Chemical Engineering Journal xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Improving the pollutant removal efficiency of packed-bed plasma reactors incorporating ferroelectric components

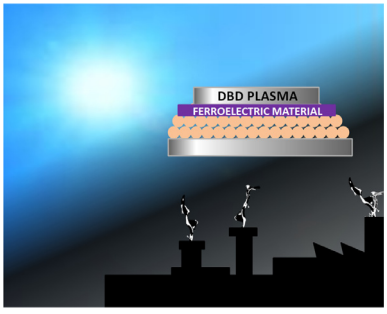
Ana Gómez-Ramírez [a,b,*,1], Antonio M. Montoro-Damas [b,1], Miguel A. Rodríguez [c], Agustín R. González-Elipe [b], José Cotrino [a,b,*]

[a] Departamento de Física Atómica, Molecular y Nuclear, Universidad de Sevilla, Avda. Reina Mercedes, 41012 Sevilla, Spain
[b] Laboratory of Nanotechnology on Surfaces, Instituto de Ciencia de los Materiales de Sevilla (CSIC-Universidad de Sevilla), Avda. Américo Vespucio 49, 41092 Sevilla, Spain
[c] Instituto de Cerámica y Vidrio (CSIC), C/Kelsen, 5, 28049 Madrid, Spain

HIGHLIGHTS

- Pollutant removal is investigated using packed-bed dielectric barrier plasmas.
- Electrode size and ferroelectric material design influence the removal efficiency.
- Addition of a ferroelectric plate enhances the process efficiency.
- Results are discussed in terms of the electrical performance of the reactors.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 June 2016
Received in revised form 25 October 2016
Accepted 8 November 2016
Available online xxxx

Keywords:
Plasma decontamination
Dielectric barrier discharge
Ferroelectric materials
Pollutant removal
VOC's removal
Packed-bed plasma reactor

ABSTRACT

In this work we have studied the plasma removal of air contaminants such as methane, chloroform, toluene and acetone in two parallel plate packed-bed dielectric barrier discharge (DBD) reactors of different sizes. Removal and energy efficiencies have been determined as a function of the residence time of the contaminated air within the reactor, the kind of packed-bed material (ferroelectrics or classical dielectric materials), the frequency and the incorporation of a ferroelectric plate onto the active electrode together with the inter-electrode ferroelectric pellets filling the gap. Results at low frequency with the small reactor and the ferroelectric plate showed an enhancement in energy efficiency (e.g., it was multiplied by a factor of six and three for toluene and chloroform, respectively) and in removal yield (e.g., it increased from 22% to 52% for chloroform and from 15% to 21% for methane). Such enhancements have been attributed to the higher energy of plasma electrons and a lower reactor capacitance found for this plate-modified configuration. A careful analysis of reaction efficiencies and electron energy distributions for the different investigated conditions and the simulation of the electric field at the necks between ferroelectric/dielectric pellets complete the present study. Overall, the obtained results prove the critical role of the barrier architecture and operating conditions for an enhanced performance of pollution removal processes using DBD systems.

* Corresponding authors at: Departamento de Física Atómica, Molecular y Nuclear, Universidad de Sevilla, Avda. Reina Mercedes, 41012 Sevilla, Spain (A. Gómez-Ramírez).
E-mail addresses: anamaria.gomez@icmse.csic.es (A. Gómez-Ramírez), cotrino@us.es (J. Cotrino).
[1] These authors contributed equally.

http://dx.doi.org/10.1016/j.cej.2016.11.065
1385-8947/

1. Introduction

One of the most common applications of dielectric barrier discharge (DBD) plasmas is the decomposition removal of gaseous pollutants [1–4]. A great number of works have been published about the use of these plasma discharges for the removal of volatile organic compounds (VOCs) present in the air as a result of different industrial and in-door activities [5–18]. However, although a large variety of reactor set-ups and working conditions have been proposed to maximize the efficiency of these processes [19–23], most studies have addressed the kinetics of the removal process and paid little attention to the analysis of the plasma, the electrical operation parameters or the effect of the reactor configuration. Common working conditions in these works are a low concentration of pollutants in air, of the order of hundreds or, maximum, thousands ppms, and the pursuit of the full oxidation of VOCs to CO_2 and H_2O (and other fully oxidized sub-products if the pollutant contains heteroatoms) with no formation of intermediate hazardous molecules.

Advanced arrangements of DBD reactors for gas reaction processes such as the reforming of hydrocarbons, CO_2 conversion or the synthesis of ammonia incorporate a ferroelectric moderator between the metallic electrodes [24–28]. This design is advantageous with respect to classical configurations incorporating dielectric materials because the operating voltages can be smaller [29,30] and high plasma currents can be maintained for relatively large separation gaps between electrodes [31,32]. Among other factors, these improvements could be linked with the substantial amount of electrons that, emitted by polarized ferroelectric materials [33,34], may contribute to increase the plasma current and to decrease the breakdown voltage. In this work we have used pellets of lead zirconate titanate (PZT), a rather seldom ferroelectric material when dealing with plasma DBD reactors. The study presents a fundamental study about the design of DBD reactors and the effect of ferroelectric materials on their performance for the abatement of VOCs and other hazardous gases like methane in air. For this purpose, a series of ferroelectric packed bed reactors with a parallel electrode configuration (most geometrical configurations in the literature use a cylindrical geometry and a two coaxial electrodes system [12,15,16]) have been used to test the influence of the electrode area (i.e., size of the reactor) and the effect of incorporating a ferroelectric plate together with the ferroelectric pellets filling the inter-electrode space. Although ferroelectric plates incorporated onto DBD electrodes have been demonstrated to be quite effective in reducing the ignition voltage in surface discharge plasmas [35], to our knowledge their incorporation together with pellets in a packed-bed reactor has not been intended up to now. This unprecedented trial has effectively demonstrated that these kinds of mixed barriers render more efficient the packed-bed reactors. Besides analyzing the influence of the ferroelectric material distribution within the reactor, we have also studied the effect of reactant flow and other working parameters on the process efficiency. Finally, a comprehensive study of the electrical response of the reactor, both theoretically by means of the COMSOL software [36] and experimentally through the determination of the average electron energy and system capacitance, has allowed us to correlate the efficiency of the decontamination processes with the architecture of the ferroelectric barrier and other operating parameters. Such an analysis has provided important clues to understand the system behavior and the possibilities for improvement and extrapolation to other reactor configurations. We think that the obtained results can be relevant to design more efficient packed-bed plasma reactors through the adjustment of the average energy of plasma electrons to values higher than the threshold required to effectively oxidize organic pollutant compounds in air.

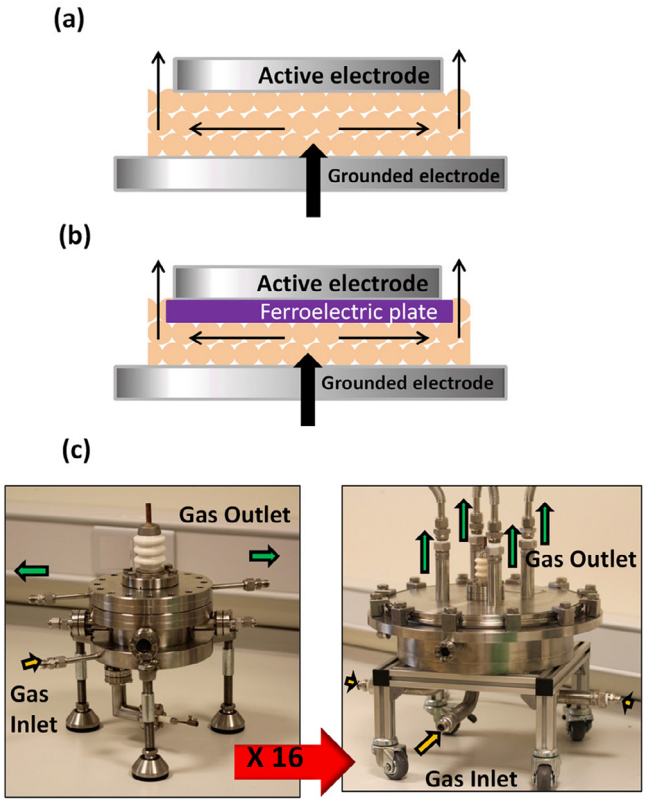


Fig. 1. Schemes of the parallel plate reactors used in the present work: (a) small reactor with ferroelectric pellets. (b) Small reactor with ferroelectric pellets and a $LiNbO_3$ plate onto the active electrode. (c) Photographs of the small (left) and big size reactors (right), the latter had a 16 times bigger electrode area. Green and yellow arrows indicate the flow direction in each case. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Materials and methods

According to Fig. 1(a), the reactors utilized for the present investigation have a parallel plate configuration with a fixed gap space of 3 mm. The inter-electrode space was filled with quasi-spherical pellets of PZT (lead zirconate titanate) with 1.25 mm of average diameter that were synthesized in our laboratory according to a complex process described in detail in [26] and that involves the sintering and sieving of pellets. The relative dielectric constant of PZT is approximately 1900 (APC International, LTD). The Curie point phase transformation of these ferroelectric pellets was 332 °C as determined by differential scanning calorimetry (DSC, TA Instruments Q600). The choice of this ferroelectric material instead of others like $BaTiO_3$ more popular for DBD applications [5,16] has been dictated by the prevalence of a high dielectric constant within a broader range of temperatures (although $BaTiO_3$ dielectric constant can be as high as 10000 [37] it losses its ferroelectric behavior above 120°) and a higher reaction performance obtained for the ammonia synthesis with the same reactor filled with PZT [27]. To ascertain the convenience of using ferroelectrics as filling materials, some comparative abatement experiments were also carried out using similar size pellets of a dielectric material (Al_2O_3, RGPBALLS S.r.l., Italy).

The active upper circle electrode was directly connected to the AC voltage supply, while the bottom electrode was grounded. In an alternative operating mode, a ferroelectric $LiNbO_3$ 0.5 mm thick disc supplied by Roditi (Roditi International Corporation Ltd, England) was fixed onto this upper electrode (Fig. 1(b)). These

Please cite this article in press as: A. Gómez-Ramírez et al., Improving the pollutant removal efficiency of packed-bed plasma reactors incorporating ferroelectric components, Chem. Eng. J. (2016), http://dx.doi.org/10.1016/j.cej.2016.11.065