Odorous emission biofiltration with new synthetic packing materials: essential nutriment release

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ABSTRACT. The aim of the present work is to develop original packing materials used as biofiltration support which provides a nutriments release added to the compounds present in the treated gas stream and required for the biological development.
In a first step, UP20 material was formulated and produced by extrusion using calcium carbonate and urea phosphate for providing the mineral element to the micro-organisms and 20 % of an organic binder. Its physical and chemical characterizations show that the organic binding agent gives a significant cohesion capacity to the material even in drastic conditions (submerged in water) and allows a low release of nutrients. In a second step, UP 20 was test to determine its ability to enhance a micro-organisms population growth. For this purpose, Oxitop® tests were performed using activated sludge as biomass, water, sodium sulfide and UP20. The results were compared to those measured with pine bark or pouzzolan packing materials. Some experiments with a mixture of these latter products and UP 20 were also done. It could be deduced from that the addition of UP 20 in a biofilter treating H_2S could improve the process performances.
In a third step, a 3 columns pilot-scale biofilter packed respectively with pine bark, UP20 and a mixture of pouzzolan and UP20, was set up to study the effects of these new packing materials under real conditions for H_2S emission biofiltration.

1 INTRODUCTION

Biofiltration is increasingly used as a method to decontaminate gas streams containing low concentrations of biodegradable volatile organic and inorganic compounds. This process has gained worldwide acceptance as an economical air pollution control technology for low concentration gas treatment (Devinny *et al.*, 1999; Kennes and Veiga, 2001; Le Cloirec *et al.*, 2005). In biofiltration, the gas stream containing the pollution is injected through a bed packed with a solid medium that supports a biofilm. The pollutant substances transfer from the air flow to the biofilm where they are degraded by microorganisms, mostly into by-products such as carbon dioxide, water, biomass and energy. In many cases, the gas stream and the water flow used to humidify the biofilm provide all the nutrients required for the development of the microorganisms. However, the contaminant concentrations in most waste gas streams can vary with time

due to either the inherent nature of the processes that generate them or process stops. Moreover, some air flows may contain only some of the elemental compounds needed for microorganism growth thus leading to disease and an inefficient biofiltration process. Focusing on their characteristics, packing materials can be described by five main properties (Perry and Green, 1997), which have a strong influence on both system efficiency and cost: (i) particle size, (ii) void fraction and specific surface; (iii) nutritive capacity; (iv) strong mechanical resistance and low bulk density; (v) significant water retention capacity; (vi) high buffer capacity. As well as presenting strong mechanical properties, packing materials should also favor the conditions for biomass attachment (Cohen, 2001) and growth. Packing materials can be organic solids, which have been widely used for the treatment of odorous compounds (Kim *et al*., 2000; Elias *et al.*, 2002; Sheridan *et al.*, 2003; Otten *et al.*, 2002) and volatile organic compounds (VOC) (Sene *et al.*, 2002). Organic materials are currently the most used supports for biofiltration because of their low cost and high nutrient content. The most common are peat, soil and compost but also wood bark (Ramirez-López *et al.*, 2000), sugarcane bagasse (Sene *et al.*, 2002) and peanut shells (Ramirez-López *et al.*, 2003). However, these materials lead to the bed packing down and cause pressure drops thus decreasing the biofilter efficiency. Inorganic materials like glass beads or perlite have also been studied (Hirai *et al.*, 2001; Rousselet *et al.*, 2002; Woertz *et al.*, 2002) since they show much better hydrodynamic and mechanical properties than organic ones (Gemeiner *et al.*, 1994). The most commonly used are metal oxides like porous ceramics, calcinated cristobalite (Hirai *et al.*, 2000) or perlite (Kennes *et al*., 1996). However, their cost remains much higher and they do not provide any nutrients to the biomass. Consequently, combinations of organic and inorganic materials have also been used (Zilli *et al.*, 2001; Ergas *et al.*, 1995).

The aim of the present work is to formulate original packing materials to be used as biofiltration supports, which provide a release of nutrients to meet biomass needs in addition to the compounds in the gas stream. The main advantage of these new materials could be a simplification of the biofiltration process as the addition of a nutritive solution in the liquid phase could no longer be required. Moreover, when the process is totally stopped, these materials could keep the biofilm viable.

2 MATERIALS AND METHODS

2.1 Support formulation

UP20 materials containing calcium carbonate, urea-phosphate and an organic binder were extruded in a cylindrical shape. First, the dry salt powders were mixed in a container by shaking for 15 min. The organic binder was introduced into water. Finally, the mixture of compounds was added to water. The amount of water was 66 % of the dry salt mixture weight. Extrusion was performed with a meat mincer and the granules were dried at 50°C for 20 hours. The C/N/P molar ratio was set at 100/10/5. The organic binder was a white fluid powder commonly used in the building industry and mainly constituted of ethylene and vinyl acetate.

2.2 Physical properties

Porosity was measured by the mercury porosimeter (Micromeritics® autopore IV). Mechanical cohesion in water was determined as the time when 10 g of formulated material started to break up when put in 500 mL water. Moisture retention capacity was

established as the mass of retained water per mass of dry granules after a 24-hour immersion in water.

2.3 Microbial properties

In order to evaluate the capacity of the packing materials to enhance microbial development, the measurement of oxygen consumption was chosen. The initial biomass came from activated sludge of a wastewater treatment plant. Oxygen consumption measurements were carried out with a WTW OxiTop® OC-110 system to compare the effect of formulated materials on microorganism growth with that of pine bark and pozzolan. A known mass of material was introduced into a 500 mL bottle filled with 100 mL of substrate. After 24 hours, pH was measured as the initial pH of the experiments. Before introducing 2 mL of the bioreactor biomass (concentration was around 3.5 g of dry biomass L^{-1}) into each bottle, a 50 mL sample was washed twice using centrifugation. A stirring table ensured the homogeneity of the suspensions and an incubator set at 20 ± 1°C was used. After five days, final pH was measured and data were collected. Table 1 presents the different materials. The combinations of the studied materials in a 50/50 mass ratio were also tested. All experiments were performed twice and a mean error of 0.27 mg O_2 L^{-1} per gram of material was calculated between these two data series. In the first step, a saccharose solution (1 g L^{-1}) was used as substrate to check that formulated materials did not inhibit microorganism metabolism. In the second step, a sodium sulfide solution (100 mg L^{-1}) was used to simulate the treatment of H_2S, as these are target compounds in further experiments under real biofiltration conditions. Non-consumed sulfide was measured by spectrophotometry using respectively the Merck® Spectroquant kit. Experiments were also carried out without biomass inoculation to evaluate the adsorbed quantities of substrate on the packing materials.

2.4 Biomass colonization

Packing material colonization by microorganisms was followed by three successive experiments. A 100 mL solution of sodium acetate (1 g L^{-1}) was used as substrate to simulate the biodegradation of a VOC. After 5 days, packing materials were washed and replaced in 100 mL of fresh substrate solution. No additional biomass was inoculated in the OxiTop® system and the oxygen consumption assays were restarted from this point. After each 5-day period, attached biomass was measured using a protein extraction procedure and a colorimetric determination. All experiments were performed twice.

For the protein determination a known mass of packing material was put in 10 mL of NaOH (1N) for 24 hours. Then, the liquid phase was diluted in 60 mL of distilled water and neutralized by the addition of HCl (1N). The Sigma-Aldrich Protein Total Lowry Micro Method (690 A) based on the biuret and Lowry procedures was used to measure the protein concentrations of the samples. A correlation had been experimentally established between protein concentration and the dry biomass amount:

$$[\text{Protein}]\ (\mu g\ L^{-1}) = 488\ .\ [\text{dry biomass}]\ (\mu g\ L^{-1})$$

2.5 Pilot studies

The reactors were made by column of 150 cm length and 10 cm diameter. The bed humidity was maintained by sprinkling tap water. The ascending gas flow in the pilot unit use for this experiment was 1 $m^3.h^{-1}$ and the H_2S concentration was near 5 $mg.m^{-3}$. The column where respectively filled with 4.950 kg of UP20, 1.555 kg of pine bark and

a mixture of 1.012 kg UP20 and 5.064 kg pouzzolan. Each reactor was inoculated with an activated sludge sample (1.31 g of dried matter).

3 RESULTS AND DISCUSSION

3.1 Microbial properties

In this part, a set of experiments were carried out using biomass inoculations in order to check that formulated materials did not inhibit biomass growth. Then, the effects of UP 20 on biomass growth were evaluated and the results compared with those obtained using classical supports. Pine bark was chosen as an organic material and pozzolan as an inorganic one. Combinations of UP 20/pine bark and UP 20/pozzolan were also studied to collect indications of their reliability when used in a pilot biofilter. Table 1 gives the main properties of these two supports in comparison with UP 20. Finally, the support colonization was studied and comparisons were established between UP 20 and pozzolan.

Table 1. Main properties of packing materials used for oxygen consumption assays.

	Pine bark	Pozzolan	UP 20
Physical aspect			
Bulk density ($kg.m^{-3}$)	367	2000	925
Median pore diameter (nm)	519	52	517
Moisture retention capacity (%)	67	21	47
pH (24hrs in 100 mL H_2O)	4.5	6.9	8.6
Composition	C ($g.kg^{-1}$) 537 N ($g.kg^{-1}$) <3 O ($g.kg^{-1}$) 398 H ($g.kg^{-1}$) 55 S ($g.kg^{-1}$) <3 K ($g.kg^{-1}$) 0.63 Mg ($mg.kg^{-1}$) 62 Ca ($g.kg^{-1}$) 0.37 Na ($mg.kg^{-1}$) 0.29 Fe ($mg.kg^{-1}$) 7.78 Cu ($mg.kg^{-1}$) 1.3	MgO (% m.) 5.21 Al_2O_3 (% m.) 14.97 SiO_2 (% m.) 44.16 P_2O_5 (% m.) 0.35 1 MnO (% m.) 0.25 Fe_2O_3(% m.) 15.15 K_2O (% m.) 1.29 CaO (% m.) 9.99 TiO_2 (% m.) 2.89 S ($\mu g.g^{-1}$) 384 Cl ($\mu g.g^{-1}$) 291 Sr ($\mu g.g^{-1}$) 778 Ba ($\mu g.g^{-1}$) 626 Zn ($\mu g.g^{-1}$) 104	$CH_4N_2O.H_3PO_4$ / $CaCO_3$ / C/N/P=100/10/5 (molar) } 80 % (w.) Organic binder C: 52.57 % H: 7.06 % O: 32.23 % Ash content: 10.57 % } 20 % (w.)

3.2 Biomass growth

Table 2 gives initial and final pH data for each assay. With a saccharose solution, the results showed only slight variations during 5 days except for the assay containing pozzolan and UP 20 mixed with pine bark. These greater variations can be explained by a biomass production of acidic compounds that are not neutralized by basic ones as shown by the initial pH. The combination of UP 20 and pine bark materials induced a pH close to neutrality. This combination could therefore be an interesting alternative to avoid too much basic conditions for biomass growth. Thus, the UP type materials could be preferred to set up an experimental biofilter.

Table 2. Initial and final pH obtained for each experiment assay with the various substrates.

Packing material	Saccharose (1 g L^{-1})		Na_2S 100 mg L^{-1}	
	Initial pH	Final pH	Initial pH	Final pH
UP 20	8.1	8.6	8.4	8.2
Pine bark	4.6	3.9	7.1	6.4
Pozzolan	6.9	4.4	10.9	10.5
UP 20 / Pine bark (50/50 w.)	6.4	7.6	7.6	7.7
UP 20 / Pozzolan (50/50 w.)	8.1	8.1	8.8	8.7

Figure 1B describes the evolution of the oxygen consumption during the whole experiment. Since all assays received the same biomass inoculation and the consumed oxygen was calculated per gram of material, the graphs can be directly linked to the capacity of each material to make the microorganisms grow. The blank set (Figure 1A) presents a very low oxygen consumption with all materials as expected (around 1 mg L^{-1}) except for pine bark, where it reached 2 mg L^{-1}, because this constitutes the best organic carbon provider. For the set using the saccharose solution, it is notable that the formulated materials had no inhibitory effect on biomass growth.

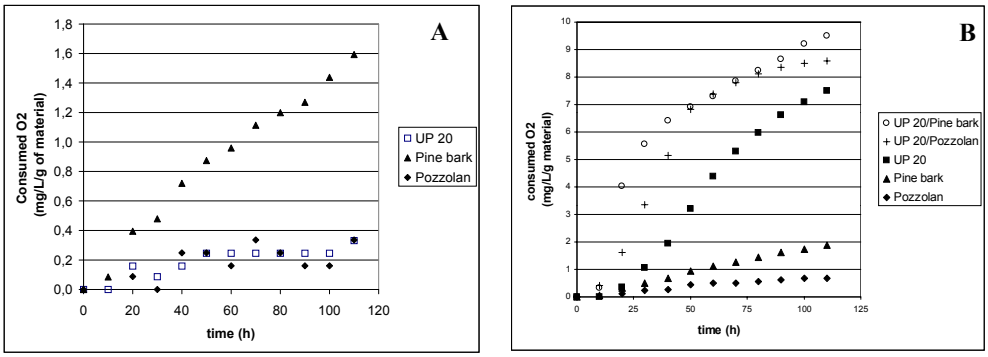

Figure 1. 1A Evolution of the oxygen consumption using no substrate (distilled water); 1B Evolution of the oxygen consumption using a saccharose solution (1g L^{-1}) as substrate

Moreover, all assays using UP 20 material presented a higher oxygen demand after 5 days than pozzolan or pine bark. This result demonstrates the efficiency of the

formulated materials to complete the biomass needs. Secondly, assays containing UP 20 showed significantly higher final microorganism activity (approximately 4 times higher than pine bark). These assays displayed the fastest growth, especially when UP 20 was combined with pozzolan or pine bark. As can be noted in Table 2, this packing material led to a neutral pH. These media conditions could allow a better microbiological growth corresponding to a higher oxygen demand.

3.3 Sodium sulfide removal

Figure 2 presents the evolution of the oxygen consumption when a 100 mg L^{-1} sodium sulfide solution was used as the substrate. It could be noticed that all assays containing UP 20 show the highest and fastest oxygen consumption.

In this experiment the substrate did not provide any nitrogen. As a consequence, the formulated material UP 20 could entirely fulfill its nutritive function by providing the biomass with the nitrogen it needs and therefore stimulate its growth. Table 2 shows that pine bark generated the best pH conditions: pH varied from 7.1 to 6.4 when they were used alone and from 7.6 to 7.7 in combination with UP 20. Associated with the previous remark, this result could explain why the combination UP 20/pine bark generated the highest and fastest oxygen consumption. As expected, pozzolan, which has no nutritive function, generated very poor oxygen consumption throughout the 5 days (around 0.5 mg L^{-1}).

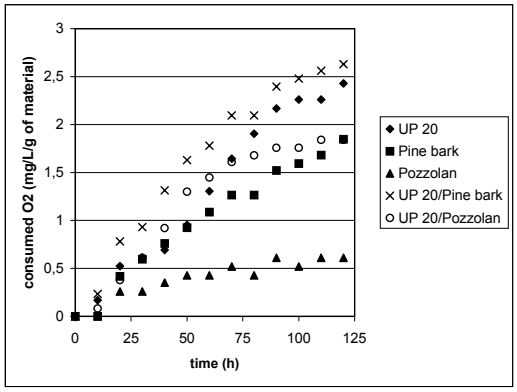

Figure 2. Evolution of the oxygen consumption with a 100 mg L^{-1} sodium sulfide solution.

Figure 3 presents the mass balance of sulfide for the five types of support studied. Pine bark still shows the best adsorptive properties: the adsorbed amount of sulfide ranges between 25 and 30 % of the initial amount. Except for pozzolan, non-adsorbed sulfide is almost entirely biotransformed by the biomass. Concerning the treatment of hydrogen sulfide under real biofiltration conditions, the results obtained here are encouraging to study UP 20 as a packing material in pilot experiments. Although the addition of pozzolan will have no effect on hydrogen sulfide biodegradation, it could be used to improve the mechanical resistance of the filter bed.

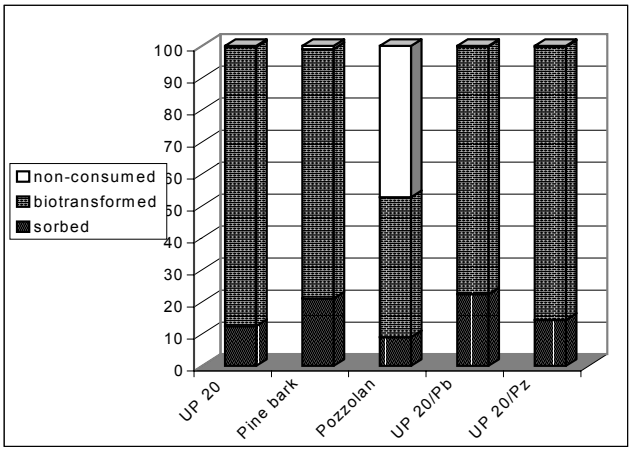

Figure 3. Percentage of sulfide removed on the support.

3.4 Packing material colonization

For these experiments, assays containing pine bark could not be studied because the protein determination procedure generated samples that were too strongly coloured thus obstructing the measurement of absorbance.

Protein determination allowed a closer look at the support colonization. Table 3 gives the final amount of attached biomass on UP 20 and pozzolan after 5, 10 and 15 days. First, it can be observed that a distinctly greater amount of biomass was found on UP 20, especially after 15 days of experiment when the attached biomass reached 0.20 mg per gram of material compared to 0.11 mg in the case of pozzolan. However, the most interesting result is the increase in the values with time. In the case of UP 20, the amount of attached biomass ranges from 0.09 mg after 5 days to 0.20 mg after 15 days, showing a significant colonization of this support.

Table 3. Attached biomass after 5, 10 and 15 days.

	Attached biomass (mg of dry biomass g^{-1} of material)	
Time (day)	UP 20	Pozzolan
5	0.090	0.061
10	0.126	0.075
15	0.194	0.109

3.5 Reactor operation

Figure 4 presents the first results of the use of UP20, pine bark and the UP20/pouzzolan mixture material in a pilot scale biofilter. After 5 days the H_2S removal is close to 100 % for all conditions. Nevertheless, UP20 shows a high buffering capacity.

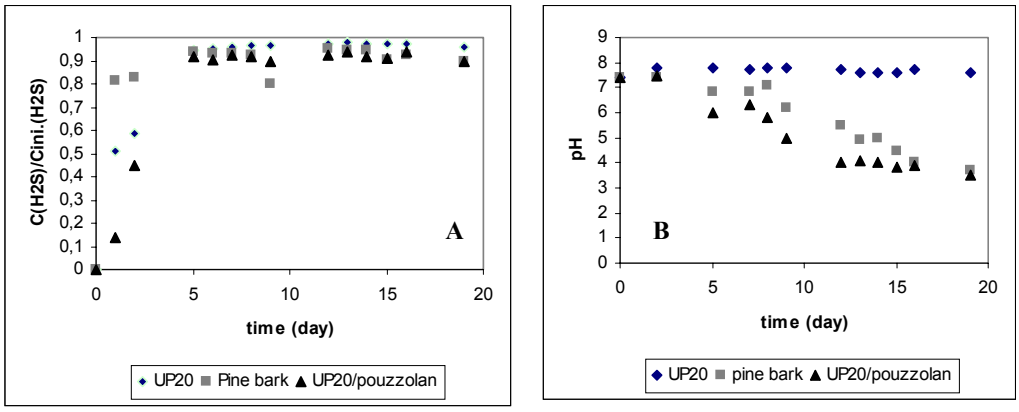

Figure 4. **4A**: H_2S removal; **4B**: pH variation in the water collected at the bottom of the column.

In conclusion, these experiments shown that the UP20 packing material has:

(i) no inhibitory impact,
(ii) a nutritive function under different conditions of pH and substrate
(iii) a good effect on colonization of formulated materials by biomass after a few weeks.

Finally, the pilot scale tests are really encouraging to use UP 20 as the packing material of an experimental biofilter, especially in the case of hydrogen sulfide removal.

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