Vacuum 101 (2014) 86–91

Contents lists available at ScienceDirect

Vacuum

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

Transport characteristics of gas phase ozone in soil during soil remediation by pulsed discharge plasma

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ARTICLE INFO

Article history:
Received 14 May 2013
Received in revised form
11 July 2013
Accepted 13 July 2013

Keywords:
Soil remediation
Discharge plasma
Ozone transfer
p-Nitrophenol
Ozonation

ABSTRACT

In order to investigate transport characteristics of chemically active species in soil during soil remediation by pulsed discharge plasma, gaseous ozone, as a model active species, was chosen in the present research. Ozone transport characteristics in soil were investigated by laboratory column experiments. Effects of soil organic matter, metal oxides, soil pH, soil moisture, and ozone initial concentration on the fate and transport of ozone were evaluated. The experimental results showed that ozone transport velocity was inversely proportional to soil organic matter. Metal oxides could decompose ozone by catalytic reactions, and thus exhibited negative effect on ozone transport. Alkaline soil was not beneficial for ozone transport, due to reactions of ozone with OH^- ions. Water molecules could cover on soil particles to form water film, which interfered with reaction of ozone with soil organic matter and also blocked the catalytic ozone decomposition over metal oxides, and thus a certain amount of water in soil could quicken ozone transport. The relationship of *p*-nitrophenol (PNP) removal in soil column and ozone transport was also studied. Compared with clean soil, ozone transport velocity in PNP contaminated soil was obviously retarded, and more ozone was consumed by PNP molecules. After 30 min of ozone treatment, the maximum PNP degradation efficiency (73.5%) was achieved in the column packed with quartz sand, and followed in descending order, with sand (65.2%), with sandy soil (51.8%) and with clay soil (45.6%). Organic matter and metal oxides resulted in the different PNP removal characteristics in these porous media.

1. Introduction

Soil contamination by biorefractory organic compounds has been of great concern for many decades [1–3]. These organic compounds come from leaky fuel storage tanks, refineries, factories, and improper waste disposal, and have huge impacts on human health and environment [4,5]. Many methods have been proposed for remediating soils contaminated with various organic pollutants [6–9]. Recently, in-situ ozonation technology has been viewed as a promising alternative for removing biorefractory organic pollutants in soil [10,11]. Ozonation offers several advantages for soil remediation. Ozone can be delivered directly to contaminated soil zone by injection, and can react quickly with some biorefractory organic pollutants in soil, improving their biodegradable potentials [12,13]. Furthermore, ozone can increase the amounts of small organic acids in soil and enhance the hydrophilic properties of soil organic matter, and then improve soil structure [14].

Ozone oxides organic pollutants in two ways: by direct oxidation with ozone molecules and by generation of OH radicals [15]. The generation of OH radicals can shorten the remediation time and can also expand the range of organic pollutants to be treated, due to its higher oxidation potential and nonselective g property for pollutants. Metal oxides such as MnO_2, Al_2O_3 and Fe_2O_3 on soil surface can accelerate ozone decomposition to generate OH radicals by catalytic effects [15].

Recently, the application of ozone in the remediation of organic pollutants contaminated soil has been widely studied [16–18]. The mathematical model considering mass transfer process at gas–liquid interface in soil ozonation has also been developed [11]. Based on the application of ozone in soil remediation, gas phase pulsed discharge plasma technology has been developed for soil remediation in our previous studies, and great performances for

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0042-207X/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.vacuum.2013.07.020

pentachlorophenol and *p*-nitrophenol (PNP) contaminated soil remediation were presented [19,20]. During soil remediation by pulsed discharge plasma, two processes exist, that is, transport processes and chemical reaction processes of pollutants and chemically active species. The transport processes can influence the chemical reaction processes, and inversely, the chemical reactions can also improve the transport processes [21]. Therefore, it is necessary to explore the transport characteristics of the active species in soil.

Due to the relatively stability of ozone, in the present research, we mainly chose ozone as a model active species to investigate its transport characteristics in soil. The effects of soil intrinsic properties such as soil organic matter, metal oxides, soil pH, and soil moisture on ozone transport were evaluated. Furthermore, the relationship between PNP degradation in soil and ozone transport was also studied. It is expected to provide references for soil remediation by pulsed discharge plasma.

2. Experimental

2.1. Materials

PNP (purity $> 95\%$) and other inorganic reagents (analytical grade) were used as purchased without further purification.

In this study, four different types of porous media (quartz sand, sand, sandy soil, and clay soil) were employed. Quartz sand and sand were purchased from a chemical plant of Dalian, China. Sandy soil and clay soil were collected from a suburb of Dalian, China. Before use, the porous media were all pretreated as follows. Firstly, they were passed through a 20 mesh standard sieve, and washed with n-hexane and acetone ($v/v = 1:1$) for several times to remove residual impurities to eliminate their impacts on analysis processes, and then air-dried. Tables 1 and 2 showed the main properties and the results of X-ray fluorescence analysis of these porous media, respectively. The preparation processes of PNP contaminated soils and sands were the same as our previous study [20].

2.2. Experimental methods and chemical analysis

The schematic diagram of the experimental apparatus was presented in Fig. 1, which consisted of ozone generation system, ozone transport column, and ozone detection system. Ozone was generated by pulsed discharge in a multi-needle-to-plate reactor, and dry oxygen (99.99%) was used as carrier gas. The detailed introduction on this multi-needle-to-plate reactor could be seen in previous research [20]. Pyrex glass column (350 mm length and 10 mm internal diameter) was used for the column experiments. A stainless-steel wire netting placed on each end cap provided an even distribution of ozone in the soil column. Gaseous ozone was trapped in potassium iodide solution (550 mL) to calculate the amount of ozone, and the capture time for each sample was 2 min, and the detailed measurement method was reported by Suarasan [22]. The ozone concentration in the inlet and outlet of the column were both monitored.

In each transport experiment, 25.0 g soil sample with the desired moisture was filled in the column. Soil pH values were adjusted with NaOH and HCl solutions and determined as described by Hultgren [23]. The methods for PNP extraction from soil and analysis were the same as previous research [20].

Table 1
Main properties of the porous media used in this study.

Contents	Quartz sand	Sand	Sandy soil	Clay soil
pH	8.18	7.73	7.30	7.51
Organic matter (%)	0.03	0.28	2.38	5.54
Particle size (mesh)	20 ∼ 30	20 ∼ 30	20 ∼ 30	20 ∼ 30

Table 2
Results of X-ray fluorescence analysis of different porous media.

Contents	Analysis data (wt. %)			
	Quartz sand	Sand	Sandy soil	Clay soil
SiO_2	98.95	90.01	79.37	56.02
Al_2O_3	0.54	4.03	10.23	17.61
Fe_2O_3[a]	0.40	1.15	3.04	8.86
K_2O	0.03	2.13	2.19	4.09
CaO	0.01	0.06	1.00	2.36
MnO	0.01	0.10	0.42	2.12
MgO	0.01	0.04	0.03	1.81
Na_2O	–	2.01	1.05	0.85
P_2O_5	–	0.01	0.08	0.16
BaO	–	–	0.03	0.11
CuO	–	0.01	0.01	0.10
TiO_2	–	0.03	0.04	0.09
ZrO_2	–	0.08	0.05	0.07
ZnO	–	0.02	0.01	0.05
L.O.I.[b]	0.05	0.32	2.45	5.70
Total	100.00	100.00	100.00	100.00

[a] Fe_2O_3: Total iron.
[b] L.O.I.: Loss on ignition.

Ozone consumption efficiency was calculated as follows:

$$\beta = \frac{C_{O_3\ in} - C_{O_3\ out}}{C_{O_3\ in}} \tag{1}$$

where β was ozone consumption efficiency (%); $C_{O_3\ in}$ and $C_{O_3\ out}$ were ozone concentrations (mg L^{-1}) in the inlet and outlet of the soil column, respectively.

Ozone retardation factor during transport in soil column was calculated as follows [24]:

$$R = \int_0^{T_{max}} \frac{C_{O_3\ in} - C_{O_3\ out}}{C_{O_3\ in}} dT \tag{2}$$

where R was ozone retardation factor; T_{max} (min) was the total time when $C_{O_3\ in}$ and $C_{O_3\ out}$ were equal; T was the sampling time (min).

Considering ozone could react with water in soil pores to generate OH radicals, and it could also suffer from catalytic decomposition to generate OH radicals over metal oxides by the metal oxides catalysts, HCO_3^-, as OH radicals scavenger, was chosen to capture OH radicals in soil column in this study. The evolution of HCO_3^- concentration could indirectly reflect OH radicals transport characteristics in the soil column.

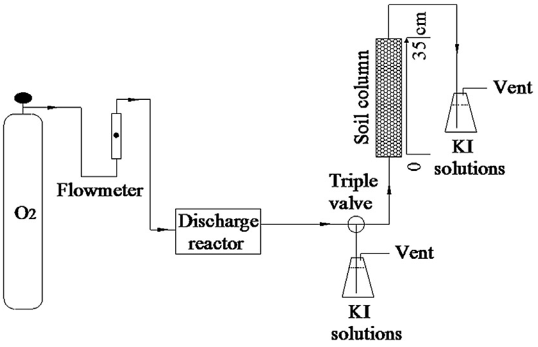

Fig. 1. Schematic diagram of the experimental setup of O_3 diffusion in soil column.