



# *In situ* electrochemically generated peroxymonophosphoric acid as an oxidant for the effective removal of gaseous acetaldehyde



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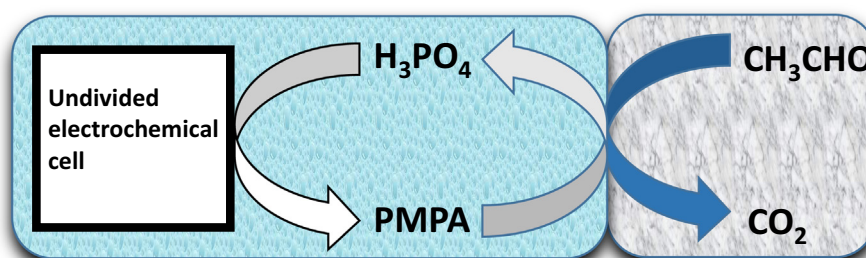
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## HIGHLIGHTS

- Undivided cell evidenced to prepare peroxymonophosphoric acid.
- Ti cathode favored to prepare high concentration of peroxymonophosphoric acid.
- High concentration of peroxymonophosphoric acid at equal cathode size seems to be influence of OH<sup>-</sup>.
- With the 1.71% current efficiency, 30 ppm of acetaldehyde was removed successfully.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Peroxymonophosphate in salt form has a wide range of applications. In this study, peroxymonophosphoric acid (PMPA) was generated *in situ* in an undivided electrolytic cell (single cell) and applied to the removal of acetaldehyde, a model air pollutant. PMPA was characterized by titration methods and <sup>31</sup>P-nuclear magnetic resonance spectroscopy. The generation of PMPA was initially optimized using boron-doped diamond as the anode and different cathode materials (Pt-coated Ti, DSA, Ti, and Cu) in constant current mode. Of the cathodes assessed, the maximum concentration of PMPA (6 mM) was achieved from an initial concentration of 1 M H<sub>3</sub>PO<sub>4</sub> using the Ti cathode. This study examined the influence of the applied current density, temperature, and initial H<sub>3</sub>PO<sub>4</sub> concentration. A higher PMPA concentration was produced using an anode and cathode with equal sizes than that with smaller sized cathodes. This shows that a larger cathode produces a greater number of OH<sup>-</sup>, which is responsible for the production of PMPA. Under optimized cell parameters (electro-scrubbing), the oxidative removal efficiency of acetaldehyde from a wet-scrubbing column with the online production of PMPA was approximately 95% for a 30 ppm inlet concentration. The removal of 30 ppm of acetaldehyde required only 6 mM of electrogenerated PMPA, which makes it competitive with the high concentration metal ion mediator that is used to remove the same concentration of acetaldehyde.

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## 1. Introduction

Peroxyphosphoric acid is an environmentally friendly oxidant in biological and disposal aspects because the spent peroxydiphos-

phate (phosphate) can be removed easily and economically from waste compared to peroxydisulfate (sulfate) [1]. The salt forms of peroxymonophosphate (PMP) and peroxydiphosphate (PDP) are used as oxidants in organic synthesis [2], agriculture [3], waste water treatment [4], and bleaching agents in the detergent industry [5], and are prepared commercially [6]. These compounds can be produced on a large scale via a chemical reaction between P<sub>2</sub>O<sub>5</sub> and H<sub>2</sub>O<sub>2</sub> under biphasic conditions [7] and acid hydrolysis

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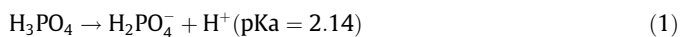
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of lithium peroxymonosulfate (PMS) salts [8]. On the other hand, peroxyphosphoric acid (PMPA) ( $\text{H}_3\text{PO}_5$ ), which is also known as perphosphoric acid (PPA), is difficult to synthesize because of the exothermal chemical reactions that lead to rapid decomposition of the peroxy-compounds generated, resulting in low efficiency [9]. The synthesis of PMPA is also limited by the high cost and poor reproducibility despite the addition of surfactants [10], powerful external agents [7], and inert diluents [9]. Canizares et al. [1,11] reported the preparation of PMPA *in situ* by an electrochemical method. Their main focus was to prepare PMP and PDP at  $\text{pH} = 2.5\text{--}12.5$  using a divided electrochemical cell configuration [11]. They reported that the cationic membrane separator was expensive and required periodical activation. Moreover, the periodical addition of NaOH is required, which makes the process impractical for scale-up [11].

To the best of the authors' knowledge, no attempt has been made to apply the electrogenerated PMPA to the removal of environmental air pollutants. Acetaldehyde causes air pollution, such as photochemical smog, ground-level ozone, sick house syndrome, and chemical sensitivity, and it is harmful to human health [12–14]. Therefore, reliable methods for acetaldehyde removal before its release into the atmosphere are needed to improve health and achieve a clean environment. Several techniques have been proposed to remove VOCs (volatile organic compounds), such as chemical, physical, or biological technologies, including incineration, absorption, chemical scrubbing, bioscrubbing, and biofiltration [14,15]. Of these, the chemical scrubbing of acetaldehyde by total oxidation to carbon dioxide and steam is simple and clean, and can be performed at low temperatures with few adverse side effects, such as  $\text{NO}_x$  production [16]. The electrochemical degradation of air pollutants is promising because the electrons produced can be used for catalyst activation, and the fundamental electron transfer behavior of acetaldehyde oxidation has been reported [17–21]. Cyclic voltammetry (CV) and Fourier transform infrared (FTIR) spectroscopy have demonstrated the adsorption of acetaldehyde on Pt [22]. The alloy electrodes of Pt/Os and Pt/RuO<sub>2</sub>/Os showed the good electrocatalytic oxidation of acetaldehyde [20]. Few studies have applied electrochemistry in industry to degrade acetaldehyde in combination with an electrochemically assisted scrubbing process [23], where direct electrochemical oxidation (DEO) was used. The authors assessed mediated electrochemical oxidation (MEO) in an electrochemically assisted scrubbing process for the removal of various liquid and air pollutants [24–26]. As part of an ongoing study, acetaldehyde was degraded using an electrogenerated  $\text{Co}^{3+}$  mediator via an electro-scrubbing process [27]. Despite metal ion mediators being good for the removal of air pollutants, metal free mediators, such as PMPA, are expected to minimize the cost and make a sustainable operation possible.

In the present study, PMPA was generated *in situ* using an undivided electrolytic cell and applied to the removal of gaseous acetaldehyde. The preparation of PMPA by paired electrolysis in a  $\text{H}_3\text{PO}_4$  solution was considered to be more suitable because the precursor forms at acidic pH [11], as shown in Eq. 1.



An undivided cell configuration can be a good choice because it can avoid the membrane and its related problems but the cathode may reduce the rate of PMPA formation [1]. The boron-doped diamond (BDD) electrode has been reported to be a good choice as the anode material because of its wide water splitting window [28]; however, it is important to prevent the reduction of electrogenerated PMPA to  $\text{H}_3\text{PO}_4$  at the cathode. Consequently, the smallest cathode size has been adopted to help prevent, possibly, the reduction of the electrogenerated peracid to its precursor. Accordingly, PDSA (peroxydisulfuric acid) was prepared using this cathode size variation approach and utilized in the removal of  $\text{SO}_2$  gas [29].

Because of the undivided cell and acid medium, a cheaper iron cathode can contaminate the electrogenerated PMPA owing to its lower oxidation potential [30]. Therefore, appropriate cathode selection must consider effective PMPA generation, and the following electrode materials were assessed for effective PMPA generation: Pt-coated Ti, DSA, Ti, and Cu. In addition, the roles of temperature, concentration, current density, and quantity of pollutants were also analyzed. Further, this study examined the role of *in situ* formed PMPA as an oxidant for the effective removal of gaseous acetaldehyde using an electro-scrubbing system in continuous flow mode. The process was monitored using an online FTIR gas analyzer.

## 2. Experimental

### 2.1. Electrogeneration of $\text{H}_3\text{PO}_5$ and its estimation

The PMPA mediator was generated quantitatively from a 1–6 M  $\text{H}_3\text{PO}_4$  solution by electrolysis, as reported previously [11,29]. Briefly, an electrolyte volume of 500 ml containing 1 M  $\text{H}_3\text{PO}_4$  in a 1000 ml double walled glass tank was connected to a undivided flow-through electrolytic cell with a working electrode area of  $35 \text{ cm}^2$  (Fig. 1A). Electrolysis was conducted by applying different current densities with an electrolyte flow rate of  $1 \text{ L min}^{-1}$ . The electrolyte was circulated continuously through the cell using magnetic pumps. A BDD anode with any one of the tested cathodes (Pt coated Ti, DSA, Ti, and Cu), was used to generate PMPA. For the divided cell electrolysis experiments, Nafion324 membrane was used as separator and the remaining electrolysis conditions were done as similar to the undivided cell. All solutions were prepared using reverse osmosis purified water (resistivity =  $18 \text{ M}\Omega\text{-cm}$ ), and all experiments were performed in triplicate.

The PMPA concentration was measured by an iodometric titration, as reported elsewhere [11]. Briefly, a 3 ml sample was withdrawn from the electrolytic cell and added to 6 ml of 0.02 M KI. After the addition of 1 ml starch to the same sample solution, the sample was titrated against 0.001 M sodium thiosulfate to quantify the PMPA concentration, which was derived from the thiosulfate value. The additional long-lived intermediate,  $\text{H}_2\text{O}_2$ , which formed during electrolysis on the BDD electrode was quantified using a slight modification of the standard  $\text{Ce}^{4+}$  titration method [31]. An additional 3 ml sample was withdrawn separately from the electrolytic cell at a similar time interval to that of PMPA analysis and equal volume of 0.001 M Ferroin ( $[\text{Fe}^{\text{II}}(\text{o-phenanthroline})_3]\text{SO}_4$ ), as a redox indicator, was then added to the drawn sample. The sample was then titrated against  $\text{Ce}^{4+}$  (already calibrated) to derive the  $\text{H}_2\text{O}_2$  concentration according to the electrolysis time.

The formation of  $\text{H}_3\text{PO}_5$  was cross checked by the changes in the oxidation/ reduction potential (ORP) using an ORP electrode (EMC 133, 6 mm Pt sensor electrode and Ag/AgCl reference electrode containing a gel electrolyte, iSTEK, USA) connected to an iSTEK multimeter (pH-240L, USA).  $\text{H}_3\text{PO}_4$  had an initial oxidation potential of approximately 457 mV, which increased with increasing electrolysis time at a constant current density. The ORP value of the sample solution decreased to the initial ORP value during the iodometric titration, suggesting that the quantification of *in situ* oxidants, PMPA and  $\text{H}_2\text{O}_2$ , is possible (data not used in the present work) and is similar to the quantification of  $\text{Co}^{3+}$  by a potentiometric titration [27].

<sup>31</sup>P-nuclear magnetic resonance (NMR) spectroscopy: The <sup>31</sup>P NMR spectra of 1 M  $\text{H}_3\text{PO}_4$  were collected from the 1 h-electrolyzed sample without dilution and any internal or external standard using a Bruker Avance III HD-400 MHz spectrometer equipped with a 5 mm QNP probe with z-gradients and operated at 162.0144 MHz utilizing the following parameters: Inverse gated

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