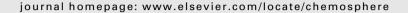
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# Chemosphere





# H<sub>2</sub>S Abatement in a biotrickling filter using iron(III) foam media

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### ABSTRACT

Airstreams polluted with H<sub>2</sub>S at inlet loads ranging from 2.4 to 40.9 g H<sub>2</sub>S m<sup>-3</sup> h<sup>-1</sup> were treated in a biotrickling reactor packed with hematite bearing, open pore foam units, at Empty Bed Residence Times (EBRT) ranging from 20 to 60 s over a period of 80 d, with almost complete removal of the pollutant from the startup of the system. The media had been seeded with sludge from a local water works facility, and removal efficiencies in excess of 80% were consistently observed along the operation of the reactor, with an average of 98%. Based on section performance, being a section one third of the bed length, observed elimination capacities (EC) reached up to 88.7 g H<sub>2</sub>S m<sup>-3</sup> h<sup>-1</sup> and 72.0 g H<sub>2</sub>S m<sup>-3</sup> h<sup>-1</sup> at section EBRT of 10 and 7 s, respectively. The observed EC values compared much better than data reported on other packed bed reactors using biological iron oxidization to treat H<sub>2</sub>S airstreams indirectly, and so did it when comparing the EC per unit of specific area in a similar study using polyurethane (PU) foams. Further, and unlike PU packed biofilters, no compaction occurred due to the iron foam rigidity, which translated in much better observed gas phase pressure drop as opposed to other conventional biofilters. Denaturing gel gradient electrophoresis was performed on the biomass collected in the packing after the biofilter service, and it was found that though a multi bacterial colony was seeded in the system via the sludge, the only surviving genus was the iron oxidizing *Alicyclobacillus* spp.

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## 1. Introduction

Iron sponges have been reported to remove hydrogen sulfide from airstreams due to the chemisorption of the pollutants in the active hematite ( $Fe_2O_3$ ) sites of the adsorbent. This reaction has been widely documented elsewhere, and, in general, it can be described as follows (Davis et al., 1985):

$$Fe_2O_3 \cdot 3H_2O + 3H_2S \rightarrow 2FeS + S + 6H_2O$$
 (1)

$$Fe_2O_3 \cdot 3H_2O + 3H_2S \rightarrow Fe_2S_3 + 6H_2O$$
 (2)

In the presence of high concentrations of dissolved oxygen, and at slightly alkaline pH, the iron sulfides of the reactions described in Eqs. (1) and (2) further react to partially recover the original hematite, increasing the adsorbent removal capability

$$4FeS + 6H_2O + 3O_2 \rightarrow 2(Fe_2O_3 \cdot 3H_2O) + 4S \tag{3}$$

$$2Fe_2S_3 + 6H_2O + 3O_2 \rightarrow 2(Fe_2O_3 \cdot 3H_2O) + 6S$$
 (4)

The high amount of sulfur produced quickly translates in clogging and performance depletion for these systems (Davis et al., 1985). This problem is alternatively overcome by means of a biologically mediated recovery of the ferric ions instead of the oxidation described by Eqs. (3) and (4) owing to iron oxidizing bacteria at acidic pH, yielding high concentrations of soluble sulfates and diminishing

the amounts of elemental solid sulfur (Mesa et al., 2002). The reactions can be described as follows:

$$4Fe_2O_3 + H_2S + 7H_2SO_4 \to 8FeSO_4 + 8H_2O \eqno(5)$$

$$4 FeSO_4 + 2 H_2 SO_4 + O_2 \xrightarrow{\text{IRON OXIDIZING BACTERIA}} 2 Fe_2 (SO_4)_3 + 2 H_2 O \quad \ (6)$$

When the iron media are seeded with municipal sludge, direct degradation of H<sub>2</sub>S by sulfur oxidizing bacteria is additionally expected to occur in parallel over the first stages of acclimatization. This releases high amounts of sulfates that increase the acidity in the system, which favors the leaching and maintenance of iron ions. At increased acidity, the activity of both types of microbial species, the sulfur and iron oxidizing ones, is enhanced; thus, when these microorganisms are seeded in the iron containing system, reactions Eqs. (1) and (2) are progressively replaced as the bacterial communities grow, and the direct biooxidation of H<sub>2</sub>S and/or indirect H<sub>2</sub>S abiotic reaction are responsible for the pollutant abatement. Interestingly, previous studies have shown that the microbial consortia from municipal sludge used to seed iron containing media (lavarock packed biofilters) as biomass carriers treating H<sub>2</sub>S evolved into single iron oxidizing species, even though sulfur oxidizing bacteria were expected to survive (Truesdail et al., 1998; Li et al., 2005).

All synthetic media biofilters suffer from low initial efficiency when the biofilms are getting established, during which the biofilter is emitting relatively untreated and odorous air, resulting in odor complaints. Even after these biofilters have established the biofilms, whenever the inlet concentration increases abruptly,

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odorous air is emitted since it takes time to grow additional biomass, corresponding to the higher inlet concentrations. The use of iron rich media is advantageous since such media achieve complete removal during initial start-up, can effectively handle abrupt changes in inlet concentration and do not get saturated like an adsorbent, due to continuous regeneration of the media. The goal of this study was, therefore, to develop and experimentally test Iron Open Pore Foam (IOPF) units for the abiotic and biotic removal of odorous airstreams at room conditions, simulating typical emissions encountered in water works facilities. Open pore foam units were used since it had been reported that biofilters packed with foam structures and geometries exhibit better pressure drop and biomass clogging characteristics compared to other systems packed with natural or more compact synthetic media (Moe and Irvine, 2000; Goncalves and Govind, 2005).

#### 2. Materials and methods

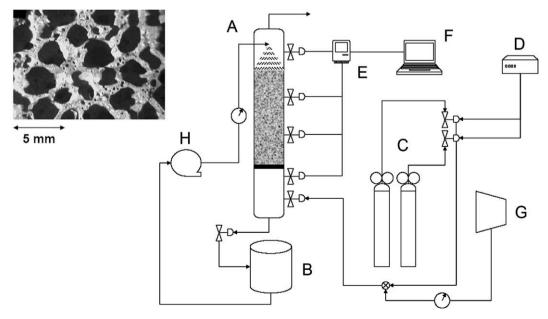
The IOPF material was synthesized by Nanodynamics, Inc. (Buffalo, NY) and is manufactured by gelation of soluble silicates

**Table 1** Properties of the IOPF packing media and operation conditions for the dry and wet basis, abiotic  $H_2S$  uptake experiments, as well as the biological runs carried out after seeding of the IOPF with sludge from a local water works facility

IOPF property	Value	IOPF property	Value
IOPF sample amount (g)	1,187	Intrinsic solid moisture content (wt%)	14
Bed height (cm)	60	Average iron surface composition measured with EDS (wt%)	4.6
Bed volume (1)	4.8		
Bed porosity (%)	53	Gas phase EBRT (s)	20-60
Average unit sample size (m)	0.022- 0.036	Nutrients/water flow rate (L min <sup>-1</sup> cm <sup>-2</sup> )	0.0025
Average solid macropore size $(\mu m)$	525	Inlet airstream H <sub>2</sub> S concentration (ppmv)	20- 280
Sample macroporosity (%)	69	Inlet airstream H <sub>2</sub> O concentration (ppmv)	30

(13 wt% Na<sub>2</sub>O, 26 wt% SiO<sub>2</sub>, balance water) with soluble aluminates (17.5 wt% Na<sub>2</sub>O, 22 wt% Al<sub>2</sub>O<sub>3</sub>, balance water) combined with powdered ion oxide (Fe<sub>2</sub>O<sub>3</sub>) material, surfactant (DC 190, Dow Chemical Co.; 0.05 wt% of total composition), and aluminum powder (7 μm average particle size, 0.5 wt% of the total composition). All ingredients are combined at 15 °C to reduce the gelation rate, and then are poured in a mold at room temperature, resulting in rapid gelation and hydrogen gas production, thereby creating open cell porosity. The resultant shape, which is a self-supporting gel, is dried to reduce the water content. A final open-cell porous material with a bulk density of about 512 kg m<sup>-3</sup>, compressive strength of 2-3 MPa, a modulus of rupture of 1-2 MPa, and a final iron bulk content of 14 wt% is then obtained. The design and operation properties of the IOPF packing media and reactor used during the abiotic uptake and biological experiments carried out in the present study are summarized in Table 1. A schematic of the experimental set-up where the continuous tests were carried out and a snapshot of the IOPF are shown in Fig. 1. A pressurized stream of 5% by volume H<sub>2</sub>S in nitrogen source (Matheson, IL) was diluted with the incoming lab air at concentrations up to 280 ppmv. H<sub>2</sub>S concentrations were measured in real time by means of an inline electrochemical sensor (iTrans, Industrial Scientific Corp., PA). The reactor was equipped with 4 sampling ports separated 30 cm from each other. Environmental Scanning Electron Microscopy (ESEM), Energy Dispersive Spectroscopy (EDS) and Fourier Transformed Raman Spectroscopy (FT-Raman) were used to help observe the biomass attached on the foams and analyze the chemical iron content of the outermost foam surface and of some spots of interest. EDS and ESEM data were obtained in a Philips XL-30 apparatus, whereas FT-Raman spectra were taken with triple monochromator T 64000 (Jobin Yvon) in backscattering configuration using KrC laser (647.1 nm excitation line) and laser power of 3 mW at a sample and spectral resolution of 1 cmK1; flux density was 3 mW mm<sup>-2</sup>. Spectra were acquired at 1 cmK1 resolution.

The abiotic  $\rm H_2S$  uptake was carried out on a dry basis (air from lab supply containing a relative humidity of 0.1%) and on a wet basis on the media exhausted after the dry basis tests finished, in which deionized water was trickled down the bed from the column



**Fig. 1.** Schematic of the system used in the abiotic and biological uptake of H<sub>2</sub>S with the IOPF media and PU foam. (A) PVC reactor (diameter 10 cm and length 90 cm) equipped with 4 sample ports. Bed height was always 60 cm. (B) Nutrients tank. (C) H<sub>2</sub>S cylinder (H<sub>2</sub>S 5% by volume, N<sub>2</sub> 95% by volume). (D) H<sub>2</sub>S mass flow controller. (E) Electrochemical sensor for the measurement of H<sub>2</sub>S in the sampling ports. (F) H<sub>2</sub>S concentration data acquisition system. (G) Lab air compressor (relative humidity 0.1%). (H) Nutrient solution recirculating pump. Snapshot of the IOPF foam is shown in left upper corner.

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