

Co (III) AS MEDIATOR IN PHENOL DESTRUCTION USING ELECTROCHEMICAL OXIDATION

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ABSTRACT

Electrochemically processing for organic waste treatment has been developed widely because the advantages of low cost, efficient, the exhausted gas that does not contain toxic materials, and can be operated in a relative low temperature. Electrochemical oxidation of organic compounds using metal ion mediator is one alternative method that is appropriate for the management of organic waste. Cobalt (III) is a strong oxidizing agent is prepared by the electrochemical oxidation method and as a mediator in the process of mediated electrochemical oxidation. At potential of 6 volt, with 4 M nitric acid and temperature of 25°C give result 23.86% where Co (II) is converted to Co (III) within 2 hours of the initial concentration of Co (II) 0.1 M. The addition of AgNO₃ to catholyte can increase the concentration of Co (III). At the optimum conditions, the mediator metal ion Co (III) can destructed to 66.44% of phenol compounds are oxidized to CO₂ for two hours.

Keywords: mediated electrochemical oxidation (MEO), Co (III), phenol.

1. INTRODUCTION

With the development of technology today, the more the waste generated, both organic and inorganic waste, which may be or may not be recycled. This waste product performed in the household, community or industrial, mostly composed of liquid waste and solid waste. Inadequate waste handling with application of technology that does not comply will cause negative effects for the environment because these wastes can contain chemicals which are hazardous and toxic. Wastewater treatment technologies is the key in maintaining environmental sustainability. Whatever kinds of industrial wastewater treatment technology that is built must be operated and maintained by local industry [2].

Various processing techniques to eliminate waste water pollutant materials have been tested and developed over the years, generally divided into three treatment methods such as physical processing, chemical processing and biological treatment

In general, waste processing currently done traditionally with regular combustion or by using an incinerator. Burning organic wastes using an incinerator can cause pollution in the form of exhaust gas emissions of toxic although incinerator has been equipped with Exhausted Gas Treatment System that has been standard in wastewater treatment processes and environmental standards. However, if the combustion conditions are not in controlled, the toxic waste in the gas can occur. This problem especially occur if the phenol compounds, chlorinated aromatic compounds and polychlorinated biphenyl (PCB) either radioactive or non-radioactive burned in the incinerator. To overcome with this, an electrochemical treatment of organic waste has been developed in developed countries in Europe, America, Korea and China. Electrochemical processing organic waste has advantages in terms of safety compared to using an incinerator, because the process can be done at relatively low temperatures, no exhaust gases are toxic and pose no secondary waste. Disadvantages of this process is the limited capacity, which could only process a minimal amount of organic waste in a day [2,9].

In this research will be described one of electrochemical process called mediated electrochemical oxidation method. The electrochemical process for the ambient temperature (below 373 K) and atmospheric pressure, in the processing of organic waste hazardous and mixed waste for the conversion of low-level radioactive waste are being developed. Oxidizing agent, is produced by anodic oxidation, will react with dissolved organic compounds to produce CO₂ and H₂O, because of the oxidizing agent play as a mediator in the electrochemical

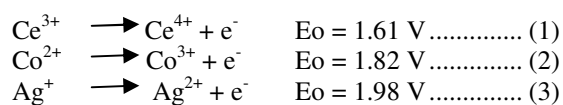
reaction, this process known as mediation electrochemical oxidation (MEO). Ambient temperature on the oxidation of organic waste components mixture done at this stage to avoid the possibility of condensing the high temperature which can carry out the evaporation of radioactive compounds when incineration takes place.[1,3]

In previous investigations by Farmer, (1992) reported the complete MEO of ethylene glycol (EG) and reported the complete MEO of ethylene glycol (EG) and benzene (BZ) by Ag(II). EG and its intermediates were completely converted to CO₂, (100% conversion efficiency). Coulombic efficiencies of 83-88% were achieved at 24-40% iL (336-673 mA), where $i_{\sim}$ is the limiting current for mediator generation. Unfortunately, the coulombic efficiency diminished to 39-44% at 58% iL (1346 mA). EG and its intermediates were oxidized by Ag(I) in close proximity to the surface of the rotating cylinder anode. Gas chromatography/Mass Spectrophotometry (GC/MS) was used to identify formaldehyde and formic acid in the anolyte, the two primary reaction intermediates formed during the MEO of EG. A model was developed to explain observed nonlinearity in the conversion-time curves by accounting for the sequential formation of reaction intermediates. With the exception of organics volatilized from the anolyte, BZ and its intermediates were also completely converted to CO₂. [3]

Electrochemical methods based on reduction and oxidation reaction of an anolyte that generates the electron transfer amount of current that can be measured. The amount of current is proportional to the measured anolyte concentrations. Electrochemical techniques based on electron transfer are controlled by an electric potential differences. In anode oxidation reaction occurs and in cathode reduction reaction. This electrochemical technique can be applied to the processing of waste, including radioactive waste and for decontamination. The range of organic materials which can be destroyed by this technique is very wide. The process is extensively employed for nuclear industry application, rubber, some plastics, poly urethane, ion exchange resins of various types and hydraulic and lubricating oils, aliphatic and aromatic compounds, chlorinated aliphatic and aromatic compounds etc.[10]

Electrochemical techniques for the decontamination can be carried out with the direct oxidation method and indirect. The waste is directly oxidized, applied using one of the electrodes (called "electro polishing"), while the indirect, if the oxidation uses media as a catalyst), wherein the catalyst has been reduced to be re-oxidation at the anode, Some mediators which have successfully applied this technique are silver,

cobalt and cerium, the oxidation potential (in 4 M HNO₃) as follows[11.12.16]:



In MEO process metal ions oxidized in acidic medium from lower level to a higher level of oxidation and the oxidized species will destroy organic compounds into carbon dioxide and water and the organic compound will be reduced. Therefore, the metal ions are not consumed in the reaction and act as a mediator. Mediator ion used is usually transition metals with high oxidation potential.[6.7.13.14]

The process of destruction of organic compounds can be done in two stages. In the first stage, experiments performed at low temperature which conducted a laboratory-scale system, variety of acid cocentration, and variety electrolyte. Second stage, the destruction of organic compounds made in large-scale system with the size of the commercial industry. In this experiment, organically fed and measured continuously during the anolyte running. Farmer et al. [3] reported that the oxidation of ethylene glycol and benzene carried out with silver as a mediator ion using a rotating cylindrical gold electrodes and also destruction of chlorinated organic carried out with the cobalt as a mediator using a rotating cylindrical platinum electrodes. Nelson [18] discusses the application equipment commercially developed for organic destruction with cerium mediator in the nitric acid. [17] examine the damage pesticides using silver mediator in the nitric acid medium. Chiba [19] studied the oxidation of model compounds of cellulose and using Mn (II) as a mediator. It was concluded from the above reference MEO process can be used for both the concentrated organic waste and wastewater. Although various metal ions work as a mediator, cobalt found either based on the following aspects. It does not form a precipitate as silver salts that form precipitates with anions liberated during the destruction of halogenated organic. Co leakage through electrode separator amount is less than the use of silver as a mediator. The more investigation frequently used Ce(IV)/Ce(III) redox couple MEO systems have less strength compared to cobalt in the oxidation of nitric acid medium. Electro-oxidation of cobalt nitrate in acid medium has been patented, but the electrochemical oxidation and damage the data have not been reported.[3.4.5]

Phenol were one of the most common pollutants found in the effluents of many industries such as and was chosen as the target organic species in the present investigation. [4.5.7.15] The aim of the present work were: to investigate Co(III) electro-oxidation in presence of nitric acid medium using a simple electrochemical cell, and to investigate the influence of applied cell potential, temperature, and concentration of nitric acid over Co(III) yield and to evaluate the degradation of organic compound, by the produced Co(III) mediator ion, in electrochemical cell.

2.0 EXPERIMENTAL

Glassware used in analytical chemistry laboratories like beaker, flask, magnetic stirrer, glass stirring rod, measuring cups, bowls watch, test tubes, funnel, pipette, measuring pipette and pipette volumes used for the preparation of the solution. Other equipment used in this study is the bottle spray, spatula, as well as containers of substances. The main tool used for electrochemical oxidation experiments were laboratory-scale cells

Materials used are Ag wire as anode, Pt wire as chatode, saturated KCl 3.0 M, cobalt(II) nitrate hexahydrate 1.0 M (M.W= 291.03), Ce(IV) sulfate tetrahydrate 0.1 M (M.W = 404.30) in 0.5 M sulfuric acid (96% m/v; ρ=1.84 kg/L), Fe(II) sulphate heptahydrate 0.1 M (M.W= 278.02) in 0.5 M sulfuric acid, barium hydroxide octahydrate 0.1 M (M.W= 315.33), anhydrous potassium dichromate 0.02 M (M.W= 294.21), silver nitrate 1.0 M, anhydrous sodium carbonate 0.1 M (M.W= 105.99), phenolphtalien indicator, methyl red indicator, indicator ferroin which is 1,10-phenantroline monohydrate(M.W=198.21), nitric acid p.a (65% m/v; ρ=1.40 g/cm³), hydrochloric acid 0.2 M (32% m/v; ρ= 1.16 g/cm³), sulfuric acid p.a, aquadest, nitrogen gas, ethylene glycol 0.05M, phenol solution 0.05 M (M.W= 94.11), and ethanol p.a 96% .

Overall, this study has divided into three stages of preparation, the first is to design an electrochemical cell and testing electrode Ag/AgCl as the reference electrode, the second optimization of the oxidation of Co (II) to Co (III) which to oxidize the organic compound. And the last stage is the oxidation and the destruction of organic compounds itself.

To see the potential effect on the oxidation of Co(II) into Co(III), was made a series of solution of Co (II) 0.1 M in 1.0 M nitric acid solution and then each solution is electrochemically oxidized at temperatures 25°C in hotplate and stirred within 2 hours and at potential 2 Volt - 8 Volt. Concentration Co(III) is formed at various intervals determined by reversible Potentiometry titration using electrode Ag/AgCl and Pt as indicator electrode, by adding 2 mL aliquots into 5 ml of Fe(II) sulfate, then Fe(II) which does not react with Co(III) is titrated with a solution of Ce(IV) by using indicators Ferroin. The data obtained were plotted between Co (III) concentration formed to reaction time at various potential.

Effect of nitric acid concentrations, was made a series of solution Co (II) nitrate 0.1 M in nitric acid which varied between 1.0 M and 6.0 M. Then each solution was oxidized electrochemically at 25°C stirred in the hotplate at constant potential 6 Volt. The concentration of Co (III) formed is titrated, by adding 2 ml aliquots into 5 ml solution of Fe(II) and excess of Fe(II) which does not react titrated with a solution of Ce(IV) use indicators Ferroin. Data were plotted between concentrations of Co (III) to reaction time to determine the optimum concentration of nitric acid.

Effect of temperature, made a series of solutions Co(II) in 4.0 M nitric acid and then oxidized electrochemically at potential 6 Volts with varied temperature 25°C, 40°C and 60°C and stirred in a hotplate. Potentiometric titration performed using an electrode behind the Ag / AgCl and Pt By adding 2 mL aliquot to 5 ml of Fe(II) sulfate. Excess of Fe(II) which does not react titrated with a solution of Ce(IV) by using indicators Ferroin. The data obtained were plotted between Co (III) formed to reaction time to determine the optimum temperature.

Effect of AgNO₃, into the catholyte added a amount of AgNO₃ so the concentration become 0.1 M, while in the anolyte solution of Co(II) in 0.1 M HNO₃ 4 M. Then the solution is electrochemically oxidized at a

constant temperature of 25 °C at a potential of 6 Volt and stirred with a magnetic stirrer. After the process done, 2 mL aliquot is added to 5 ml of Fe(II) sulfate. Excess of Fe (II) which does not react titrated with a solution of Ce (IV) use indicators Ferroin. And the data obtained were plotted between Co (III) concentration to reaction time to determine effect of AgNO₃.

Destruction of organic compounds, for the oxidation of phenols and ethylene glycol, mixed 100 mL of Co (II) 0.1 M solution with 25 mL organic solution 0,05 M in 4.0 M nitric acid.

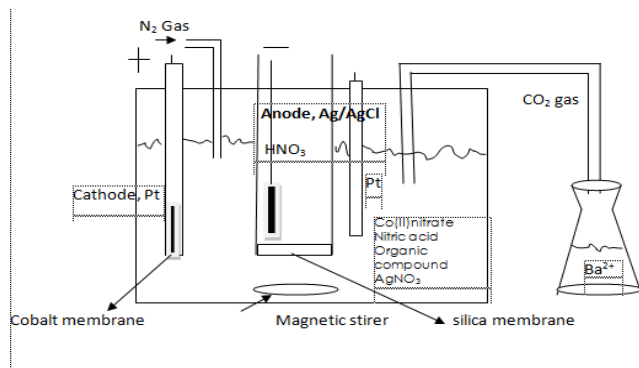


Figure 1. Electrochemical cells scheme

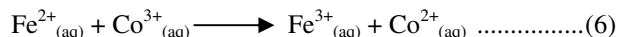
Then the solution is electrochemically oxidized at a temperature of 25 °C and at potential 6 Volt for 120 minutes. CO₂ gases liberated during the oxidation reaction were flow with nitrogen gas into the solution Ba(OH)₂. The excess solution of Ba(II) which does not react with carbon dioxide titrated with a solution of HCl using indicator methyl red. The amount of Ba(OH)₂ which reacts is proportional to the amount of CO₂ which released from the oxidation reaction of organic compounds. It can be calculate from the following equation:

$$\text{Oxidation Efficiency (\%CO}_2\text{)} = \frac{\text{mmol CO}_2 \text{ experiment}}{\text{mmol CO}_2 \text{ theory}} \times 100\% \quad \dots (\text{Eq.1})$$

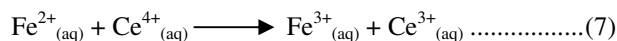
3.0 RESULTS AND DISCUSSION

3.1 Potential Effect

After the electrochemical oxidation performed at various intervals, then reverse potentiometric titration begin by adding 2 mL aliquots of Co(III), which formed during the electrochemical oxidation process, to 5 mL Fe(II) solution, and Fe(II) which does not react titrated with Ce(IV) by using indicators ferroin. At the beginning of the addition, Fe (II) is oxidized by Co (III) according to the reaction:



Furthermore, excess of Fe (II) which does not react with Co(III) is oxidized by Ce(IV) in the process of reverse potentiometric titration according to the reaction:



By determining mmol Fe(II) in early process and mmol Fe(II) residual unreacted with Co(III) in the process of titration will be obtained mmol Fe(II) reacted. Where mmol Fe(II) will be comparable to react mmol Co(III) that is in aliquots. With plotting concentration Co (III) which is formed on the oxidation time we get a graph as shown in Figure 1 below:

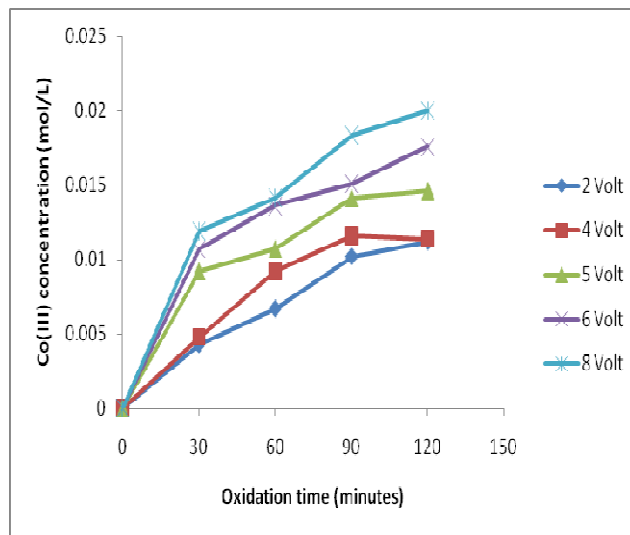


Figure 2. The relationship between the concentration of Co (III) to the oxidation reaction time on a variety of potential

Concentration Co(III) increases with the increase in potential, it is due to the greater potential given will speed up the process of electrochemical oxidation of Co (II) to Co (III). From the graph concentration Co(III) was significant at a potential of 6 V to 8 V, thus potentially been used for the subsequent oxidation process is at a potential of 6 Volt.

3.2 Effect of HNO₃ Concentration

The concentration of nitric acid was made in range 1.0 M to 6.0 M. The electrochemical oxidation start at potential 6 Volt and at temperature 25°C. Data of concentration Co(III) formed were plotted against time oxidation and obtained the following graph:

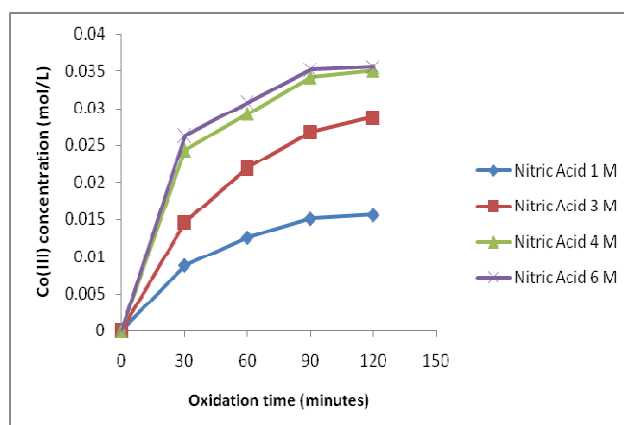
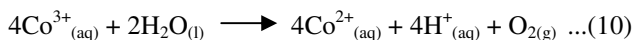
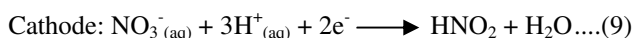
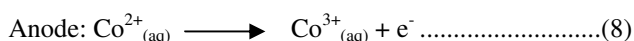


Figure 3. The relationship between concentration of Co(III) formed in the electrochemical oxidation to oxidation time at various concentrations of nitric acid

In figure 3, the increasing of the nitric acid concentration, concentration of Co (III) formed is also increased, this is due to the nature of Co(III) which very quickly reduced by water, as per following reaction:



From Fig.3 above, at concentration of nitric acid 4.0 M and 6.0 M to the increasing of concentration Co(III) is not too significantly, it is likely due to nitric acid which is also a

strong oxidizing agent, so that when the nitric acid concentration increased there will be a reaction to the form Co(III) prior to electrochemical oxidation process begins. So in this case for the addition of nitric acid in oxidation process Co (II) to Co (III) is selected for the optimum concentration is nitric acid 4.0 M.

3.3 Effect of Temperature

Oxidation temperature was kept at 25°C, 40°C and 60°C by using a nitric acid 4.0 M and at potential 6 Volt can be seen from the graph of concentration of Co(III) which formed during oxidation process versus oxidation time at various temperatures as below:

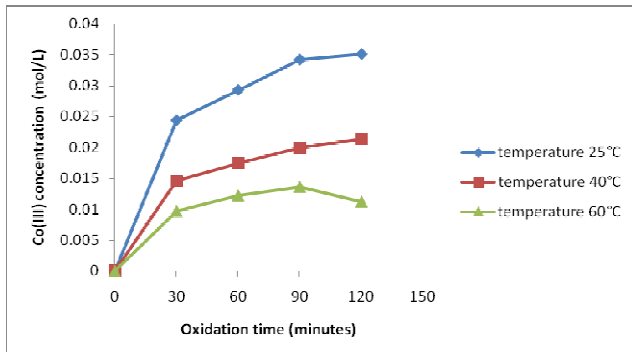


Figure 4. Relations between Concentration Co (III) which formed versus oxidation time at various temperatures

From the figure 4 above, shows with the increasing temperature at which the oxidation takes place, the concentration of Co(III) formed is decreased. This is because at the time during the anodic oxidation reaction Co (II) took place, the formation of complex compounds of cobalt nitrate not yet occurred. So that, to form Co(III), it may happened because of oxidation from HNO₃. By increasing the temperature, the formation of nitrous acid complex also increased in the anolyte and as a result the concentration of nitric acid itself will be reduced in the anolyte. Reduction of nitric acid levels will decreased the stability of formation Co(III) which causes the concentration of Co(III) will also decrease. And in this study, the temperature selected for the electrochemical oxidation process is at a temperature of 25°C.

3.4 Effect of AgNO₃ Addition

The amount of silver nitrate was added to the catholyte solution so that the concentration became 0.1 M. In the Figure 5, showed that the concentration of Co(III) formed during the electrochemical oxidation process increases with the presence of AgNO₃.

Figure 5 below shows the relationship between the addition of AgNO₃ to formation of Co (III) as follows:

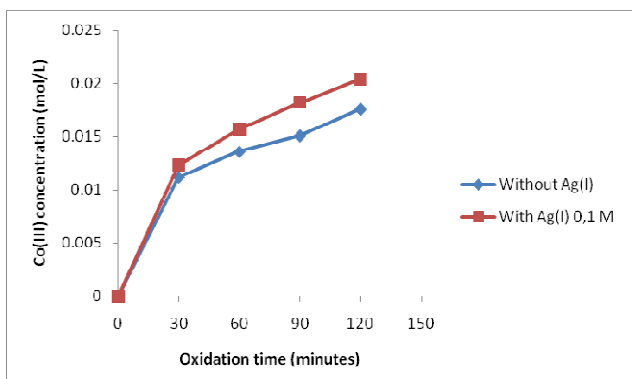
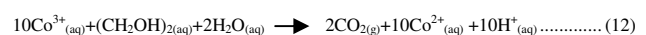
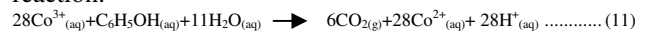


Figure 5 Relation between concentration Co (III) to the reaction time with the addition of AgNO₃

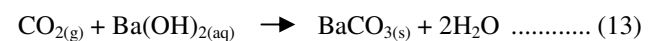
From Fig.5, it can be shown that the addition of AgNO₃ can increase the formation of concentration Co(III) this is due to the presence of Ag⁺ ions will decrease the rate of reduction of nitric acid in the catholyte and prevent the diffusion of H⁺ ions from the anolyte to the catholyte. So that the electrochemical oxidation process, improving the metal oxidizer ingredient in acid medium will increase, if the concentration of the acid medium increased and decreased with increasing temperature.

3.5 Oxidation of Organic Compounds

Organic compounds are oxidized in this case are phenol and ethylene glycol. In electrochemical oxidation of organic compounds with the mediator Co(III) will produce carbon dioxide gas, according to the following chemical reaction:



Carbon dioxide liberated during the oxidation reaction of organic compounds supplied to a solution of Ba(OH)₂ will form a precipitate BaCO₃ according to the following reaction:



In this research, the value of oxidation efficiency obtained for phenol is 66.44% and ethylene glycol is 86.47% by using Co (III) as a mediator in the MEO in a separate cell system with oxidation time for 2 hours at a temperature of 25°C.

4. CONCLUSION

Cobalt (III) is a strong oxidizing agent prepared by electrochemical oxidation method and as a mediator in the process mediated electrochemical oxidation. At potential 6 Volt, with 4.0 M nitric acid and temperature 25°C 23.86% Co (II) converted to Co (III) within 2 hours of an initial concentration of Co (II) 0.1 M. The addition of AgNO₃ to catholyte can increase the concentration of Co(III). At the optimum conditions, the mediator metal ion Co(III) has been successfully destructed 66.44% phenolic compounds and 86.47% ethylene glycol compound electrochemically oxidized to CO₂ for 2 hours with an initial concentration of each organic compound of 0.05M

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