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Removal of volatile organic compounds by heterogeneous ozonation on microporous synthetic alumina silicate

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ABSTRACT

A hybrid process combining adsorption and ozonation was examined as an alternative treatment for odorous volatile organic compounds (VOCs). Methyl ethyl ketone (MEK) was chosen to study the influence of operating parameters. Two synthetic aluminosilicates (faujasite-Y and ZSM-5) were tested for adsorption and reactivity with ozone. The adsorption equilibrium measurement on both adsorbents showed that adsorption performance depends on temperature but is not sensitive to relative humidity, due to the hydrophobic properties of the materials. Adsorbed VOCs were oxidized at low temperature when ozonated flow was sent to the reactor. Regeneration of the fixed bed was achieved at the same time, releasing mainly CO_2 and H_2O. Intermediates of oxidation, such as 2,3-butanedione and acetic acid, were identified, leading to incomplete mineralization. The influence of concentration and humidity are discussed. Four successive cycles were tested: after the first adsorption/ozonation cycle, the adsorption efficiency was not affected during subsequent cycles. These results show that the same sample of adsorbent can be used in the treatment process for a long time. Ozonation regeneration is a promising process for VOC removal.

Key words | adsorption, alumina silicate, odours, ozonation, volatile organic compounds

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INTRODUCTION

Among many techniques available for controlling volatile organic compound (VOC) emissions, adsorption on activated carbon (AC) has been found to be effective at low concentration levels (Zhao *et al.* 1998). However, the regeneration of AC remains a problem because the regeneration process is slow, expensive and may cause irreversible damages to AC (Alvarez *et al.* 2004). The crystalline and mineral structures of aluminosilicate adsorbents give them strong thermal and chemical stability, and new ways of regeneration, such as oxidation with powerful oxidants like ozone (Sagehashi *et al.* 2005; Monneyron *et al.* 2007), have been explored recently. Oxidation using ozone, and supported by catalysts, has already been used for the treatment of air polluted with hazardous compounds (Konova *et al.* 2006; Einaga & Ogata 2009). Very few studies focused on the coupling of ozone and aluminosilicates to remove VOCs (Monneyron *et al.* 2007; Kwong *et al.* 2008; Valdes *et al.* 2009; Einaga *et al.* 2010). In the present work, methyl ethyl ketone (MEK; butan-2-one) was chosen as a common odorous pollutant. This compound was also chosen for its very weak reactivity with ozone in the gaseous phase.

METHODS

Adsorbents and adsorbate

Two types of aluminosilicate were used, supplied by TOSOH Corp. in the form of pellets: a de-aluminated faujasite Y (Fau-Y) and a silicalite ZSM-5. The main characteristics of the adsorbents are given in Table 1. Prior to experimentation, the adsorbents were heated in a drying oven at 500 K for 24 h and kept in a desiccator. The VOC used in this study was MEK (purity >99%), purchased from Aldrich.

Table 1 | Characteristics of the adsorbents

Type (symbol)	Faujasite	ZSM-5
Crystalline framework	α-cages	Interconnected channels
Pore diameter (Å)	7.4(aperture) - 13(cage Ø)	(5.7×5.1) and 5.4
SiO_2/Al_2O_3 (mol mol^{-1})	360	1,880
Active porous volume (cm^3 g^{-1})	0.24	0.18
BET^a surface area (m^2 g^{-1})	650	300
Granular diameter (mm)	3	1.5

[a]Brunauer–Emmett–Teller.

Laboratory-scale pilot

Adsorption isotherms were performed using a static volumetric apparatus, described in a previous study (Brosillon *et al.* 2001). Adsorbed quantities were normalized for pure zeolite material, assuming that the inert clay binder mass does not participate in the adsorption phenomena. The experimental fixed bed is shown in Figure 1. It is composed of a polluted air generator, an ozonated air generator (5LO Trailigaz model) and a glass reactor (internal diameter (ID): 8 cm, length: 20 cm) in which adsorbents are introduced (from 100 g to 200 g). Experimental conditions were: air flow rate 5 m^3 h^{-1}, VOC concentration 1.35 g m^{-3} and ozonated air flow fixed between 0.1 and 0.25 m^3 h^{-1}. Ozone concentration was 18 g m^{-3}. The adsorption and ozonation occurred at room temperature (24 °C ± 2 °C).

On-line gas analysis was performed using a Varian 3800 gas chromatograph (GC) equipped with flame ionization (FID) and thermal conductivity (TCD) detectors. VOCs were analysed with a CP-SIL 8 capillary column (30 m × 0.53 mm ID) with a 1.0 µm film thickness, and CO_2 with a Hayesep Q 60/80 column (1 m × 3 mm). Ozone concentration was determined by a UV BMT 964 Ozone Analyzer.

RESULTS AND DISCUSSION

### Adsorption equilibrium isotherms of MEK

Adsorption isotherms were determined for both adsorbents at a low partial relative pressure range, corresponding to $P/P_0 \leq 0.1$ or $C \leq 35$ g m^{-3}. As previous research seemed to prove that temperature could enhance adsorption capacity of aluminosilicates (Wang *et al.* 2006), the influence of temperature (T) on isotherms was investigated. Furthermore, the influence of moisture (relative humidity) was studied on the adsorption capacity of these adsorbents.

The experimental adsorption isotherms are presented in Figure 2(a) (influence of T) and 2(b) (influence of relative humidity; RH). A sharp increase in capacity is observed at low partial pressures for ZSM-5, corresponding to micropore filling, followed by a flat plateau region at relatively high partial pressures indicating good adsorption affinity. The isotherm curves are of type I of the IUPAC classification (Sing *et al.* 1985) and can be modelled by the Langmuir equation as expected for this kind of microporous adsorbent (Monneyron *et al.* 2003). For Fau-Y adsorption, a weaker increase can be observed at low partial pressures but stabilization is found at higher values than for ZSM-5. This result is explained by a greater porous volume for Fau-Y than for ZSM-5: 0.24 cm^3 g^{-1} versus 0.18 cm^3 g^{-1}.

The increase in temperature of adsorption decreases the quantity of MEK adsorbed on ZSM-5 and Fau-Y. Using the assumption that the adsorbed phase is comparable with a liquid state, micropore filling was calculated at this plateau region. The volumes of MEK adsorbed on ZSM-5 at this plateau are 0.148 cm^3 g^{-1} at 298 K and 0.141 cm^3 g^{-1} at 333 K, corresponding to filling rates of 82% and 78%, respectively. On Fau-Y, the filling rate of MEK is 87% (298 K) and 51% (333 K), indicating a higher loss of adsorption capacity with temperature. These differences can be explained by the pore structure and pore diameter. The pores of ZSM-5 (5.5 Å) are narrower than Fau-Y (7.4 Å). The MEK molecules with a kinetic diameter of 5.2 Å interact strongly with the channel walls of ZSM-5, whereas this interaction is much smaller in large pore aluminosilicates, such as Fau-Y (Meininghaus *et al.* 2000).

Regarding the influence of humidity, results presented in Figure 2(b) showed that the adsorption capacity was not significantly affected by moisture content. The hydrophobicity of both materials is proven.
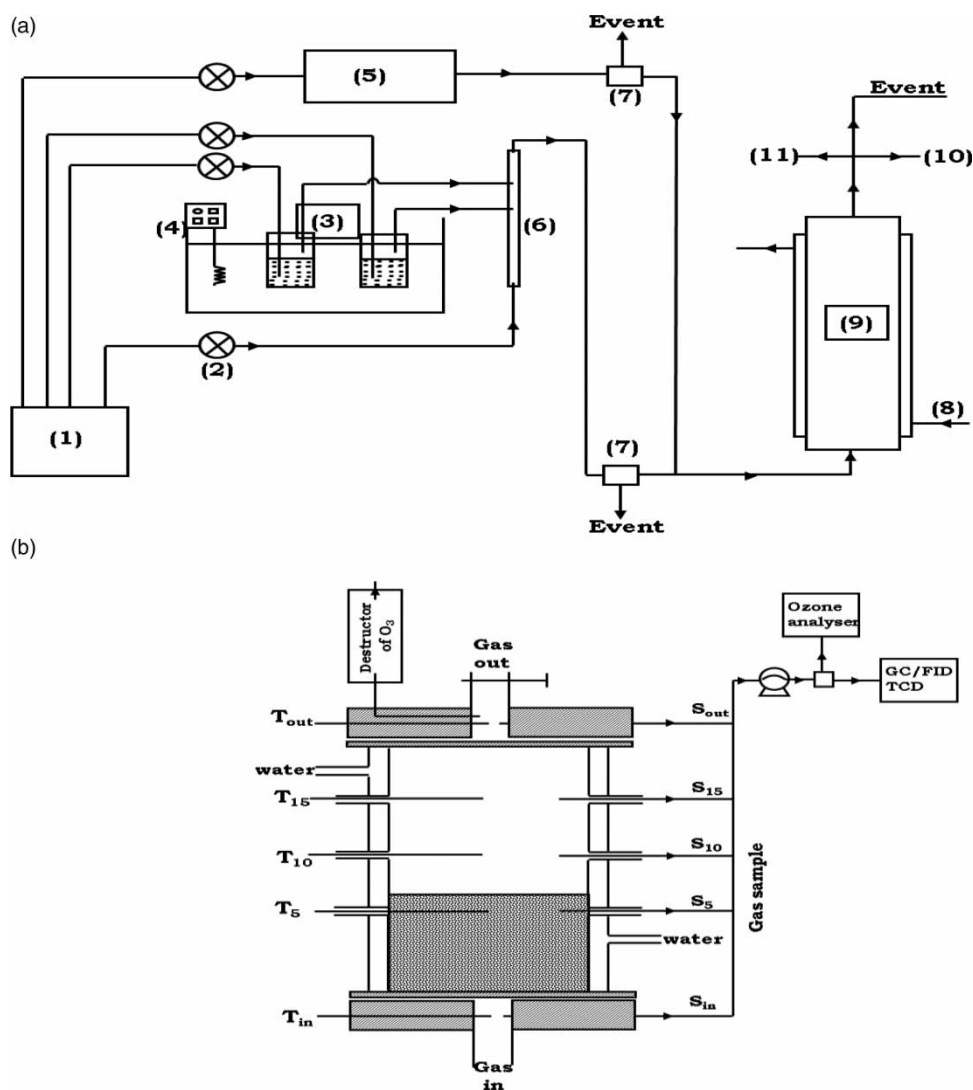
Figure 1 | (a) Scheme illustration for the experimental set-up of adsorption/ozonation. (1) air supply; (2) mass flow controller; (3) saturators; (4) thermostatic bath; (5) ozone generator; (6) mixing volume; (7) 3-way valve; (8) temperature control fluid; (9) reactor; (10) GC/FID/TCD and (11) ozone analyser; (b) Schematic diagram of the reactor designed for this application.

The adsorption/ozonation treatment

The treatment of polluted air was carried out in the laboratory-scale pilot by a sequential process: adsorption then ozonation. The typical course of an experiment is represented in Figure 3 for one cycle of adsorption/ozonation of MEK at room temperature.

Adsorption step

A classical breakthrough curve can be observed, with different curve shapes for the two adsorbents. The weak slope of the ZSM-5 curve can be explained by a wide mass transfer zone and a probable limitation by the internal resistance to transfer. The Fau-Y curve slope is slightly greater ($702\ \text{mg m}^{-3}\,\text{h}^{-1}$ versus $440\ \text{mg m}^{-3}\,\text{h}^{-1}$) and the mass-transfer zone is smaller, representative of better affinity with MEK.

The total amount of MEK adsorbed was obtained by integration of the breakthrough curve (hatched part on Figure 3). The results obtained for extrapolation to total saturation (0.103 and 0.043 g g^{-1} for ZSM-5 and Fau-Y respectively) are in quite good agreement with the static adsorption equilibrium. For a concentration of MEK of 1.35 g m^{-3}, the adsorption capacity from isotherm experiments was 0.108 g g^{-1} for ZSM-5 and 0.062 g g^{-1} for Fau-Y.
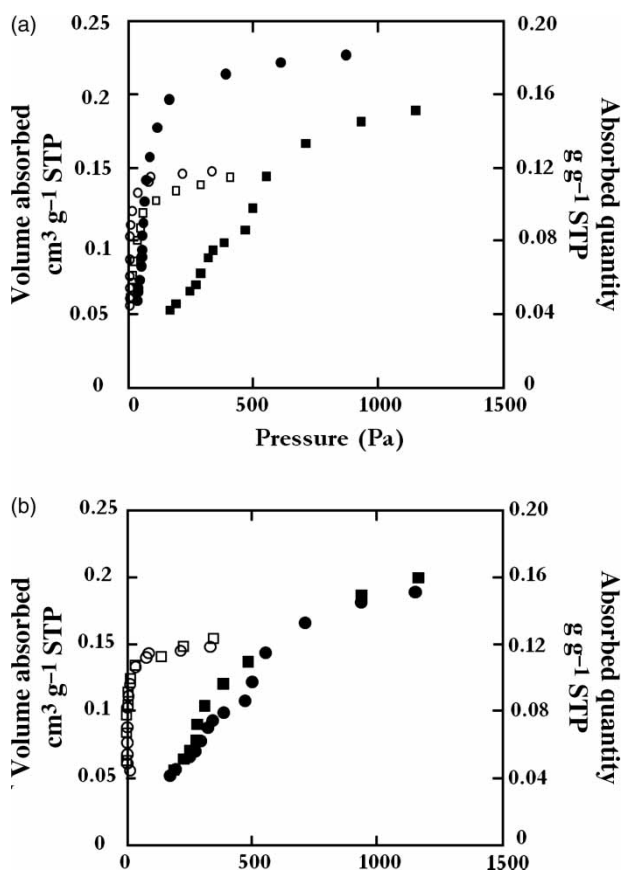
Figure 2 | (a) Adsorption isotherms of MEK on two high-silica zeolites: influence of T: ZSM-5: ○ 298 K; □ 333 K ; Fau-Y: ● 298 K; ■ 333 K. (b) Adsorption isotherms of MEK on two high-silica zeolites: Influence of humidity (333 K): ZSM-5: ○ dry air; □ RH = 50%; Fau-Y: ● dry air; ■ RH = 80%.

Ozonation step

When a given partial saturation rate ($C_{out}/C_{in} = 0.50$) is reached, inlet polluted air is stopped and ozonated air (18 g m^{-3} under a flow of 0.25 m^3 h^{-1}) is sent through the reactor. A very high peak is observed (Figure 3) as soon as the ozonation begins, an indication of strong desorption of MEK. This thermal desorption is probably caused by the local heating induced by the oxidation. During this phase, very high temperature increases are seen (Figure 3B1 & Figure 3B2): $\Delta T = 106\,°C$ for ZSM-5 and 145 °C for Fau-Y.

The desorbed amount was determined by integration of the curve. The desorbed quantity is about 2.03 g of MEK for Fau-Y and 2.42 g for ZSM-5, which accounts for 26% and 15% of the initially adsorbed quantity for Fau-Y and ZSM-5 respectively. In an industrial situation, the adsorption step would be stopped before 50% saturation, and the thermal desorbed VOCs would be less important and could be adsorbed in the bed zone free of adsorbate or could be recycled.

The regeneration of adsorption capacity was estimated by comparing the adsorbed quantities of MEK before and after each ozonation. The regeneration is very weak for ZSM-5 (22%) whereas it is much stronger for Fau-Y (79%). The structure of this channelled adsorbent may explain this result. If molecular ozone is not able to diffuse easily to meet adsorbed MEK, oxidation cannot take place, whereas the large cage structure of Fau-Y allows easy
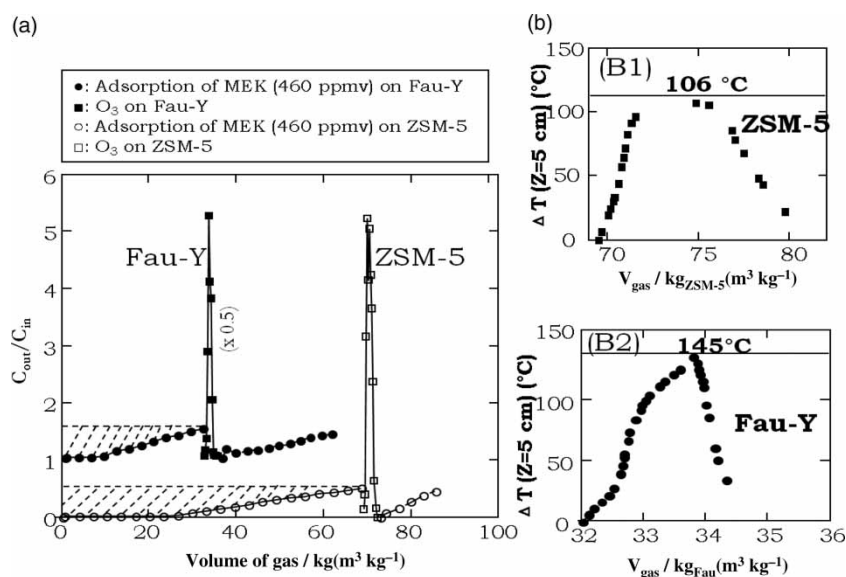
Figure 3 | (a) VOC concentration profiles during a discontinuous adsorption/ozonation cycle of MEK (1.35 g m^{-3}) on two adsorbents: ZSM-5 (202 g) and Fau-Y (205 g). (b) (B1) Temperature increase in ZSM-5 during ozonation. (B2) Temperature increase in Fau-Y during ozonation

diffusion of ozone in the porous volume and an easy oxidation of the adsorbed component.

Mass balance during ozonation step

Using measurements of concentrations versus time the mass balance was determined for carbonated compounds and for ozone, and is presented in Table 2 for the experiment on ZSM-5. A comparison is made between the theoretical mineralization reaction (Equation (1)) and the real oxidation reaction due to stoichiometry coefficients:

$$C_4H_8O + 11/3O_3 \rightarrow 4CO_2 + 4H_2O \tag{1}$$

It can be seen that the mass balances of carbon and oxygen are incomplete and hence experimental and theoretical coefficients values are quite different. The lack of CO_2 production and the weak ozone consumption are indicative of incomplete oxidation, with the formation of sub-products. These components are probably oxidation reaction intermediates, such as aldehydes, organic acids, ketones and alcohol. Indeed, the formation of other peaks was observed, showing the presence of sub-products such as acetone and ethanol. 2,3-butanedione and acetic acid were identified and their production was quantified (Table 2); traces of other sub-products were also detected.

Successive cycles of adsorption/ozonation

In order to evaluate the stability of the adsorbent during the cycle of adsorption and regeneration by O_3, the reuse experiment was carried out. The operating conditions for the adsorption and ozonation steps were the same as described above. Tests of adsorption were carried out on a mass of 200 g of ZSM-5 and 205 g of Fau-Y, with a concentration of MEK of 1.35 g m^{-3} in the air for a total flow of 5 m^3 h^{-1}. The ozonation phase was carried out after each step of adsorption (50% partial saturation) with a concentration of O_3/air of about 18 g Nm^{-3} for a flow of 0.25 m^3 h^{-1}. Figures 4 and 5 show the changing MEK concentration on Fau-Y and ZSM-5.

The quantities of MEK adsorbed after the first phase of adsorption (cycle 1) are 15.4 g MEK on ZSM-5 and 7.18 g MEK on Fau-Y, confirming the better adsorption of ZSM-5 in the low concentration range. The breakthrough time of the second cycle of adsorption–ozonation is lower than the first, especially for ZSM-5, from 86 min to 8 min for ZSM-5 and from 30 min to 18 min for Fau-Y. This seems to indicate a decrease of the adsorption capacities of the

Table 2 | VOC oxidation mass balance on ZSM-5 (t_s = 4.36 s; [MEK] = 1.35 g m^{-3})

Mass balance of C					
MEK adsorbed (non desorbed) (g)	CO$_2$ produced (g)	Acetic acid (g)	2,3-butanedione produced (g)	Experimental stoichiometry (mol CO$_2$ mol$_{voc}$⁻¹)	Theoretical stoichiometry (mol CO$_2$ mol$_{voc}$⁻¹)
13.5	7.7	4.2	1.8	1	4.0

Mass balance of O			
O$_3$ consumed (g)	O$_3$ sent (g)	Experimental stoichiometry (mol O$_3$ mol$_{voc}$⁻¹)	Theoretical stoichiometry (mol O$_3$ mol$_{voc}$⁻¹)
11	17.6	1.2	3.7
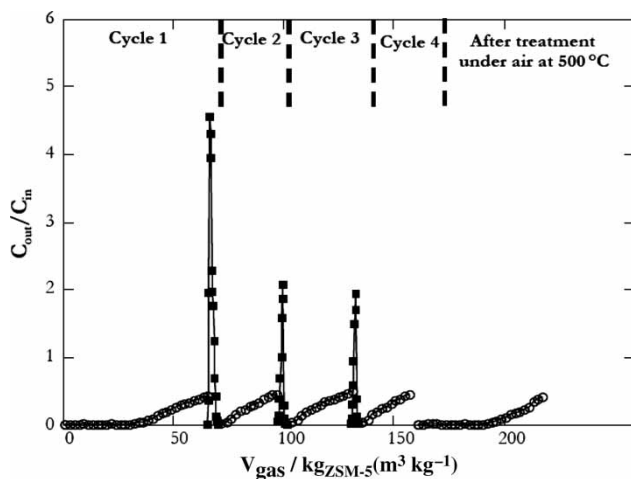
Figure 4 │ Cyclic study of adsorption/ozonation of MEK on Fau-Y. ○: adsorption of MEK (1.35 g m^{-3}) on Fau-Y, ■: O_3 on Fau-Y.
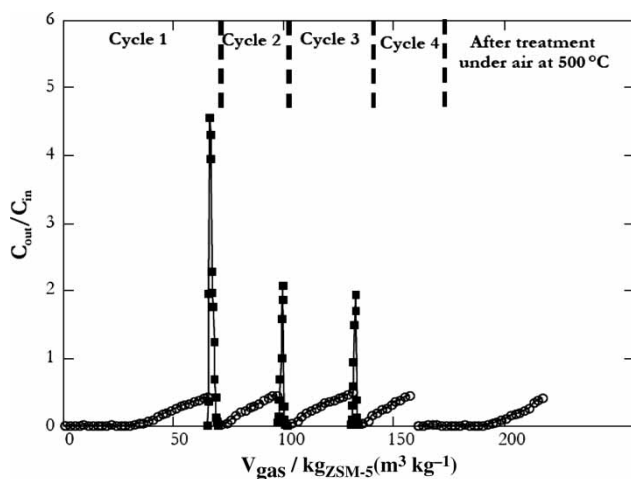
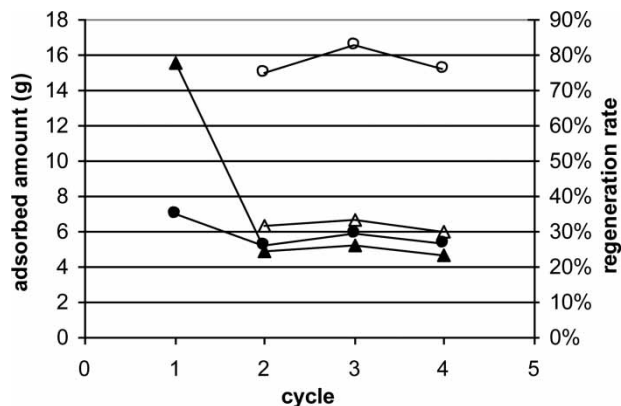**Figure 5** │ Cyclic study of adsorption/ozonation of MEK on ZSM-5. ○: adsorption of MEK (1.35 g m^{-3}) on ZSM-5, ■: O_3 on ZSM-5.

Figure 6 │ Evolution of adsorption capacity during the adsorption/ozonation process. ●: adsorbed amount on Fau-Y, ▲: adsorbed amount on ZSM-5; ○: regeneration rate of Fau-Y, △: regeneration rate of ZSM-5.

material, probably caused by some remaining adsorbed by-products. A change in the physical or chemical surface of aluminosilicate is also possible (Valdes *et al.* 2010) and could be the origin of the decrease of adsorption.

The regeneration of adsorption capacity was estimated by comparing the adsorbed quantities of MEK on the two adsorbents before and after each ozonation. Results are reported in Figure 6.

Stabilization was observed after the first adsorption/ozonation cycle, showing a constant regeneration rate. Fau-Y has better results than ZSM-5, with a constant regeneration rate of about 75–83%. For ZSM-5, the regeneration rate is weaker (28–32%) but the interesting point is that it is stable. Strong heating of the ZSM-5 (500 °C), showed

that the adsorbed compounds could be desorbed. The re-adsorbed quantity of MEK was 14.3 g, corresponding to 93% of the adsorbed quantity at the first cycle of adsorption–ozonation for the ZSM-5. Thus, it can be deduced that no real irreversible poisoning of catalysts occurred during ozonation.

CONCLUSIONS

Experimental results of static adsorption and those conducted in the laboratory-scale pilot showed the feasibility of this treatment, coupling adsorption on microporous synthetic aluminosilicate and oxidation with ozone.

Good capture of MEK in dry or wet conditions was found and a good regeneration of the adsorbent occurred at ambient temperature and pressure, with better results for Fau-Y. The main products of oxidation were CO_2 and H_2O. Intermediates of oxidation such as 2,3-butanedione and acetic acid were identified, leading to incomplete mineralization. The adsorbents' efficiency was not highly affected after four consecutive cycles of MEK adsorption–ozonation. These results show that the same sample of adsorbent can be used in the treatment process for a long time. Ozonation regeneration is a promising process for VOC removal.

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