Reductive Photocatalytic Degradation of Triclosan by UV Light and P25: Influence of Experimental Parameters

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Abstract: *Concentration of emerging pollutant entering into the environment from the use of personal care products is increasing rapidly. One such pollutant is triclosan (5-chloro-2-(2,4 dichloropheonxy)phenol. Few oxidation methods and AOPs are tried by some researchers for triclosan degradation. But reports related to reductive dechlorination of triclosan are very scares. In this study an attempt has been made to use reductive photocatalytic dechlorination of triclosan using TiO_2 (P25) and UV light. Oxalic acid was found to be best hole-scavenger among the different organic hole-scavengers tried. Alkaline pH gave better removal compare to acidic pH. Under optimum condition, almost complete removal of triclosan was obtained after 120 mins of irradiation time. GC-FID analysis and pH monitoring during the reaction indicates that the probable pathway for triclosan degradation was reductive dechlorination.*

Keywords: *Triclosan, Photocatalytic reduction, Hole scavengers, Reducing radicals*

I. INTRODUCTION

In recent years there has been increasing concern regarding emerging pollutants entering into the environment through the use of products for different purposes like personal care, surfactants, flame retardants and water treatment. Most of these pollutants belong to the unregulated contaminants [1]. One such example of emerging pollutant is triclosan, 5-chloro-2-(2, 4 dichloropheonxy)phenol. It is extensively used in household cleaners, skin care creams, soaps and toothpastes as a broad spectrum antimicrobial and preservative agent. It is also used in socks, under garments, and toys due to its capacity of inhibiting microbial growth. Triclosan is bacteriostatic at low concentrations, but higher levels are bactericidal [2]. At sub-lethal concentrations, it acts by inhibiting the activity of the bacterial enoyl-acyl carrier protein reductase (FabI), a critical enzyme in bacterial fatty acid biosynthesis [3-4]. At bactericidal concentrations, it is suggested to act through multiple nonspecific mechanisms including membrane damage [5]. Approximately 1500 t of triclosan is produced annually worldwide [6-7]. Up to 96% of triclosan can come in to the sewerage system during normal use, and ultimately come in to the aquatic environment [8]. Incomplete removal of triclosan from wastewater treatment plants (WWTPs) as well as spreading the triclosan laden biosolids into soils, leads to triclosan being distributed in soil and surface waters. This poses a potential environmental and ecological hazard, particularly for aquatic systems. In a study on effluent from wastewater treatment facilities, approximately 75% of triclosan was present in sludge [9]. Triclosan can attach to other substances suspended in aquatic environments, which potentially endangers marine organisms and may lead to further bioaccumulation. Table 1 shows environmental concentration of triclosan. Increase in concentration of triclosan can involve serious environmental implications derived from its toxicity to several aquatic organisms like algae (Scenedesmus subspicatus) [10], fish (LV50 rainbow trout=0.35 mg/L) [11] or micorganisms like Daphnia magna (EC50=0.39mg/L[11].Attention has been drawn to triclosan and its degradation products recently due to their chemical structural similarity with highly toxic contaminants, such as dioxins. Although triclosan is regarded as a compound with low toxicity, it is a precursor for formation of the more toxic dioxin. Studies suggested that triclosan can be undergone cyclization to form 2,8-dichlorodibenzo-p-dioxin (2,8-Cl_2DD) in aqueous solution under UV irradiation [8,12]. Moreover, presence of triclosan in water can lead to formation of chloroform and related trihalomethanes as well as chlorinated dioxins during disinfection using chlorine [13].

To remove triclosan several researcher have proposed chemical oxidation using chlorine [13] and ozonation [6]. AOP's like Fenton [1, 14] and photocatalytic oxidation [15-16] has also been used. But these methods have shown some draw backs. Chlorination can produce highly toxic by-products, while oxidation which is considered to be a destructive pathway of pollutant removal can produce toxic dioxins.

Reduction is considered to be a selective method for degradation of pollutant. Photocatalytic reduction has been an under explored mechanism of photocatalysis. When photocatalyst is irradiated by light of sufficient energy to overcome the band gap of the catalyst, electron and hole are produces as shown in eq. (1)

$$TiO_2 + h\nu \rightarrow e_{cb}^- + h_{vb}^+ \quad (1)$$

Valence balance electron is responsible for photocatalytic reduction (PCR) of the pollutant, while the hole either directly or indirectly through production of hydroxyl radical will cause photocatalytic oxidation (PCO). Any one of the mechanism can be enhance by using a suitable scavenger. PCR can be enhance by using hole scavengers/electron donors which would trap the hole there by making more electron available for PCR. Oxygen can act as an electron acceptor, so oxygen free environment is preferred for PCR.

In this study reductive dechlorination of triclosan has been tried using P25 (TiO_2) and UV light. Effect of types of hole-scavenger and initial pH of the solution has been studied. PCO of triclosan using TiO_2 has been found in the literature but PCR of triclosan has not been reported to best of our knowledge.

Table1: Environmental concentration of triclosan [5]

Environmental Matrix	Triclosan Concentration
Surface water (lake/river streams with known input of raw wastewater)	1.4 ng/L-40000 ng/L
Wastewater Influent	20-86161 ng/L
Wastewater Effluent	23-5370 ng/L
Sea water	<0.001-100 ng/L
Sediment(Lake/River/other surface water)	<100-53000 µg/kg (Dry Weight)
Sediment(Marine)	0.02-35 µg/kg ((Dry Weight)
Biosolid from WWTP	20-133000 µg/kg (Dry Weight)
Activated/digested sludge	580-15600 µg/kg
Pore water	0.201-328.8µg/L (calculated)

II. MATERIALS AND METHODS

TiO_2 (P25) (>99.5%) was obtained from Evonik (formerly known as Degussa) in powder form. Formic acid (HCOOH, 98%), oxalic acid ($H_2C_2O_4.2H_2O$) supplied by Merck were of analytical standard (Guaranteed Reagents). Triclosan (Irgasan) ($C_{12}H_7Cl_3O_2$) (>97%) was supplied by Sigma-Aldrich and was of Analytical grade. Argon gas used was of 99.995% purity and was supplied by local supplier. All the solutions were prepared using distilled water.

Photocatalytic Experiments

Photocatalytic experiments were performed in the cylindrical acrylic reactor (60mmφ and 300 mm high). 500ml aqueous solution of triclosan with concentration of 20 mg/L was mixed with adequate quantity of photocatalyst TiO_2 (P25) and hole scavenger followed by stirring for 30 min in dark to obtain adsorption-desorption equilibrium. The mixture was then irradiated by 11W UV light ((Philips) UVC<254 nm) light located concentrically in the reactor for one hour. Argon gas was purged during the entire experiment. Contents of the reactor were mixed throughout the experiment by magnetic stirrer. 3 ml of suspension was sampled at regular interval for GC-FID analysis. All the experiments were carried out at room temperature (33±1 ˚C) with the reactor placed in a water jacket to limit the rise in temperature to < 1 ˚C of the initial temperature during the irradiation period. TiO_2 dose of 1.0 g/L was used in all the experiments unless specified. All the experiments were done in duplicates and average values are reported.

Analytical Method

The Collected samples were first acidified using 5 N H_2SO_4. The content of the test tube was thoroughly mixed by the vortex mixture. Subsequently the acidified samples were extracted thrice with 1 ml of cyclohexane

Gas chromatographic (GC) analysis was done using Bruker 456 model equipped with FID and DB-5 column (30 m × 0.32 mm ID × 0.25 µM film thickness). Oven temperature and ramp used are as used by Liu et al. (2013).The temperature program use for FID analyses was: GC oven temperature was held constant at 40˚C for 2 min, Temperature ramp 1: 40–250˚C at 10˚C /min, hold time 5 min, Temperature ramp 2: 250–280˚C at 15˚C /min, hold time 5 min Injector and detector temperatures were set at 260˚C and 300˚C, respectively. Injections were performed in split-less mode using nitrogen as carrier gas (gas velocity 25 cm/s). Injection volume was 1 µL

III. RESULTS AND DISCUSSION

Results of initial trial experiments using different hole-scavengers

Initial trial experiments for PCR of triclosan were tried using oxalic acid (2mM) as hole-scavenger. Oxalic acid was tried initially as it was found to be better Hole-scavenger compared to other in our previous study on PCR of azo dyes. pH of 20 mg/L triclosan containing 2mM OA was found to be 2.8. 96.7% of triclosan removal was found after 120 mins of irradiation. The rate of removal was very rapid initially with almost 71 % removal obtained in first 15 mins. Also dark adsorption was very significant ca. @48.5%. The reason for higher

dark adsorption has been discussed in the following section. When methanol and iso-propanaol were tried as hole-scavenger removal obtained was 74.999% and 79.32%. The removal obtained in both the cases was lesser than when oxalic acid was used as Hole-scavenger. Higher removal when oxalic acid was used, may be due to the fact that Oxalic acid can produce a strong reductant, i.e carboxyl anion radical $CO_2^{\bullet-}$ having normal potential E^0 ($CO_2/CO_2^{\bullet-}$) = -1.85 V [17]. It has more reduction potential than the electron (-1.5 V) produce by irradiation of TiO_2. Due to Carboxyl radical it may be acting as better hole-scavenger. In oxygen free atmosphere oxalate may be oxidized by photogenerated holes resulting in formation of CO_2 and $CO_2^{\bullet-}$ as shown in Eq. 2

$$C_2O_4^{2-} + h^+ \rightarrow CO_2 + CO_2^{\bullet-} \quad (2)$$

Another probable reason may be formation of oxalate radical $C_2O_4^{\bullet-}$ which has reduction potential of 2.1 V [18]. Due to formation of $CO_2^{\bullet-}$and $C_2O_4^{\bullet-}$ oxalic acid may have acted as a better hole scavenger and was used for further experiments

GC-FID chromatograms (Fig. 1) obtained at different time points shows decrease in peak corresponding to RT of triclosan (20.64 min) with formation of new peaks before the peak of triclosan. These peaks may be due to the intermediates formed during PCR of triclosan. To indentify the intermediates, chromatograms of phenol and 2 4 DCP were also obtained. Peaks corresponding to the retention time of both the intermediates (10.05 min for 2 4 DCP and 7.33 min for phenol) were not found in any of the trials. Yu et al (2006) [16] & Song et al. (2012)[14] detected 2 4 Dichlorophenol (2, 4 DCP) as an intermediate when the oxidative mechanism was used for triclosan removal. As 2, 4 DCP was not detected in any trials; probable pathway for removal of triclosan can be reduction. Son et al. (2009)[15] detected phenol using TiO_2 photocatalytic (oxidation). Absence of peak corresponding to phenol further indicates that probable pathway for removal of triclosan can be reduction. Literature shows that PCR of triclosan will not result in 2, 4 DCP. Wang et al. (2013) [19] found dichlorohydroxydiphenyl ether as reductive dechlorination product of triclosan by Chlorella pyrenoidosa. Knust et al (2010) [20] found intermediates like 5-chloro-2-(4-chlorophenoxy) phenol and 5-chloro-2-phenoxyphenol, as well as traces of 2-phenoxyphenol by using Electrochemical reduction of 5-chloro-2-(2,4-dichlorophenoxy)phenol (triclosan) in dimethylformamide. So from the published literature it could be said that degradation of triclosan is occurring through a reductive path way. The exact mechanism could be delineated only after identifying all the possible intermediates.

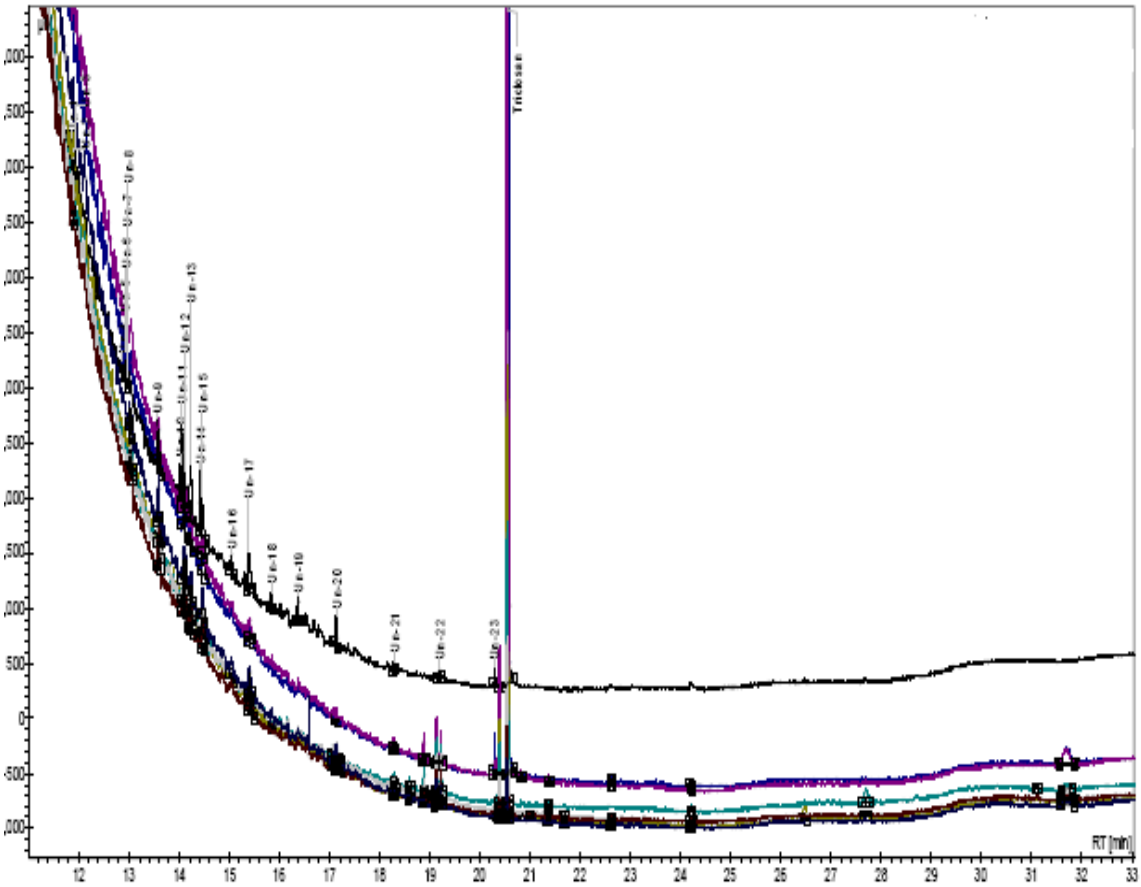

Figure1: GC –FID chromatogram at different time points during PCR of Triclosan
(*Reaction conditions*: Triclosan concentration: 20 mg/L; Oxalic acid concentration: 2mM; TiO_2 dose: 1g/L; pH 2.8)

Effect of initial pH on PCR of triclosan

To study the effect of pH on the photocatalytic degradation of triclosan, experiments were done at natural pH of 2mM oxalic acid and pH adjusted to 9. Fig 2 shows time course profile for triclosan degradation at different pH.

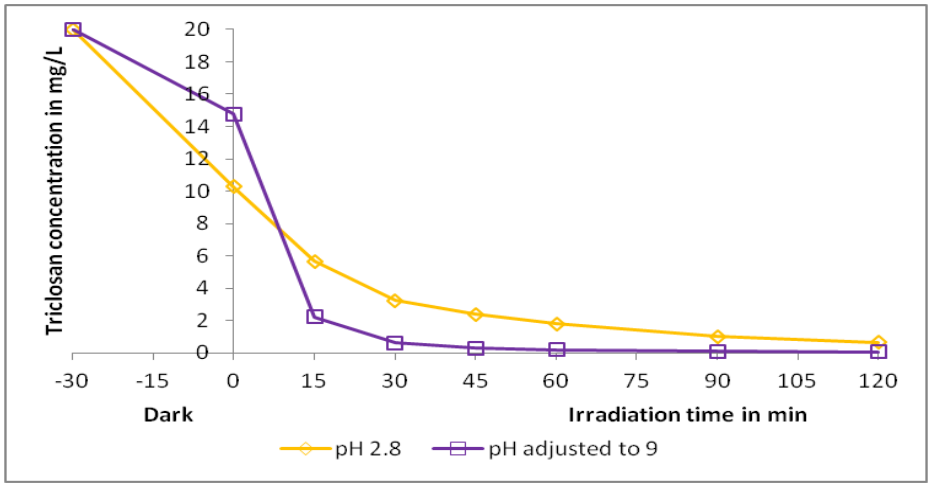

Figure2: Time course profile for triclosan degradation at different pH

(Reaction Condition: Triclosan concentration, 20 mg/L;TiO_2 dose, 1g/L; OA dose,2mM)

It can be observed from fig. 2 that dark adsorption at pH 2.8 was about 20% more than adsorption at pH 9. This may due to the fact that at pH 9.0 TiO_2 surface would be negatively charge, as pH_{zpc} of TiO_2 is 6.25. The pKa of triclosan is reported to be in the range of 7.9-8.1. So at pH 9 it would be in present in an anionic form, thereby there would be lesser attraction for the negatively charged TiO_2 surface. At pH 2.8 the TiO_2 surface would be positively charged, thereby triclosan would be attracted to the positively charge TiO_2 surface resulting in higher dark adsorption. It can be seen from fig 2 that even though degradation of triclosan after 120 mins of irradiation differs by only 3-4%, the rate of degradation of triclosan is much higher at pH 9 compare to pH 2.8. It has been reported in the literature that triclosan can be degraded by photolysis using UV light [7, 15]. Fig. 3 shows the time course profile as well as pH variation during photolysis and photocatalysis of Triclosan. Around 76% of triclosan was degraded after only one minute and almost 99% was degraded after 10 mins of irradiation time respectively in photolysis. While in the photocatalysis with TiO_2 82% of triclosan was degraded in 10 mins and 99% of degradation of triclosan was achieved in 60 mins. Not only the rate of degradation was different in PCR and photolysis, some of the intermediates identified in PCR were not found in photolysis. Intermediates at RT of 11.86, 12.1, 19.17 and 19.21 mins were found only in PCR. Also it can be seen from fig. 3 that the pH is been lowered at a faster rate in PCR compare to photolysis. Lowering of pH may be due to liberation of chloride ions. This indicates that probable pathway of triclosan degradation might be different in both the cases, with dechlorination as a possible path way in case of PCR. It was observed that the intermediates formed were not accumulated in proportion to the reduction of triclosan concentration, indicating that the intermediates formed may be degraded by Photocatlysis/photolysis.

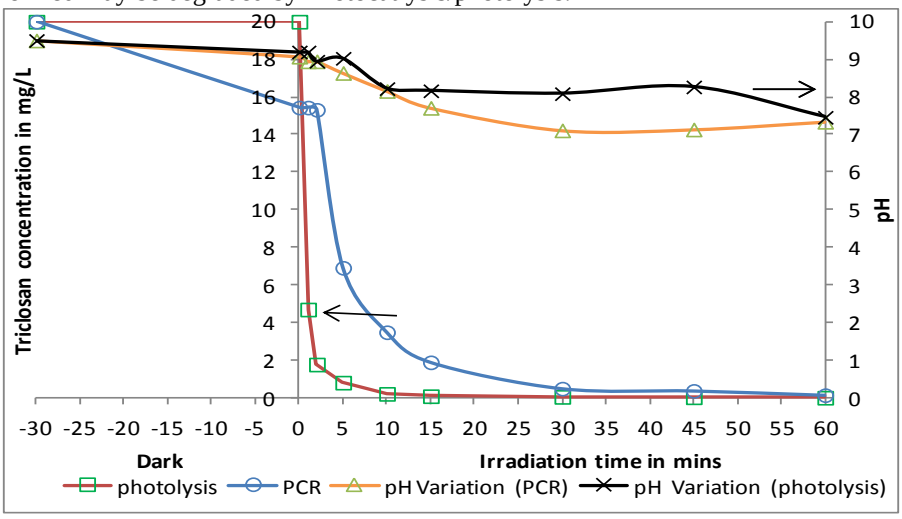

Figure3: Time course profile for PCR and photolytic degradation of triclosan

(*Reaction Conditions*: Triclosan concentration, 20 mg/L;TiO_2 dose, 1g/L; OA dose,2mM; initial pH,~9)

IV. CONCLUSION

Form this study it could be concluded that triclosan can be effectively degraded by PCR. The intermediate formed as well as the pattern of pH change during the reaction indicates that possible pathway for triclosan degradation is through photocatalytic dechlorination. Excessive photolysis of triclosan can be considered as an impending issue for application of PCR for triclosan degradation, but use of UV B or C or visible light can solve the problem.

V. REFERENCES

[1] *M. Munoz, Z. M. De Pedro, J. A. Casas and J. J. Rodriguez, Triclosan breakdown by Fenton-like oxidation, J. Chem. Eng., 198-199 (2012) 275-28.*
[2] *M. Suller and A. Russell, Antibiotic and biocide resistance in methicillin-resistant Staphylococcus aureus and vancomycin resistant Enterococcus, J. Hosp Infect., 43(1999) 281–291.*
[3] *R. Heath, S. White and C. Rock, Inhibitors of fatty acid synthesis as antimicrobial chemotherapeutics, Appl. Microbiol. Biotechnol., 58 (2002) 695–703.*
[4] *Y. Zhang and C. Rock, The reductase steps of the type II fatty acid synthase as antimicrobial targets, Lipids, 39(2004)1055–1060.*
[5] *Opinion on triclosan, Scientific Committee on Consumer Safety, 2010 (SCCS/1414/11)*
[6] *X.J. Chen, J. Richard, Y.L. Liu, E. Dopp, J. Tuerk and K. Bester, "Ozonation products of triclosan in advanced wastewater treatment," Water Research. 46 (7) (2012) 2247-2256.*
[7] *H. Liu, X. Cao, G. Liu, Y. Wang, N. Zhang, T. Li and R. Tough, Photoelectrocatalytic degradation of triclosan on TiO2 nanotube arrays and toxicity change,Chemosphere, 93(2013) 160–165.*
[8] *Y. Gao, Y. Ji, G. Li and T. An, Mechanism, kinetics and toxity assessment of OH-initiated transformation of triclosan in aquatic environments, Water research, 49(2014) 360-370.*
[9] *B.O. Clarke and S. Smith, Review of 'emerging' organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids, Environ. Int., 37(1) (2011) 226-247.*
[10] *H. Singer, S. Muller, C. Tixier and L. Pillonel, Triclosan: occurrence and fate of a widely used biocide in the aquatic environment: field measurements in wastewater treatment plants, surface waters, and lake sediments, Environ. Sci. Technol.,36 (2002) 4998–5004.*
[11] *M. Adolfsson-Erici, M. Pettersson, J. Parkkonen and J. Sturve, Triclosan, a commonly used bactericide found in human milk and in the aquatic environment in Sweden, Chemosphere, 46 (2002) 1485–1489.*
[12] *D.E. Latch, J.L. Packer, W.A. Arnold and K. McNeil, J. Photochem. Photobiol: A, 158 (2003), 63-66.*
[13] *K.L. Rule, V.R. Ebbett and P.J. Vikesland, Formation of chloroform and chlorinated organics by free-chlorine-medited oxidation of triclosan, Environ. Sci. Technol. 39 (2005) 3176-3185.*
[14] *Z. Song , N. Wang, L. Zhu , A. Huang, X. Zhao and H. Tang, Efficient oxidative degradation of triclosan by using an enhanced Fenton-like Process, Chem. Eng. J, 198–199 (2012) 379–387.*
[15] *H. Son, G. Ko and K. Zoh, Kinetics and mechanism of photolysis and TiO2 photocatalysis of triclosan, J Hazard Mater. 166 (2009) 954–960.*
[16] *Jimmy C. Yu, T.Y. Kwong , Q. Luo , Zongwei Cai, Photocatalytic oxidation of triclosan, Chemosphere 65 (2006) 390–399.*
[17] *Y. Wang and P. Zhang, Photocatalytic decomposition of perfluorooctanoic (PFOA) by TiO2 in the presence of oxalic acid. J. Hazard. Mater, 192 (2011) 1869-1875.*
[18] *Y. Li and F. Wasgestian, Photocatalytic reduction of nitrate ions on TiO2 by oxalic acid, J. Photochem. Photobiol. A: Chemistry, 112 (1998) 255-259.*
[19] *S. Wang , X. Wang , K. Poon , Y. Wang , S. Li , H. Liu , S. Lin and Z. Cai , Removal and reductive dechlorination of triclosan by Chlorella pyrenoidosa, Chemosphere, 92 (2013)1498–1505.*
[20] *K N. Knust , M.P. Foley, M. Mubarak, S. Skljarevski, K. Raghavachari and D. G. Peters, Electrochemical reduction of 5-chloro-2-(2,4-dichlorophenoxy)phenol (triclosan) in dimethylformamide, J. Electroanal. Chem., 638 (2010) 100–108.*