthalic acid at 170-190 °C in the presence of urea and nitrobenzene using CuCl₂/ammonium molybdate catalyst and subsequent direct sulfonation with oleum or sulfuric acid [2]. Figure 1 shows the chemical structure of the dye copper phthalocyanine tetrasulfonic acid tetrasodium salt (Cu-pc).

Metallophthalocyanines are widely used in the pigment industry for many things including printing inks, paints, painting, coating, enamels, plastics, textiles, linoleum and rubber goods [3]. Recently, metallophthalocyanines have

been reported in literature to support the electro-oxidation of methanol in direct fuel cells [4]. They also exhibit an anti-HIV activity by blocking infection and preventing the fusion of HIV envelop proteins to host cells [5].

Common methods for treatment and remediation of dye bearing wastewaters are oxidative processes such as chlorination or ozonation [6], advanced oxidation processes such as Fenton, photo-Fenton [7-9], photocatalytic [10] sonochemical processes [11] and biological processes.

The discharge of dye waste and effluent containing parent phthalocyanines or their sulfonated metal complexes remains a problem. Conventional biological and oxidation treatment processes are often less successful because these dyes are barely or non biodegradable [9, 12]. Degradation of copper phthalocyanines by heterogenous or homogenous photocatalytic processes [13] and UV irradiation in the presence of H₂O₂ [8, 9] have been reported.

Electrochemical processes for pollution abatement have been proved viable alternatives or complementary to biological treatment in some instances, especially when pollutants are recalcitrant to biological processing. They are based mainly on direct anodic oxidation at dimensionally stable electrodes [14, 15], advanced electrochemical oxidation [16, 17] and electrocoagulation with sacrificial aluminium or iron electrodes [18-20]. The advantages of electrochemical treatment are various and well documented:

* E-mail address: demerz@otenet.gr

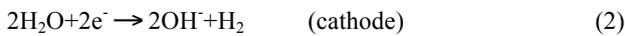
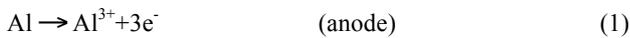
the catalyst/electrode is immobilized i.e. without the need to separate the catalyst from the reaction mixture, the variables such as current and potential are easily controlled facilitating automation of the process.

To the best of our knowledge, literature does not mention any study on electrochemical decolorization treatment of the reactive dye copper phthalocyanine tetrasulfonic acid tetrasodium salt. What is reported refers to electrocoagulation of the non sulfonated parent copper phthalocyanine [21], photo-degradation of di- or tetrasulfonated phthalocyanine [8, 9, 13] and ultrasound degradation of parent phthalocyanine [11].

The present paper discusses an integrated electrochemical decolorization/degradation treatment of the Cu-pc dye, which comprises electrocoagulation with aluminium sacrificial electrodes, direct and indirect anodic oxidation at dimensionally stable Ti/Pt and graphite anodes in NaCl and Na₂SO₄ electrolyte solutions and advanced electrochemical oxidation using the electro-Fenton process with iron sacrificial anode and added amounts of hydrogen peroxide. The efficiencies of the three different electrochemical processes are compared and evaluated.

1.1 Electrocoagulation

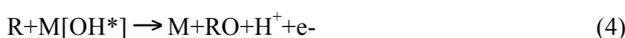
Electrocoagulation is a process consisting of creating metallic hydroxide flocs inside the wastewater by electrodisolution of soluble anodes made of aluminum or iron. The main reactions occurring during electrocoagulation produce aluminum ions at the sacrificial anode and hydroxide ions as well hydrogen gas at the cathode:



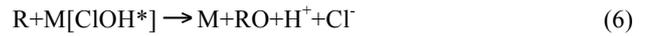
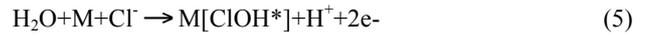
The generated Al³⁺ and OH⁻ ions react to form various monomeric and polymeric species such as Al(OH)²⁺, Al(OH)₂⁺, Al₂(OH)₂⁴⁺, Al(OH)₄⁻, Al₆(OH)₁₅³⁺, Al₇(OH)₁₇⁴⁺, Al₈(OH)₂₀⁷⁺, Al₁₃O₄(OH)₂₄⁷⁺, Al₁₃(OH)₃₄⁵⁺ which finally result in situ formation of gelatinous Al(OH)₃ effecting the coagulation and coprecipitation or H₂ flotation of particulates from the solution by adsorption [19].

1.2 Anodic oxidation

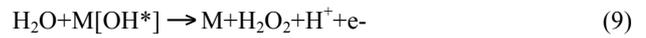
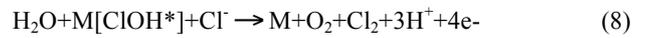
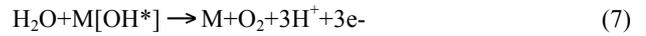
Organic matter can be anodically destroyed in two different mechanisms, namely: direct electrooxidation, where the pollutants are adsorbed on the anode surface and destroyed by the electron transfer reaction and (b) indirect electrooxidation in the liquid bulk by the electrochemically mediated oxidants, such as chlorine, hypochlorite, hydroxyl radicals, ozone and hydrogen peroxide. In anodic oxidation organic pollutants are attacked by the absorbed hydroxyl radicals formed as intermediates from water oxidation to O₂ at the surface of dimensionally stable anodes (graphite, Pt, TiO₂, IrO₂, PbO₂ or boron doped diamond electrodes).



In the presence of NaCl, chlorohydroxyl radicals are also formed on the anode surface which then oxidize the organic matter:



Reactions between water and radicals near the anode can yield molecular oxygen, free chlorine and hydrogen peroxide:



Furthermore, hypochlorite can be formed as follows:



Where M, R and RO represent the anode surface, organic matter and oxidized organic matter respectively.

The radicals OH* , O* and ClOH* have very high oxidation potential and therefore very short half-lives. They are either converted to other oxidants, such as Cl₂, O₂, ClO₂, O₃ and H₂O₂ or oxidize organic contaminants. The primary oxidants Cl₂, O₂ and the secondary ones ClO₂, O₃ and H₂O₂ produced from the destruction of radicals have longer half-lives and diffuse into the bulk solution away from the electrode where they continue the oxidation process [14, 22] (indirect oxidation).

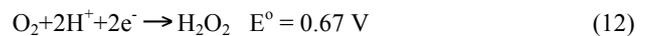
1.3 Electro-Fenton process

Fenton's reagent is an acidic mixture of hydrogen peroxide and Fe²⁺, where free hydroxyl radicals with high oxidative power are produced as follows;



Recently, the Fenton's reagent has been produced in situ electrochemically (electro-Fenton) in two ways:

(a) by addition of a catalytic amount of Fe²⁺ ions, reduction of oxygen and regeneration of Fe²⁺ on a suitable cathode in acidic media:



and

(b) by addition of H₂O₂ and electrochemical production of Fe²⁺ ions with a sacrificial Fe anode according to the anodic reaction:



In this case, a part of Fe³⁺ ions is produced from Fenton's reaction (3) between supplied H₂O₂ and electrogenerated Fe²⁺ which precipitates as Fe(OH)₃. Therefore, the organic pollutants can be removed by oxidation with OH* radicals and simultaneously by electrocoagulation with the Fe(OH)₃ precipitate [16, 22].

2. Experimental

2.1 Chemicals

NaCl, Na₂SO₄ and H₂O₂ were of analytical grade (Merck). pH was adjusted with 0.1 M solutions of H₂SO₄ and NaOH as required. The reactive dye Cu-pc (Mr = 988.28) was purchased from Aldrich. Its structure is shown in Figure 1.

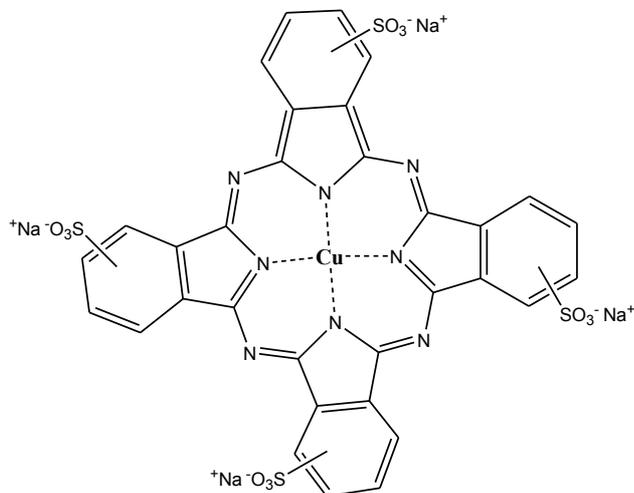


Fig. 1. Chemical structure of reactive dye copper phthalocyanine tetrasulfonic acid tetrasodium salt (Cu-pc), Mr: 988.28, Molecular Formula: C₃₂H₁₆N₈O₁₂CuNa₄S₄

2.2 Apparatus

A laboratory model DC power supply apparatus (Agilent E3612A, USA) was used to measure voltage and current and maintain constant DC current. Conductivity was measured by means of a conductometer (inoLab Cond. Level 1, WTW). pH was measured by a WTW pH-meter. Electrolyses were conducted at room temperature in a cylindrical glass cell of 500 ml and the solution was rigorously stirred with a magnetic bar at 500 rpm. The electrodes used for electrooxidation were two platinized titanium plates (Ti/Pt), while for electrocoagulation and electro-Fenton two aluminium and two iron plates respectively (obtained commercially) were used with an effective area of 30 cm² each.

2.3 Analytical Procedures

Hitachi 2000 (Japan) UV-Vis Spectrophotometer was used for spectrographic analysis of dye concentrations. Known concentrations of the Cu-pc dye solution were scanned at optimum absorption wavelength of 613 nm wavelength for generating the calibration plot. The equation used to calculate the percentage of color removal efficiency (R%) was:

$$R\% = \frac{C_o - C}{C_o} \times 100 \quad (1)$$

where C_o and C are the initial and final concentrations of the dye in solution in mg L⁻¹ respectively.

Samples were diluted using distilled water if the absorbance exceeded the range of calibration curve. All

samples were filtered using polytetrafluorethylene filters with a pore size of 0.45 μm (Whatman).

2.4 Experimental Procedures

All electrochemical experiments: electrocoagulation, electrooxidation and electro-Fenton were conducted in the 500ml electrochemical reactor. The interelectrode distance was 1.5 cm. During the indirect electrooxidation and electro-Fenton processes H₂O₂ was added to the reactor continuously. The concentrations of Na₂SO₄ and NaCl were 6 g L⁻¹. The applied current densities were 2.5 and 5 mA cm⁻² for electrocoagulation, 10 mA cm⁻² for electrooxidation and 5 mA cm⁻² for electro-Fenton. pH was not adjusted for electrocoagulation, while for electrooxidation and electro-Fenton experiments it was adjusted to 3.

3. Results and discussion

3.1 Removal of Cu-pc by electrocoagulation

The electrocoagulation process for decolorization of the Cu-pc wastewater was investigated using aluminum electrodes as anode and cathode at different current densities in 6 g L⁻¹ NaCl electrolyte solution. According to Fig. 2, for the two current densities 2.5 and 5 mA cm⁻² the initial concentration of 50 mg L⁻¹ Cu-pc fell under the detection limit (0.008 mg L⁻¹) in 4 and 2 minutes of electrolysis time respectively. The removal rate is faster with increasing current density. This is a presumable phenomenon, as the current density determines the coagulant dosage rate, the bubble production and the flock size and growth [23]. The initial solution pH of 6.4 changed to 7.6, i.e. no significant pH change was observed during electroprocessing. This is due to the buffering species Al(OH)₃/Al(OH)₄⁻ which is formed during the electrocoagulation process [24].

During the electrocoagulation process the Cu-pc dye is not destructed. The dye molecule consisting of both, the metallic copper central atom and the organic ligand is absorbed and relocated as a whole in the electro-generated Al(OH)₃ precipitate. Consequently, the effluent after electrocoagulation contains no copper or other heavy metal ions. The concentration of aluminum ions originated from the electro-generated Al(OH)₃ flocs is in the appropriate range for effluent discharge.

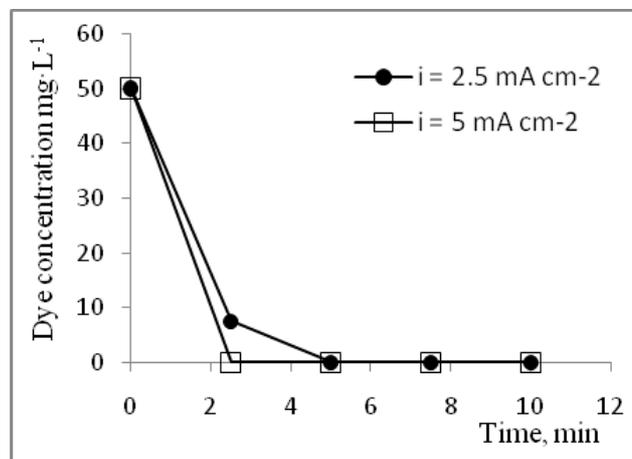


Fig. 2 Residual dye concentration versus time during electrocoagulation of Cu-pc at different applied current densities.

The electrical energy consumption for electrocoagulation treatment at the two current densities 2.5 and 5 mA cm⁻² calculated from the Faradaic equation (2):

$$E = \frac{U \cdot I \cdot t}{m} \quad (2)$$

where

U = voltage (Volts)

I = current intensity (A)

t = time (s)

m = mass of dye removed from wastewater.

are 0.460 and 0.683 Kwh/Kg of dye removed respectively.

3.2 Indirect electrooxidation in NaCl electrolyte solution

The indirect electrooxidation of Cu-pc dye was carried in 6 g L⁻¹ NaCl electrolyte solution with Ti/Pt and graphite plate electrodes at the current density of 10 mA cm⁻². As already stated, electrooxidation conducted in the presence of NaCl leads to the formation mainly of free chlorine in acidic conditions and to hypochlorite in slightly alkaline conditions. Both, chlorine and hypochlorite are known strong oxidizing agents which cause oxidative degradation of organic substances in the bulk solution. According to Fig. 3, however, the initial dye concentration of 50 mg L⁻¹ was only slowly and partially degraded. Even after 90 minutes of electroprocessing with Ti/Pt and graphite plate electrodes 11.4 and 9.4 mg L⁻¹ of the dye remained respectively undegradable. The Cu-Pc complex is a very stable and recalcitrant dye. [6, 11]. Therefore, this electrochemical method by electrooxidation for degradation of Cu-pc is not energy efficient.

The degradation of Cu-Pc is faster at graphite than at Ti/Pt electrode. Unlike Ti/Pt the graphite electrode promotes the electrooxidation of Cl⁻ ions to free Cl₂ rather than the electrooxidation of H₂O to O₂.

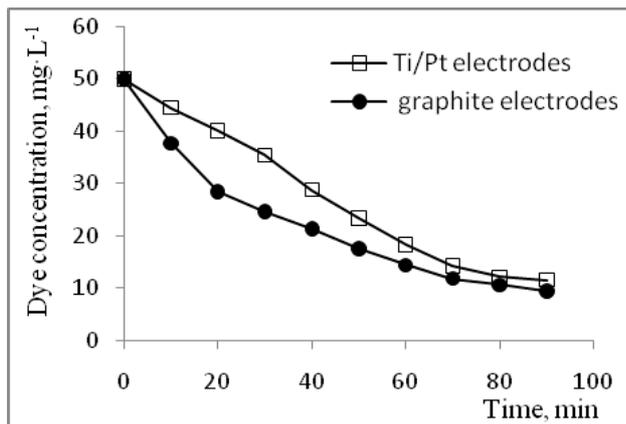


Fig. 3. Residual dye concentration versus time during direct electrooxidation of Cu-pc in NaCl electrolyte at different electrodes

The decolorization-degradation of such binary metallic-organic dyes like Cu-pc by electrooxidation present another drawback. Only the organic ligand is destructed, while the heavy metal ions are released in the treated solution. The effluent after electrooxidation contains 6 mg/L Cu²⁺ ions and for their removal it needs further treatment, such as ion exchange, chemical precipitation [25], membrane assisted electrodeionization [26], membrane-less electrostatic

shielding based electro dialysis/electrodeionization [27], or electrocoagulation [20, 28, 29].

3.3 Direct and indirect electrooxidation in Na₂SO₄ electrolyte and added H₂O₂ solution

The degradation treatment of Cu-Pc from aqueous solution of 50 mg L⁻¹ was investigated by direct electrooxidation at platinized titanium (Ti/Pt) electrodes as anode and cathode and graphite plate electrodes as anode and cathode as well. Na₂SO₄ (6 g L⁻¹) was used as supporting electrolyte to increase the solution conductivity and therefore reduce the resistance and the electrical energy consumption. H₂SO₄ was added to the dye solution until it reached pH = 3. For the indirect electrooxidation also H₂O₂ was added to the treated solution. The applied current density was held at 10 mA cm⁻².

As can be obtained from Figs 4 and 5 the Cu-pc dye can not be oxidized anodically neither at Ti/Pt nor at graphite plate electrodes. Only by the indirect electrooxidation at Ti/Pt electrodes and supplied H₂O₂ the initial concentration of 50 mg L⁻¹ of dye fell slightly to 46 mg L⁻¹ in 60 minutes (Fig. 4).

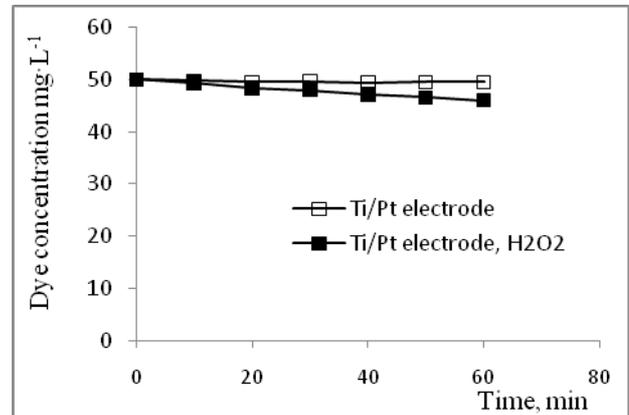


Fig. 4. Residual dye concentration versus time during direct and indirect electrooxidation of Cu-pc at Ti/Pt electrodes

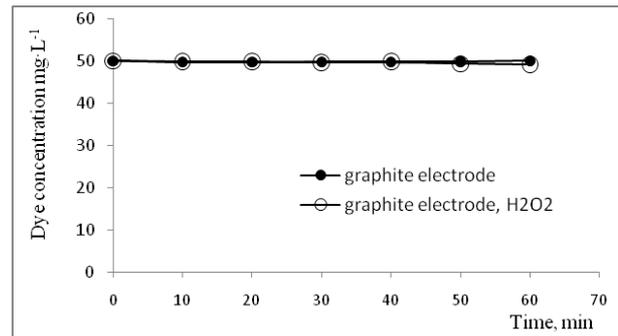


Fig. 5. Residual dye concentration versus time during direct and indirect electrooxidation of Cu-pc at graphite electrodes

3.4 Degradation of Cu-pc by advanced electro-Fenton oxidation

Fenton reagent is generally conducted in acidic solutions with pH values ranging from 2 to 4 with pH = 3 being the optimum. Hence, the dye solution was acidified with H₂SO₄ until it reached pH = 3. The electro-Fenton experiment was conducted at the applied current density of 5 mA/cm² with iron plate electrodes as anode and cathode and adding 2 ml of H₂O₂ 1M solution every 5 minutes during electroprocessing. The solution pH tending to increase

slightly during the process was monitored and adjusted with a dilute NaOH solution to the optimal pH value of 3. Fig. 6 shows that the initial concentration of 50 mg L⁻¹ Cu-pc dye was completely decolorized and degraded in 15 minutes of electrolysis time. Compared to the direct and indirect electrooxidation with Na₂SO₄ and NaCl electrolytes respectively the electro-Fenton process is faster, due to the fast reaction of the Cu-pc dye and its oxidation products with the very reactive OH* radicals generated from chemical reaction (11).

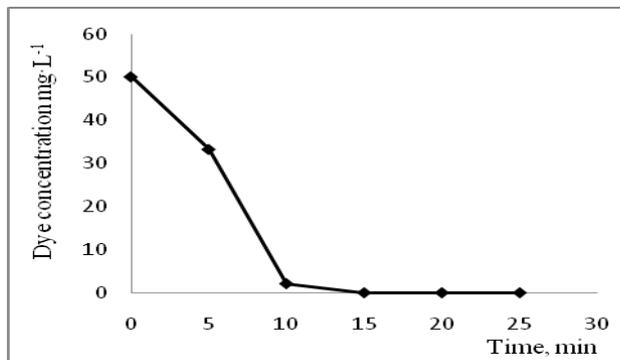


Fig. 6. Residual dye concentration versus time during the advanced electro-Fenton oxidation of Cu-pc with Fe electrodes and added H₂O₂

In addition to electro-Fenton degradation the Cu-pc dye or its organic intermediates can partially be absorbed and coprecipitate with the generated Fe(OH)₃ flocs and therefore be removed by electrocoagulation as already pointed out. Here, however, this way of dye removal by electrocoagulation is slow because of the low solution pH.

The electrical energy consumption for complete dye degradation after 15 minutes of electrolysis time at the applied current density of 5 mA cm⁻² is 3.296 Kwh/Kg of dye removed.

4. Conclusions

References

- Ullman's Encyclopedia of Industrial Chemistry A22, Phthalocyanine Dyes, 5th Eds, Wiley-VCH, p.660.
- Linstead R.P., Weiss F.T., *J. Chem. Soc.* (1950) 2975.
- Stillman M.J. & Nyokong T., Phthalocyanines: Properties and Applications, in: C. Leznoff, A.B. Lever (Eds.), VCH, New York. (1989), p.133.
- Jingjie W., Haolin T., Mu P., *Electrochem. Acta* 54 (2009) 1473.
- Vzorov A.N., Marzilli L.G., Compas R.W., Dixon D.W., *Antiviral Res* 59 (2003) 99.
- Perkins W.S., Namboodri C.G., Walsh W.K., *Chem Oxid* 3 (1993) 202.
- Georgiou D., Melidis P., Aivasidis A., Gimouhopoulos K., *Dyes Pigm.* 41 (1999) 211.
- Dos Santos A.C.V., Masini J.C., *J. Braz. Chem. Soc.* 20 (2009) 1800.
- Shu H-Y., Chang M-C. *J. Hazard. Mater.* B125 (2005) 96.
- Height M.J., Pratsinis S.E., Makasumwandrumong O., Praserttham P., *Appl. Catal. B: Environ.* 63 (2006) 305.
- Tu S.P., Kim D., Yen T.F., *J. Environ. Eng. Sci.* 1 (2002) 237.
- Beydill M.I., Matthews R.D., Pavlostathis S.G., *Water Sci. Technol.* 43 (2001) 333.
- Caliman A.F., Berberidou Ch., Lazar L., Poullos I., Macoveanu M., *Environm. Engin. Manag. J.* 6 (2007) 85.
- Chatzisyneon E., Xekoukoulotakis N.P., Coz A., Kalogerakis N., Mantzavinos D., *J. Hazard. Mater.* B137 (2006) 998.
- Gotzi M., Kalogerakis N., Psillakis E., Samaras P., Mantzavinos D., *Water Res.* 39 (2005) 4177.
- Oturan M.A., Brillas E., *Portugal. Electrochim. Acta* 25 (2007) 1.
- Wang A., Qu J., Ru J., Liu H., Ge J., *Dyes Pigm.* 65 (2005) 227.
- Arslan-Alaton I., Kabdasli I., Vardar B., Tünay O., *J. Hazard. Mater.* 164 (2009) 1586.
- Koby M., Can O.T., Bayramoglu M., *J. Hazard. Mater.* B100 (2003) 163.
- Körbahti B.K., Artut K., Gecgel C., Öyer A., *Chem. Engin. J.* (2011) Doi: 10.1016/j.cej.2011.02.018.
- Phalakornkule C., Polgumhang S., Tongdaung W., Karakat B., Nuyut T., *J. Environ. Manage.* 91 (2010) 918.
- Yatmaz H.C., Uzman Y., *Int. J. Electrochem. Sci.* 4 (2009) 614.
- Koshla N.K., Venkachalam S., Sonrasundaram P., *J. Appl. Electrochem.* 21 (1991) 986.
- Can O.T., Bayramoglu M., Koby M., (2003), *Ind. Eng. Chem. Res.* 42, 3391.
- Tünay O., Kabdasli N.I., *Water Res.* 28 (1994) 2117.
- Lu H., Wang J., Bu S., Fu L., *Separ. Sci. Technol.* 46 (2011) 404.
- Dermentzis K., Davidis A., Dermentzi A., Chatzichristou C., *Water Sci. Technol.* 62 (2010) 1947.
- Dermentzis K., Christoforidis A., Valsamidou E., *Int. J. Environ. Sci.* 1 (2011) 696.
- Akbal F., Camci S., *Environ. Progr. Sust. Energy* 30 (2011) n/a, doi:10.1002/ep.10546.

A study for decolorization/degradation of copper phthalocyanine reactive dye was investigated using electrochemical methods such as electrocoagulation, direct and indirect electrooxidation and electro-Fenton processes. Based on the results, following conclusions can be drawn:

- The dye is recalcitrant and barely degradable by direct and indirect electrooxidation treatment using Ti/Pt and graphite plate electrodes in acidic medium with Na₂SO₄ electrolyte and added H₂O₂ respectively.
- The electrooxidation process was improved by substituting Na₂SO₄ with the same amount of NaCl, due to indirect electrooxidation of the dye in the bulk solution by the anodically generated chlorine and hypochlorite. The initial dye concentration of 50 mg L⁻¹ fell to 11.5 and 9.4 mg L⁻¹ after 90 minutes of electrolysis time for the treatment with Ti/Pt and graphite plate electrodes respectively. The process is slow and not energy efficient. In addition, only the organic ligands of the metalocyanine complex are destructed, while Cu²⁺ ions are released to the treated solution. The effluent, therefore, needs further treatment.
- The electro-Fenton process with Fe electrodes and supplied H₂O₂ in acidic solution is a more efficient method for degradation of copper phthalocyanine dyes. 100% degradation of the dye was achieved in 15 minutes. The energy consumption was 3.296 Kwh/Kg of dye removed.
- The electrocoagulation process with Al electrodes is the fastest and more efficient method for decolorization of aqueous copper phthalocyanine solutions achieving 100% color removal in less than 4 and 2 minutes at applied current densities of 2.5 and 5 mA cm⁻² with the corresponding energy consumptions 0.460 and 0.683 Kwh/Kg of phthalocyanine removed from wastewater. In this process the dye is not degraded but absorbed and relocated in the Al(OH)₃ precipitate.