Removal of Benzene from Oil Refinery Wastewater Treatment Plant Exhausted Gases with a Multi-stage Biofiltration Pilot Plant

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Benzene removal from exhausted gases is a tricky issue and is usually carried out by the means of chemical processes. Such systems require reactants, produce waste and are energy demanding. Biological systems can be a cost-effective solution. The paper presents the results obtained in a multi-stage biological system for benzene and other aromatics removal from exhausted gases of a wastewater treatment plant working with oil refinery pavement wastewaters. The system, based on a bioscrubber, two biotrickling filters and one biofilter, obtained removal efficiencies always over the 70%, also giving good results with fluctuating inlet concentrations.

Keywords: air pollution, benzene, biofiltration, biotrickling filter, oil refinery wastewater

Benzene is, together with other aromatics as toluene, ethylbenzene and xylene isomers (the so-called BTEX), typically contained in petroleum products [1, 2]. BTEX polluted wastewaters can be collected and treated by the means of activated sludge processes. Due to its high volatility and carcinogen properties, exhausted gases containing benzene coming for the first stages of wastewater treatment plants (WWTPs) need to be treated because of workers and population health concerns (table 1 for the main exposure threshold limits). Some of these type of chemicals can reach the environment in small quantities and their pollution effect is not immediate, they accumulate over time [3]. Traditionally, exhausted gases containing BTEX are treated by the means of physical and chemical processes, such as adsorption, condensation, thermal incineration or catalytic conversion [4,5]. Such systems have usually high removal efficiencies, even if they have high operative costs (e.g. reactant use, transport and storage; waste disposal; energy consumption).

Table 1

SAFETY AND ODOUR EXPOSURE THRESHOLDS (mg Nm^{-3}) FOR BENZENE

IDLH* [5]	STEL** [7]	TWA*** [7]	Odour [5]
1,742	8.7	1.7	14-24

*: Immediately Dangerous for Life and Health.
**: Short Term Exposure Limit.
***: Time Weighted Average.

In recent years biofiltration, that was originally aimed at removing low odorous concentrations [8,9], has received increased attention as a low-cost, energy-efficient and effective method to treat waste air streams containing low/medium concentrations of biodegradable compounds. The importance of the biofiltering performances optimization has been pointed out recently, taking into account that these devices usually release the treated gas at very low concentration levels [10].

Different sectors including waste aerobic treatment facilities and WWTPs have selected biofilters to convert gas phase chemical compounds into common biological degradation products such as carbon dioxide, water and mineral salts [9,11-14]. In biofilters (BF), as the exhausted air is passed through a bed of media, the contaminants and oxygen are first transferred to the biofilm formed on the surface of the media particles and, then, metabolized by bacteria. In order to sustain microbial growth, moisture is provided by saturating the processed air before it enters the biofilter unit. Moisture is also provided by intermittent and occasional spray irrigation of the media. The media within a biofilter are normally composed of natural material or synthetically manufactured media.

Even biotrickling filtration is one of the many promising biological techniques for odour and VOC control. The trickling liquid provides moisture, salts, metabolites and supplemental nutrients to the process culture; moreover it is a convenient mean to control pH. Biotrickling filters (BTF) show several advantages over biofiltration technologies for air pollution control: little bed height limitation (up to 2-3 m); smaller footprints; packing longevity over 10 years; lower pressure drops due to high media porosity; easy control of temperature, *p*H, salt concentration and metabolites accumulation; wider range of treatable pollutants [4].

For all these features biotrickling filters can be used both in combination and in substitution of conventional biofilters to improve odour control and diminish pollutants emission.

The paper presents the results obtained with a multi-stage pilot plant treating the exhausted gases drawn from the pumping station and the primary settling tanks of a WWTP treating oil refinery pavement wastewaters containing high benzene loads.

Experimental part

Equipment and methods

The pilot plant is composed of four biological stages (fig. 1):

- a bioscrubber (BS1) filled with Pall Rings (volume: 4.0 m^3);
- a BTF filled with Mitilus edulis shells (Monashell® patent), exhibiting a high buffering power [9] (BTF2; volume 6 m^3);

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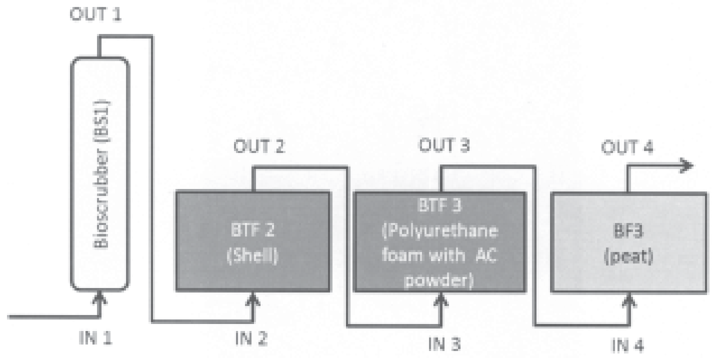

Fig. 1. Four-stages pilot plant layout

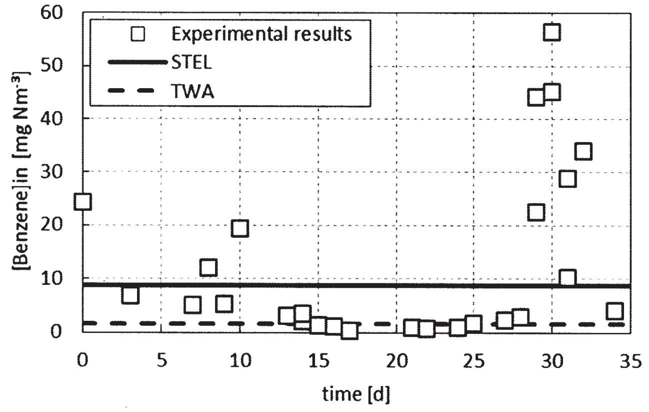

Fig. 2. Benzene inlet concentration

- a BTF filled with synthetic foam cubes charged with activated carbon (AC) powder (BTF3; 8 0 m^3);
- a finishing single-stage biofilter (BF4; volume: 6 m^3) that uses peat as support media (Monafill® patent).

While BS1 uses tap water which is directly treated by the WWTP after the process, BTF2 and BTF3 trickling liquid is recirculated and maintained at 30°C by the means of two thermostat-equipped electric heaters placed into the respective tanks. No nutrients and oligoelements have been added to the trickling liquid (aqueduct water). A selected consortium of microbial population was decided to be inoculated in order to lower start-up times and, meanwhile, improve biotrickling filters efficiency in terms of total abatable mass.

The pilot plant ran for a period of 35 days, during which chemical analysis on air samples was conducted. Air samples were taken upstream and downstream each stage and collected onto suitable sorbent tubes using SKC sample pumps. Following desorption, the samples were analyzed by Gas Chromatography Mass Spectrometry (GC-MS) in order to determine BTEX and cumene. Temperature (T) and flow rate (Q) were measured by the means of a Delta Ohm HD 2303.0 Hot Wire Anemometer [15] with an AP471 S1 probe.

Pollutant loading rate (Ls, g h^{-1} m^{-3}of packing material) and removal efficiencies (REs, as percentage) and elimination capacity (ECs, g h^{-1} m^{-3} of packing material) of each stage were calculated: (1)

$$L_s = \frac{Q\,C_{in\,s}}{V_s} \qquad (2)$$

$$RE_s = \frac{C_{in\,s} - C_{out\,s}}{C_{in\,s}}100 \qquad (3)$$

$$EC_s = \frac{C_{in\,s} - C_{out\,s}}{V_s}Q$$

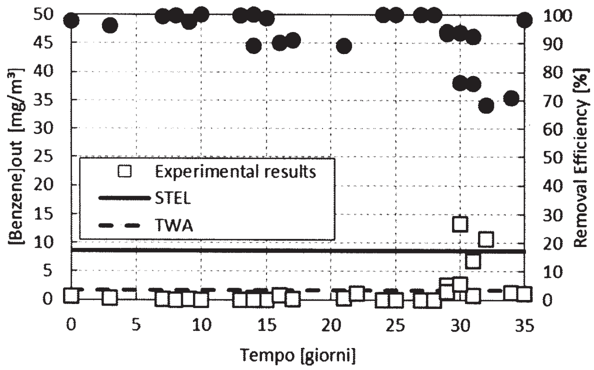

Fig. 3. Benzene outlet concentration and overall removal efficiencies of the biofiltration system

where C_{in} and C_{out} are, respectively, the inlet and outlet pollutant concentrations (g m^{-3}), V is the volume of the packed bed (m^3).

Results and discussions

The system was tested with two flow rates (300 and 600 m^3 h^{-1} during the last 10 days). Inflow air temperature ranged between 22 and 28°C. Data analysis on the five sampled chemicals showed that benzene is the most recalcitrant pollutant; for such reason only benzene results are presented. Inlet concentrations are shown in figure 2, while outlet concentration and overall removal efficiencies are reported in figure 3.

Benzene concentrations has a huge variability (almost two orders of magnitude) with peaks of more than 40 mg Nm^{-3}; TWA and STEL threshold were exceeded respectively, 11 and 20 times. This was due to the WWTP operating conditions.

The overall system removal efficiency was over the 89%, except when inlet concentrations were over 30 mg Nm^{-3}. In such case REs were about the 70% and the outlet concentrations exceeded the STEL threshold only in two cases (days 30 and 32).

This is a good result, considering that benzene is substantially insoluble in water [16] and biological removal is based on dissolution of pollutant to remove in water [4].

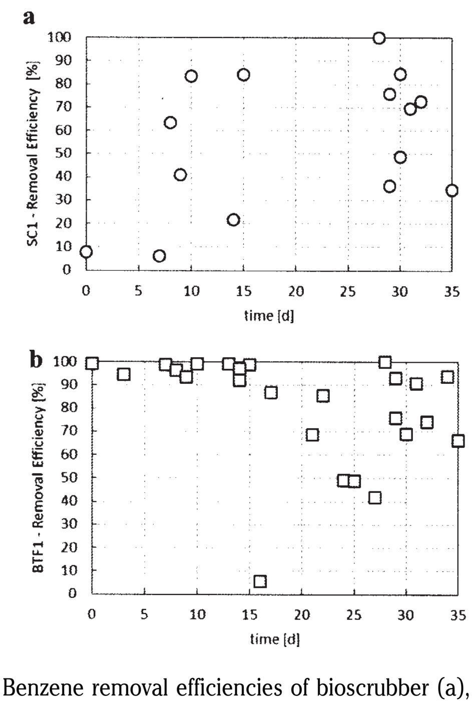

Fig. 4. Benzene removal efficiencies of bioscrubber (a), BTF2 (b)

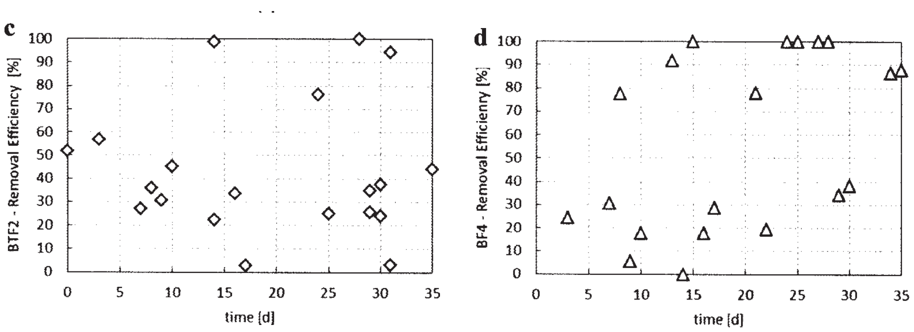

Fig. 4. Benzene removal efficiencies of BTF3 (c) and BF4 (d)

Figure 4 shows removal efficiencies of each filtering stage.

BS1 removal efficiencies are fluctuating, ranging from 10 to 99%, with an average value of about 50% (fig. 4a). During days 16-27 BS1 was not running because of a packing material cleaning period due to an excess of suspended solids in washing water.

BTF2 removal efficiency is more stable than BS1 (fig. 4b); only the increasing loading during days 16-27, due to BS1 inactivity, reduced the performances, but average RE were above 90%.

Variable performances of BTF3 and BF4 (fig. 4c and 4d, respectively) can be explained with (i) a low pollutant load, unable to allow biofilm growth, coupled with (ii) a short acclimation period. In fact, a good acclimation period is fundamental for achieving good biological system resilience.

No positive effect seems to be attributed to activated carbon powder added to BTF3 filling material.

Conclusions

Only 35 day long experimental activity carried out on a four-stage system based on a bioscrubber, two biotrickling filters, filled with different packing material, and a peat-filled biofilter demonstrated that benzene removal is possible with biological systems. The outlet concentrations are usually below the threshold limit for short term exposure even if no nutrients or oligoelements were added to the trickling liquid and strong peak of inlet benzene concentration occurred. The exceeding outlet concentrations can be ascribed to the short acclimation period.

Analysing the single stage performance, the biotrickling filter filled with Mitilus edulis shells seems to be the best as removal efficiency and stability.

Further developments of research will be focused on (i) the improvement of the biofilm growth as well as stability adding oligoelements and the (ii) increase of loading rates in order to better understand the limits of biofiltration process.

The subject has also been studied by other researchers [17].

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