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Hybrid processes for the removal of VOCs in gaseous emissions

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Abstract

Since new regulations on volatile organic compounds (VOC) emissions have been decided, industrial companies are interested in ways to reduce their pollution. Conventional chemical engineering processes are industrially used to remove VOCs, such as incineration, condensation, scrubbing or adsorption. Each technique has its own field of use, however they generally do not permit recovery of the pure component. Moreover, the low loaded VOC emissions in large flows induce a particular problem. This work proposes two new hybrid processes : absorption coupled with pervaporation and absorption coupled with adsorption. First experimental results are introduced and interests of these processes are discussed like their ability to treat the air and to re-use water and VOCs.

1 Introduction

Recently, new regulations on volatile organic compounds (VOCs) emissions in air have been imposed in Europe. In France, in most of industrial cases, the maximal average concentration authorised for VOCs emissions is about 150 mg/m^3. Since February 1998, new industrial activities are concerned by these last

Destructive techniques	Advantages	Disadvantages
Incineration (thermal , catalytic, , regenerative)	Economic; treatment of mixed gas possible; Large field of use; heat recovery possible.	No recovery; toxic exhaust (HCl,HF,Nox..), catalyst erosion.
bioepuration	Low cost; treatment of mixed gas possible; weak concentration.	No recovery; high pressure drop; fouling; big installation.
Recovery techniques		
Condensation	Recovery of cost solvent; hybrid process possible.	High cost; not for light VOC; pretreatment required.
Absorption or scrubbing	easy use; high efficiency; treatment of mixed gas and hybrid process possible.	Large plant; waste water; not feasible for hydrophobic COV.
Adsorption	Easy use; easy control, high efficiency; hybrid process possible.	Large plant; cost of desorption; carbon is combustible.

Table 1.Conventional unit operations of chemical engineering for gas treatment [1]

regulations such as car or plane and metal coating. Generally, VOC pollution is very diluted (1 to 5 g/m^3) in large flow rate (20 000 to 70 000 m^3/h) which is a very particular problem. Conventional chemical engineering processes can be used to remove VOCs, table 1 introduces the more often used. The main drawback of conventional processes is their lack to treat low VOC concentration in large flow rates. In fact economic problems or efficiency problems limit their use.

The aim of this paper is to propose a new process which would be well adapted to treat large flow rates with diluted concentration with respect to the following constraints : To produce the more pure air (according to the regulation); to allow solvent recovery and eventually re-use. A process consisting in a coupling of three unit operations was then imagined. Principle of this hybrid process is introduced in figure 1. This work introduces experimental results obtained for the two hybrid processes : absorption coupled with pervaporation and absorption coupled with adsorption.The first treatment stage consists in an absorption, that deals to transfer all soluble VOC to water. Air pollution is then changed to water pollution. In the hybrid process I, aims to treat water coming from the absorption step with a pervaporation technique. Two flows are then produced. One is quite pure water which could be re-used for absorption and the second one is rich in VOC and could allow VOC recovery. the hybrid process II deals to purify the air coming from absorption stage. The process used is adsorption on a granular bed.

2 Principle of the unit operations (absorption, adsorption and pervaporation) :

Principle of the three unit operations used in the hybrid process is briefly described.

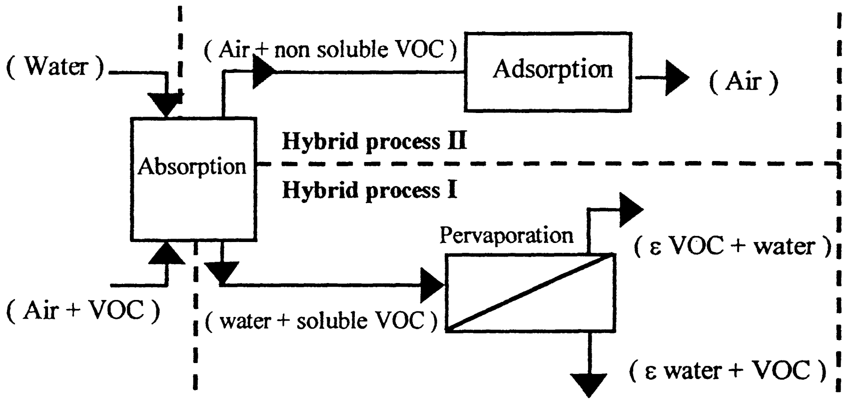


Figure 1 diagram of the principle of the hybrid processes.

Gas absorption : Consists in transferring compounds from the gas phase to a liquid phase. A soluble compound in the vapour is absorbed by means of a liquid in which the compound is more or less soluble[2]. this operation is often realised in packed tower which are designed to offered a large contact area between the liquid and the gas. The liquid wets uniformly the packing surface and flows downward contercurrent to the gas upward flow.

Process efficiency depends mainly on hydrodynamics, Bravo, Fair [3] (mainly ratio of gas flow rate to liquid flow rate) and Henry's constant values[2] (solubility), hydrodynamics imposes the tower sealing.

Pervaporation : Pervaporation is a membrane unit operation, which means that it divides the feed stream into two streams : a permeate which passes through the membrane and a retentate containing all the species retained by the membrane. In the case of an aqueous feed containing VOCs the permeate will be enriched in VOCs and the retentate VOCs concentration will be lower. The principle of pervaporation lies on a partial vaporization of the most volatile components of the liquid through a dense (non-porous) organic membrane. Vaporization is due to an activity difference maintained between the two membrane sides by creating a partial vacuum on the permeate side. The permeate is removed as a vapour and recovered by condensation.

The transfer mechanism through the membrane is currently considered as including three successive steps : 1) adsorption of the compounds on the membrane surface; 2) diffusion through the membrane from the feed to the permeate side; 3)desorption in the permeate side as a vapour.

As this mechanism requires solubility and diffusivity of the compounds in the membrane it induces a great influence of the membrane material and thickness on both permeate flux (process productivity) and on selectivity (permeate and concentrate quality). These performances are also influenced by the raw water composition and by the operating parameters like temperature, downstream pressure and feed velocity inside the module which controls the mass transfer coefficients and thus the organic compound flux.

Gas adsorption : consists in transferring compounds from gas phase to the surface of a solid adsorbent. This unit operation can be used as a separation or as a concentration process. The gas flows continuously through the bed until the solid is nearly saturated[2]. Adsorbent are highly porous materials (activated coal, zeolite, silica gel ....) having a very large internal surface ranges (800 to 2000 m²/g). Process efficiency depends on the mass transfer rates and solid/gas equilibria, Ruthven[4]. Adsorption kinetics is generally controlled by intracrystalline transport[4]. Knowledge of the breakthrough curve (outlet concentration versus time) and adsorption isotherm (amount adsorbed versus initial concentration) are necessary to design an adsorber.

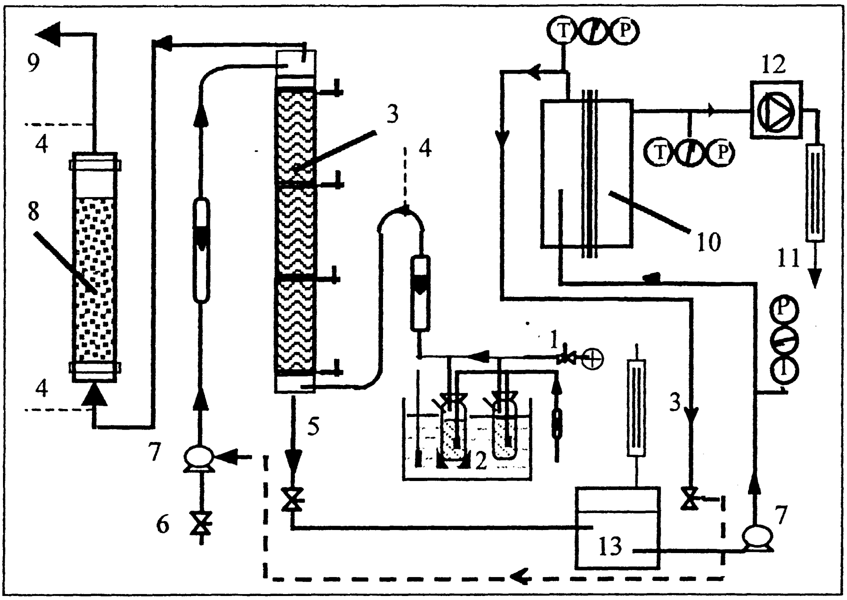
3 Materials and methods

3.1 Pilot plant

The experimental set-up for absorption and adsorption is shown in figure 2. It mainly consisted of an absorption tower which contained a metallic structured packing, Sulzer BX, was in line with an adsorption column which contained synthetic zeolites (HISIV 3000;UOP). Characteristics of the absorption tower are : 2.7 m height, 0.072 m diameter and 1.5 m packing height. Adsorption column : 0.5 m height, 0.052 m diameter and 0.2 m fixed bed height. The adsorbent is a molecular sieve whose mean pore diameter is dp = 6 10^{-10} m, specific area 1180 $m^2.g^{-1}$, pellet size :1 10^{-3} m diameter and 5 10^{-3} m height.
The mixture air/VOC are obtained by the use of two separate air bubblers for each compound. Different VOCs have been used : heptane and acetone alone or in mixture.

A pervaporation pilot plant was built to study performances of pervaporation membranes during batch runs realised with a constant volume of water (3 litres) charged with VOCs. The pilot shown on figure 2 integrates : a pervaporation module, a vacuum pumping group equipped with a vacuum regulator and followed by a condenser, a circulating pump which controls feed velocity at the module inlet (Re=3800), a heating system allowing to regulate water temperature at the module inlet at 60°C, a cryostat system necessary for the condenser, pressure and temperature gauges disposed at the module inlet and outlet, a data acquisition system for on-line measurements.

Feed water is pumped from a thermostated tank to the pervaporation module. Retentate is send back to the tank and the vapour permeate is pumped by the vacuum pump and then condensed. Feed water temperature was fixed
The pervaporation module is a flat sheet module with a filtration area of 4.8 10^{-3} m^2.The membrane chosen for the trials was a silicone membrane from GFT (ref. 1060). This hydrophobic organic material preferentially adsorbs VOCs from water.
Analytical measurement are realised with a gas phase chromatography equipped with a flame ionisation detector.



1 air inlet - 2 generation of VOC - 3 packed column - 4 gas outlet sample 5 liquid out - 6 cleaning liquid inlet - 7 centrifugal pump – 8 adsorption bed - 9 cleaned gas- 10 pervaporation unit (plane) - 11 VOC (acetone) 12 vacuum pump.- 13 thermostat tank.

Figure 2 pilot plants

3.2 Results and discussions

During the experiments, operating fluid flows were 0.44 $kg.m^{-2}.s^{-1}$ for gas and 4 $kg.m^{-2}.s^{-1}$ for liquid. The inlet concentration in air is about 0.014 to 0.046 $mol.m^{-3}$. Heptane and acetone are always in equimolar ratio in the mixed gas for the hybrid process II.

3.2.1 Absorption

Experiments showed a very good efficiency for acetone removal. In fact the efficiency ranges from 98.5 % to 99 % for all concentrations of inlet mixing gas tested. For an equimolar acetone/heptane mixed gas, heptane removal is very low, efficiency ranges from 3 % to 6 %. This result is in good agreement with the weak solubility in water of linear paraffin.

The outlet VOC concentration in water is about 6.2 10^{-5} $g.m^{-3}$ to 13.53 10^{-3} $g.m^{-3}$ for acetone and 1.8 10^{-6} $g.m^{-3}$ to 1.2 10^{-5} $g.m^{-3}$ for heptane. the absorption rate calculated acetone is equal to 7. This value explains the good efficiency removal, Dang Van[5].

A very low pressure drop (10 $Pa.m^{-1}$) was measured during the experiments, thus inducing a low energy consumption. This is a specific feature of the structural packing used. As well known, it is observed that presence of heptane does not modify acetone absorption. This let us assume that only heptane would be present in the scrubber outlet gas if a mixture of acetone, MEK and heptane would be treated by absorption, with the operating conditions previously used (gas concentration, liquid and gas flow rate).

3.2.2 Pervaporation ; Hybrid process I

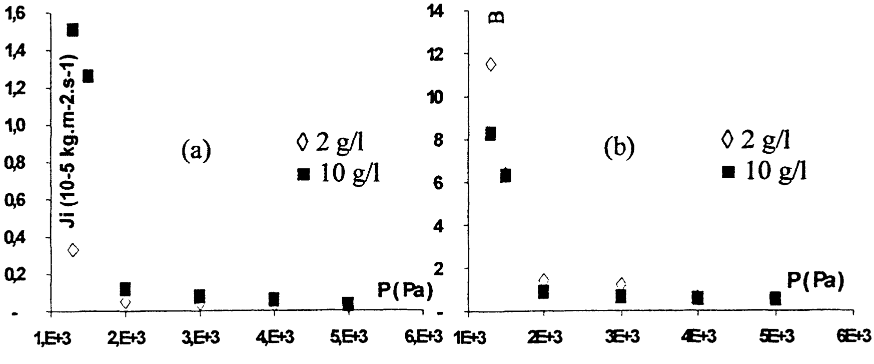
Batch pervaporation runs were realised with solutions of acetone in water at 2 g/l and 10 g/l which are in a range of the concentrations obtained in the water at the outlet of the absorption column after treatment of a gaseous effluent containing less than 15 g of acetone per m^3 of air.

Criteria to estimate the process performances are the acetone permeation flux and the VOC enrichment coefficient (β) defined from the mass fraction of VOC in the permeate ($w_{VOC\text{-}p}$) and in the feed ($w_{VOC\text{-}f}$) by the equation 1:

$$\beta = \frac{w_{VOC-p}}{w_{VOC-f}} \qquad (1)$$

Permeation flux depends on the feed water composition and on downstream pressure. For the two concentrations used and for downstream pressures between 1300 to 5000 Pa the permeation flux (Ji) varied in the range between 0.01 10^{-5} to 1.7 10^{-5} kg.m^{-2}.s^{-1}, whereas β varied between 0.5 and 12. For both flux and selectivity, best results were obtained for the lower downstream pressures.

Modelling of the process was realised on the basis of the model proposed by Rautenbach and Albrecht [6]. It was improved taking into account an equation relating the surface distribution coefficient of the COV to the feed concentration and to the downstream pressure. The modelling was based on a set of non-linear equations and was then solved numerically. It requires parameters of the liquid solution and parameters characterising the interactions between the solutes and the membrane (diffusivity coefficients, interaction parameters, distribution coefficients ...). The last six parameters are not experimentally accessible. They were adjusted to minimise the distance between experimental and modelled values. The empirical model obtained allows predicting experimental fluxes and enrichment coefficients with a good accuracy (error less than 15 %).



Figures 3 a) and b) Variation of acetone flux and β with downstream pressure
T= 60°C – Re = 3800 - membrane GFT 1060

Acetone conc. in the gas effluent (g.m^{-3})	5			15		
Acetone conc. in the gas after absorption (g.m^{-3})	0.1			0.3		
Acetone conc. in the liquid after absorption (g.l^{-1})	1.6			4.9		
P (10^2 Pa)	3	5	13	3	5	13
Acetone conc. in the permeate (g.l^{-1})	150	103	18	273	211	49

Table 2: Simulated performances of the hybrid process working in a continuous way for a 5000 Nm^3.h^{-1} plant

This model was then used to simulate and to design an industrial plant treating a gas effluent with a flow rate of 5000 Nm^3.h^{-1}. Design was based on the hybrid process integrating a well-designed absorption column (treatment rate = 98 %) and an industrial pervaporation module (70 m^2) with a GFT1060 membrane. VOCs concentrations which could be obtained in the permeate were calculated as a function of acetone concentration in the gas effluent and of the downstream pressure in the pervaporation process.

This simulation clearly demonstrates the interest of the hybrid process : very high VOCs concentration can be reached in the permeate. This process thus allows recovery and eventually re-use of the VOCs and this could be interesting for numerous industries to spare solvent. Optimisation of the process should now be realised together with economics considerations.

3.2.3 Adsorption, Hybrid process II

3.2.3.1 Adsorption capacities adsorption isotherms of single heptane, of single heptane after absorption (wet heptane), and the partial co-adsorption isotherm of heptane in mixture with acetone are shown in figure 4.

The maximum adsorption for heptane mixed with acetone was estimated to 0.26 mol.kg^{-1} which is three times less than the maximum capacity for wet heptane. This great difference emphasises the interest of removing acetone before the adsorption column.
The maximum adsorption capacities of for HISIV 3000 for single heptane and wet heptane were estimated to 0.8 mol.kg^{-1} and 0.77 mol.kg^{-1} respectively.
Gas humidity after absorption never exceeds 65 %, this can explain the small difference between isotherms of wet and pure heptane. It demonstrates the feature of the hydrophobic zeolite.

3.2.3.2 Heptane Breakthrough curves Experimental breakthrough curves are not S shaped, like usual breakthrough curves. For this reason adsorbent saturation was considered when $C/C_o = 1$ and not for the more usual value : $C/C_o = 0.5$.

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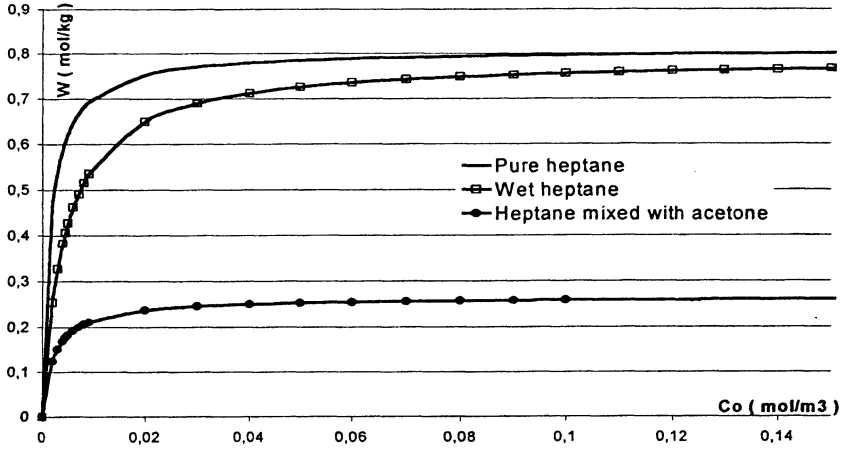

Figure 4 Adsorption isotherms of heptane, (pure, wet, mixed); at 298 K

A more favourable adsorption is observed for wet heptane than for heptane mixed with acetone figure 5. The amount injected (mole.kg^{-1}) in the case of wet heptane, for $C/C_0 = 0.05$ and $C/C_0 = 0.5$ is respectively 48 % and 45 % higher than the amount injected in the heptane/acetone mixture case.

The kinetic evolution for wet heptane is very similar to pure heptane under $C/C_0 = 0.8$ figure 5 b. Above this value the curve slope for wet heptane increases less than the one of pure heptane. The little amount of water present in the adsorbent can explain this slowdown.

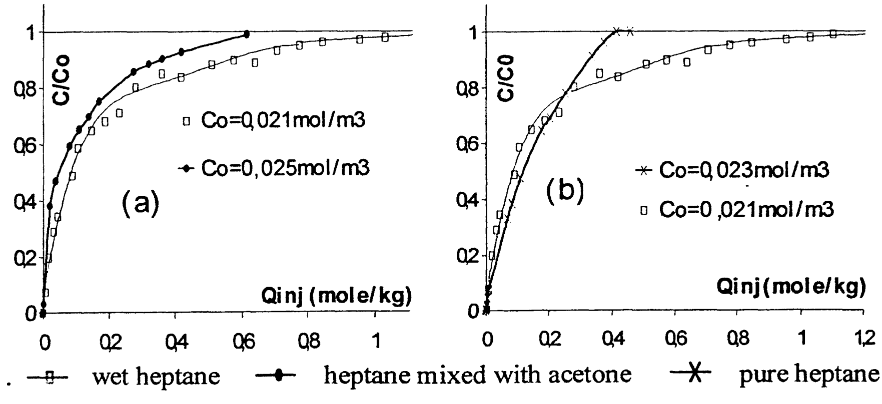

Figure 5 Heptane breakthrough curves : C/C_0 versus amount injected

3.2.3.3 Kinetic adsorption modelling Mass transfer during adsorption can be considered as mainly limited by two phenomena : external film control, or pore diffusion. Two models describe these limiting cases : Mickael model [7] and Hall model [8],

Mickael's model considers that mass transfer is limited external film :

$$\frac{C/Co}{(1-C/Co)^{r}} = \exp[(1-r)(NET(T-1)-1)] \qquad (2)$$

Hall's model makes the assumption that mass transfer limited by pore diffusion :

$$\frac{(C/Co)^{r}}{(1-C/Co)} = \exp[(1-r)(NET(T-1)+1)] \qquad (3)$$

These models are not predictive, however we can estimate by this way the predominant controlling phenomenon. Experimental breakthrough curves and modelling breakthrough curves are shown in figure (6), for wet heptane and heptane mixed with acetone.

Comparison between experimental data and modelled values demonstrates that the models fits well the data. The pore diffusion mechanism could be due to the small size of the microporous adsorbent (dp = 6 10^{-10} m).

The absorption tower which contains structured packings have a very good efficiency for soluble COV. For the hybrid process II, the maximum adsorption capacity is three time more than the maximum adsorption capacity for adsorption alone. Then removal of acetone is very interesting. A diffusion control seem do be predominant at high filling.

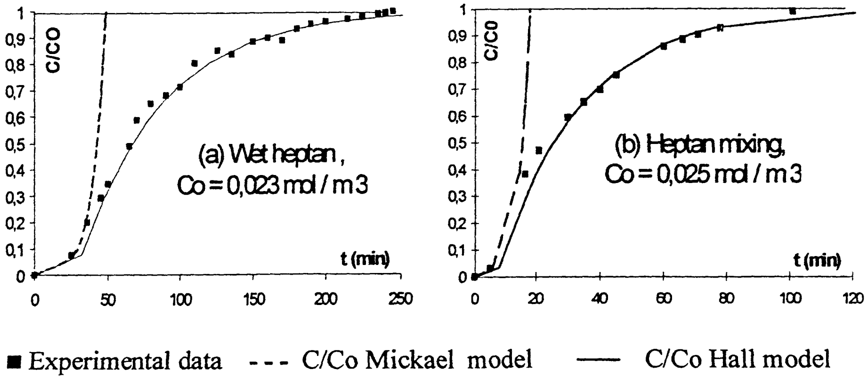

Figure 6 Experimental breakthrough curves compared with model

4 Conclusion

This study based both on experimental and modelling approaches puts in evidence the potential interests of two hybrid processes both including a first absorption step. The first process uses adsorption to improve the gas treatment : it allows a better removal of non soluble compounds which are not treated by absorption alone. Moreover for these compounds, pretreatment by absorption increases the saturation time of the adsorbent bed. The second process uses pervaporation to treat the outlet liquid from the absorption column. Great enhancement of the VOC concentration in the liquid can be obtained. VOC re-use is then possible.

These processes appear as an interesting way of development. Further research is necessary mostly focusing on process optimisation based on economics.

Notation :

C : gas concentration at the time t (mol.m^{-3})
Co : gas concentration at the inlet (mol.m^{-3})
Qinj : amount injected per kg of zeolite (mol.kg^{-1})
MEK : Methyl Ethyl Ketone
T = t / ts dimensionless time
K = Langmuir Constant

NET : number of theoretical plate
ts: time at the saturation
r = 1/(1 + K)

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