Intensification of the temperature-swing adsorption process with a heat pump for the recovery of dichloromethane

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A B S T R A C T

The temperature-swing adsorption process (TSA) is a widely used process for solvent recovery. Steam or a heated gas is used for the desorption of organic pollutants from activated carbons. This study aims to show the efficiency of coupling the TSA process with a heat pump. Hence, the adsorption column was cooled down whereas the column under regeneration was warmed by the heat pump. An experimental unit was designed and experiments were conducted with dichloromethane. The advantages of coupling the TSA process with a heat pump are twofold: the first benefit was for the adsorption step whose efficiency was increased. The decrease of temperature inside the fixed bed enabled a significant increase of breakthrough times (+30% on average). The second benefit of using the heat pump during regeneration cycle is the warming of the activated carbon bed prior to steam desorption. Temperatures up to 45 °C were measured during desorption when using the heat pump alone. Experimentally, the results have shown an interesting recovery efficiency (up to 71%) during dichloromethane desorption if using only the heat pump. Numerical simulations, via the software ProSim DAC, predicted the expected process behaviors for dichloromethane on a larger scale: a TSA unit containing 15 t of activated carbon. The results showed that the regeneration rate was not totally sufficient, 38.5%, and the use of a heat pump alone was not able to ensure the desorption of the VOC. Although the heap pump by itself was not sufficient to ensure the regeneration, the combination with the steam desorption shed light on new perspectives for the reduction of energy consumption.

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1. Introduction

Volatile organic compounds (VOC) involved in photochemical pollution phenomenon react with nitrogen oxides to form tropospheric ozone, which plays a part in the greenhouse effect. Moreover, tropospheric ozone is the third main greenhouse gas after CO_2 and CH_4 [1–3]. In addition to being precursors of air pollution, some VOCs are flammable, explosive, toxic, carcinogenic or mutagenic. Thus, both national and international policies have been adopted to reduce VOC emissions from all sources (transportation, industries . . .) and these regulations cover a wide range of solvents used in different industrial activities, e.g. printing, surface cleaning, dry cleaning, footwear manufacturing and pharmaceutical products [4]. Among these compounds, DCM is a widely used solvent in chemical industries, up to 2.3% of the total VOC in 2002 in the United Kingdom [5]. DCM is known for having adverse effects on human beings and the environment [6,7] but this solvent has convenient properties (inertness towards many types of reagents and reaction conditions) although its low boiling temperature (39.6 °C) remains a major drawback [8]. Strict regulations are applied to this particular VOC such as banning DCM in paint-strippers by the European Commission [9].

Adsorption on fixed beds of granular activated carbon (GAC) is widely used in VOC recovery and is also used in the case of DCM removal [10–13]. The design and the associated optimizations play a key role in the overall performance of the process. Because the adsorption of VOC is an exothermic phenomenon (enthalpy of adsorption estimated between −40 and −90 kJ mol^{-1}) [3], high temperature increases were observed when high concentration

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Nomenclature

b_0 Parameter of the langmuir model (atm^{-1})

b_T Parameter of the langmuir model (K)

C Dichloromethane concentration in the gas phase ($mol\,m^{-3}$)

C^* Equilibrium DCM concentration in the gas phase ($mol\,m^{-3}$)

Cp_a Specific heat capacity of the adsorbed phase ($J\,mol^{-1}\,K^{-1}$)

Cp_g Specific heat capacity of the gas phase ($J\,kg^{-1}\,K^{-1}$)

Cp_s Specific heat capacity of the adsorbent ($J\,kg^{-1}\,K^{-1}$)

D Axial mass dispersion coefficient ($m^2\,s^{-1}$)

d_c Diameter of the column (m)

D_H Axial heat dispersion coefficient ($W\,m^{-1}\,K^{-1}$)

d_p Equivalent particle diameter (m)

h_S Gas–solid heat transfer coefficient ($W\,m^{-2}\,K^{-1}$)

h_p Heat transfer coefficient of the wall ($W\,m^{-2}\,K^{-1}$)

H Enthalpy of the gas phase ($J\,kg^{-1}$)

k Overall mass transfer coefficient (s^{-1})

K_f External mass transfer coefficient ($m\,s^{-1}$)

P_e Equilibrium DCM partial pressure (atm)

q Adsorbed DCM concentration ($mol\,kg^{-1}$)

q^* Equilibrium DCM concentration in the solid adsorbent ($mol\,kg^{-1}$)

q_m Parameter of the langmuir model (K)

S_p Specific surface area of adsorbent bed ($m^2\,m^{-3}$)

T Temperature of the gas phase (K)

T_s Temperature of the solid particle (K)

T_p Wall temperature (K)

$tp_{10\%}$ Breakthrough time for 10% of the inlet concentration (s)

v Superficial velocity ($m\,s^{-1}$)

z Thickness of the column wall (m)

Greek letters

ΔH_{ads} heat of adsorption ($kJ\,mol^{-1}$)

ε Bed porosity (−)

ρ_p Bulk adsorbent density ($kg\,m^{-3}$)

ρ_g Density of the gas phase ($kg\,m^{-3}$)

and the main consequence will be a reduction of process efficiency [17–20].

There are several types of adsorption process used in chemical industries such as temperature swing adsorption (TSA) or pressure swing adsorption (PSA) [21]. The main difference between these two types of processes is their regeneration mode. The TSA process uses hot inert gas (nitrogen at 170–200 °C for example) or steam (between 120 and 150 °C) for VOC desorption and subsequent recovery (by condensation) [10,11,22].

In conventional TSA processes, saturated steam at low pressures is the most common desorbing medium. Regeneration by steam is fast and very efficient but has the disadvantage of requiring a subsequent drying and cooling step, which takes usually a long time [10,23–28]. In the aim to control temperature during adsorption process, various intensification methods have already been used to increase TSA process productivity by heating or cooling adsorbent beds which include thermoelectric elements in order to accelerate the dynamics of temperature changes (Peltier effect), likewise adsorption columns with internal and external heat exchangers have been developed [25,29,30].

Numerous processes (adsorption, condensation) have been developed for solvent recovery [31–33]. Among these developments, a new technology was patented by Marvillet and Chaix in 2003 [32]. As illustrated in Fig. 1, this optimization is a combination of the conventional TSA method with two adsorption columns used alternately in adsorption and in regeneration mode. The particularity is highlighted by the use of a heat pump for adsorption column cooling (left side in Fig. 1). The heat released during the adsorption step was transferred to the regeneration column (right side in Fig. 1). Thus, the heat brought by the pump is used for VOC desorption. Furthermore, at the outlet of the column under regeneration, the gas-phase is enriched with VOC and this flow is then feeding the lower part of the adsorber so that VOC is condensed and recovered.

This technology was already modeled by Bonjour and Clausse [34] who proposed thermodynamic charts applied to the adsorption and desorption of toluene. Although this process shows promising performances, further experimental and simulation work should be carried out to confirm these expected benefits. Until now, to our knowledge, no comprehensive synthesis has been reported about energy savings or cost reductions for this specific adsorption process.

Therefore, the main objectives of this research work are to assess the performance of coupling the TSA process with a heat pump for the adsorption and recovery of DCM. An experimental unit was designed. Then, from experimental results, the best operating conditions were determined. The mass and heat
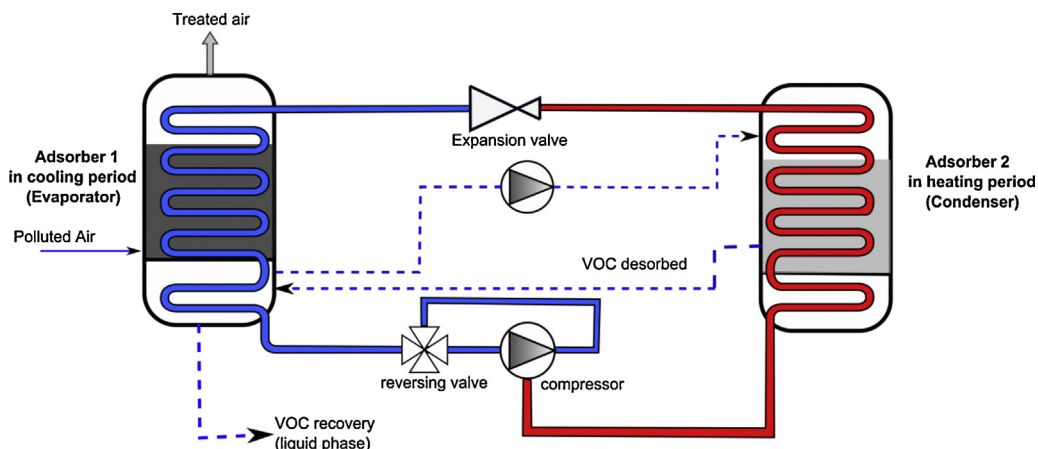
levels are treated [15,16]. A safety limit thus exists since the temperature must remain lower than the temperature of oxidation of either the adsorbent or the adsorbate. More importantly, the adsorption capacities would decrease as the temperature increases

Fig. 1. Process and device for the capture of vapors contained in a gas effluent [32].