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# Non-selective rapid electro-oxidation of persistent, refractory VOCs in industrial wastewater using a highly catalytic and dimensionally stable Ir–Pd/Ti composite electrode

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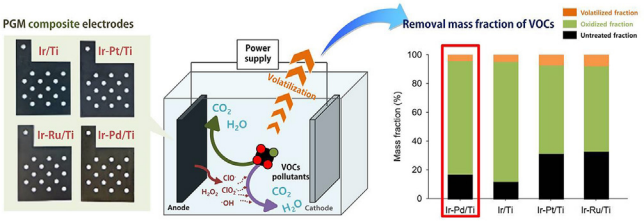
## HIGHLIGHTS

- DSAs composite electrodes were investigated for electro-oxidation of VOCs.
- Both of VOCs' oxidization and volatilization were evaluated to maximum treatment.
- Energy consumption was calculated as a key-factor for electro-oxidation.
- Ir–Pd/Ti achieved the highest removal efficiency compared to other electrodes.
- Current density and electrolyte concentration were adapted for proper operation.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Volatile organic compounds (VOCs) are highly toxic contaminants commonly dissolved in industrial wastewater. Therefore, treatment of VOC-containing wastewater requires a robust and rapid reaction because liquid VOCs can become volatile secondary pollutants. In this study, electro-oxidation with catalytic composite dimensionally stable anodes (DSAs)—a promising process for degrading organic pollutants—was applied to remove various VOCs (chloroform, benzene, toluene, and trichloroethylene). Excellent treatment efficiency of VOCs was demonstrated. To evaluate the VOC removal rate of each DSA, a titanium plate, a frequently used substratum, was coated with four different highly electrocatalytic composite materials (platinum group metals), Ir, Ir–Pt, Ir–Ru, and Ir–Pd. Ir was used as a base catalyst to maintain the electrochemical stability of the anode. Current density and electrolyte concentration were evaluated over various ranges (20–45 mA/cm$^2$ and 0.01–0.15 mol/L as NaCl, respectively) to determine the optimum operating condition. Results indicated that chloroform was the most refractory VOC tested due to its robust chemical bond strength. Moreover, the optimum current density and electrolyte concentration were 25 mA/cm$^2$ and 0.05 M, respectively, representing the most cost-effective condition. Four DSAs were examined (Ir/Ti, Ir–Pt/Ti, Ir–Ru/Ti, and Ir–Pd/Ti). The Ir–Pd/Ti anode was the most suitable for treatment of VOCs presenting the highest chloroform removal performance of 78.8%, energy consumption of 0.38 kWh per unit mass (g) of oxidized chloroform, and the least volatilized fraction of 4.4%.

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Ir–Pd/Ti was the most suitable anode material for VOC treatment because of its unique structure, high wettability, and high surface area.



## 1. Introduction

The increase of organic materials in water pollution is a worldwide concern due to the high resistance of these materials to traditional treatment methods, such as coagulation, biological oxidation, adsorption, ion exchange, and chemical oxidation (Zollinger, 2003; Sharma et al., 2007). These materials have been discharged in lakes, rivers, and oceans without an environmentally acceptable treatment option. This discharge causes serious environmental health problems in living organisms, including humans (Damalas and Eleftherohorinos, 2011).

Among the different organic categories, volatile organic compounds (VOCs) are still the most dangerous due to their toxicity, potential hazardous effects, and rapid evaporation to the atmosphere, which can create secondary air pollution (Mudliar et al., 2010; Pollack et al., 2013). Benzene, chloroform, trichloroethylene, and toluene are the most common VOC pollutants emitted by the different chemical and petrochemical industries, including petroleum refining, paint manufacturing, large steel-structure manufacturing, and automobile manufacturing (Cheng et al., 2008).

From an environmental point of view, it is important to remove VOCs and limit and control their vapor emissions to avoid their negative effects on climate change, plant growth, and human health. Over the past three decades, significant efforts have been exerted to develop more effective techniques for removing VOCs from wastewater. These techniques are basically classified into three different groups: physical treatment, such as air stripping, various membrane filtrations, and the adsorption process (Shah, 2004; Wu et al., 2004; Celebioglu et al., 2016) biological treatment, such as the aerobic/anaerobic treatment process (Easter et al., 2005; Mudliar et al., 2010); and electrochemical treatment (Moreira et al., 2017). In the electrochemical treatment process, electrical activity and chemical activity are integrated to achieve the highest removal percentage of undesirable organic pollutants.

There is great diversity within the electrochemical treatment approaches, such as electro-coagulation, electro-cementation, electro-floatation and electrochemical advanced oxidation (Curteanu et al., 2014; Palma-Goyes et al., 2015; Ahmadzadeh et al., 2017). The unique advantages of electrochemical advanced oxidation processes (EAOPs), including simplicity, high efficiency, environmental friendliness, and cost-effectiveness, make them the most effective treatment techniques because coagulated or floated sludge treatments are unnecessary.

Many forms of EAOPs have been investigated with various selectivity and reaction rates, which is accomplished as a result of direct and/or indirect oxidation on the electrode surface, such as electro-Fenton oxidation, photocatalytic oxidation, and electro-oxidation (Moreira et al., 2017). Electro-Fenton oxidation, a well-known electrochemical process, requires excessive $Fe^{2+}$ concentration and produces a significant amount of chemical sludge during treatment (He and Zhou, 2017). Moreover, photocatalytic oxidation exhibits a low organic pollutant degradation rate over a narrow photocatalytic region and a small fraction (<5%) of solar irradiation absorbance (Dong et al., 2015). However, electro-oxidation does not produce sludge, while degrading pollutants rapidly and non-selectively (da Silva et al., 2013; Särkkä et al., 2015; An et al., 2017).

Electro-oxidation reactions mainly depend on the electrochemical oxidizing agents, such as •OH, $H_2O_2$, $O_3$, $ClO^-$, and $ClO_2^-$, which have the ability to oxidize the organic compounds to the simplest structure such as $CO_2$ without the generation of secondary pollution (Rivera-Utrilla et al., 2013). The oxidation reaction mechanism can be classified as a direct or indirect mechanism. For direct mechanisms, the organic pollutants are selectively oxidized on the active oxidation sites of the metal, acting as oxidizing agents with high oxidation potentials. In contrast the indirect mechanisms, when the electrodes have no active oxidation sites, organic matter is oxidized using other oxidized agents generated from the supporting electrolyte solution, such as hydroxyl radical groups or chlorine species (Basha et al., 2009; Curteanu et al., 2014; Rahmani et al., 2015; Murillo-Sierra et al., 2018).

There are many factors affecting the generation and concentration of the oxidants' agents, such as the electrode properties, pH, electrolyte type, electrolyte concentration, current density, and temperature (Moreira et al., 2017). The electrode materials are still the most important due to the direct connection between their active surface and the oxidant agent materials. As a result, most researchers seek to develop novel, effective, low-cost, and appropriate electrode materials to increase the efficiency in removing VOCs from wastewater solutions (López Peñalver et al., 2013; Rivera-Utrilla et al., 2013). $PbO_2$ and $SnO_2$ were investigated as effective oxidizing-agent anodes with high oxidation potentials (oxygen evolution over potential 1.9 V); however, their low corrosion resistance, particularly with regard to chloride content, is a major drawback for these electrodes (Cossu et al., 1998; Anglada et al., 2009). When $IrO_2$ and graphite were used as anodes, they exhibited low performance and poor ability during the electro-oxidation process due to their lower oxygen evolution potentials of 1.6 and 1.7 V, respectively (Pulgarin et al., 1994). Platinum group metal (PGM) electrodes have also been studied as high oxygen potential anode materials (2.7 V), and the obtained results confirmed they were dimensionally stable with excellent performance; however, their high cost and short lifespans restrict their application (Britto-Costa and Ruotolo, 2012; Martins et al., 2012). Modified titanium electrodes with a thin layer of ruthenium dioxide ($RuO_2$/Ti) have been presented as promising electrode materials for organic pollutant degradation of wastewater effluents (Chae et al., 2004; Yavuz and Koparal, 2006; Hamida et al., 2017). The cost-effective $RuO_2$/Ti electrode possesses good stability, a high oxygen evolution potential of 2.0 V (Anglada et al., 2009), chemical resistance, and high electrocatalytic activity for chlorine evolution and other strong oxidants (•OH, $H_2O_2$, and $O_3$) (Panizza and Cerisola, 2009). Pd is well known for its high electrochemical activity and thermal stability. Moreover, its high anode anti-poisoning effect improves catalytic anodic oxidation, while minimizing adverse electrode oxidation by oxygen molecules, as compared with other platinum group metals (Feng et al., 2016; Mahajan et al., 2017).

In spite of the previously mentioned studies, none of them, to date, has addressed the optimum conditions for controlling the vapor emissions of VOC pollutants in wastewater. This study introduces material groups with high dimensional stability as novel, effective oxidizing-surface sites; they are cost-effective, have anodes with long lifetimes, and are suitable for the degradation of