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#### Research article

# Efficacy of wood charcoal and its modified form as packing media for biofiltration of isoprene



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#### ABSTRACT

The efficacy of wood charcoal (WC) and nutrient-enriched wood charcoal (NWC) as biofilter packing media were assessed for isoprene biodegradation in a bioreactor comprising bioscrubber and a biofilter connected in series and inoculated with *Pseudomonas* sp. The bioreactors using WC and NWC exhibited >90% removal efficiency and around 369 g m<sup>-3</sup> h<sup>-1</sup> elimination capacity at around 404 g m<sup>-3</sup> h<sup>-1</sup> inlet loading rate. In both the bioreactors, the biofilter component showed better degradation capacity compared to the bioscrubber unit. The kinetic parameters, maximum elimination capacity,  $EC_{max}$ ; substrate constant,  $K_s$  and  $EC_{max}/K_s$  for Michaelis-Menten model were evaluated. The lower  $K_s$  for the WC packed bioreactor indicated that  $EC_{max}$  achieved, was faster compared to others, while higher  $EC_{max}$  and  $EC_{max}/K_s$  for the NWC packed bioreactor suggests its superiority in isoprene abatement in the continuous mode. A comparison of the available published information on biofiltration of isoprene reflected polyurethane foam as the superior packing media.

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### 1. Introduction

Volatile organic compounds (VOCs), including non-methane hydrocarbons (NMHCs), are important species to play the key role(s) in altering the atmospheric chemistry. Isoprene (2-methyl-1,3-butadiene), which comprises one-third of VOCs, ranks the most abundant NMHCs in the atmosphere with its global emission in the range 450-700 Tg C yr<sup>-1</sup> (Ashworth et al., 2010). Most of the isoprene emitted is biogenic in origin (Fall and Copley, 2000). However, in the urban areas, anthropogenic sources of isoprene dominate (Barletta et al., 2002; Hellen et al., 2006). It reacts with the oxides of nitrogen in ambient air to generate one of the criteria pollutants: tropospheric ozone (EPA US, 1990). Besides generating ground level ozone, isoprene also contributes to the formation of secondary organic aerosols and carbon monoxide. Anthropogenic sources of isoprene include emissions during ethylene manufacture, wood burning, automobile exhaust, cigarette smoking, and from industries that extensively use isoprene as the monomer to manufacture polyisoprene, styrene-isoprene-styrene (SIS) copolymer, butyl rubber, paints, etc (OECD, 2005). The global consumption of isoprene has increased from 700,000 metric tons in 2004 to over a 900,000 metric tons in 2012 (Faisca and Ping, 2013) thus increasing the potential for human exposure. It affects human health by causing various dermal and respiratory problems. Deterioration of olfactory organs has been reported in isoprene rubber plant workers (IARC, 1994), and is also identified as the carcinogen (NTP, 1999). Hence its removal from the contaminated environment seems imperative.

Biofiltration has proved to be a promising technology for elimination of VOCs from the contaminated gas streams (Delhomenie and Heitz, 2005; Zhao et al., 2014; Kauselya et al., 2015). It utilizes microorganisms grown on biofilter media to degrade pollutants present in the gas stream. Different configurations of biofilters namely: biofilter, biotrickling filters, bioscrubber and membrane biofilter have been used (Mudliar et al., 2010). Each of these techniques has its own merits and demerits (Shareefdeen and Singh, 2005). Hence, in present scenario a combination of these units is used in order to get the optimum removal of the VOCs from the contaminated stream.

Apart from the microbial species, being of major importance, the nature of biofilter media has been reported as the other key factor in biofilter performance (Corsi and Seed, 1995; Devinny et al., 1999; Krailas et al., 2000; Tawil, 2001) as it provides a favourable environment in terms of moisture, temperature, pH, and nutrients (Elias et al., 2002). The biofilter media have been categorized into natural and synthetic (Malhautier et al., 2005; Kennes et al., 2009).

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Natural media are organic in nature and include compost, peat, wood chips, bark mulch, etc. Although they provide nutrients for microbial growth, they have a major drawback of being themselves deteriorated, thus compacting and clogging of the bed and declining the biofilter performance during extended durations (Gaudin et al., 2008). Synthetic packing media could be the one derived from the natural source such as wood charcoal (WC) or completely synthetic as polyurethane foam (PUF). They have uniform structure and size that reduces compaction, and allows better air inflow. However, the system requires additional mineral nutrients (Ortiz et al., 2008). Recently, new synthetic media enriched with nutrients have being formulated (Dumont et al., 2008; Hernandez et al., 2010; Acosta et al., 2012). Several VOCs like styrene, toluene, hexane, etc. are effectively removed using biofilters (Malhautier et al., 2005; Hassan and Sorial, 2011).

Studies related to biofiltration of isoprene are scanty. Till date, only natural packing media viz. soil, compost and peat were used for biofiltration of isoprene in the VOCs mixture (Yoon and Park, 2002; Yoon et al., 2002; Gray et al., 2015). In our previous study, synthetic media, PUF, was used as the packing media in a specially designed bioreactor (Srivastva et al., 2015). In the present study, WC and nutrient-enriched wood charcoal (NWC) are used as packing media to assess their effect on isoprene biofiltration.

#### 2. Material and methods

#### 2.1. Preparation of inoculum

The bacterial culture used in the present study, was the same as isolated earlier from contaminated soils of the waste rubber dumping site (Srivastva et al., 2015). The most efficient bacterial isolate [Pseudomonas sp. (NCBI accession number: KM226326)], as revealed by the degradation kinetics in batch mode, was used as the inoculum during continuous mode operation. The bacterial culture grown in mineral salts medium (MSM) was passed through the packing media via an overhead nutrient tank.

#### 2.2. Preparation of packing media

Wood charcoal was obtained from the domestic fuel market and cut into cubes (approx 1 cm). The pieces were washed in distilled water and dried ( $60 \, ^{\circ}$ C, 2 days).

The second packing media was prepared from the WC. The nutrient enrichment of WC pieces was done as described earlier with slight modifications (Singh et al., 2012). Approximately, 200 g of dried WC powder (average diameter 0.85 mm) was added to 1.26 M potassium nitrate (KNO<sub>3</sub>) solution and kept for 24 h. Polyvinyl alcohol (PVA) (200 g) was dissolved in 0.63 M KNO<sub>3</sub> solution by heating (90 °C). The incubated WC/KNO<sub>3</sub> mixture was slowly added to PVA/KNO<sub>3</sub> mixture under constant stirring for 1.5 h at 90 °C. The viscous lump formed by cooling mixture to 40 °C, was cut into cubes (approx 1 cm). The cubes were then incubated in aqueous phosphate solution (150 g NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O and 335 g Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O in 450 ml water) for 0.5 h at room temperature. The modified NWC was finally dried (100 °C, 24 h) before packing it into the bioreactor.

#### 2.3. Biodegradation of isoprene in continuous mode

Biodegradation of isoprene was carried out in a bioscrubber-cum-biofilter bioreactor connected in series as described earlier (Srivastva et al., 2015). The two bioreactors, one with WC while the other with NWC as packing media, were operated simultaneously. The lower part (I.D. 5 cm  $\times$  L 28 cm) in both the cases, was operated as bioscrubber (the suspended growth), while the upper part (I.D.

5 cm  $\times$  L 70 cm) as the conventional biofilter. Isoprene vapor generated in the bubbler, was fed to the bioscrubber unit at four different flow rates i.e. 0.06, 0.18, 0.36–0.48 m<sup>3</sup> h<sup>-1</sup> during the Acclimation Phase and Phases I, II and III, respectively. Isoprene concentrations at the inlet and two outlets located at the top of bioscrubber and biofilter units were estimated by gas chromatographic method (Srivastva et al., 2015). The biodegradation was carried out for 130 days and the performance of the bioreactors were assessed during operation in terms of following parameters:

% Removal efficiency (RE) = 
$$\frac{C_{in} - C_{out}}{C_{in}} \times 100$$
 (1)

Elimination capacity (EC) = 
$$\frac{Q(C_{in} - C_{out})}{V}$$
 (2)

At varying inlet loading rates:

$$Inlet \ loading \ \ rate \ (IL) = \frac{C_{in}Q}{V} \tag{3}$$

where, V is the working volume (m $^{-3}$ ), Q is the volumetric flow rate (m $^{-3}$  h $^{-1}$ ),  $C_{in}$  is the inlet concentration (g m $^{-3}$ ),  $C_{out}$  is the outlet concentration (g m $^{-3}$ ).

#### 2.4. Biodegradation kinetics

The Michaelis-Menten model, modified for continuous system as derived by Mathur et al. (2006):

$$\frac{V}{Q(C_{in}-C_{out})} = \frac{K_s}{EC_{max}} \frac{1}{C_{ln}} + \frac{1}{EC_{max}}$$
(4)

was applied to the experimental values of Phases I to III for determining the kinetic parameters. Here,  $EC_{max}$  is the maximum elimination capacity (g m<sup>-3</sup> h<sup>-1</sup>),  $K_s$ , the saturation constant of

substrate (isoprene) (g m<sup>-3</sup>) and 
$$C_{ln} \left\{ = \frac{C_{in} - C_{out}}{ln \frac{C_{in}}{C_{out}}} \right\}$$
, the logarithmic

average of inlet and outlet concentrations of isoprene. The equations corresponding to the best fit straight line in  $\frac{1}{EC}$  vs  $\frac{1}{C_{in}}$  plot for bioscrubber and biofilter were generated using least-squares method. The intercept gave the value  $1/EC_{max}$  and the slope of  $K_s/EC_{max}$ .

#### 3. Results and discussion

#### 3.1. Wood charcoal as the packing media

The performance of the bioscrubber and biofiltration units of WC packed bioreactor at varying inlet concentrations is depicted in Fig. 1. In the bioscrubber section (Fig. 1A), the initial high RE (96.4%) during Acclimation Phase could be due to the increased dissolution of isoprene in liquid medium at low inlet concentrations  $(0.01-0.05 \text{ g m}^{-3})$  (Pedersen and Sehested, 2001). With the attainment of saturation level, the RE gradually declined to 53.5%. From the 4th day onward, the increment in the RE was observed owing to biodegradation until it reached 73% at the steady state of Acclimation Phase. The steep decline in RE (73–08%) was observed with the increase in inlet concentration  $(0.3-12.3 \text{ g m}^{-3})$ , which subsequently increased and became stable at around 15% from 40th day onward in Phase I. The steady state continued till 60th day where approx 20% RE was achieved. The increase in flow rate from 0.18 to 0.36 m<sup>3</sup> h<sup>-1</sup> during Phase II was again accompanied by steep decline in RE. The steady state during this phase was obtained after 72nd day where approx 13% RE was observed. A further decline in

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