An innovating process for pollutants concentration in gaseous effluents: application to high gas flow rates with low VOC concentrations

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ABSTRACT. Among all kinds of atmospheric pollution, volatile organic compounds (VOCs) have raised a lot of interest recently. For high flow rates of low polluted gaseous effluents, the Bioprocess and Biotechnology Laboratory of the INSA of Toulouse has developed a cost-effective process to concentrate polluting molecules into a smaller gas flow rate.

The concentration process is based on mechanical desorption of dissolved gases. The first step consists in an absorption step. The next step is a desorption step. Micro-bubbles are then separated from the liquid flow using an in-house designed gas/liquid separator (improved gas/liquid cyclone) and constitute the high polluted gas effluent. The ratio between the high polluted gas flow rate and the initial low polluted gas flow rate is the concentration factor. The cleaned liquid phase is recycled for a new absorption step.

First results have shown a 90% recovery of VOCs from the liquid flow to the high polluted gas flow with the three target molecules. According to these results, this concentration technology seems to be of particular interest to improve economic efficiency of degradation processes, such as thermal incineration, reducing the gas flow rate to treat. Thus, it would facilitate purification steps in the case of economically interesting molecules because of the smaller gas flow rate treated.

1 INTRODUCTION

The treatment of waste gas containing Volatile Organic Compounds (VOCs) is a major environmental problem for such industries as refineries, transport, incineration, painting and surface treatment. Nowadays, numerous treatment processes are available and can ensure satisfactory purification rates. We can quote for example processes such as incineration or adsorption that represent at least 70% of gas treatment installations in Europe and the United States (Dueso and Lambert, 1997). However, the application domain of these technologies is not universal (Ademe, 1997; Ceccaldi et al., 1993; Le Cloirec, 1998; Siegell, 1996). Costs induced by the use of an efficient process which is poorly adapted to effluent characteristics constitute a limitation to the development of an environmental strategy for gaseous effluent dumping. Effluent purification often highlights the problem of the treatment of large gas flow rates (from 10^3 to $2\ 10^5$ m^3.h^{-1})

polluted with low VOC concentrations (from 0.1 10^{-3} to 10^{-2} kg.m^{-3}). Because of high gas flow rates, high volumes are needed to reach satisfactory treatment efficiency. One solution can be the use of a cost-effective process to concentrate polluting molecules into a smaller gas flow rate to reduce the treatment unit size.

The Bioprocess and Biotechnology Laboratory of the INSA (National Institute for Applied Sciences) of Toulouse has developed, with financial support from the Biotrade company (innovating solutions for aerobic treatment of industrial effluents, http://www.biotrade.fr) and the ADEME (agency for environment preservation and energy control), a concentration process for gaseous polluting molecules. This technology allows:

➢   to improve economic efficiency of degradation processes, such as thermal incineration, reducing the gas flow rate to be treated.

➢   to retrieve molecules of interest in a smaller gas flow rate, facilitating following purification steps.
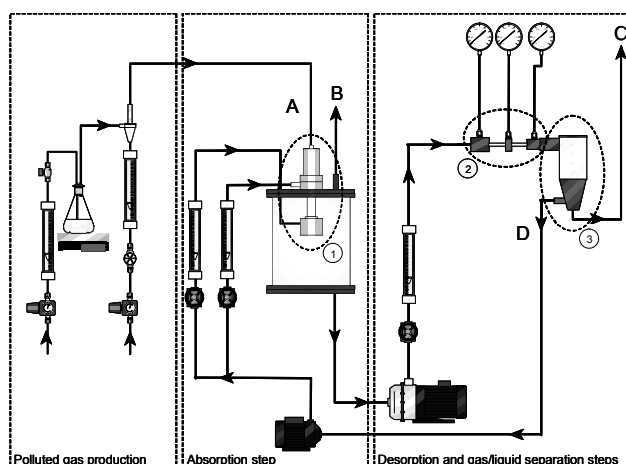

Figure 1. Concentration process schema. Polluted gas is generated at the left part of the schema. (A) It is carried to the aero-ejector (1) for the absorption step. VOCs are transferred into the solvent and cleaned gas is obtained (B). The polluted solvent passes through the desorption device (2) and gas/liquid separation is achieved in the in-house designed separator (3). The high polluted gas flow rate is obtained at the gaseous outlet (C) and cleaned solvent is recycled to the absorption step (D).

As shown in Figure 1, the concentration process is based on mechanical desorption of dissolved gases. The first step consists in an absorption step. The "aero-ejector", an in-house developed gas/liquid contactor (De Billerbeck and Fonade, 1995), ensures an improved mass transfer of molecules from the polluted gas flow to the liquid flow (water) with small volumes. A previous study of its hydrodynamic and mass transfer characteristics was achieved with model molecules such as oxygen, ethanol, butyl acetate and methyl ethyl ketone: a 90% elimination of VOCs was obtained with a single treatment of the gaseous phase (Daubert *et al.*, 2001; De Billerbeck *et al.*, 1999; Rainer *et al.*, 1995). The next step is a desorption step. The liquid flow passes through a desorption device which allows nucleation of gas bubbles and mass transfer of dissolved VOCs from the liquid flow to the gas flow (the pressure decrease provoked by the desorption device implies a thermodynamic imbalance between the VOCs

concentrations in the liquid phase and the gas phase, contributing to a high mass transfer). Micro-bubbles are then separated from the liquid flow using an in-house designed gas/liquid separator (improved gas/liquid cyclone) and constitute the high polluted gas effluent. The ratio between the high polluted gas flow rate and the initial low polluted gas flow rate is the concentration factor. The cleaned liquid phase is recycled for a new absorption step.

The present study deals with the process optimization (i.e. the design of the new gas/liquid separator). Thus, it shows first results obtained for pollutants recovery into the final gaseous phase (high polluted).

2 MATERIALS AND METHODS

2.1 Volatile Organic Compounds
During this study, we used three target pollutants, frequently encountered in industrial gaseous effluents (as for example in printing or in pharmaceutical industries): ethanol (EtOH), methyl ethyl ketone (MEK) and butyl acetate (BA). All VOCs (99% purity) were provided by Prolabo. Added to their non-toxicity and their processing facility, the major interest of these molecules is their difference in solubility in water, which enables us to test process efficiency in different cases (Henry's constant H varying from 0.29 10^5 to $7.8 \ 10^5$ Pa).

2.2 The polluted gas generation
The main air stream was saturated with water vapour by sparging the air through a 20 L reactor containing tap water. Three smaller compressed air streams were sparged in a 1 L bottle, hermetically closed, containing liquid VOC (either ethanol, methyl ethyl ketone or butyl acetate as required) and subsequently mixed with the main humidified air stream. One scale (Sartorius EA6DCE1, accuracy $0.2 \ 10^{-3}$ kg) allowed the amount of entrained VOCs to be measured. The streams were measured with float flowmeters (main air stream: Krohne, 20°C, $1.0132 \ 10^5$ Pa, range $1.4 \ 10^{-4} - 1.4 \ 10^{-3}$ $m^3.s^{-1}$, for the smaller main flow air streams: Krohne, 20°C, $1.0132 \ 10^5$ Pa, butyl acetate: range $0.17 \ 10^{-3} - 1.7 \ 10^{-3}$ $m^3.s^{-1}$; ethanol and methyl ethyl ketone: range $5 \ 10^{-5} - 5 \ 10^{-4}$ $m^3.s^{-1}$).

2.3 Experimental set-up for concentration experiments
Experimental set-up is shown on figure 1. All liquid flow rates are measured using Krohne flowmeters (main liquid stream: Krohne, 20°C, range 1.4 10-4 – 1.4 10-3 m3.s-1, recycled liquid streams: Krohne, 20°C, range 2.78 10-5 – 2.78 10-4 m3.s-1). Pressures were measured with Bourdon manometers in the desorption device (range 0; -1 bar).

2.4 Analysis
The pollutant concentrations in the gas phase were determined by mass spectrometry (VG Prima 600S). The ratio between VOC mass and air flow rates enables the VOCs' concentration to be determined and thus the mass spectrometer to be calibrated. Sampling was carried out independently at points A, B and C as shown in figure 1 (i.e. for the inlet gaseous stream, the cleaned gaseous stream and the high polluted outlet gaseous stream) in a continuous mode. Every 3 minutes, the gas outlet concentration was measured, allowing to determine the process efficiency.

VOC concentrations in the liquid phase were measured by gas chromatography (HP 5700 A chromatograph) using a Porapack Q80-100 column (1 m × 3.2 mm) and a flame

ionisation detector (FID) according to the internal standard method (2-propanol, 0.5 kg.m^{-3}, Prolabo). The operating conditions were as follows: nitrogen was the carrier gas (3 10^5 Pa, 27 ml.min^{-1}) and the temperature of the injector and detector was 260°C. The oven temperature increased from 140°C t 240°C using a 20°C.min^{-1} gradient. Then, it stayed at 240°C for 5 min. The injected volume was 0.1 µl. The detection thresholds were 0.02 kg.m^{-3} of ethanol (2% accuracy), 0.02 kg.m^{-3} of methyl ethyl ketone (3% accuracy) and 0.05 kg.m^{-3} of butyl acetate (6% accuracy). Quantification was achieved by integration of peak areas (integrator HP 3396A).

2.5 Numerical modeling of gas/liquid separation

Numerical modeling of gas/liquid separation was performed using Fluent 6.1 software. For fluid hydrodynamic modeling in the separator, a k- model was chosen.

3 RESULTS AND DISCUSSION

3.1 Improvement of gas/liquid separator geometry

The objective of such a process is to concentrate VOCs in a smaller gas flow rate. Performances of the concentration process were evaluated using three model molecules (EtOH, MEK and BA). In the case of gaseous BA treatment, the size of bubbles obtained at the outlet of the desorption device is very small (< 0.1 mm). This implies that effective separation of the gas flow and the liquid flow can not be performed with conventional gas/liquid separators (Figure 2).
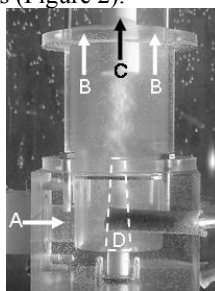

Figure 2. Conventional gas/liquid separator. (A) Gas/liquid tangential inlet. (B) Liquid outlet. (C) Gas outlet. (D) Conic core element.
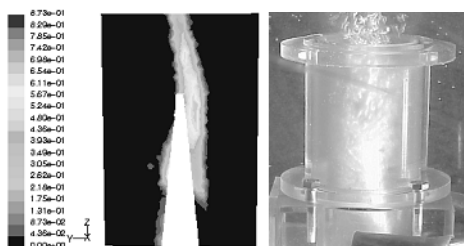

Figure 3. Numerical modelling validation with bubbles size of 1 mm. The gaseous volume fraction is represented on the left part (the maximum is 87.3% of gas). As predicted by the modelling, the picture shows a conic gaseous flow at the middle of the separator.
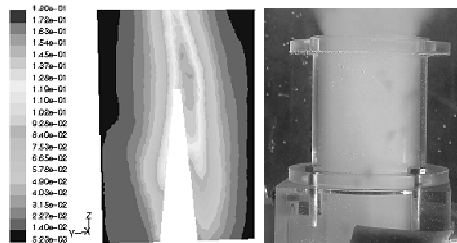
Figure 4. Numerical modelling validation with bubbles size of 0.1 mm. The gaseous volume fraction is represented on the left part (the maximum is 18.0% of gas). As predicted by the modelling, the picture shows a dispersed gaseous flow in the whole separator.

So, a new geometry of gas/liquid separator was designed by numerical modeling. Our model was validated by visual observation (Figures 3 and 4).

The influence of four parameters was evaluated on separation performances (separator diameter, separator length, inlet geometry and presence of a conic core element). This led to the following results: the diminution of separator diameter (in order to increase radial velocity of fluid), the decrease of device length and the presence of the conic element are favorable elements for an efficient separation. The design of the inlet geometry does not influence separation.
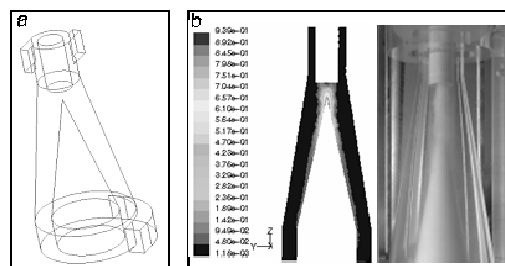

Figure 5. (a) New geometry of the gas/liquid separator. (b) The gaseous volume fraction is represented on the left part for bubbles size of 0.1 mm (the maximum is 93.9% of gas). The picture shows a conic gaseous flow at the middle of the separator (bubbles size of 0.1 mm).

The new geometry is presented in figure 5a. It provides efficient gas/liquid separation even for bubbles which size is smaller than 0.1 mm (Figure 5b).

3.2 Process performances for BA treatment

Since gas/liquid separation is effective even for small bubbles size (< 0.1 mm), concentration process performances can be measured. Previous studies were performed to evaluate the mass transfer characteristics of the aero-ejector with model molecules such as oxygen, ethanol, butyl acetate and methyl ethyl ketone: a 90% elimination of VOCs was obtained with a single treatment of the gaseous phase (Daubert *et al.*, 2001; De Billerbeck *et al.*, 1999; Rainer *et al.*, 1995). So, the attention was focused on performances of desorption and gas/liquid separation steps.

The desorption and gas/liquid separation steps were run starting from an aqueous solution of BA (BA concentration in solvent = 0.04 g.L^{-1}). The evolution of BA concentration in the solvent flow and in the outlet gas flow was followed during experiment (Figure 6).
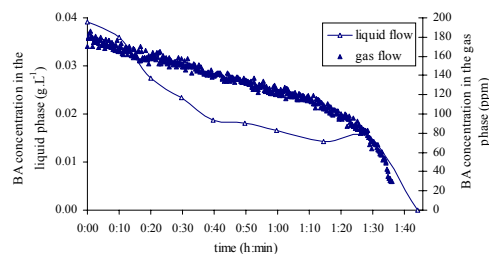
Figure 6. Evolution of BA. concentration in the solvent and in the outlet gas flow.

To estimate the transfer performance, a mass balance was carried on BA provided in solvent and total mass of BA recovered in the gas. Results showed that 89% of VOC were transferred in gas.

Considering transfer performances of the aero-ejector, we can expect to recover more than 80% of the VOCS in the outlet gas flow for the whole concentration process with a theoretical flow rate ratio of 1/100 between the low polluted inlet gas flow rate and the high polluted outlet gas flow rate. According to these results, this concentration technology of VOCs in gaseous effluents seems to be of particular interest as a preliminary step for degradation processes such as thermal incineration. Thus, it would facilitate purification steps in the case of economically interesting molecules.

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