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Electrochemical Oxidation Process for Mineralization of Solvent

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Abstract

A silver mediated electrochemical oxidations is a promising technique for the destruction of organic compounds. The destruction of 30%tributyl phosphate in dodecane in a nitric acid medium containing electrogenerated Ag(II) to carbon dioxide was studied by using a laboratory scale electrochemical oxidation cell. The electrolyte used in this system was 0.5 M $AgNO_3$ in the range of 3 - 7 M HNO_3, at operating temperatures of 60ºC ± 5ºC, under ultrasonic agitation and the output of a DC power supply at constant the current was 60 A, respectively. Electrolysis was carried out for 5 hours. The results show that, in silver mediated electrochemical oxidation method, destruction of 30%TBP/Dodecane was increased with increase of concentration of HNO_3.

Key word : Electrochemical Oxidation, Silver mediated, Ag(II), Tributyl phosphate, Dodecane

Introduction

Much attention has recently been paid to electrochemical processes designed to treat organics wastes containing 30%Tributyl Phosphate (TBP) in Dodecane, used in the NUCEF process as an extractant for uranium and plutonium and as a solvent, had to be dealt with. Typically, these problems arise due to the reactivity of certain organics when treating waste at elevated temperatures and attention has therefore been focused on low temperature alternatives. One of these alternatives, Mediated Electrochemical Oxidation (MEO), mineralizes organics species to carbon dioxide and water while operating at near ambient pressure and temperature in an aqueous system. An electrolysis cell is used to generate an active metal ion, Ag(II) in the MEO process. The metal ion is the powerful oxidant chemical agent; it may react directly with the organic material to be destroyed or it may first react with water to form hydroxyl radicals, which in turn oxidize the material.

At the heart of the Ag(II) process is the chemical oxidation of organic molecules by the Ag(II) ion. This is one of the most oxidizing species that can be generated at an anode in an electrochemical cell in aqueous solution. Radical species initiated by Ag(II) attack the organic substrate, progressively converting it in a series of steps irreversibly to CO_2, water and residual salts from hetero-atoms. During the oxidation step, Ag(II) is reduced back to Ag(I). This is then regenerated to Ag(II) again at the electrochemical anode. This “catalytic” use of silver makes this a Mediated Electrochemical Oxidation (MEO) Process.

The complete TBP and Dodecane conversion balance equation may be expressed as follows: (1) and (2)

$$C_{12}H_{27}PO_4+72Ag^{+2}+24H_2O\rightarrow 12CO_2+72Ag^{+}+H_3PO_4+72H^{+} \quad (1)$$

$$C_{12}H_{26}+74Ag^{+2}+24H_2O\rightarrow 12CO_2+74Ag^{+}+74H^{+} \quad (2)$$

Although this equation is purely theoretical and does not reflect the actual process, it

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approximates the overall phenomenon sufficiently to prepare balances and calculate the reaction yield.

Silver(II) Process Chemistry

The silver(II) process is based on the highly oxidizing nature of silver (II) (Ag(II)) ions in a nitric acid solution. Ag(II) is one of the strongest oxidizing agents known; nitric acid also makes a significant contribution to the oxidizing process. In this process, a solution of silver nitrate in nitric acid is electrolyzed to produce the Ag(II) cation.(4)

Thus, the standard electrode potentials, E° of the half-cell reaction for the desired electrolysis under standard conditions at 25°C (77°F) would be:

$Ag^+ \rightarrow Ag^{+2} + e^-$ E° = -1.98 V

$NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O$ E° = 0.94 V

The overall reaction and standard potential for the electrolysis of the silver nitrate solution are therefore :

$2Ag^+ + NO_3^- + 3H^+ \rightarrow 2Ag^{+2} + HNO^2 + H^2O$ E° = -1.04 V

The electrode potentials at other concentrations are given by the Nernst equation:

$$E = E0 + \frac{RT}{Fn} \ln (Q)$$

Where Q represents the standard expression for the Law of Mass Action,

$$Q = \frac{[Ag^{+2}]\,[HNO_2]}{[Ag^{+1}]\,[NO_3^-]\,[H^+]^3}.$$

Also, T is the temperature in Kelvin, R is the universal gas constant, F is the Faraday constant (charge on one mole of electrons), and n is the number of electrons transferred in the reaction.

The high concentration of nitric acid used in the silver(II) process prevents the electrolysis of water that would occur at a lower potential (-1.23 volts[V]) than the electrolysis of silver nitrate in aqueous solution. For a simple 1.0 M silver nitrate solution, the following reactions would take place:

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ E° = -1.23 V

$NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O$ E° = 0.94 V

For an overall reaction;

$2H_2O + 2NO_3^- + 2H^+ \rightarrow O_2 + 2HNO_2 + 2H_2O$ E° = -0.29 V

These standard electrode potentials are valid only at 25°C (298K) and at unit activity of all reactants and products. However, the silver (II) process is normally carried out at about 90°C (194°F) and at 8.0 M HNO_3. The potentials at this temperature and at these high concentrations of nitric acid are not well know. More over, the reaction is aided by the formation of a brown complex, $Ag(NO_3)^+$, which lowers the required potential for the oxidation of Ag^+. The association constant for its formation is unknown.

Although the electrochemistry for the conditions used is not know. There is no doubt that Ag(II) is formed and that it reacts only slowly with water to produce intermediates, such as OH and other radicals. The Ag(II) formed in the electrolytic cells is then transported into a reaction vessel. The generation of Ag(II) ions depends entirely on the electrical current to the cells, and it stops rapidly when the power is switched off. However, because Ag(II) is such a strong oxidizing agent, it will corrode most metal systems that are not glass-lined or coated with a noble metal. Concentrated nitric acid is also a strong oxidizing agent.

Ag(II) can oxidize all elements to their highest oxidation state if allowed to reach equilibrium. Thus, the following general theoretical reaction should occur;

Organic$+O_2 \rightarrow CO_2$ + inorganic salt/acids in water

The NO_x formed is converted to NO_3^-, but in practice, amines (RNH_2) are only converted to elemental nitrogen.

Silver(II) Process Arrangement

Ag(II) ions are generated by passing an Ag(I) nitrate/nitric acid solution past a platinum anode. A semi permeable membrane (to cations) separates the anode and cathode compartments of this cell, thus preventing bulk mixing of the anolyte and catholyte solutions and allowing the transport of cations and water (but not anions) across the membrane.

According to the technology provider, Ag(II) ions generated at the anode of^{-} the electrochemical cell react with the water and nitric acid of the anolyte solution to form a range of other oxidizing radicals (OH, NO_3). The Ag(II) ions and other oxidizing species then react with the organic material delivered into the anolyte vessel and are reduced to Ag(I) ions, nitrate ions, and water. The organic material itself is completely oxidized to carbon dioxide, oxides of nitrogen (NO_x) and traces of carbon monoxide, protons (H^+), and inorganic salts. No hydrogen is produced in the process. Off-gas from the reaction passes from the anolyte tank via a chiller (to condense nitric acid vapors) to an NO_x reformer.

To balance the electrochemical reaction in the anolyte vessel, a cathode reaction reduces nitric acid to nitrous acid and water, while other reduction reactions generate NO_2. The evolved gases pass from the catholyte tank to the NO_x reformer.

During the electrochemical reaction, nitric acid is consumed in the catholyte circuit, and water is transferred across the semipermeable membrane in the electrochemical cell from the anolyte to the catholyte. Some Ag(I) ions are also transferred across the cell membrane. In order to maintain steady-state operating conditions, proportions of the anolyte and catholyte circuits are bled to a nitric acid and silver recovery unit, which includes the previously mentioned NO_x reformer.

Process Chemistry for Organics Destruction

The organic oxidation process chemistry in the Ag/HNO_3 system, the cathodic reaction is the reduction of nitrate ions, which can result in the formation of NO_X. To prevent this, the nitrous acid can be converted back to nitric acid by reacting it with oxygen. Also, this cathodic reaction is electrochemically reversible and a cationic exchange membrane must be employed to prevent the reoxidation of nitrite ion at the anode and consequent loss of current efficiency.

Experimental Procedure

The experimental setup was divided in to electrolysis and mixing sections as shown on Figure 1. For laboratory scale experiments, the organics destruction test of 30%TBP/Dodecane was carried out in a bench–scale electrolytic cell made of glass and polytetrafluoroethylene (Teflon) with ‘square box’ configuration type and platinum electrode as shown in Figure 2. This two channel cell contained a platinum cylinder anode compartment of 3.2 dm^3 in one arm and a platinum cylinder cathode compartment of 0.6 dm^3 in the other arm; the two compartments were separated by a Nafion membrane. This system has ultrasonic a capability of up to 60%, with a flow rate of 180 watt per liter and anolyte and catholyte fluid volumes of 3 and 0.450 liters respectively. The mediator concentration of $AgNO_3$ was 0.5 M, a value which allowed reasonable current densities without exceeding solubility limits, while the acid concentration were varied from 3–7 M for the HNO_3 system, at operating temperature of 60°C ± 5°C and the output of a DC power supply (Model SB 31SD-080-101, Chuo Seisakusho, Ltd.) under constant current was 60 A (output voltage of 4.4 - 4.8 V), respectively. Electrolysis was carried out for 5 hours. The organic substrate was introduced into the cell in a batch mode, and the off-gas was then pumped through a flow rate 2 liters per minute, and then was analyzed for carbon dioxide by infrared gas analyzer (Model CGT-7000, Shimadzu Corporation) at a flow rate 1 liter per minute, and % carbon dioxide in the off-gas was recorded in real time. By integrating the volume of carbon dioxide produced on the period of a run was used calculate to the destruction of 30%TBP in terms of mole at every 5 minutes, at a current of 60 A and the actual voltage (4.4 – 4.8 V) applied to the electrochemical cell.

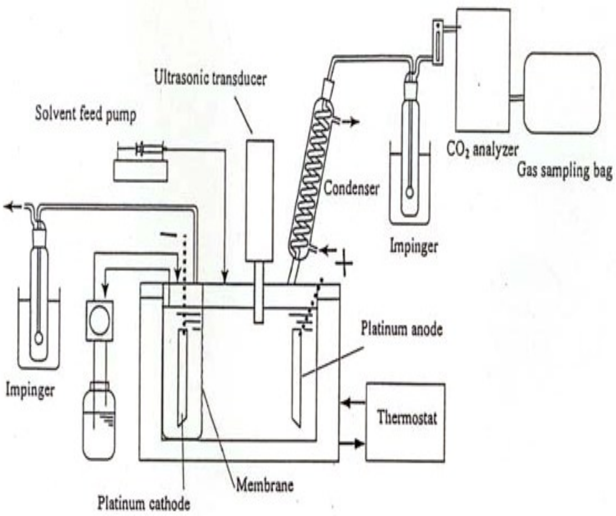

Figure 1. Principle of the experimental setup divided into an electrolysis

Figure 2. Schematic of laboratory scale experiment

Results and Discusion

The experimental process was validated for mineralization of 30%TBP/Dodecane, the first step of organic destruction by this process, the brown-black color characteristic of Ag(II) gradually appears as soon as a current was applied across the electrodes. However, direct anodic oxidation of 30%TBP/Dodecane also forms CO_2, off-gas profiles were obtained during electrolysis tests with a mediator in solution; carbon dioxide was detected as soon as current is applied.

Dissolved organics are ultimately converted to carbon dioxide and water in such a process. Measurements of 30%TBP/Dodecane conversion; an overall reaction for the TBP/Dodecane oxidation to carbon dioxide may be expressed as follows:

$$C_{12}H_{27}PO_4+C_{12}H_{26}+146Ag^{+2}+48H_2O \rightarrow 24CO_2+146Ag^{+}+H_3PO_4+146H^{+} \quad (3)$$

Although this equation is purely theoretical and dose not reflects the actual process, it approximates the overall phenomenon sufficiently to prepare balances and calculate the reaction yield.

Having demonstrated the feasibility of destroying 30%TBP/Dodecane by the Ag(II) process. The results show that CO_2 can be efficiently produced by electrolysis oxidation from organic solvent. Higher concentration of HNO_3 raises the chemical efficiency, the experimental volume of CO_2 increased with the progress of electrochemical oxidation. Since CO_2 gradually increased at the first electrolysis aqueous intermediates of 30%TBP/Dodecane seem to accumulate in anolyte. At the end of the first electrolysis, CO_2 evolution became almost constant in after 60 minis. It was suggested from the behavior of CO_2 evolution that intermediates of 30%TBP/Dodecane were very quickly decomposed to CO_2. Figure 3 shows the destruction of 30%TBP/Dodecane in terms of mole at every 5 minutes, at various concentration of HNO_3, which the mole destroyed of 30%TBP/Dodecane was increased according to concentration of HNO_3. The destruction of 30%TBP/Dodecane calculated from the CO_2 evolution, At 7 M HNO_3, the rate destruction increases to greater than 50% by comparison with 5 M HNO_3. However, the resulted from electrolysis at 3 M HNO_3 longer than 2 hours can not be interpreted due to carbon dioxide in the off-gas, the result shows that the concentration of HNO_3 have an influence with potentials of electrochemical reaction.

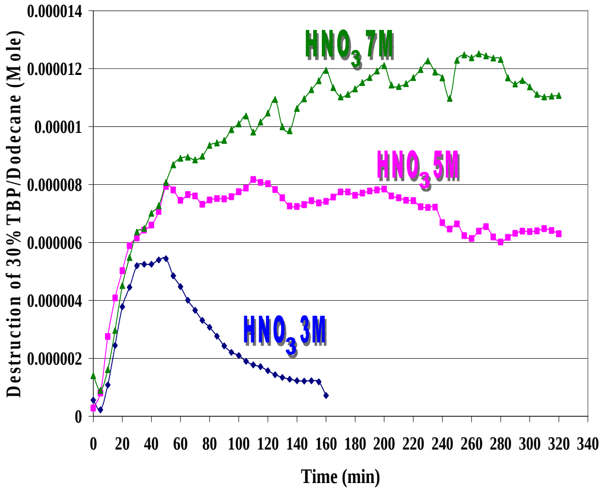

Figure 3. The destruction of 30%TBP/Dodecane in terms of mole at various concentration of HNO3

Conclusion

Electrochemical oxidations have been developed for many of organic chemical syntheses. Processes have been developed for carrying the oxidation to completion, with all of the carbon in the original hydrocarbon converted to CO_2. The complete oxidation process appears to be best carried out by using a combination of electrolysis and chemical reaction.

The experimental process was validated for mineralization of organic compounds; having demonstrated the feasibility of destroying 30% TBP/Dodecane by the Ag(II)/HNO_3 process. The electrolyte used in this system was 0.5 M $AgNO_3$

in 3-7 M HNO_3, at operating temperature of 60ºC ± 5ºC, under ultrasonic agitation and the output of a DC power supply at constant the current was 60 A and the output voltage of 4.4 - 4.8 V, respectively. The infrared spectrum recorded during the experiment showed characteristic CO_2 line. The destruction rate of 30%TBP/Dodecane was increased according to concentration of HNO_3; an estimate of the total destruction time could be obtained.

Acknowledgements

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Reference

1. Balazs, G. B., Chiba, Z., Hsu, P., Lewis, P. R., Murguia, L. and Adamson, M. G. 1997. *Destruc-tion of Hazardous and Mixed Wastes using Mediated Electrochemical Oxidation in a Ag(II)/HNO Bench Scale System.* Livermore, CA, UCRL-126754.

2. Judd, L. 2002. *A Demonstration of SILVER II^{TM} for the Decontamination and Destruction of Organics in Transuranic Wastes*. AEA Technology Engineering Services Inc. Sterling, VA 20166.

3. Paire, A., Espinoux, D., Broudic, J.C., Lecomte, M.and Masson, M. 1997. *Organic Compound Oxidation Mechanisms by The Silver(II) Process.* Commissariat a l'Energie Atomique (CEA), DRDD/SPHA, France.

4. National Academy Press 1999. *AEA SILVER II Technology Package. Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons.* Washington, D.C.

5. Sugikawa, S., Umeda, M., Kobayashi, F., Nagata, M., Dojiri, S. and Amano, M. 2005. *Enhanced Electrochemical Oxidation of Spent Organic Solvent under Ultrasonic Agitation.* Global, Japan.