

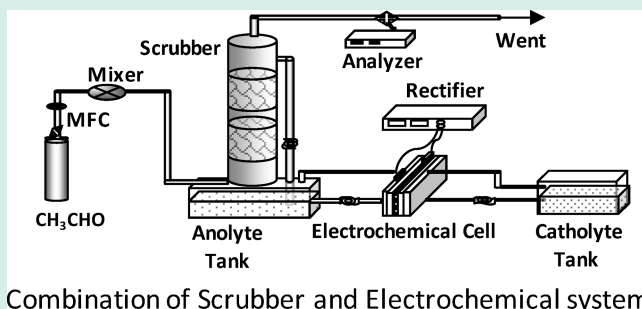
# Mineralization of Gaseous Acetaldehyde by Electrochemically Generated Co(III) in H<sub>2</sub>SO<sub>4</sub> with Wet Scrubber Combinatorial System

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**ABSTRACT:** Electrochemically generated Co(III) mediated catalytic room temperature incineration of acetaldehyde, which is one of volatile organic compounds (VOCs), combined with wet scrubbing system was developed and investigated. Depending on the electrolyte's type, absorption and removal efficiency is varied. In presence of electrogenerated Co(III) in sulfuric acid, acetaldehyde was mineralized to CO<sub>2</sub> and not like only absorption in pure sulfuric acid. The Co(III) mediated catalytic incineration led to oxidative absorption and elimination to CO<sub>2</sub>, which was evidenced with titration, CO<sub>2</sub>, and cyclic voltammetric analyses. Experimental conditions, such as current density, concentration of mediator, and gas molar flow rate were optimized. By the optimization of the experimental conditions, the complete mineralization of acetaldehyde was realized at a room temperature using electrochemically generated Co(III) with wet scrubber combinatorial system.

**KEYWORDS:** electrochemically generated Co(III), wet scrubber, combinatorial system, room temperature incineration, acetaldehyde



Combination of Scrubber and Electrochemical system

## 1. INTRODUCTION

Acetaldehyde is harmful to human health and the environment, as recognized to cause air pollution, such as photochemical smog, ground-level ozone, sick house syndrome, and chemical sensitivity.<sup>1–3</sup> Acetaldehyde causes oral cavity, esophagus, and pharyngeal cancers, as well as the sick building syndrome in many incidences because it is being used as a solvent for paints and adhesives and a responsible chemical substance. Another potential source of acetaldehyde exposure is municipal waste disposal area where it is evolving along with many odorous compounds.<sup>4</sup> For good health and a clean environment, it is necessary to remove acetaldehyde released in air atmosphere. For the effective abatement of VOCs, several methods have been proposed, such as chemical, physical, or biological technologies, including incineration, absorption, chemical scrubbing, bioscrubbing, and biofiltration.<sup>5</sup> Among these methods, chemical scrubbing of acetaldehyde by total oxidation into carbon dioxide and steam is an ecologically simple and clean technology to eliminate it at low temperatures and to minimize the negative side effects such as NO<sub>x</sub> production.<sup>6</sup> Further, at high concentrated air pollutants source, the chemical scrubbing the only technique can be used instead of biofilter or bioscrubbing.<sup>7</sup> A number of chemical catalysts for acetaldehyde abatement have been reported.<sup>8–12</sup> However, it is significantly difficult to realize complete oxidation of acetaldehyde at low temperatures,<sup>13</sup> and actually, the active catalyst required more at each time.

In this context, alternative techniques to generate active catalyst have been introduced, such as photochemical and

electrochemical way.<sup>14,15</sup> Drawbacks of photochemical process are, for example, reactivation of catalyst will not be a 100% because of prevention of light rays in to the core of the column reactor. Electrochemical techniques have started being used in air pollutant degradation with promising since electrons can be used as source to activate the catalyst. Many of the electrochemical studies demonstrated the fundamental electron transfer behavior of acetaldehyde oxidation.<sup>16–20</sup> Adsorption of acetaldehyde on Pt has been proven by cyclic voltammetry and FTIR techniques.<sup>21</sup> Then alloy electrodes of Pt/Os and Pt/RuO<sub>2</sub>/Os were shown to have good electrocatalytic oxidation of acetaldehyde.<sup>19</sup> In industrial applications, a few works attempted to use electrochemistry to degrade acetaldehyde in combination of electrochemically assisted scrubbing process,<sup>22</sup> where direct electrochemical oxidation was applied. Our group's many publications demonstrate our experience in electrochemically assisted-degradation, where mediated electrochemical oxidation was used, and in the scrubbing process for various liquid and air pollutants successfully.<sup>23–25</sup> In continuation of our work, acetaldehyde degradation was initiated because of its major presence in municipal waste disposal area of Suncheon city.

This study focuses on the complete degradation of acetaldehyde using electrochemically generated Co(III) with a wet scrubbing combination system. To proceed, absorption of

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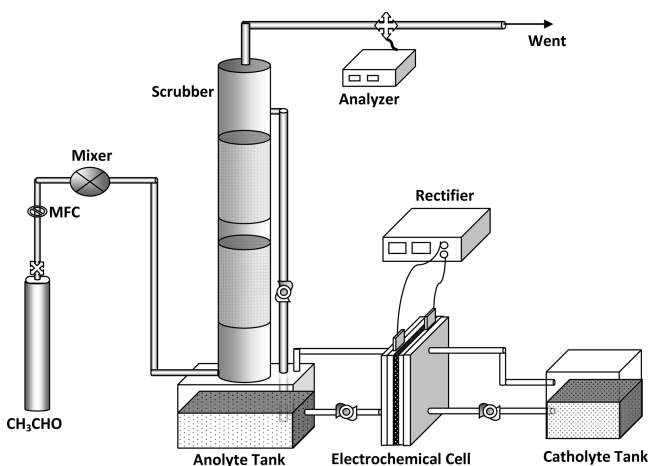
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acetaldehyde in  $\text{H}_2\text{SO}_4$  solution was carried out to determine if the acetaldehyde was removed by mediated oxidation of Co(III). Further, the possible method of elimination of acetaldehyde was investigated by cyclic voltammetry study, acid–base titration, and  $\text{CO}_2$  analyzer in anolyte solution and outlet scrubber column, respectively. Finally, the experiential variables for the effective removal efficiency of acetaldehyde, such as concentration of Co(II), current density, and molar flow rate, were studied and discussed.

## 2. EXPERIMENTAL SECTION

**2.1. Chemicals.** Cobalt sulfate ( $\text{Co}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ , 99.9%) from TERIO Corporation, China, sulfuric acid ( $\text{H}_2\text{SO}_4$ , 60%) from Sam Chun Chemicals, Korea, and ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) from Junsei Chemical Co., Ltd., Japan, were used as received without any further purification. Nafion 324 membrane was purchased from Dupont, U.S.A., and mesh-type Pt-coated-Ti and Ti plate electrodes were from Wesco, Korea. All the solutions were made using water purified by reverse osmosis (Human Power III plus, Korea). The cylinder gases of  $\text{CH}_3\text{CHO}$  (2%  $\text{CH}_3\text{CHO}$  in  $\text{N}_2$ ) supplied by P.S. Chem. Co., Ltd., Korea, and oil free air compressor supplied by Kyungwon Co., Korea, were used.

**2.2. Apparatus and Process.** The experimental setup that used for  $\text{CH}_3\text{CHO}$  removal consisted of two main domains: an electrochemical cell unite and a wet scrubber column unite, as shown in Figure 1. The electrochemical cell, used for Co(III)



**Figure 1.** Schematic diagram of the electrochemical cell with wet scrubber experimental setup used in this study for removal of acetaldehyde using the Co(III)/Co(II) based mediated electrochemical oxidation.

generation, was of plate-and-frame type narrow gap divided flow cell configuration with a mesh type Pt-coated-Ti anode and Ti cathode separated by a Nafion 324 membrane. The interelectrode gap was maintained at 5 mm with the help of two Viton rubber gaskets (thickness = 2 mm). The electrode assembly setup was tightly clamped to Ti end plates of thickness 5 mm with the help of a series of Teflon plates (thickness = 5 mm) and rubber gaskets by filter press technique. Provisions were made with separate channel paths by which the anolyte and catholyte solutions flew across the respective electrodes. A 2.0 L solution of cobalt sulfate in 4 M sulfuric acid and a 1.0 L of 4 M sulphuric acid, taken in separate anolyte and catholyte glass tanks, were continuously circulated through the anode and cathode compartments of the

electrochemical cell at different constant flow rates ( $\text{L min}^{-1}$ ) with the help of magnetic pump (Pan World Co., Ltd., Taiwan). The electrolysis for generation of Co(III) active mediator was generated galvanostatically by applying different constant current by a locally made constant current source from Korea Switching Instrument. The effective surface area of each electrode exposed to the solution was  $140 \text{ cm}^2$ .

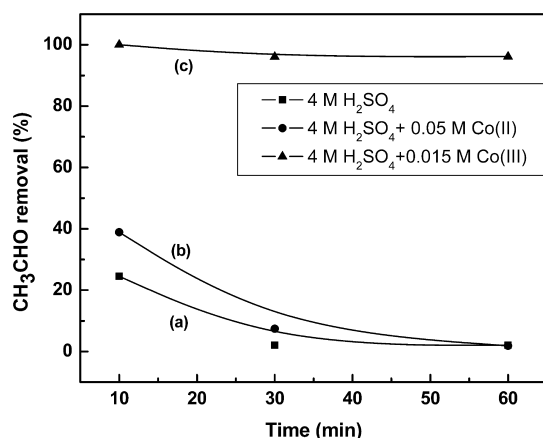
The  $\text{CH}_3\text{CHO}$  removal at scrubbing reactor system was composed of air supply, scrubbing liquid tank, the scrubber reactor column, data logging, and gas analysis systems. The scrubber column of ID = 9.5 cm was an 85 cm height glass vessel filled with 25.4 mm diameter Tripak packing material. The  $\text{CH}_3\text{CHO}$ –air mixture, obtained by controlled mixing of air, using mass flow controllers (MFC), was introduced at the bottom of the scrubber at a constant gas flow rate, and the activated catalyst containing solution (4 M  $\text{H}_2\text{SO}_4$  with Co(III)) was introduced at the top of the scrubber in counter current flow pattern at a given constant liquid flow rate. The outlet scrubbing solution containing the reduced form of Co(II) was passed through the electrochemical cell for Co(III) generation and was further recirculated.

**2.3. Analysis.** The outlet gas concentration of  $\text{CH}_3\text{CHO}$  was measured at regular time intervals by online FTIR analyzer (1200-MIDAC Corp., Irvine, California, U.S.A.). The reproducibility in the  $\text{CH}_3\text{CHO}$  removal experiments the FTIR instrument was tested with 25 and 50 ppm samples, respectively, measured three times and confirmed. Outlet  $\text{CO}_2$  gas was measured using  $\text{CO}_2$  analyzer from U.S.A. (MultiRAE-IR(PGM-54)).

First, the electrochemical cell was run until Co(II) to Co(III) oxidation conversion attained steady state (45%), as followed by measuring Co(III) in the anolyte by titrating it with Fe(II) by potentiometry, before allow to react  $\text{CH}_3\text{CHO}$  and Co(III) at scrubbing column. To get products in the anolyte solution, the anolyte sample was taken during  $\text{CH}_3\text{CHO}$  purging at desired time interval using a measuring syringe via a suitable provision made on anolyte solution flow tube and titrated against with NaOH using phenolphthalein as indicator. For  $\text{CO}_2$  analysis test, the  $\text{N}_2$  was used as carrier gas, and  $\text{N}_2$  was purged into anolyte solution about 30 min before allow the  $\text{CH}_3\text{CHO}$  for  $\text{CO}_2$  analysis. Cyclic voltammetry experiments were carried out using PAR-290 instrument from U.S.A. Platinum (2 mm) and graphite rod (5 mm) served as working and counter electrode and Ag/AgCl served as reference electrode, respectively. All the  $\text{CH}_3\text{CHO}$  removal and cyclic voltammetry experiments were carried out at  $20 \pm 1 \text{ }^\circ\text{C}$  temperature.

## 3. RESULTS AND DISCUSSION

**3.1. Identification Path of  $\text{CH}_3\text{CHO}$  Removal.** The effect of removal of  $\text{CH}_3\text{CHO}$  was carried out at a given gas flow rate of  $50 \text{ L min}^{-1}$  with the scrubbing liquid of 4 M  $\text{H}_2\text{SO}_4$  at a liquid flow rate of  $4 \text{ L min}^{-1}$  in the absence and presence of Co(II) (M). Figure 2 shows the  $\text{CH}_3\text{CHO}$  removal efficiency profile with respect to time at different experimental solutions for comparison. The removal efficiency of  $\text{CH}_3\text{CHO}$  shows 25% at initial time and then start decreases with time and become 0% (120 min) when only 4 M  $\text{H}_2\text{SO}_4$  is used as scrubbing solution (Figure 2, curve a). Also, similar trend was observed with little increased removal efficiency (40% curve b) initially and become 0% at 120 min duration in presence of 0.05 M Co(II). At the same time,  $\text{CH}_3\text{CHO}$  shows 100% removal efficiency at studied time in the presence of Co(III), as shown

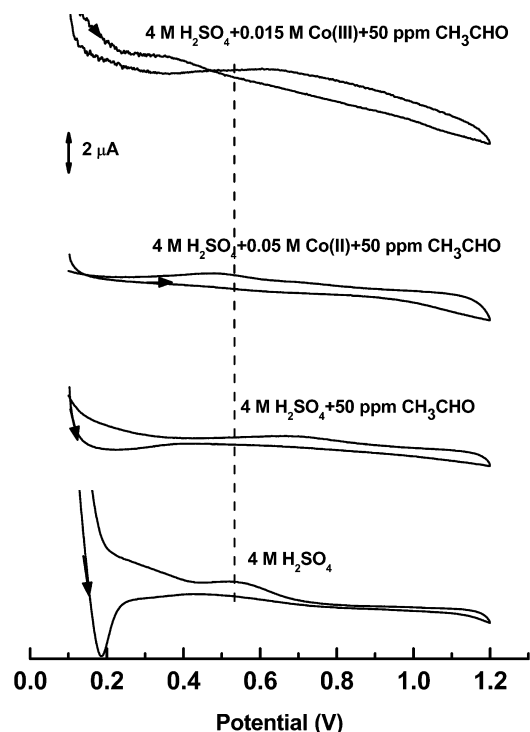


**Figure 2.** Comparative plot of the CH<sub>3</sub>CHO removal efficiency with respect to time in 4 M H<sub>2</sub>SO<sub>4</sub>: (a) CH<sub>3</sub>CHO; (b) 0.05 M Co(II) + CH<sub>3</sub>CHO; (c) Co(III) (0.015 M) + CH<sub>3</sub>CHO. Experimental conditions: Feed concentration of CH<sub>3</sub>CHO = 50 ppm; gas flow rate = 50 L min<sup>-1</sup>; liquid flow rate = 4 L min<sup>-1</sup>.

in Figure 2 (curve c). These comparative results clearly tell that the high % removal efficiency of CH<sub>3</sub>CHO is achieved only by electrogenerated Co(III) in 4 M H<sub>2</sub>SO<sub>4</sub> medium.

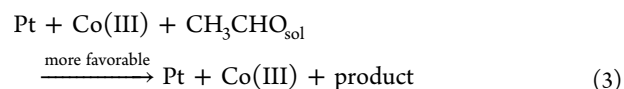
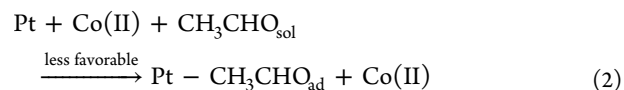
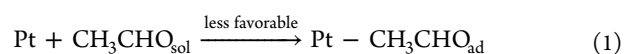
Electrochemical study may be expected to give direct impacts on electron transfer phenomena that could have occurred in working solution. With this assumption, the CV experiments have been performed at Pt electrode in 4 M H<sub>2</sub>SO<sub>4</sub> with various experimental solutions separately.

Figure 3 depicts the cyclic voltammetry response of Pt electrode in 4 M H<sub>2</sub>SO<sub>4</sub> solution in different experimental solutions such as (a) 4 M H<sub>2</sub>SO<sub>4</sub>, (b) 4 M H<sub>2</sub>SO<sub>4</sub> + 50 ppm



**Figure 3.** CV response of CH<sub>3</sub>CHO in different working solutions (mentioned in figure) in 4 M H<sub>2</sub>SO<sub>4</sub>. Working electrode: Pt. Scan rate: 50 mV s<sup>-1</sup>. Cobalt(II) concentration: 0.05 M (Co(III) 0.015 M). CH<sub>3</sub>CHO concentration: 50 ppm.

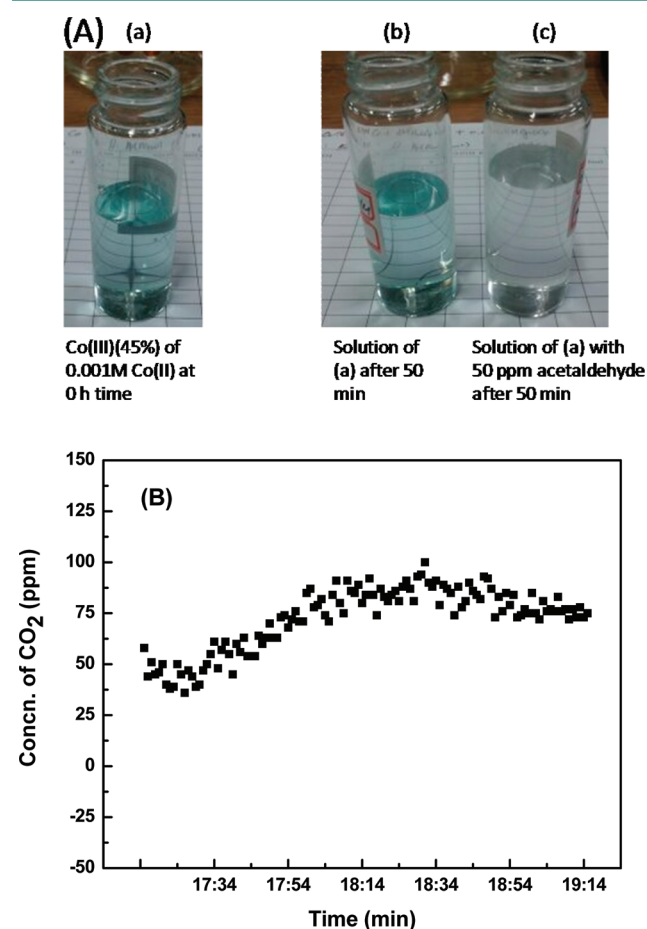
acetaldehyde, (b) 4 M H<sub>2</sub>SO<sub>4</sub> + 0.05 M Co(II) + 50 ppm acetaldehyde, (c) 4 M H<sub>2</sub>SO<sub>4</sub> + 0.015 M Co(III) + 50 ppm acetaldehyde at a scan rate of 10 mV s<sup>-1</sup>. Two oxidative current peaks appear in the positive-going scan, one centered at 0.2 V, which is from H<sub>upd</sub> and another one starting at about 0.75 V, which is from CO<sub>ad</sub> with a small shoulder on the middle potential side. In the reverse scan, there observed one peak at 0.55 V, which is for CO<sub>des</sub> and another steep rising in current for H<sub>des</sub>. All correlates well with the typical of polycrystalline or rough macro electrode of Pt behavior in H<sub>2</sub>SO<sub>4</sub>.<sup>26,27</sup> On the other hand, in the presence of 50 ppm acetaldehyde, the both H<sub>upd</sub> peak and CO<sub>ad</sub> peak get largely suppressed and broadened in positive going run. A positively shifted peak (0.65 V) of CO<sub>ad</sub> was observed in the negative going run, which is 100 mV positive than the pure 4 M H<sub>2</sub>SO<sub>4</sub> solution. In the presence of Co(II), the H<sub>ad</sub> peak completely minimized and CO<sub>ad</sub> peak shifted to 0.55 V in forward scan and 0.45 V (CO<sub>des</sub>) in reverse scan, respectively. An curve crossing at 0.5 V in presence of Co(III) and 50 ppm acetaldehyde with absence of H<sub>ad</sub> and CO<sub>ad</sub> (Peaks II) shifted still more negative 0.5 V in positive going cycle. Minimization of H<sub>ad</sub> peak and positive shift in CO<sub>ad</sub> and CO<sub>des</sub> peak potentials in presence of acetaldehyde, indicates the competitive adsorption of acetaldehyde. But, in presence of Co(II) and Co(III), there shows a catalytic reaction, negative shift in CO<sub>ad</sub> and CO<sub>des</sub> peak and curve crossing between forward and reverse scan, respectively, apart from adsorption. Note that acetic acid adsorption due to adsorptive oxidation of acetaldehyde does not cause a measurable formation of stable irreversibly adsorbed species.<sup>28,29</sup> Further, on the basis of the finding that CO<sub>2</sub> formation was only observed in a peak corresponding to the low potential shoulder of the first Faradaic current peak in the positive-going scan, which starts at 0.5 V and passes through a maximum at 0.78 V, the authors of the latter study attributed this shoulder to the oxidation of CO<sub>ad</sub> formed by dissociative acetaldehyde decomposition at lower potentials.<sup>20</sup> It is believed that the present results follow less adsorptive oxidation and more of mediated catalytic oxidation of acetaldehyde, which means solution phase catalytic oxidation as



where CH<sub>3</sub>CHO<sub>sol</sub> and CH<sub>3</sub>CHO<sub>ad</sub> are acetaldehyde in solution and adsorbed on Pt, respectively.

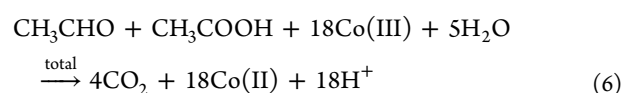
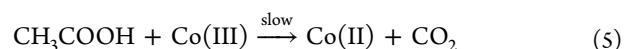
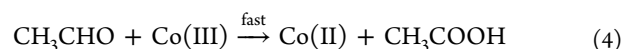
In literature view, gaseous acetaldehyde directly converted to CO<sub>2</sub> by solid catalyst CoOx-doped silica xerogels but through some fast intermediates steps.<sup>11</sup> If solution phase concerned, Chou et al.,<sup>30</sup> have done the both heterogeneous and homogeneous catalytic oxidation of acetaldehyde and its fundamental electrode transfer phenomena using cobalt as catalyst.<sup>30,31</sup> They found peracetic acid (PAA) and acetaldehyde monoperacetic acid (AMP) as the reaction product. Noteworthy here is that peracetic acid as the reaction product in solution phase oxidation<sup>30</sup> and acetic acid is one of the major product in many oxidation reaction.<sup>32</sup> In the present study, combined the both that gaseous acetaldehyde decontaminated in solution

phase reaction, which means combination of products may occur possibly. To know further, the anolyte solution was checked through titration, and the outlet gas was run in to CO<sub>2</sub> analyzer. First, the anolyte solution was titrated before and after purging of acetaldehyde with base, but it shows no noticeable change. It is believed that the high concentration of H<sub>2</sub>SO<sub>4</sub> (4 M) and Co(III) presence, which is highly reactant, could have cause the error on anolyte solution estimation for acetic acid and acetaldehyde. According with Chou et al., peracetic acid will generate Co(III) because of its highly oxidant nature.<sup>29</sup> By simple experiment, the peracetic acid presence can be proved that anolyte solution (low concentration of Co(II) were taken to minimize the reaction time) of before and after purging acetaldehyde were kept and monitor the reduction rate by color change (Co(III) and Co(II) in sulfuric acid are green and pink in color). The acetaldehyde purged sample changed to pink color (here color less due to low concentration) at faster rate (Figure.4A) evidence the peracetic acid is not in anolyte solution and proves indirectly some other intermediate likely acetic acid. CO<sub>2</sub> was checked at inlet of the scrubber column and it considered as zero time. The found difference between



**Figure 4.** (A) Pictorial representation of anolyte solution with 45% oxidation efficiency of Co(II) at 0 h (a), after 50 min without CH<sub>3</sub>CHO (b) and with 50 ppm CH<sub>3</sub>CHO (c). Conditions: 0.001 M Co(II) feed concentration, current density = 71.4 mA cm<sup>-2</sup> (2 h), electrolyte = 4 M H<sub>2</sub>SO<sub>4</sub>. (B) CO<sub>2</sub> analysis of before and after purging the 50 ppm CH<sub>3</sub>CHO into scrubber. Experimental conditions: CH<sub>3</sub>CHO molar flow rates = 110.6 × 10<sup>-6</sup> mol min<sup>-1</sup>; feed concentration of Co(II) = 0.05 M; liquid flow rate = 5 L min<sup>-1</sup>; electrolyte = 4 M H<sub>2</sub>SO<sub>4</sub>.

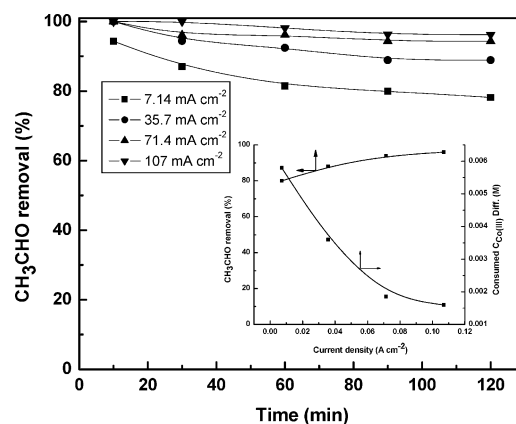
inlet and outlet CO<sub>2</sub> is almost 80 ppm, which is shown in Figure.4B. Although, which is not equal to mole equivalent of 50 ppm of feed concentration of acetaldehyde, absence of peracetic acid in solution believed to be the CO<sub>2</sub> will be the final product. If measure the kinetic constant at this experimental conditions may give exact conclusion, but which is far from this present focus. We are planning to focus the kinetics between acetaldehyde and Co(III) at said conditions in separate study. Based on the above evidence, the reaction scheme can be as follows:



Corroborating with the CV, the titration and CO<sub>2</sub> results give evidence the CH<sub>3</sub>CHO is completely mineralized and not just absorbed into solution or converted to some other intermediates in total.

### 3.2. Current Density Variation on Co(II) Oxidation.

Different current densities were studied to explore how effectively the Co(III) formed. Despite the fixed distance between the two electrodes, the applied current density may influence the rate of the mediator's (Co(II)) oxidation. Figure 5



**Figure 5.** Co(II) oxidation efficiency as a function of the current density. Experimental conditions: Gas flow rate = 110.5 × 10<sup>-6</sup> mol min<sup>-1</sup>; liquid flow rate = 4 L min<sup>-1</sup>; Electrolyte 4 M H<sub>2</sub>SO<sub>4</sub>. Insert shows the consumed concentration difference of Co(III) variation during reaction with 50 ppm CH<sub>3</sub>CHO against various concentration of Co(III) produced at different current densities.

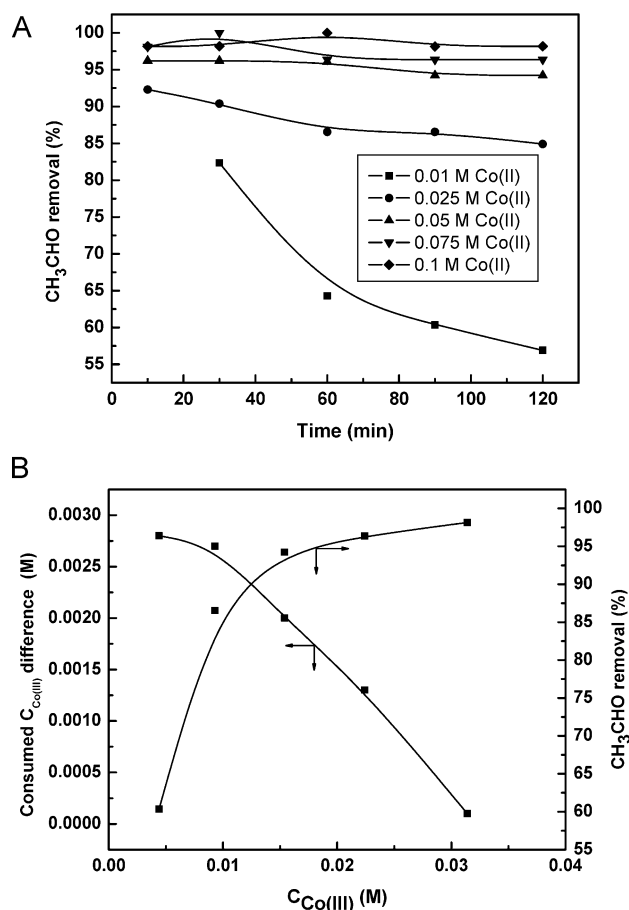
shows the effects of four different current densities (7.14, 35.7, 71.4, and 107 mA cm<sup>-2</sup>) of 140 cm<sup>2</sup> area of Pt coated Ti electrode on the removal of CH<sub>3</sub>CHO. At lower current densities, the removal efficiency of CH<sub>3</sub>CHO decreases initially and retained almost constant with increasing time. At higher current densities, the removal efficiency of CH<sub>3</sub>CHO is higher and maintained almost constant with studied time. These results explain that the generated Co(III) concentration is more higher at initial time that could have utilized fully to remove CH<sub>3</sub>CHO at higher level. In consecutive time interval, the utilization rate of Co(III) is more than it is generation rate at lower current densities, which leads to the removal efficiency of CH<sub>3</sub>CHO decrease at longer time. Note that Co(II) oxidation

and  $\text{CH}_3\text{CHO}$  purging is continuing constantly at their own rate. In the case of higher current densities, the regeneration rate of  $\text{Co(III)}$  is well cop up with the studied concentration of  $\text{CH}_3\text{CHO}$  that may be the reason for almost constant removal efficiency (98%) with all studied time intervals. This is more clearly explained if look at the insert figure of Figure.5. The exact consumed concentration difference, initial concentration of  $\text{Co(III)}$  after introduction of  $\text{CH}_3\text{CHO}$  subtract with final concentration of  $\text{Co(III)}$  at certain time interval (where the  $\text{Co(III)}$  becomes constant), of  $\text{Co(III)}$  at each current density shows decrease with increasing current density, which explains the rate or number of  $\text{Co(III)}$  generated at given current density. It is well correlates with removal efficiency of  $\text{CH}_3\text{CHO}$  and reaches maximum at higher current density. On the other hand, the distance between the two electrode being optimum at  $71.4 \text{ mA cm}^{-2}$  for the most efficient oxidation of  $\text{Co(II)}$  under the test conditions.

**3.3. Feed  $\text{Co(II)}$  Concentration Variation.** In consideration of economic and effective utilization, experiments were performed to find the influence of the active catalyst  $\text{Co(III)}$  concentration on effective removal of  $\text{CH}_3\text{CHO}$  in our packed column reactor. For a given liquid flow rate  $4 \text{ L min}^{-1}$ , the redox ion ( $\text{Co(III)}$ ) concentration was varied from 0.0044 to 0.032 M in 4 M sulfuric acid solution. Figure 6A (respective symbol in figure) shows the effect of  $\text{Co(III)}$  concentration on  $\text{CH}_3\text{CHO}$  removal efficiency. For these measurements, the concentration of  $\text{CH}_3\text{CHO}$  was kept to a molar value-cum-gas flow rate  $110.5 \times 10^{-6} \text{ mol min}^{-1}$ . There shows better removal of  $\text{CH}_3\text{CHO}$  at higher concentration of  $\text{Co(III)}$  ion (0.032 M). For example, the steady state removal was 58% at 0.0044 M  $\text{Co(III)}$  concentration, but increased to almost 100% within 0.032 M  $\text{Co(III)}$  concentration, as shown in Figure 6A (respective symbol), apparently indicating that working with higher (0.032 M)  $\text{Co(III)}$  concentration was more advantageous. But, as depicted in Figure.6B, the steady state removal of  $\text{CH}_3\text{CHO}$  is attained almost at 0.015 M and further increase of 50%  $\text{Co(II)}$  will leads only 5% improve in removal efficiency of  $\text{CH}_3\text{CHO}$ . The consumed concentration difference decreases with increasing concentration of  $\text{Co(III)}$  explains the more number of active  $\text{Co(III)}$  available at high feed concentration, as similar with high current density in insert of Figure.5.

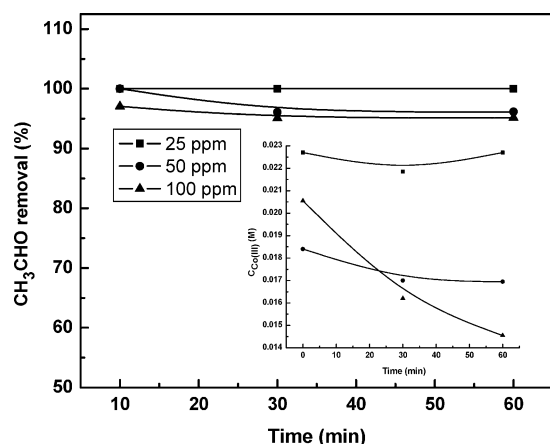
**3.4. Variation of  $\text{CH}_3\text{CHO}$  Concentration and Molar Flow Rates.** Figure 7 shows the removal efficiency variation of  $\text{CH}_3\text{CHO}$  with different feed concentration of the same at given concentration of  $\text{Co(II)}$ . There observed 100% removal efficiency with studied time intervals at lower concentration of  $\text{CH}_3\text{CHO}$  (25 ppm). At higher feed concentration (50 and 100 ppm), the removal efficiency was decreased to 98 and 95% respectively. This is an expected phenomenon that excess of  $\text{CH}_3\text{CHO}$  comes out due to devoid of  $\text{Co(III)}$ , that is, reactants  $\text{CH}_3\text{CHO}$  and  $\text{Co(III)}$  concentration ratio is not well matched. the removal efficiency decreased to 95% with increasing feed concentration of  $\text{CH}_3\text{CHO}$ . This is well explained through  $\text{Co(III)}$  concentration in each feed concentration of  $\text{CH}_3\text{CHO}$ , as depicted in insert figure. There, excess of  $\text{Co(III)}$  remain in the reaction solution at low feed concentration. At the same time, the  $\text{Co(III)}$  concentration decreased to almost zero concentration at 100 ppm of feed  $\text{CH}_3\text{CHO}$ , which is well correlated with removal efficiency of  $\text{CH}_3\text{CHO}$ .

Figure 8 shows variation in the removal efficiency of  $\text{CH}_3\text{CHO}$  as a function of different molar gas flow rates of the 50 ppm acetaldehyde with air mixture ( $\text{mol min}^{-1}$ ). These data were collected for different acetaldehyde flow rates varied

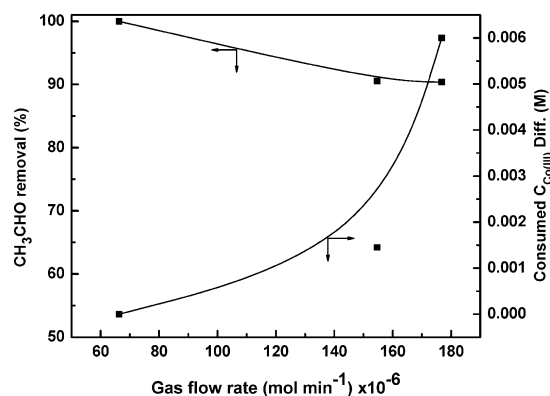


**Figure 6.** (A)  $\text{CH}_3\text{CHO}$  removal efficiency as a function of time for various concentrations of active  $\text{Co(III)}$  (M) in 4 M  $\text{H}_2\text{SO}_4$ : (■) 0.0044, (●) 0.0093, (▲) 0.015, (▼) 0.022, and (◆) 0.032. Experimental conditions:  $\text{CH}_3\text{CHO}$  molar flow rates =  $110.5 \times 10^{-6} \text{ mol min}^{-1}$ ; liquid flow rate =  $4 \text{ L min}^{-1}$ ; current density =  $71.4 \text{ mA cm}^{-2}$ , electrolyte 4 M  $\text{H}_2\text{SO}_4$ . (B) Dependence of the  $\text{CH}_3\text{CHO}$  removal efficiency at 120 min on the initial  $\text{CH}_3\text{CHO}$  (50 ppm) feed concentration and consumed concentration difference of  $\text{Co(III)}$  with various concentrations of active  $\text{Co(III)}$ . Experimental conditions are as in Figure 6A.

from  $55.6 \times 10^{-4}$  to  $218 \times 10^{-4} \text{ mol min}^{-1}$  at a constant feed concentration of  $\text{Co(III)}$  (0.015 M) in 4 M  $\text{H}_2\text{SO}_4$ . One could attain the outlet removal efficiency a steady state, it was considered that lower the  $\text{CH}_3\text{CHO}$  contained solution flow rate the better the acetaldehyde removal; as shown in the Figure.8, It can be observed that the removal of  $\text{CH}_3\text{CHO}$  decreased with increase in molar flow rate,  $\text{CH}_3\text{CHO}$  showing greater depression. This was quite expected since at high gas flow rate, as there was more  $\text{CH}_3\text{CHO}$  to oxidize, the  $\text{Co(III)}$  concentration in the scrubbing solution could decrease resulting in poor performance. On top of this, one could realize that at higher gas flow rates the gas phase would be allowed to remain in contact with the scrubbing solution with  $\text{Co(III)}$  oxidant only for a shorter residence time, which could also add-up in lowering the removal efficiency of the  $\text{CH}_3\text{CHO}$  gas treated in the scrubber or packed column. In other words, if look at consumed  $\text{Co(III)}$  difference in insert figure, which is higher at high molar flow rate. It tells that devoid of  $\text{Co(III)}$  at high  $\text{CH}_3\text{CHO}$  flow rate and directly confirms the removal efficiency follow certain concentration ratio between  $\text{Co(III)}$  and  $\text{CH}_3\text{CHO}$ .



**Figure 7.** CH<sub>3</sub>CHO removal efficiency as a function of the CH<sub>3</sub>CHO feed concentration (indicated in the figure). Experimental conditions: Gas flow rate =  $110.5 \times 10^{-6} \text{ mol min}^{-1}$ ; liquid flow rate =  $4 \text{ L min}^{-1}$ ; electrolyte =  $4 \text{ M H}_2\text{SO}_4$ . Insert shows the consumed concentration difference of Co(III) variation on CH<sub>3</sub>CHO removal against different CH<sub>3</sub>CHO concentrations. Insert shows the consumed concentration difference of Co(III) with various feed CH<sub>3</sub>CHO concentrations.



**Figure 8.** CH<sub>3</sub>CHO removal efficiency as a function of the CH<sub>3</sub>CHO molar gas flow rates ( $\text{mol min}^{-1}$ ) against constant feed concentration of Co(II) ( $0.05 \text{ M}$ ). Experimental conditions: Gas flow rate =  $110.5 \times 10^{-6} \text{ mol min}^{-1}$ ; liquid flow rate =  $4 \text{ L min}^{-1}$ ; electrolyte  $4 \text{ M H}_2\text{SO}_4$ . Insert shows the consumed concentration difference of Co(III) variation with various molar flow rate of CH<sub>3</sub>CHO.

#### 4. CONCLUSIONS

The developed electrochemically assisted-scrubbing process was successfully applied to remove the acetaldehyde. Our experimental results confirmed that this process can effectively mineralize CH<sub>3</sub>CHO. The removal efficiency of CH<sub>3</sub>CHO in the presence of  $0.05 \text{ M Co(III)}$  showed 100% compared to that of  $4 \text{ M H}_2\text{SO}_4$  solution only confirms the strength and influence of Co(III) mediator in reaction with destruction efficiency. The experiment results demonstrated that the low gas and high liquid flow rates are suitable for CH<sub>3</sub>CHO removal. The CV and titration of anolyte results suggested that the destruction pathway for CH<sub>3</sub>CHO follow mediated electrochemical oxidation, i.e., electrochemically generated Co(III) assisted pathway. In fact, unlike the other methods developed for acetaldehyde gas removal, the electrochemically assisted-scrubbing process is more efficient and safer, since it works at room temperature and atmospheric pressure utilizing the conventional electrodes more commonly used in industrial

applications. Now, we are testing this developed process at municipal waste disposal site in our Suncheon city.

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##### Notes

The authors declare no competing financial interest.

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