Removal of Heavy Metal Ions by Electrocoagulation for Continuous Use of Fe^{2+}/Fe^{3+}-Mediated Electrochemical Oxidation Solutions

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Removal of heavy metal ions (Cd^{2+} and Zn^{2+}) by electrocoagulation (ECG) was investigated in an acidic condition, which is necessary for re-using or discharging the mediated electrochemical oxidation (MEO) media. Effects of various parameters such as electrolytes, current densities, and electrode materials were examined for a metal-contaminated MEO system using Fe^{2+}/Fe^{3+} pairs as a mediator. It was found that ECG with Al electrodes is greatly affected by the presence of Fe^{2+}. [Cd^{2+}] and [Zn^{2+}] remain constant until [Fe^{2+}] reaches a certain concentration level (*ca.* 10 mM). This preferential removal of Fe^{2+} during ECG with Al electrodes is not alleviated by controlling current densities, potential programs, and solution mixing. ECG with Fe electrodes, on the other hand, resulted in relatively fast removal of Cd^{2+} and Zn^{2+} under coexistence of Fe^{2+}, indicative of the different role between Fe^{n+} generated from an electrode and Fe^{2+} initially present in a solution. When ECG was performed with Fe electrodes until [Fe^{n+}] became the same as the concentration of initially present Fe^{2+}, [Cd^{2+}] and [Zn^{2+}] were reduced to one-tenth of the initial concentrations, suggesting the possibility of a continuous use of the medium for a subsequent MEO process.

Key Words : Electrocoagulation, MEO, Metal ions, Fe electrode, Al electrode

Introduction

Since the electrochemical treatment of wastewater is environmentally friendly and appropriate for applying to an effluent system, it has been widely studied during a last few decades in spite of large capital investment and energy consumption.[1] Electrochemical methods include electroflotation,[2] electrodeposition,[3] direct/indirect electrochemical oxidation,[4-6] and ECG.[7,8] Among these, ECG is probably the most versatile method in that various polluting materials, including a wide range of ionic species[9-15] as well as organic materials such as textile dyes,[16,17] phenolic compounds,[18] and polymer latex[19] can be successfully treated. This is possible because ECG utilizes various forms of monomeric and polymeric metal hydroxide complexes which can interact with polluting materials *via* several routes (electrostatic force, surface adsorption, physical entrapment, and coprecipitation).[7,8] In general, an ECG cell is equipped with Fe or Al electrodes. Upon applying a potential between two electrodes, metal dissolution at the anode and cathodic reaction of electroactive species in solution take place to produce coagulants. ECG therefore, usually requires frequent change of sacrificial anodes and cleaning of cathodes for maintenance.

In this regard, when limited to the decomposition of organic wastes,[4-6] indirect electrochemical oxidation (MEO) has advantages over ECG since mediators can completely decompose organic hydrocarbons to CO_2 and H_2O.[5,6,20-25] Reactive and high-valent metal ions which are electrochemically generated from stable and low valent state are utilized as oxidants. Various redox couples such as Ag^{+}/Ag^{2+},[20] Co^{2+}/Co^{3+},[21] Fe^{2+}/Fe^{3+},[22] and Ce^{3+}/Ce^{4+} [23-25] have been examined to degrade organic pollutants.

For economical and environmental reason, the overall MEO system is operated as a closed loop. The mediator-containing anolytes are circulated through an electrochemical cell, in which high-valent metal ions are electrochemically produced, and mixed with organic wastes. The concentration of mediators is maintained *via* appropriate dehydration and gas evolution processes, in principle making repeated use of the solution possible.[25] Repeated treatments of wastewater, however, essentially result in the accumulation of heavy metal ions which can be problematic to continuous operation.

In this paper, we describe the removal of Cd^{2+} and Zn^{2+} from Fe^{2+}/Fe^{3+}-MEO media by ECG. Cd^{2+} and Zn^{2+}, which are commonly found in various wastewater sources, were tested as heavy metal ions accumulated in a MEO solution. A Fe^{2+}/Fe^{3+}-MEO system was chosen since we considered that its halide-tolerance and facile change of redox states would make it beneficial to specific MEO systems. It has been addressed that, despite the relatively low standard reduction potential (E^0), Fe^{3+} is an efficient oxidant for the complete destruction of organic compounds such as ethylene glycol.[22]

<u>MEO process</u>

$10Fe^{2+} \rightarrow 10Fe^{3+} + 10e^-$
[generation of mediator in anolyte]

$10H^+ + 10e^- \rightarrow 5H_2$ [reduction in catholyte]

$10Fe^{3+} + (CH_2OH)_2$ in wastewater $+ 2H_2O$
$\rightarrow 10Fe^{2+} + 2CO_2 + 10H^+ +$ (concentrated M^{n+})
[destruction of organics]

Subsequent ECG process

$4Fe(s) \rightarrow 4Fe^{2+} + 8e^-$ [dissolution of anode]

$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3$ (flocs) $+ 8H^+$ [in solution]

flocs + concentrated $M^{n-} \rightarrow M^{n+}$ adsorbed flocs [precipitation]

Experimental

HNO_3, $FeCl_2$, $Fe(NO_3)_3 \cdot 9H_2O$ (from Junsei, Japan), $Zn(SO_4) \cdot 7H_2O$ (from Daejung, Korea), $Cd(NO_3)_2 \cdot 4H_2O$, NaCl, $NaNO_3$, Al plates (99.9+), and Fe plates (99.9+) (from Aldrich) were used as received. Water was purified through a Milli-Q Plus system (Millipore Co.) until its resistivity was over 18 MΩ cm.

ECG was carried out using 2 parallel Al or Fe electrodes separated by 0.8 cm. The electrolytic cell was filled with solutions of 3 mL and various constant currents were applied between the electrodes through an EC Epsilon electrochemical analyzer. During electrolysis, samples of 10 μL were periodically taken from the ECG solution. After filtration, samples were diluted 100 times with 0.1 M HNO_3 and the concentration changes of metal ions were measured by atomic absorption spectrophotometry (Hitachi, Z-5000).

Results and Discussion

Figure 1 shows the concentrations of Fe^{2+}, Zn^{2-}, and Cd^{2+} vs. energy consumed during ECG in 0.1 M NaCl, $NaNO_3$, and HNO_3. A current density of 4.3 mA cm^{-2} was applied between two Al plates. The concentration changes were monitored by atomic absorption spectrophotometry after dilution of sampled solutions. On passing the current in NaCl, the concentration immediately decreases and reaches negligible values when *ca.* 80 J is consumed (Figure 1A). A slightly faster decrease in Fe^{2+} is observed during the initial period. In $NaNO_3$, on the other hand, the energy efficiency is reduced and the difference between metal ions becomes distinguishable throughout the whole time period examined.

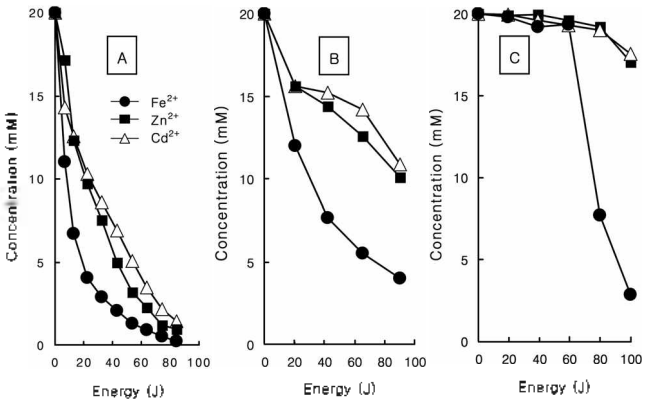

Figure 1. Concentration changes during ECG in 0.1 M (A) NaCl, (B) $NaNO_3$, and (C) HNO_3. j = 4.3 mA cm^{-2} was applied between Al electrodes in a mixed solution containing Fe^{2-}, Zn^{2-}, and Cd^{2+}.

Figure 1B indicates that appreciable amounts of metal ions remains even after energy consumption of 90 J in 0.1 M $NaNO_3$ and the removal of Fe^{2-} are favored. This behavior becomes more distinct in HNO_3 (Figure 1C). After an initial retardation period, $[Fe^{2+}]$ suddenly decreases to *ca.* 2 mM, but $[Cd^{2-}]$ and $[Zn^{2+}]$ show only a small depletion.

The difference in the removal efficiency with different electrolytes is not surprising. Since the ionic conductivity is not an issue here, it is likely that the electrolyte dependence results from the properties of the anions (Figure 1A *vs.* 1B) and solution pH (Figure 1B *vs.* 1C). It is known that passivation of the electrode surface is reduced at high $[Cl^-]$.[14] The effect of pH on ECG has also been reported by numerous authors. As a result, it is now well known that the increase in initial pH enhances the removal efficiency of metal ions by ECG[9,10,13,15]

Since the goal of this work is to consecutively treat wastewaters by ECG after repeated Fe^{2-}/Fe^{3+}-MEO processes, the solution pH should be maintained highly acidic. We re-examined the effect of pH to identify the pH ranges appropriate to both ECG and MEO. Table 1 compares the changes of $[Zn^{2-}]$ and pH before and after ECG (120 min) in various $[HNO_3]$ with Al electrodes. It is obvious that decrease in $[HNO_3]$ leads to rapid removal of Zn^{2-} with greater energy consumption resulting from the lower solution conductivity. Considering MEO processes performed in high $[H^-]$ and ECG efficieny, we carried out further ECG experiments in 0.1 M HNO_3. The energy efficiencies in the cases of initial $[HNO_3]$ of 0.05 and 0.1 M are similar.

Another important feature of Figure 1 is the preferential

Table 1. Effect of HNO_3 concentrations on Zn^{2+} removal with an Al electrode. j = 4.3 mA cm^{-2}

$[HNO_3]$	initial		final		energy consumption (J)	energy efficiency (mol J^{-1})
	$[Zn^{2-}]$ (mM)	pH	$[Zn^{2+}]$ (mM)	pH		
0.05 M	50	1.60	2.1	6.38	420	3.4×10^{-7}
0.10 M	50	1.27	9.9	4.68	336	3.6×10^{-7}
0.25 M	50	0.95	41	2.50	291	9.2×10^{-8}
0.50 M	50	0.64	50	1.52	267	0

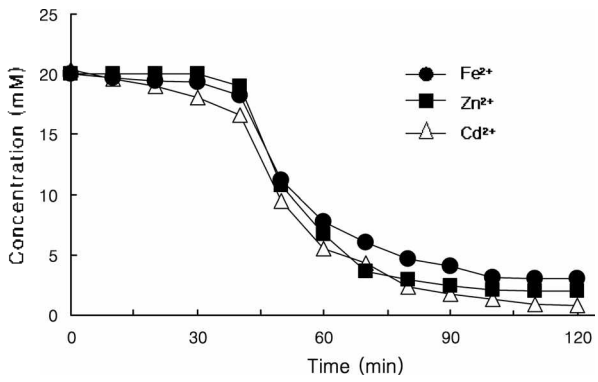

Figure 2. Concentration changes during ECG in 0.1 M HNO_3 solutions containing a single component of metal ions. j = 4.3 mA cm^{-2} was applied between Al electrodes.

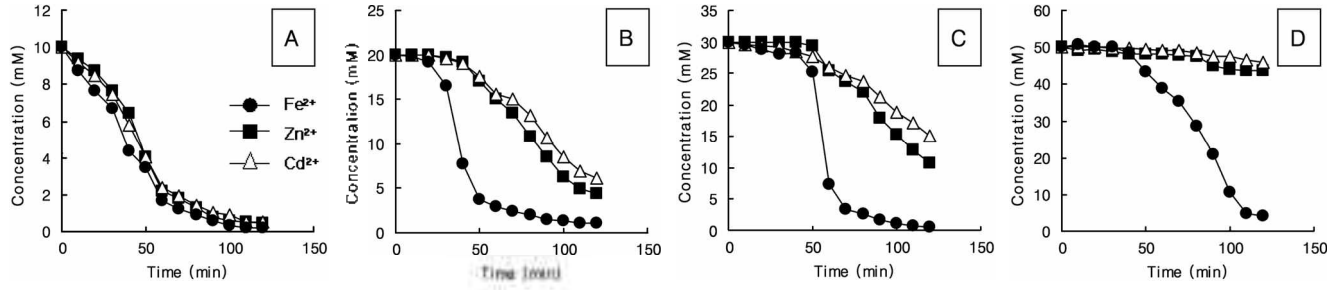

Figure 3. Concentration changes during ECG in 0.1 M HNO_3 solutions containing $[Fe^{2+}] = [Zn^{2+}] = [Cd^{2+}]$ = (A) 10, (B) 20, (C) 30, and (D) 50 mM. j = 4.3 mA cm^{-2} was applied between Al electrodes in a mixed solution containing Fe^{2+}, Zn^{2+}, and Cd^{2+}.

removal of Fe^{2+}. Since we are examining ECG coupled with Fe^{2+}/Fe^{3+}-MEO, this behavior must be properly controlled. Figure 2 demonstrates that the concentration changes during ECG in 0.1 M HNO_3 solutions containing a single metal ion of 20 mM. Unlike Figure 1C, no significant difference with ionic species is observed, implying that the slow removal of Zn^{2+} and Cd^{2+} in a mixed solution is due to the presence of Fe^{2+}.

The preferential removal of Fe^{2+} in a mixed solution becomes more obvious as the increase of metal ion concentrations. Figure 3A to 3D compare the decrease in metal ion concentration during ECG in 0.1 M HNO_3 (j = 4.3 mA cm^{-2}). The initial concentrations of each metal ion were 10, 20, 30, and 50 mM, respectively. While no difference between ionic species is observed in a mixed solution of 10 mM each, the preferential removal of Fe^{2+} becomes significant as the increase of concentrations. When the concentrations of each ion are 50 mM (Figure 3D), negligible amounts of Zn^{2+} and Cd^{2+} are removed within an experimental time scale. Figure 3 implies that the presence of Fe^{2+} hampers the ECG of other metal ions until $[Fe^{2+}]$ drops below a certain concentration level (*ca.* 10 mM).

The effect of current density was also examined to see whether the preferential removal can be controlled. Figure 4 shows the fraction of each metal ion remaining after the passage of *ca.* 32 C cm^{-2} between two Al plates (*i.e.*, ECG for 120, 80, 53, and 32 min at j = 4.3, 6.7, 10.0, and 16.7 mA cm^{-2}). The increase in current density removes metal ions more efficiently. Note that, while *ca.* 50% of Zn^{2+} and Cd^{2+} are removed for 32 min at 16.7 mA cm^{-2}, 90% of Zn^{2+} and Cd^{2+} remain in a HNO_3 solution after 120 min. at 4.3 mA cm^{-2}. Although Figure 4 suggests the possibility that Zn^{2+} and Cd^{2+} dissolved in a mixed solution can be completely removed by lengthening the ECG time at high current densities, the preferential removal of $[Fe^{2+}]$ is still uncontrollable. The application of AC current and vigorous mixing of a solution do not improve this behavior.

Since the presence of Fe^{2+} above *ca.* 10 mM hampers precipitations of Zn^{2+} and Cd^{2+}, it is reasonable to speculate that the use of Fe electrodes retards the removal of Zn^{2+} and Cd^{2+} to a greater extent. Expecting no change in $[Zn^{2+}]$ and $[Cd^{2+}]$ within an experimental time scale, we performed ECG with Fe electrodes in a mixed solution. Figure 5 shows the concentration variations of 3 metal ions under the

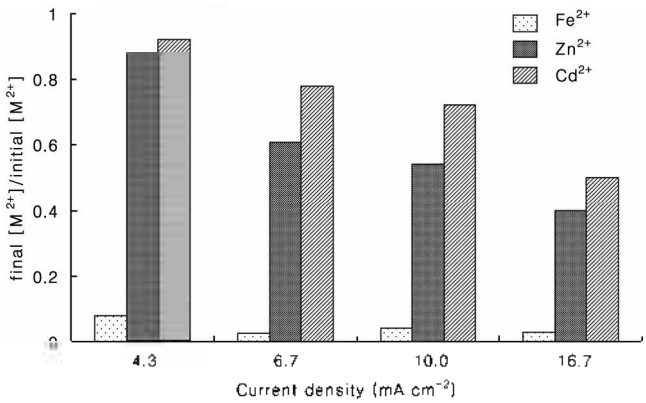

Figure 4. Fractions of each metal ion remaining after the passage of *ca.* 32 C cm^{-2}. Different current densities were passed between two Al plates in a mixed solution.

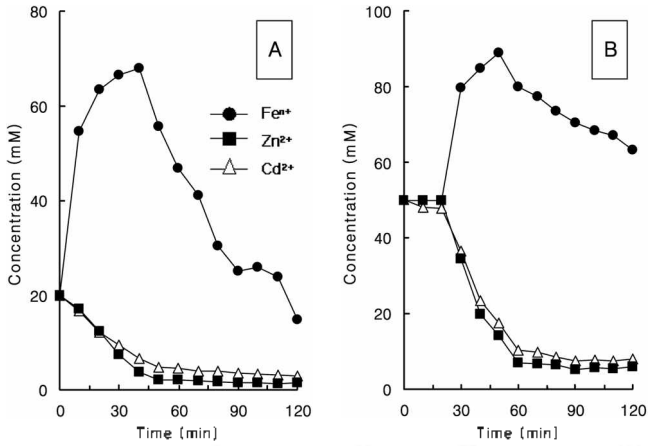

Figure 5. Concentration changes during ECG with Fe electrodes in 0.1 M HNO_3 solutions of $[Fe^{2+}] = [Zn^{2+}] = [Cd^{2+}]$ = (A) 20 and (B) 50 mM. j = 4.3 mA cm^{-2}.

application of 4.3 mA cm^{-2}. When the initial concentrations of each ion are 20 mM (Figure 5A), $[Fe^{n+}]$ immediately increases on passing current due to oxidation of the sacrificial Fe electrode (Fe^{n+} stands for both Fe^{2+} and Fe^{3+}). $[Fe^{n+}]$ then begins to decrease after reaching 68 mM at 40 min. $[Zn^{2+}]$ and $[Cd^{2+}]$, on the other hand, decrease regardless of the concentration level of $[Fe^{n+}]$. This is quite surprising because the results using Al electrodes (Figure 3B) showed no concentration changes of Zn^{2+} and Cd^{2+} during the initial

Table 2. Concentrations of Zn^{2+} and Cd^{2+} after ECG until $[Fe^{n+}]$ was returned to initial $[Fe^{2+}]$ in 0.1 M HNO_3, j = 4.3 mA cm^{-2} between Fe electrodes

initial $[Fe^{2+}]$ (mM)	initial $[Zn^{2+}]$ = $[Cd^{2+}]$ = 20 mM			initial $[Zn^{2+}]$ = $[Cd^{2+}]$ = 50 mM		
	$[Zn^{2+}]$ (mM)	$[Cd^{2+}]$ (mM)	Time (min)	$[Zn^{2+}]$ (mM)	$[Cd^{2+}]$ (mM)	Time (min)
20	1.5	2.6	90	5.2	5.6	81
50	2.3	2.1	101	4.9	7.0	153
75	2.1	2.8	120	4.4	6.8	205
100	2.0	3.1	143	5.0	6.1	259

50 min due to high $[Fe^{2+}]$. We further investigated this point with a mixed solution containing 50 mM each. Figure 5B exhibits no substantial change in metal ion concentrations during the initial 20 min. followed by a sudden increase in $[Fe^{n+}]$ and simultaneous decrease in $[Zn^{2+}]$ and $[Cd^{2+}]$. This complicated behavior indicates that Fe^{n+} generated at an electrode acts differently from Fe^{2+} initially present in solution. One possible explanation is that most Fe^{n+} ions released from a sacrificial electrode are in a high-valent state (Fe^{3+}). The release of Fe^{3+} results in the abundance of $Fe(OH)_3$ since it has a much smaller solubility product constant (K_{sp} = 10^{-39}) than $Fe(OH)_2$ (K_{sp} = 10^{-17}).[26] Although Fe^{2+} can be oxidized by O_2 to Fe^{3+} in an acidic medium,[1] we believe that finite amounts of O_2 limit this reaction. It should be mentioned that the use of Fe electrodes does not weaken the preferential interaction of Fe^{2+}, but rather accelerates the removal of Fe^{2+}. The retardation for initial 20 min in Figure 5B is likely due to precipitation of Fe^{2+}.

In order to confirm the above speculation we compared the effects of initial presence of Fe^{2+} and Fe^{3+}. Figure 6 compares the concentration changes of Zn^{2+} and Cd^{2+} coexisting with Fe^{2+} (dotted line) and Fe^{3+} (solid line) under the passage of 4.3 mA cm^{-2} between Al electrodes. We chose Al electrodes to see the concentration differences more distinctively. It is obvious that Zn^{2+} and Cd^{2+} are removed more efficiently in the presence of Fe^{3+} than Fe^{2+}. Although the reason that Fe^{2+} preferentially interacts with aluminum hydroxide complexes is not clear, Figure 6 reveals that Fe^{3+} contributes to the removal of Zn^{2+} and Cd^{2+} along with aluminum hydroxide complexes. This suggests that it is necessary to maintain the oxidation state of Fe^{n+} of MEO media in a Fe^{3+} state for efficient ECG operation. However, Figure 6 does not mean that ECG with Al electrodes in the presence of Fe^{3+} is as efficient as the use of Fe electrodes. When compared with Figure 5B, Figure 6 shows substantially slower removal. Moreover, ECG with Al electrodes needs the supplementary addition of mediators for a subsequent MEO process.

Table 2 summarizes the concentration of Zn^{2+} and Cd^{2+} when $[Fe^{n+}]$ was returned to initial $[Fe^{2+}]$. The initial $[Zn^{2+}]$ and $[Cd^{2+}]$ were fixed at 20 or 50 mM, but the initial $[Fe^{2+}]$ was varied. A current density of 4.3 mA cm^{-2} was applied between Fe electrodes. It is evident that ECG with Fe electrodes enables lowering $[Zn^{2+}]$ and $[Cd^{2+}]$ to *ca.* one-tenth of the initial concentration within a reasonable time scale, indicating that ECG with Fe electrodes is a promising method for reducing the contamination level of Fe^{2+}/Fe^{3+}-MEO media without oxidizing Fe^{2+} in a MEO loop before ECG. The treated solution can be continuously utilized for a subsequent MEO process without adding mediators.

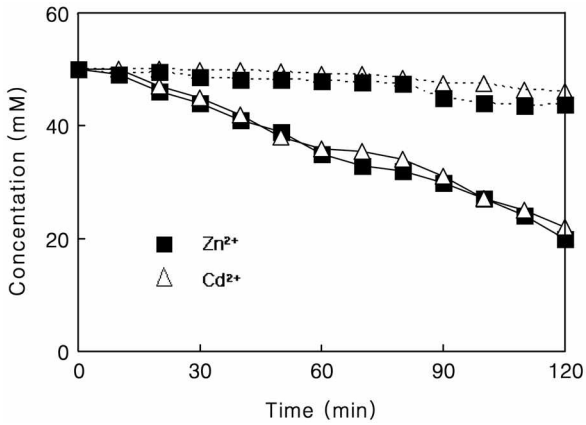

Figure 6. Comparison of the concentration changes of Zn^{2+} and Cd^{2+} during ECG in 0.1 M HNO_3 solutions coexisting with Fe^{2+} and Fe^{3+} of 50 mM. j = 4.3 mA cm^{-2} was applied between Al electrodes.

Conclusions

The removal of Zn^{2+} and Cd^{2+} coexisting with Fe^{2+}/Fe^{3+} in HNO_3 was investigated by ECG. When Al electrodes were used, Fe^{2+} was removed first and other metal ions began to precipitate when $[Fe^{2+}]$ reached a certain concentration level (*ca.* 10 mM). While the retardation of removal of Zn^{2+} and Cd^{2+} was not alleviated by adjusting experimental parameters, the use of Fe^{3+} instead of Fe^{2+} greatly improved the ECG efficiency.

ECG with Fe electrodes resulted in much faster removal of Zn^{2+} and Cd^{2+} than that with Al electrodes, indicating that Fe^{2+} initially present in a solution acts differently from Fe^{n+} generated at a Fe electrode. The retardation was not problematic even in the initial presence of Fe^{2+}. $[Zn^{2+}]$ and $[Cd^{2+}]$ were able to be reduced to one-tenth of their initial concentrations by performing ECG until $[Fe^{n+}]$ was the same as the initial $[Fe^{2+}]$.

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