Semi Batch Electrolyzer for Liquid DCM Removal Using Electrochemically Generated Homogeneous Ni(I)(CN)$_4^{3-}$

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Dichloromethane is a very strong persistent and its removal except on catalytic thermal combustion is tedious. Thus, the present investigation focuses on evaluation of non combustional technique like mediated electrocatalytic reduction (MER) towards dichloromethane removal using semi batch paired electrolyser. Mediator must possess high solubility in aqueous medium with low valent oxidation state stabilizing capacity. Here, Ni(II)(CN)$_4^{2-}$ solubility (0.1 M) and stability of low valent oxidation is considerably high in aqueous medium. Electrochemical reductive generation of Ni(I)(CN)$_4^{3-}$ was identified by oxidation reduction potential (ORP) change and the same was quantified by potentiometric titration and presented in the form of reduction efficiency. Finally, DCM removal was carried out by optimized conditions using semi batch electrolytic cell. The removal efficiency of DCM was calculated from the GC analysis and almost 81 % was found in 1 h duration. Cyclic voltammetry analysis of Ni(II)(CN)$_4^{2-}$ at the Cu electrode in presence of DCM revealed the MER of DCM followed by Ni(I)(CN)$_4^{3-}$. The removal of DCM might have been followed by radical reaction pathway that facilitates the reaction at room temperature.

1. Introduction

Growing interest of modernization in human mind causes many adverse effects in the environment, particularly water and soil contaminations by halogenated pollutants. Nevertheless, worldwide environment protecting groups like United States Environmental Protecting Agency (USEPA, 2001) keeps finding many controlling methods and also suggests to implement for healthier environment. Among many halogenated compounds, dichloromethane (DCM) found in huge quantities (USEPA, 2001) but it is a difficult compound to degrade its toxicity showing low conversions (Lopez et al., 2006; Bonarowska et al., 1999) due to the high amount of chlorinated by-products (Singuin et al., 2000). Among non-combustion methods of DCM degradation, electrochemical oxidation/reduction considered as futuristic technology due to clean reagent 'electron' (Juttner et al., 2000).

Reductive dehalogenation has found an effective method in removal of chlorinated organic compounds (COCs) from ground water effluents either by direct (Sanchez et al., 2008; Kotsinaris et al., 1998) or mediated (Yudi et al, 1988) reduction path ways. The direct electrochemical reduction of COCs present in aquatic effluents has been predominately studied to understand the fundamentals of reaction as initiative interest (Criddle and McCarty, 1991; Jiao et al., 2008). Because of the COCs solubility in organic solvents like acetonitrile, dimethyl sulfoxide, dimethyl formamide has used electrochemical reduction in the name of electro synthetic processes (Molina et al., 2003; Rondinini and Vertova, 2010). In order to minimize the applied energy, mediated electro catalytic reduction (MER, indirect reduction) has been performed on COCs reduction using the organic solvents (Skljarevski et al., 2011). The MER of COCs faced a serious problem during the separation of mediator from water after reduction reaction was completed, which is solved especially by prior separation of pollutants from water and the successive dissolution in suitable solvents (Durante et al., 2009).

Hence, certain attentions have been focused on homogenous mediators utilization in MER of COCs at aqueous medium like Co(II)(bipyridine), Ni(II)(salem), and Co(II)(tetraphenylporphyrin) (Muthuraman and Chandrasekara pillai, 2006; Wagoner et al., 2012; Trojanek et al., 2014). The Co(II)(bipyridine) mediator solubility found maximum of 2 mM and other mediators showed almost the same level of concentration

(Muthuraman and Chandrasekara pillai, 2006; Wagoner et al., 2012; Trojanek et al., 2014). Also, the solubility of COCs in aqueous medium has been facilitated by introducing surfactants like CTAB, SDS or TritonX-100 (Muthuraman and Chandrasekara pillai, 2006; Matsunaga and Yasuhara, 2005). Nonetheless, many research has been conducted towards development in upgrading the electrochemical cell, as reactor, for industrial application such as plate and frame type with filter press type (Bringmann et al., 1995) using the idea for paired electrolysis (Bringmann et al., 1995). By using the paired electrolysis method, many COCs have been oxidized (Balaji et al., 2007). Further, divided paired electrolysis have been utilized for mediated electrochemical oxidation (MEO) of many pollutants (Govindan et al., 2013; Govindan and Moon, 2015), but MER of COCs is still under infant stage. To explore the MER through divided paired electrolysis, many rooms remain like selection of high solubility mediators, generation of mediators at cathodic half-cell, reduction reaction between mediator and COCs.

In the present investigation, highly soluble $Ni(II)(CN)_4^{2-}$ mediator has been applied on liquid DCM degradation using semi batch paired electrolyser. The electrochemical reduction of $Ni(II)(CN)_4^{2-}$ was performed on Cu electrode (cathode) and the low oxidation state of $Ni(II)(CN)_4^{2-}$ was identified by oxidation reduction potential (ORP) change during electrolysis. Quantification of electrochemically generated low valent $Ni(I)(CN)_4^{3-}$ was derived from potentiometric titration with Fe(III). The electrochemically generated $Ni(I)(CN)_4^{3-}$ was subjected to reduction by DCM using semi batch reaction. At first glance, the $Ni(I)(CN)_4^{2-}$ concentration change facilitates to identify degradation of DCM. The degradation efficiency of DCM was derived by GC of benzene extracted reaction sample solution. Also, the MER was checked by cyclic voltammetry (CV) experimental analysis.

2. Experimental

2.1 Chemicals

Dichlromethane (DCM) was purchased from Aldrich. Ferrous sulphate was from Junsei Chemical (Japan), and sulfuric acid (95%) was from Sam Chun Chemicals (Korea). All chemicals were used as received.

$Ni(II)(CN)_4^{2-}$ preparation: $K_2[Ni(II)(CN)_4]$ was synthesized as reported previously (Fernelius and Burbage, 1946) Briefly, 53.77 g potassium cyanide (KCN) dissolved in 50 ml water was added to a 60 ml of a cooled solution containing 40 g of Nickel (II) nitrate under nitrogen (cyanide : Ni ratio ~4:1) and then an equal volume of chilled alcohol was added. The resulting mixture was slowly cooled until a mass of thin orange platelets appears. The obtained complex was rapidly filtered, washed with cold alcohol, recrystallized using alcohol, dried in a vacuum desiccator, and stored in an air-tight brown bottle.

2.2 $Ni(I)(CN)_4^{3-}$ generation

A thin layer flow through divided electrochemical cell configuration was used as reported elsewhere (Govindan and Moon, 2015) with suitable modification in conditions. In short, a catholyte volume of 200 ml containing 9 M KOH and 0.05 M $Ni(II)(CN)_4^{2-}$ in a 250 ml glass tank and an anolyte volume of 200 ml containing 5 M H_2SO_4 in another 250 ml glass tank, both connected to a flow through divided (by Nafion® 324 from DuPont, USA) cell. Anolyte and catholyte were continuously circulated using peristaltic pumps (Masterflex-7524-45, Cole-Parmer Instrument Company, USA) through anode and cathode compartments, respectively, at a rate of ~70 ml min^{-1}. The electrolysis experiments were conducted using constant current mode by different applied current densities between 10 to 50 mA cm^{-2} (by a D.C. power supply from Korea Switching Instruments). An electrode area of 4 cm^2 was used for electrolysis experiments.

2.3 Analysis and procedure

All experimental data were collected using a constant concentration of $Ni(II)(CN)_4^{2-}$ (0.05 M). $Ni(I)(CN)_4^{3-}$ concentration was determined using ORP changes upon titration against $Fe(II)SO_4$ (0.001 M) solution using EMC 133 (Pt (6 mm) gel electrolyte) electrode from Germany with the help of iSTEK multimeter (Model No.: pH-240L) from USA.

A 2 ml of reaction samples were withdrawn via syringe from the catholyte reaction tank (Fig.1) at defined interval and extracted by benzene (5 ml) for GC, to identify degradation efficiency. A Shimadzu Q2010 (GC/MS), Japan, equipped with an electron capture detector. The DB-5 column capillary (30 m length × 250 μm diameter × 0.25 μm thickness) was used for all chromatographic separations (J&W Scientific). The source temperature was 250°C and the GC transfer line was held at 280°C. The GC oven temperature was programmed as follows; 4 min at 45°C, increase to 100°C at 4°C min^{-1}, increase to 250°C at 8°C min^{-1}, and then held at 250°C (total run time: 50 minutes). Helium was used as carrier at a flow rate of 2 ml min^{-1}. Extracts were automatically injected into the GC inlet at a split ratio of 6:1 at 100°C.

CV studies. A potentiostat (Princeton Applied Research, versaSTAT3, USA) was used for the CV analyses and interfaced with a personal computer running VersaStudio software. For these CV studies, a three electrode cell configuration was used with Pt and Ag/AgCl as counter and reference electrodes respectively, and the working electrode used was Cu mesh.

3. Results and Discussions

3.1 Electrolytic generation of Ni(I)(CN)$_4^{3-}$

As given conditions in the figure 1A caption, the paired electrolysis started and the obtained changes in the cathodic half-cell shown in figure 1A. The initial ORP value -170 mV increases with increasing electrolysis time and attains steady state in 60 min around -800 mV (Figure 1A curve a) and finally reaches -850 mV in 6 h. This is the first indication of Ni(I)(CN)$_4^{3-}$ formation. The ORP value difference facilitates to do potentiometric titration and through which corresponding low valent concentration of Ni(I)(CN)$_4^{3-}$ was derived and presented in figure 1A curve b. The reduction efficiency is increased with electrolysis time and reaches 8 % in 6 h duration. Also, the initial yellow color solution changes to red color in 30 min and maintains the formation of Ni(I)(CN)$_4^{3-}$ (Mizuta et al., 1968). In order to check the reduction efficiency limitations, various applied current densities were conducted and the results are presented in Figure 1B. It was observed Ni(I)(CN)$_4^{3-}$ concentration increased on increasing current density from 10 to 25 mA cm^{-2}, and above 25 mA cm^{-2}, there was no predominant change in the Ni(I)(CN)$_4^{3-}$ or decrease at longer electrolysis time. This may have been due to Ni(0)(CN)44- formation and the subsequent formation of [Ni2(CN)3]3- by water reduction (Orlik and Galus, 1988). Thus, the optimum current density of reduction of Ni(II) was found to be 25 mA cm-2.
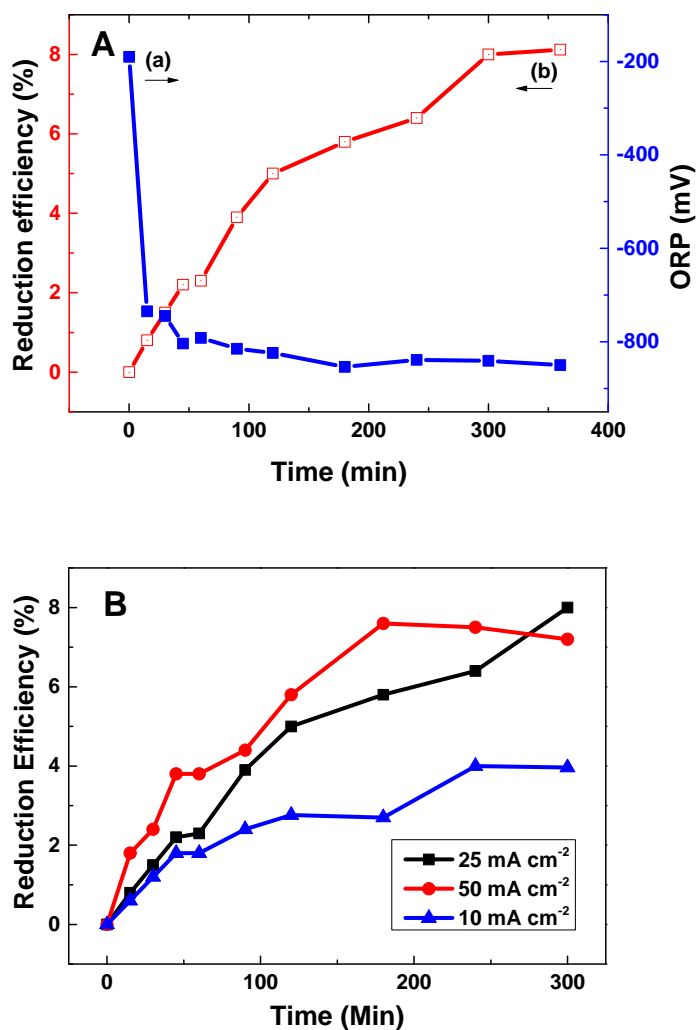

Figure 1A: ORP and reduction efficiency variation with time during electrolysis of Ni(II)(CN)$_4^{2-}$ in 9 M KOH solution. Electrolysis conditions: Electrode = Pt coated Ti (anode) and Cu (cathode); Current density = 25 mA cm^{-2}; Solution flow rate = 70 ml min^{-1}.

Figure 1B: Reduction efficiency variation with time on current density during electrolysis of Ni(II)(CN)$_4^{2-}$ in 9 M KOH solution. Current densities mentioned in the figure and remaining conditions are same as in figure 1A.

3.2 Ni(I)(CN)$_4$$^{3-}$ mediated reduction of DCM

The electrochemically generated Ni(I)(CN)$_4$$^{3-}$ was allowed to react with DCM and the obtained results are presented in figure 2A. The Ni(I)(CN)$_4$$^{3-}$ generation was allowed to reach nearly 8.7 % and then 0.026 M DCM was injected into the reactor for its degradation. Once DCM is injected, the Ni(I)(CN)$_4$$^{3-}$ concentration decreased to 6 % and maintained around 7.2 up to 1 h reaction time (Figure 2A curve a) . At the same time, the ORP value also reduced to -740 mV from -850 mV and maintained throughout the reaction time (Figure 2A curve b). The ORP and reduction efficiency change during the addition of DCM explains the reaction between Ni(I)(CN)$_4$$^{3-}$ and DCM occurred in the reactor. Additionally, the MER of DCM by Ni(I)(CN)$_4$$^{3-}$ was cross checked by CV analysis as shown in figure 2B. The only Ni(II)(CN)$_4$$^{2-}$ in 9 M KOH shows a broad reduction peak from -420 mV to -680 mV and corresponding anodic peaks at -350 mV (small hump) and -180 mV (Figure 2B curve a). The first redox peak (-420 mV and -180 mV) corresponds to a Cu redox behaviour and the second reduction peak believed to be response of Ni(II)(CN)$_4$$^{2-}$ reduction peak. At the same time, the cathodic peak current at -680 V increased in presence of 0.026 M DCM (Figure 2B curve b) with no change in Cu redox peak tells MER of DCM occurred by Ni(I)(CN)$_4$$^{3-}$.
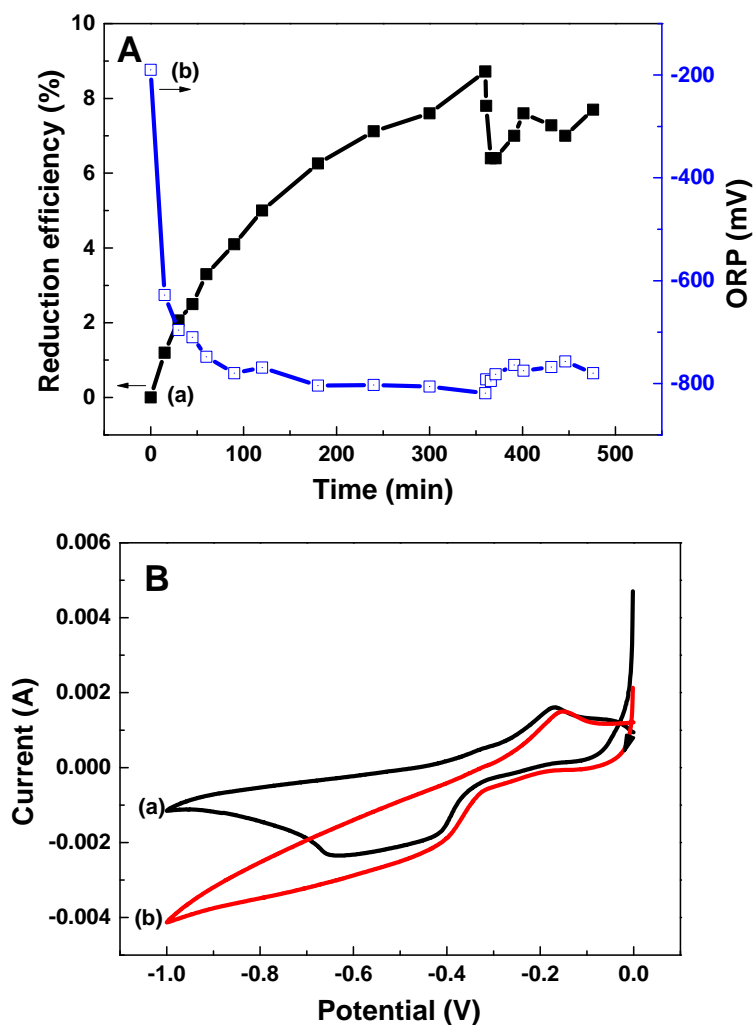

Figure 2A: Identification of DCM degradation by ORP and reduction efficiency change of Ni(II)(CN)$_4$$^{2-}$ during semi batch removal process in 9 M KOH catholyte solution. The electrolysis conditions are same as in figure 1A.

Figure 2B CV response of 0.01 M Ni(II)(CN)$_4$$^{2-}$ in 9 M KOH (a) absence and (b) presence of 0.026 M DCM at a scan rate of 20 mV s^{-1}.

The degradation efficiency of DCM during batch electrolytic reduction was analysed by GC analysis and the results are depicted in figure 3. In the just prepared solution, which contains $Ni(II)(CN)_4^{2-}$ in 9 M KOH, 0.026 M DCM was injected and extracted using benzene considering as before electrolysis (BE) sample or base sample. GC results of samples that are collected during the reaction at 30 min and 60 min samples compared with the BE sample results. According with the present GC experimental conditions, the retention time (RT) for DCM is around 7.8 min. Along with the solvent peaks, the BE sample shows a peak at 7.8 RT that confirms the detection of DCM. In the case of reaction samples, peak intensities at RT 7.8 decreases with time and diminished in 1 h. Based on the peak area at RT of 7.8 min, the degradation efficiency calculated and depicted in figure 3. The degradation efficiency of DCM reached 81 % in 1 h tells that the degradation of DCM by $Ni(I)(CN)_4^{3-}$ is occurred. In catalytic combustion, hydrodechlorination is found at 300 °C and claimed that C-Cl bond braking by strong adsorption of Lewis acidity contained Pd/Al_2O_3 catalyst (Sanchez et al., 2008). Here, the DCM dechlorination facilitated at room temperature might be, by radical reaction pathway by carbene formation that might have induced the reaction at room temperature to cleave the C-Cl bond, as supported by the CV results that the degradation reaction follows by the MER via $Ni(I)(CN)_4^{3-}$. Still more studies are needed to derive reaction mechanism and by-products confirmation.
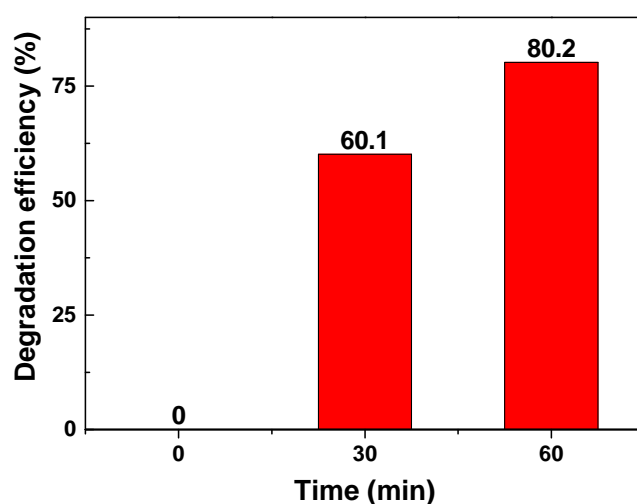

Figure 3: Removal efficiency of DCM with reaction time derived from GC analysis. Removal experimental conditions are same as in figure 2A caption.

4. Conclusions

According to the results, the electrolytic reduction of $Ni(II)(CN)_4^{2-}$ is possible to form $Ni(I)(CN)_4^{3-}$. The ORP value changes and potentiometric titration analyses have helped quantitative identification of $Ni(I)(CN)_4^{3-}$. Exceeding higher current density beyond 25 mA cm^{-2} found further reduction to $Ni(0)(CN)_4^{4-}$. So, 25 mA cm^{-2} might be optimum in generation of $Ni(I)(CN)_4^{3-}$ mediator. The degradation reaction of DCM identified at first by reduction efficiency change of $Ni(II)(CN)_4^{2-}$. Finally, degradation of DCM was confirmed by GC peak analysis and found to be 81 %. The reaction might have occurred in radical reaction pathway. Further works needed to confirm the by-products and reaction pathway.

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