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# Air ionization as a control technology for off-gas emissions of volatile organic compounds<sup>\*</sup>



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#### ABSTRACT

High energy electron-impact ionizers have found applications mainly in industry to reduce off-gas emissions from waste gas streams at low cost and high efficiency because of their ability to oxidize many airborne organic pollutants (e.g., volatile organic compounds (VOCs)) to CO<sub>2</sub> and H<sub>2</sub>O. Applications of air ionizers in indoor air quality management are limited due to poor removal efficiency and production of noxious side products, e.g., ozone (O<sub>3</sub>). In this paper, we provide a critical evaluation of the pollutant removal performance of air ionizing system through comprehensive review of the literature. In particular, we focus on removal of VOCs and odorants. We also discuss the generation of unwanted air ionization byproducts such as O<sub>3</sub>, NOx, and VOC oxidation intermediates that limit the use of air-ionizers in indoor air quality management.

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# 1. Introduction

VOCs and odorants pose nuisance and health risks in urban environments (Kim and Park, 2008). Thus, the chronic presence of those pollutants in outdoor environments requires effective emissions control strategies on large emission sources (e.g., from industry). Much research effort has been devoted to the development of various strategies to eliminate or reduce such pollutants (Luengas et al., 2015). Recent developments in air cleaning techniques have resulted in significant advances in indoor air quality (IAQ) control, enabling efficient treatment of diverse chemical (odorants, VOCs, and PMs) and biological (microbes) pollutants (Zhang et al., 2011, 2013; Luengas et al., 2015).

Airborne organic matter, such as VOCs, has human health impacts and is the prime cause of poor air quality index (AQI). To meet AQI standards, concentrations of VOCs can be controlled by either destructive or non-destructive methods. For the latter, various porous media with diverse physico-chemical properties can be

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which VOCs can be captured, either for recovery or for subsequent thermal destruction. However, these techniques have both advantages and disadvantages. For example, a broad array of VOCs has been treated using sorbents such as activated carbon or zeolites (Zhang et al., 2013). However, to adequately maintain their treatment efficiency, sorbents need to be replaced or regenerated at regular intervals taking into consideration the specific breakthrough time of each VOC. Liquid-phase solvents (such as water and organic solvents) have also been employed as sorption media to capture VOCs depending on their solubility. The VOCs can then be recovered and/or regenerated by solvent distillation, but this is an energy-intensive process. Condensation technology can be used to treat highly concentrated VOC streams. The major drawbacks of these non-destructive methods are the need for post-treatment. and the requirement to clean-up spent materials such as the solid adsorbent (zeolite or activated carbon) or liquid solvent waste.

employed for adsorption, absorption, and condensation through

Destructive methods for the removal of VOCs commonly involve thermal oxidation with or without a catalyst. Oxidative methods can efficiently convert VOCs into CO<sub>2</sub> and H<sub>2</sub>O. Despite the good performance of thermal destruction methods, they tend to consume a large amount of energy. Although catalytic oxidation is

<sup>\*</sup> This paper has been recommended for acceptance by Charles Wong.

feasible economically, catalyst poisoning can occur due to the production of undesirable byproducts (e.g., sulfur, phosphorus, and halogenated compounds). Biofiltration is a cost effective and ecofriendly alternative relative to conventional techniques. Nonetheless, it has also been found to suffer from several drawbacks (e.g., poor mass transfer from gas to biofilm, inability to separate soluble VOCs, and the release of dust/microorganisms in the process) (Luengas et al., 2015).

In recent years, air ionization methods have been proposed and investigated intensively for the treatment of diverse VOCs and odorants. In this review, we provide insights into fundamental aspects of this new, rapid, green, low-cost, synthetic, and potentially effective strategy for air quality remediation. To assess the role of air ionization methods for the air quality control, we evaluate the performance of these methods relative to conventional techniques. Last, we discuss future opportunities for air ionization techniques as reliable tools for controlling VOCs and odors to meet air quality standards. In addition, limitations of air ionization techniques, particularly the release of unwanted byproducts (e.g., NO<sub>x</sub> and O<sub>3</sub>) during the treatment of VOCs, are discussed.

#### 2. Conventional methods for VOC removal

In this review, we place great emphasis on air ionization methods for removal of VOCs. However, there are diverse approaches that can be taken. As summarized in Table 1, conventional approaches to remove VOCs fall into three categories: (a) physical (sorbent adsorption, solvent adsorption, membrane separation and condensation), (b) chemical (chemical scrubbers, thermal incineration, and catalytic oxidation), and (c) biological (bioscrubbers and biofiltration) methods. The performance of these conventional techniques with regard to VOC removal is described briefly below.

To assess whether commonly-used fan-driven cleaning technologies improve air quality, a panel of experts investigated a total of 59 of 26,000 screened articles (Zhang et al., 2011). The efficiency of air cleaning devices was assessed in terms of clean air delivery rate (CADR), which is defined as the product of single-pass removal efficiency and space velocity through the device. The most effective technologies were particle filtration and sorption of gaseous pollutants. However, none of the reviewed technologies (catalytic oxidation, filtration, ozone oxidation, plasma, sorption, or UV destruction of microorganisms) was effective at removing most pollutants, while many of them were found to generate undesirable products.

The cost of various conventional VOC control techniques was estimated with reference to high-energy electron beams (Son et al., 2010). The ranges of annual costs (per cubic foot per minute (cfm)) for various methods were 25-120 USD (absorption; product recovery can offset operating costs, but requires rigorous maintenance), 10-35 USD (adsorption, activated carbon, product recovery may offset operating costs, moisture sensitive, some compounds can clog pores, e.g., aldehydes, ketones, and esters), 15-75 USD (biofiltration, less initial investment, less secondary waste, slow, selective microbial VOC, removal), 20-120 USD (condensation, product recovery may offset operating costs, requires rigorous maintenance), 15-90 USD (catalytic oxidation, possible energy recovery (up to 70%), sensitive to operating conditions), 15-150 USD (flaring, possible energy recovery (up to 85%), halogenated compounds may need additional equipment), 15-40 USD (zeolite, effective up to 90% relative humidity, product recovery offsets operating costs, high zeolite cost and limited availability), and 15-30 USD (membrane separation, no further treatment, solvent recovery may offset operating costs, membranes are rare and costly). The removal efficiencies of these approaches are generally in the range of 60-99%.

#### 2.1. Physical methods

The physical removal of airborne VOCs is based on VOC partitioning between the gas-phase (air) and some other phase (e.g., sorbents (either liquid or solid), transport through membranes, or the VOC condensed phase). For sorbent-based removal, it is essential to consider and evaluate the following factors: partitioning coefficient, sorbent capacity, breakthrough time and volume, and sorbent regeneration (Wells, 2003). Using adsorption techniques, VOCs can be removed from the air stream by physical adsorption onto porous medium like silica gel, alumina, activated carbon, zeolites, and MOF, among other materials (Vellingiri et al., 2016; Kabalan et al., 2016; Zhu et al., 2016; Yang et al., 2013). However, adsorption techniques are limited by the need for post treatment to dispose of spent adsorbents and/or to treat the adsorbed VOCs, which increases the cost of treatment.

The use of liquid solvents (usually water, mineral oils, or petroleum oils) to strip VOCs from air streams through contact with the contaminated air results in removal efficiencies of 95–98% (Heymes et al., 2006; Ozturk and Yilmaz, 2006; Tatin et al., 2015). Despite the efficiency of VOC treatment, however, absorption has some disadvantages like the presence of insoluble VOCs and/or need for post-treatment of the absorbent liquid. Condensation based on non-destructive separation allows recovery of VOCs from the air stream in a liquid state with efficiencies as high as 99% (Shi and Huang, 2014). Nonetheless, a very low (cryogenic) condensation temperature is often required to accomplish the capture of targets (in the condensed phase) from the air stream. In addition, this method is only efficient when the concentration of VOCs in the air stream is very high (>1% v/v or > 10,000 ppm) (Gupta and Verma, 2002).

### 2.2. Biological methods

Using biological processes, a wide range of pollutants can be digested into less toxic and odorless compounds. In general, biological processes can be divided into biofiltering processes and bioscrubber processes. The latter involve absorption of contaminants in aqueous media followed by biological treatment (Koutinas et al., 2007; Potivichayanon et al., 2006; Nielsen et al., 2007). Bioscrubbing methods are easily controllable and allow removal of products by washing out to avoid inhibitory effects. However, when attempting to remove less soluble or hydrophobic VOCs (e.g., methane, hexane, toluene, and benzene), limited mass transfer may be problematic (Nikiema et al., 2005; Muñoz et al., 2007). This might be one of the reasons why bioscrubbing is less commonly used than biofiltration.

Biofilters are another type of short-contact bioreactor. Here, moist, polluted air is flowed over a porous bed of immobilized microorganisms to remove VOCs (Hwang et al., 2008; Torretta et al., 2015; Wang et al., 2009; Steinberg et al., 2005). The removal efficiency of VOCs by biofiltration is limited by mass transfer of target pollutants and the microbial metabolisms specific for target pollutants. Thus, the packing materials need to be changed frequently to enhance the performance of the system, and there may be incomplete removal of VOCs.

# 2.3. Chemical methods

Processes based on chemical scrubbing and thermal oxidation (with/without catalyst) are commonly categorized as chemical treatment methods. Chemical scrubbing is the most common method used to remove airborne pollutants, especially odors and VOCs. Acidic or alkaline solutions (e.g., sulfuric acid and sodium hydroxide (caustic soda)) are used as scrubbing media. To oxidize

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