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Electrocatalytic reduction and characterization of Tetrachlorvinphos in acetonitrile-water (1:1) media in presence of cyanocobalamin

NKUNU Zachary Njiru[1,]*, GUTO Peterson Momanyi[1] and KITHURE Joyce Gatiiria[1]

[1]Department of Chemistry, University of Nairobi, P.O Box 30197 - 00100, Nairobi, Kenya

*Corresponding author email: nkunuzach@gmail.com

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ABSTRACT

This work investigates a possible electrocatalytic degradation of tetrachlorvinphos pesticide in acetonitrile-water media using cyanocobalamin as the catalyst. The catalyst and its derivatives are employed in some organic synthesis due to their ability to form and selectively cleave Co-C bonds. There is inadequate data from previous related works. This study explores possible electrocatalytic route for degradation of tetrachlorvinphos using the catalyst at temperature of 24 ± 1° by cyclic voltammetry method. Tetrachlorvinphos exhibited two consecutive reduction peaks at ~-0.710 ± 0.004 V and ~ -1.096 ± 0.029 V Versus Ag/AgCl. The second reduction peak registered a diffusion coefficient value of 3.68 x 10^{-5} cm^2s^{-1} and current density of be 5.83 x 10^{-5} A/cm^2. The reduction potential for tetrachlorvinphos in presence of cyanocobalamin was observed to be -0.923 ± 0.03 V versus Ag/AgCl. The diffusion coefficient and current density value was reported at 3.37 x 10^{-5} cm^2s^{-1} and 2.56 X 10^{-5} A/cm^2 respectively for an electro-reduction process. This implies that, catalytic reduction of the pesticide occurred at a significantly lower potential compared to direct reduction. The over potential saving of about 0.168 V is an indication of the catalyst efficiency on the pesticide degradation.

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1. Introduction

Organophosphates (OPs) are usually esters, amides or thiol derivatives of phosphoric, phosphonic, or phosphinic acids. OPs are applied as pesticides and insecticides in agriculture and as chemical warfare agents in military practice. OP compounds worldwide account for over about 40% of the total pesticides used [1]. Most used organophosphates include parathion, Malathion, methyl parathion, chlorpyrifos, diazinon, dichlorvos, phosmet, fenitrothionazinphos methyl and tetrachlorvinphos. Malathion is commonly used in public health pest control programs such as mosquito eradication [2]. Tetrachlorvinphos is an organophosphate cholinesterase inhibitor that is used as an insecticide [3]. It is registered for use in Canada, South Africa, and Australia, as well as in the USA [4]. In 1966, it was registered for use in the United States by the United States department of Agriculture on various food crops, livestock, pet animals, and in or around buildings and later banned in 1987 [4]. However, in many African countries including Kenya, its use is evident especially in public health works [5].

Tetrachlorvinphos is a white crystalline powder [8], mild color, odour [9] and when heated to decomposition it emits toxic fumes of hydrogen chloride and phosphorous oxides [10]. It has low solubility, volatility and strong affinity to colloidal matter [6]. In the environment, tetrachlorvinphos primary route of dissipation is through biotic degradation. Under alkaline conditions, abiotic processes such as hydrolysis, photo-degradation and biodegradation are somewhat efficacious [7]. Tetrachlorvinphos is relatively toxic to pets and livestock [11]. Humans can be exposed to Tetrachlorvinphos when treating pets or through dermal contact with pets treated with pet collars, powders, or aerosol sprayers [3]. Symptoms of exposure to this chemical substance include: increased perspiration, nausea, lachrymation, salivation, blurred vision, diarrhea, pulmonary edema, respiration embarrassment and convulsions. It is classified as a group C (possible human) carcinogen by the Carcinogenicity Peer Review Committee of the EPA's Office of Pesticide programs [6].

Tetrachlorvinphos has an estimated K_{oc} value of 2,000 [4] determined from a log K_{ow} of 3.53 [4] and a regression-derived equation [4] indicates that tetrachlorvinphos is expected to have low mobility in soil. Volatilization of tetrachlorvinphos from moist soil surfaces is not expected to be an important fate process given an estimated Henry's Law constant of 1.8×10^{-9} atm-cu m/mole, derived from its vapor pressure, 4.2×10^{-8} mm Hg, and water solubility, 11 mg/L [12]. Tetrachlorvinphos is not expected to volatilize from dry soil surfaces based on its vapor pressure. A biodegradation half-life of less than 8 days in soil [13] suggests that biodegradation may be an important fate process in soil. Under abiotic conditions, tetrachlorvinphos undergoes slow hydrolysis in acid and rapid hydrolysis in base. In acid and neutral solution, de-alkylation occurs and in alkaline solution, the P=O bond is ruptured [14]. The structure of Tetrachlorvinphos is shown in figure 1.

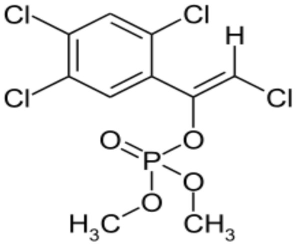

Figure 1: Structure of (Z)-2-chloro-1-(2, 4, 5-trichlorophenyl) Vinyl dimethyl phosphate.

Additional structural information is available in the PubChem compound database [4]. Effective methods for disposal of this toxic compound are needed to ensure that human and environmental health is not compromised by continuous use of organophosphate-containing pesticides. This work explores possible electrocatalytic degradation route of Tetrachlorvinphos in presence of cyanocobalamin (catalyst) at room temperature in aqueous media.

2. Materials and Methods

2.1 Chemicals and Reagents

All chemicals were of analytical grade and were used as received. Potassium nitrate salts (98%) from BDH Company, aluminium oxide, Tetrachlorviphos, and cyanocobalamin were from Sigma Aldrich and acetonitrile from Fisher Scientific Company. Analytical grade pure nitrogen gas was from BOC Gas Supply Company, Kenya. Water was de-ionized by an Elga water purification system.

2.2 Solutions

A 0.1 M KNO_3 was used as the supporting electrolyte. A 0.1mM Cyanocobalamin solution was prepared in 0.1M KNO_3 in acetonitrile/water 1:1 v/v. Sample solution of 1mM Tetrachlorvinphos was prepared freshly in 0.1M KNO_3 in acetonitrile/water 1:1 v/v for direct reduction. A 1.0 mM tetrachlorvinphos, 0.1mM cyanocobalamin and 0.1 M KNO_3 in acetonitrile/water 1:1 v/v solution was prepared for electrocatalytic reduction. Potassium ferricyanide solution was used as a standard to calibrate the potentiostat.

2.3 Characterization of Tetrachlorvinphos

Cyclic voltammetry studies were carried out using a CHI 1232B potentiostat from CH Instruments, USA. Silver/Silver (Ag/AgCl) electrode was used as a reference electrode, Platinum wire as the counter electrode and glassy carbon of diameter (Ø) 0.30cm and surface area of 0.071 cm^2 used as working electrode. The glassy carbon working electrode surface was polished using alumina slurry for about two minutes to have a new working surface before every scan. All the electrolytic solutions were de-aerated for at least 10 minutes by passing pure Nitrogen gas through them before taking measurements. This was to ensure complete removal of oxygen. Nitrogen saturated environment was maintained during entire experimental runs. All the cyclic voltammetry studies were done at ambient temperature (24 ± 1 ^{o}C). A Solution of 0.1 M KNO_3 (supporting electrolyte) in acetonitrile / water (1:1) v/v was run first to establish the potential working window. For cyclic voltammetry studies of direct and electrocatalytic reduction of Tetrachlorvinphos, the potential was swept from -0.4 to -1.5 V and then back at varying scan rate of 0.01 to 0.1 V/s. The data obtained was recorded, analyzed and interpreted using Kaleidagraph software, version 4.1.1.

3. Results and Discussion

3.1 Cyclic Voltammetry of Cyanocobalamin

The cyclic voltammetry of 0.1 mM cyanocobalamin in acetonitrile-water (1:1) media is shown in figure 2. The reduction peak potentials at a scan rate of 0.03 V/s were -0.5430 ± 0.023V and -0.922 ± 0.016 V for peaks 1c and 2c respectively while the anodic peak potential was found to be -0.600 ± 0.110 V versus Ag/AgCl.

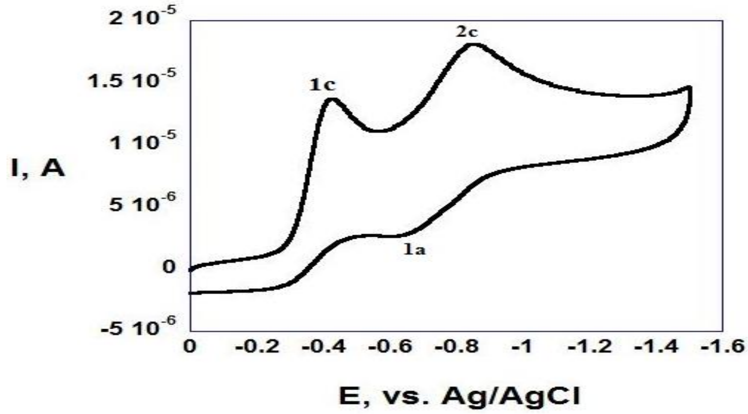

Figure 2: Cyclic voltammogram for 0.1mM cyanocobalamin in acetonitrile-water solution (1:1) containing 0.1M KNO_3 at scan rate of 3mV/s versus Ag/AgCl. (1c) is first cathodic peak, (2c) is second cathodic peak and (1a) is the anodic peak. "I" is current in "A - amperes". "E" is potential in "V - volts".

The average diffusion coefficients calculated using Randle-Sevcik equations [16] were found to be 3.4 x 10^{-7} cm^2s^{-1} for peak (1c) and 8.0 x 10^{-7} cm^2s^{-1} for peak (2c). These diffusion coefficients compare favorably with the reported diffusion coefficients for cyanocobalamin in ionic liquid media which were found to be 9.0 x 10^{-8} cm^2s^{-1} for peak 1c [18] and 1.4 x 10^{-6} cm^2s^{-1} for peak 2c [18]. The slight differences can be attributed to the higher viscosity of the ionic liquid media [16] compared to the acetonitrile/water media. It is important to note that the current densities for the cathodic peaks were found to be 5.32 x 10^{-6} A/cm^2 for peak 1c and 1.05 x 10^{-5} A/cm^2 for peak 2c.

It was also observed that, the corresponding anodic peak is smaller compared to its corresponding cathodic peaks. This peak size and symmetry difference indicates that it is a quasi-reversible (*vide infra*) reaction involving a two electron reduction of cyanocobalamin, with the oxidation state of the central cobalt species changing from +3 to +1 [16]. The symmetry of the voltammogram (figure 2.) is non-symmetrical and similar to that reported by Lagunas *et al.*, 2006 [17] due to non-linear diffusion and uncompensated solution resistance [17]. The quasi-reversible (*vide infra*) process can be explained either on the basis of transition metals shifting the geometry of their co-ordination sphere, that is, octahedral (Co(III)), square pyramidal (Co(II)), and square planar (Co(I)), with each electron transfer accompanied by the gain or loss of axial ligand [17]. Another explanation can be based on the redox reactions of the electroactive species involving the rate of conversion of 'O' to 'R' species. At equilibrium, i_{pa}/i_{pc} = 1 (reversible) and $i_{pa}/i_{pc} \neq 1$ (quasi-reversible). For quasi reversible, 'R' is converted further to other products (P), and calls for more 'R' to be generated in order to compensate for the deficiency. The deficiency leads to reduction rate increase hence, making cathodic potential (E_{pc}) more positive [15].

3.2 Electrocatalytic Reduction of Tetrachlorvinphos

Cyclic voltammetry of uncatalyzed tetrachlorvinphos in acetonitrile-water (1:1) media exhibited two reduction peak potentials at a scan rate of 0.03 V/s (figure 3). The first reduction peak (1c) was at -

0.710 ± 0.004 V and the second reduction peak (2c) was at -1.096 ± 0.029V versus Ag/AgCl as shown in figure 3. The second reduction peak at -1.096 was possibly as a result of the two consecutive one-electron reduction of C=C and the first reduction peak at ~- 0.710 ± 0.004 V can be attributed to the two consecutive one-electron reduction of P=O bond of phosphate di-ester group. The two peaks observed were irreversible (figure 3). This observation is consistent with the findings of Al-Qasmi *et al* 2018 [3] at ~ -1.35 and ~ -1.29 V at 0.1V/s versus Ag/AgCl, respectively. The C=C bond occurs at a more negative potential than P=O bond [3].

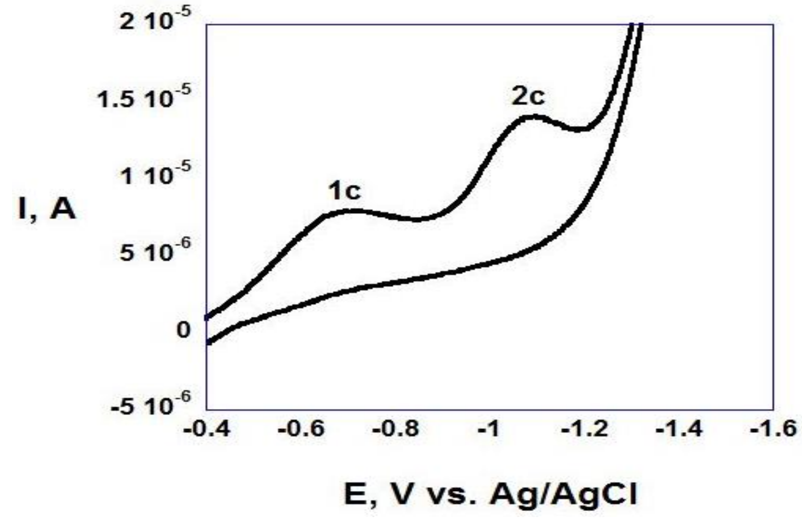

Figure 3: Cyclic voltammogram for 1.0mM Tetrachlorvinphos in acetonitrile-water solution (1:1) containing 0.1 M KNO_3 at scan rate of 3mV/s versus Ag/AgCl. (1c) is first cathodic peak and (2c) is second cathodic peak. "I" is current in "A - amperes". "E" is potential in "V - volts".

The average diffusion coefficients calculated using Randle-Sevcik equations [16] for Tetrachlorvinphos were found to be 3.68 x 10^{-5} cm^2/s^{-1} for peak (2c) while its respective current density was found to be 5.83 x 10^{-5} A/cm^2. The linearity of the plot indicated that electro-reduction of Tetrachlorvinphos is a diffusion controlled process at the electrode-solution interface. The addition of cyanocobalamin lowered the peak potential from -1.096 ± 0.029V to -0.923 ± 0.03V versus Ag/AgCl (figure 4). This shows that cyanocobalamin reduced the reduction potential for tetrachlorvinphos by a potential of about 0.168 V. From Randles-Sevcik equations, the diffusion coefficient was found to be 3.37 x 10^{-5} cm^2s^{-1} and a current density obtained was 2.56 x 10^{-5} A/cm^2. The change in current density of Tetrachlorvinphos from 5.83 x 10^{-5} A/cm^2 to 2.56 x 10^{-5} A/cm^2 with catalyst is attributed to the growth of current diffusion layer at the carbon electrode surface in solution [17]. This diffusion coefficient value is lower than the one for tetrachlorvinphos without a catalyst most probably due to a possible increase in the interfacial thickness of the diffusion layer resulting from the formation of a complex between cyanocobalamin and tetrachlorvinphos. In this reaction, electrons are donated to cyanocobalamin by the cathode (donor), which reduces the catalyst to the active form. The reduced catalyst transfers the electrons to Tetrachlorvinphos (acceptor). The reduced catalyst transfers the electrons to Tetrachlorvinphos (acceptor). The reaction occurs at the formal electrode potential at which the active form of the catalyst is generated. The product of reduction is unstable and none of it goes through oxidation [18]. The chemical process involves electrochemical generation of a 'supernucleophile' intermediate, which in the case of cyanocobalamin, Co(III)L, is the Co(I)L complex [18] as shown in scheme 1.

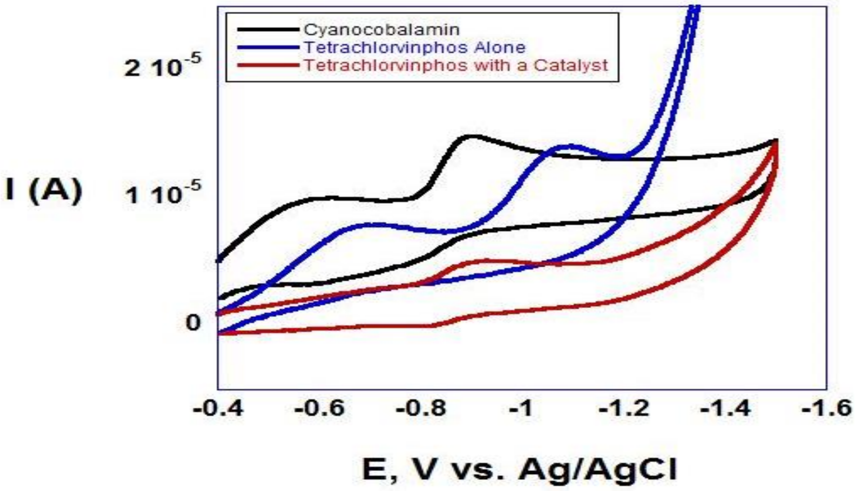

Figure 4: Overlay cyclic voltammograms of 0.1 mM cyanocobalamin (black), 1.0 mM Tetrachlorvinphos alone (blue) and 1.0 mM Tetrachlorvinphos in presence of cyanocobalamin (red) in acetonitrile-water (1:1) at 0.03 V/s versus Ag/AgCl. "I" is current in "A - amperes". "E" is potential in "V - volts".

Scheme 1

The conversion of Co(III)L to Co(I)L is either through;

$\text{Co(III) L} + e^- \leftrightarrow \text{Co(II)L}$, then $\text{Co(II)L} + e^- \leftrightarrow \text{Co(I)L}$.(1)

Or,

$\text{Co (III) L} + 2e^- \leftrightarrow \text{Co(I)L}$ ………………………………………(2)

Where 'L' is the ligand. The reduced form of Cyanocobalamin, Co(I), reacts with the organohalides (RX) according to the reaction mechanism below:

$\text{RX} + \text{Co(I)L} \rightarrow \text{R-Co(III)L} + X^-$ ………………………………….(3)

$\text{R-Co(III)L} + H^+, 2e^- \rightarrow \text{R-CH}_2(\text{CH}_2)\text{n} + \text{Co(I)L}$ …………(4)

Scheme 1 is catalytic since Co(I)L, where L is macrocyclic ligand, is regenerated. The rate determining step is the attack by Co(I) on alkyl halide. The resulting Carbon-Cobalt bond can be cleared by visible light, electrolysis, or reducing agents to give carbon-centered radicals that can add onto activated carbon-carbon double bonds [18]. Differences in cathodic currents in the presence or absence of a catalyst at similar concentrations of substrate are two significant features in the electrocatalysis process for the reduction of tetrachlorvinphos. It was also observed that, the reduction peak current (i_p) for the electrocatalytic reduction was not proportional to the square root of scan rate ($V^{½}$) implying that the electrocatalysis for the current reaction is most likely a combination of both adsorption and diffusion processes.

4. Conclusions

The electrocatalytic reduction of tetrachlorvinphos pesticide using cyanocobalamin lowered the peak potential from -1.096V to -0.923V versus Ag/AgCl. This implies that, catalytic reduction of the pesticide occurred at a significantly lower potential compared to direct reduction. The over potential saving of about 0.168 V is an indication of the catalyst efficiency on the pesticide degradation.

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References

[1] Gahlaut, A., Gothwal, A., Chhillar, A. and Hooda, V. (2012) Electrochemical Biosensors for Determination of Organophosphorus Compounds: Review. Open Journal of Applied Biosensor, **1**, 1-8.

[2] Environmental Protection Agency (EPA), "Malathion for Mosquito Control." (2008). http://epa.gov/opp00001/health/mosquitoes/malathion4mosquitoes.html, accessed on 5 March 2015.

[3] Al-Qasmi, N., Hameed, A., Khan, A. N., Aslam, M., Ismail, I. M. I., & Soomro, M. T. (2018) Mercury meniscus on solid silver amalgam electrode as a sensitive electrochemical sensor for tetrachlorvinphos. *Journal of Saudi Chemical Society*, **22**(4), 496–507.

[4] NCBI. (2015) Tetrachlovinphos. PubChem Compound Database. Compound summary for CID 5284462. Bethesda (MD): National Center for Biotechnology Information, United States National Library of Medicine. Available from: http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?cid=5284462,accessed 5 March 2015.

[5] Wanjala, C. L., & Kweka, E. J. (2018) Malaria vectors insecticides resistance in different agroecosystems in Western Kenya. *Frontiers in Public Health*, ***6***, 55.

[6] Angeluz O., Pierre B., Enrique B., Laura O. (2008) Sorption and desorption of organophosphate pesticides, parathion and cadusafos, on tropical agricultural soils. *Journal of Agronomy and Sustainable Development***, 28,** 231-238.

[7] Trivedi P., Sharma V. P., Srivastava L.P. and Malik S. (2014) Determination of organophosphorus pesticide residues in wheat and rice by QuEChERS method. *Journal of Environmental Research and Development*, **8(**4), April-June 2014.

[8] Halimah, M., Nashriyah, B. M., Yew Ai, T. & Ismail, B. S. (2004) Adsorption and desorption study of C-chlorpyrifos in two Malaysian agricultural soils. *Journal of Nuclear and Related Technologies*, **1** (1): 31-40.

[9] Spencer E. Y. (1982) Guide to the Chemicals Used in Crop Protection, 7th Edition. Publication 1093. Research Institute, Agriculture Canada, Ottawa, Canada: Information Canada, 546 p.

[10] Lewis R. J. Lewis, Sr. (2004) Sax's Dangerous Properties of Industrial Materials. 11th Edition. Wiley-Interscience, Wiley & Sons, Inc. Hoboken, NJ, pp. 3139.

[11] USEPA Office of Pesticide Programs (2006) Tolerance Reassessment Eligibility Decision and Re-registration Eligibility Decision Addenda for Tetrachlorvinphos Case No. 032 p.45. Available from, as of July 26, 2008: http://www.epa.gov/pesticides/reregistration/REDs/tcvp_red.pdf., Accessed on 25 June, 2016.

[12] Mbui D N, Mbugua J K, Kamau G N. (2014) Adsorption of Dursban (Chlorpyrifos) pesticide by loam soil from Limuru, Kenya: Apparent thermodynamic properties. Africa Journal of Physical Sciences ISSN: 2313-3317, 1(1), 1–9.

[13] Yalkowsky S. H. and He Y. (2003). Handbook of Aqueous Solubility Data. CRC Press LLC, Boca Raton, FL., pp. 639.

[14] USEPA/OPPTS (1995) Re-registration Eligibility Decisions (REDs) Database on Tetrachlorvinphos (22248-79-USEPA 738-R-95-041. Sept, 1995. Available from the Database May 6, 2008.

[15] Wanjau T. W., Geoffrey N. K., Mwaniki S. N., Muya C. N. (2015) Electrocatalytic reduction of 2, 2, 2–Trichloro-1, 1-Bis (4-Chlorophenyl) Ethanol (Dicofol) in Acetonitrile-aqueous solution using Cyanocobalamin as a catalyst. *Science Journal of Chemistry*, **3**(1), 1-10.

[16] Muya, C. N., Guto, P. M., Wangui, T. W., & Kamau, G. N. (2015) Electrocatalytic Decomposition of (3ar, 7as)-2-[(trichloromethyl) sulfanyl]-3a, 4, 7, 7a-tetrahydro-1h-isoindole-1, 3 (2h)-dione (Captan) Pesticide Residue using Cyanocobalamin. *International Journal of BioChemiPhysics*, **23**, 30-31.

[17] Lagunas, M. C., Silvester, D. S., Aldous, L., & Compton, R. G. (2006) The electrochemistry of vitamin B_{12} in ionic liquids and its use in the electrocatalytic reduction of Vicinal Dibromoalkanes. *Electroanalysis*, **18**(22), 2263–2268.

[18] Davies, T. J., Banks, C. E., Nuthakki, B., Rusling, J. F., France, R. R., Wadhawan, J. D. & Compton, R.G. (2002) Surfactant-free emulsion electrosynthesis via power Ultrasound: electrocatalytic formation of carbon–carbon bonds. *Green Chemistry*, **4,** 570–577.