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Application of high silica zeolite ZSM-5 in a hybrid treatment process based on sequential adsorption and ozonation for VOCs elimination

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\textbf{Abstract}

In this study, a hydrophobic synthetic zeolite, namely ZSM-5 is chosen as an adsorbent/catalyst for toluene removal. Experimental results showed that toluene adsorption onto ZSM-5 was favourable, following a Langmuir adsorption isotherm model. ZSM-5 zeolite was regenerated using gaseous ozone at low temperature. Adsorbed toluene was oxidised, releasing mainly CO\textsubscript{2} and H\textsubscript{2}O. Traces of oxidation by-products such as acetic acid and acetaldehyde were formed and remained adsorbed after the oxidative regeneration with ozone. After four successive cycles of adsorption/ozonation, the adsorption efficiency was not affected (92\%-99\%). These results showed that volatile organic compound (VOC) removal by adsorption onto ZSM-5 zeolite followed by ozone regeneration could be used as a promising hybrid process for the control of VOC emissions in terms of efficiency.

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**Keywords:** Adsorption, Ozone, Toluene, VOCs, Zeolite

\section{Introduction}

Volatile organic compounds (VOCs) are often considered as toxic chemicals that cause severe health problems. Their elimination has been a serious challenge for several years for many industrial companies which have to accomplish stringent environmental regulations (Ruddy and Carroll, 1993; VOC Solvents Directive, 1999/13/EC, 1999; Paints Directive, 2004/42/EC, 2004). Conventional methods used to treat VOCs include absorption, thermal and catalytic oxidations, biofiltration, condensation and adsorption (Ruddy and Carroll, 1993; Khan and Ghoshal, 2000; Brosillon et al., 2001; Ghoshal and Manjare, 2002; Yang et al., 2013; Li et al., 2014). Among them, adsorption has been considered as one of the best options to treat VOC emissions (Foster et al., 1992; Zaitan et al., 2013; Le Cloirec, 1998; Brosillon et al., 2001). However, adsorption techniques only transfer pollutants from one phase to another one, generating a new waste with a higher content of VOCs.

Regarding this problem, a variety of regeneration techniques have been evaluated and implemented. Regeneration is normally performed by changing the conditions in the adsorber bed in order to desorb the VOCs from the adsorbent (Yang, 1987; Le Cloirec, 1998; Bonjour et al., 2002; Yu et al., 2007). This process is achieved either by increasing the temperature using hot air or

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steam, by decreasing the partial pressure, or by introducing a stronger adsorbate able to displace the adsorbed VOCs (Rafson, 1998). However, the regeneration of adsorbents such as activated carbons is very difficult because of their thermal and chemical instabilities that may cause significant safety problems (Blocki, 1993; Baek et al., 2004).

Recently, the use of hydrophobic zeolites has been attracting more and more attention because of their non-flammability, thermal stability and resistance to humidity (Brosillon et al., 2001; Vinh-Thang et al., 2005; Cosseron et al., 2013). The application of hydrophobic zeolites as a dual function adsorbent/catalyst medium is justified in two aspects. Firstly, hydrophobic zeolites are safe to use in catalytic oxidation processes operating at high temperatures. Secondly, they have a high adsorption affinity toward VOC under humid conditions (Bonjour et al., 2002).

In the last years, the combined use of adsorption followed by ozone oxidation (denoted as AD-OZ process) at laboratory and at bench scale has been investigated and may offer an interesting potential for its implementation at industrial scale, since ozone can destroy adsorbed molecules, regenerating the zeolite adsorption capacity (Monneyron et al., 2007; Brodu et al., 2012). However, very few studies are focused on coupling ozone and synthetic zeolites in a same process treatment to remove VOCs (Monneyron et al., 2003, 2007; Kwong et al., 2008; Eina et al., 2011; Brodu et al., 2012).

The adsorption of VOCs on several kinds of zeolites followed by ozonation resulted in a high degree of recovery on the adsorption capacity of zeolites (Monneyron et al., 2003, 2007). In this hybrid treatment, it has been claimed that molecular ozone generates very powerful free radicals after ozone adsorption and its decomposition on strong Lewis acid sites of zeolite surface, leading to the oxidation of adsorbed VOCs (Brodu et al., 2013; Alejadro et al., 2014).

This work aims to investigate the main operating process parameters that influence the efficiency of a new hybrid process of VOC adsorption onto a fixed-bed of ZSM-5 followed by gaseous ozone oxidation in a single reactor. In particular, the maximum adsorption capacity of zeolite and the degree of adsorption capacity recovery after various cycles of adsorption–ozonation were assessed at bench scale. Moreover, oxidation by-products was identified and mass balances were established. As a result, process efficiency was evaluated in order to process design and optimisation.

### 1. Materials and methods

#### 1.1. Materials

A commercial high silica zeolite (ZSM-5) was used in the adsorption–ozonation process (AD–O2) and was supplied by (TOSOH Corporation, Tokyo, Japan) in the form of pellets (Ø = 1.5 mm). Zeolite was dried in air at 500 K for 24 hr and stored in a dessicator for further use. Table 1 shows the key physical-chemical properties of ZSM-5 zeolite.

Ozone was generated from dry air using an ozone generator (Trailigaz Model SLO, Trailigaz Ozone S.A.S., Saint Maurice, France) featuring a variable ozone production rate, with a maximum of around 24 g O₃/hr. Gaseous ozone stream was humidified (60% of relative humidity) by bubbling the outlet stream of ozone coming from the ozone generator into a water column. Toluene (purity > 99%) was supplied in liquid phase by Sigma-Aldrich (Sigma-Aldrich Chimie S.a.r.l, Lyon, France) and was used in this study as a target organic molecule representative of VOCs.

#### 1.2. Adsorption isotherms

Toluene adsorption isotherms were performed using the bottle point method, as described elsewhere (Brosillon et al., 2001). Different amounts of zeolite mass (ranging from 0.3 to 1 g) were introduced into batch glass contactors (1.1 dm³). Then, a fixed volume of liquid toluene (typically 50 µL) was injected through a septum into each adsorption chamber at 300 K and 101 kPa, leading to an initial concentration of about 0.5 mol/m³ after the complete evaporation of toluene. After that, adsorption chambers were stirred until the equilibrium was reached (2 hr). Finally, gas samples were taken from each bottle and analysed by gas chromatography (Varian CP-3800 GC, Varian Inc., Walnut Creek, USA). The total amount of adsorbed toluene per gramme of zeolite at the equilibrium, qₑ (mol/kg), was calculated from a mass balance in each isotherm batch adsorption chamber, as follows:

$$q_e = \frac{(C_0 - C_e)V}{M}$$  \hspace{1cm} (1)

where $C_0$ and $C_e$ (mol/m³) are gas phase concentration of toluene at initial and at equilibrium, respectively, $M$ (g) is the mass of zeolite sample used in each batch adsorption chamber, and $V$ ($1.1 \times 10^{-3}$ m³) stands for the total volume of the adsorption chamber. Adsorbed quantities were normalised for pure zeolite material, supposing that inert clay binder mass did not participate in the adsorption phenomena.

#### 1.3. Experimental procedures of the adsorption–ozonation process

Experimental set-up presented in Fig. 1 consists of four main parts: a toluene vapour saturator, a fixed-bed glass contactor (80 mm ID, 200 mm length), gas analysers, and an exhaust gas trap.

**Table 1 – Physical–chemical properties of ZSM-5 zeolite.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline framework</td>
<td>Interconnected channels</td>
</tr>
<tr>
<td>Pore diameters (Å)</td>
<td>Intersections: $6 \times 8$</td>
</tr>
<tr>
<td>$SiO_2/Al_2O_3$ (mol/mol)</td>
<td>Channels: $5.1 \times 5.5$ and $5.3 \times 5.6$</td>
</tr>
<tr>
<td>Total pore volume $V_T$ (cm³/g)</td>
<td>2100</td>
</tr>
<tr>
<td>Micropore volume $V_{mic}$ (cm³/g)</td>
<td>0.11</td>
</tr>
<tr>
<td>Mesopore volume $V_{mes}$ (cm³/g)</td>
<td>0.07</td>
</tr>
<tr>
<td>Specific surface area $S_{BET}$ (m²/g)</td>
<td>308</td>
</tr>
<tr>
<td>Granular diameter (mm)</td>
<td>1.5</td>
</tr>
<tr>
<td>Clay binder content (%)</td>
<td>20</td>
</tr>
<tr>
<td>Concentration of Lewis acid sites (μmol/g)</td>
<td>28 (Brodu et al., 2013)</td>
</tr>
<tr>
<td>Concentration of Bronsted acid sites (μmol/g)</td>
<td>4 (Brodu et al., 2013)</td>
</tr>
<tr>
<td>Compensating cation</td>
<td>H</td>
</tr>
</tbody>
</table>
The inlet concentration of toluene \( (C_{in}) \) was fixed by bubbling dry air into pure liquid toluene, using a temperature controlled bath (300 K), and diluted to a desired concentration by mixing with a fresh dry air stream. Sequential adsorption–ozonation experiments were carried out in the fixed-bed glass reactor loaded with 150 g of the zeolite sample. Both adsorption and ozonation steps were conducted under dynamic conditions at room temperature (300 K) and atmospheric pressure. A total flow rate of 5 m\(^3\)/hr (residence time < 0.2 sec) containing 50 ppmV (0.205 g/m\(^3\)) of toluene was continuously supplied over the zeolite bed. The adsorption step was completed when the outlet concentration of toluene reached 35% of the inlet concentration \( (C_{out}/C_{in} = 0.35) \). After that, a regeneration step was performed using a humidified gaseous ozone stream (25 dm\(^3\)/hr, 18 gO\(_3\)/m\(^3\), and 60% of relative humidity). During the regeneration step, the outlet concentration of O\(_3\), toluene and its oxidation by-products was continuously analysed. Data were recorded every 13 min. Ozone regeneration was stopped when CO\(_2\) was no longer detected at the reactor outlet stream and the reactor temperature returned to room temperature (300 K), indicating the end of the oxidation reactions. The exhaust gas stream was sent to a trap before discharging to the ambient air.

The total amount of adsorbed toluene per mass of zeolite \( (Q_{C_{H}}^{A}, \frac{g_{C_{H}}}{g_{ZSM-5}}) \) during the adsorption step was calculated according to Eq. (2):

\[
Q_{C_{H}}^{A} = \frac{F\ C_{in}}{m} \int_{0}^{t_{s}} (1 - \frac{C_{out}}{C_{in}}) dt
\]

where \( F \) (m\(^3\)/min) is the gas flow rate, \( m \) (g) is the mass of ZSM-5 zeolite, \( C_{in} \) (g/m\(^3\)) is the inlet concentration of toluene, \( t_{s} \) (min) is the adsorption time to reach saturation, and \( C_{out} \) (g/m\(^3\)) is the outlet concentration of toluene as a function of time.

The total applied load of ozone per mass of zeolite \( (Q_{O_3}^{A}, \frac{g_{O_3}}{g_{ZSM-5}}) \) during the ozonation step was calculated using
the following equation:

$$Q^L_{m} = \frac{F}{m} \int_{t_0}^{t_{eq}} \frac{C_{in}}{C_{D_{eq}}} dt$$  \hspace{1cm} (3)

where $C_{D_{eq}}$ (g/m³) is the inlet concentration of ozone, and $t_0$ and $t_{eq}$ (min) correspond to the starting and ending time of the ozonation step, respectively.

The total amount of desorbed toluene per mass of zeolite ($Q^D_{m} (\text{g/t})$, $Q^D_{m} (\text{g/t})$) due to local heating generated during the ozonation step was obtained using Eq. (4):

$$Q^D_{m} = \frac{F}{m} \int_{t_0}^{t_{eq}} C_{D_{eq}} dt.$$

(4)

The total amount of carbon dioxide formation per mass of zeolite ($Q_{CO_2} (\text{g/t})$, $Q_{CO_2} (\text{g/t})$) during the ozonation step was calculated applying Eq. (5):

$$Q_{CO_2} = \frac{F}{m} \int_{t_0}^{t_{eq}} C_{CO_2} dt.$$

(5)

where $C_{CO_2}$ (g/m³) represents the outlet concentration of carbon dioxide as a function of time.

1.4. Analytical methods

Toluene and CO₂ concentrations at the reactor outlet stream were monitored at constant intervals of time with an automatic 10-port injection valve and a digital timer by gas chromatography (Varian CP-3800 GC, Varian Inc., Walnut Creek, USA). Toluene and its oxidation by-products of high molecular weight were analysed using a CP-SIL 8 capillary column (30 m length × 0.53 mm ID) with a 1.0 μm film thickness coupled to a flame ionisation detector (FID); whereas CO₂ was analysed with a HayeSep Q packed-bed column (80–100 mesh particle size, 0.91 m length × 3.18 mm OD), using a thermal conductivity detector (TCD). Data were recorded every 5 min and processed with a Galaxie Chromatography Data System (Galaxie CDS Software, Varian Inc., Walnut Creek, USA). Ozone concentration was registered on-line, using an ozone analyser (BMT 963 Model, BMT MESSTECHNIK GMBH, Berlin, Germany).

2. Results and discussion

2.1. Adsorption equilibrium isotherms of toluene

Experimental adsorption isotherms were fitted to Langmuir (Langmuir, 1916), Freundlich (Freundlich, 1906) and Toth (Toth, 1971) equations, which have been extensively used to describe adsorption isotherms on zeolites (Einaga et al., 2011). The models express the adsorbed quantity of toluene per mass of zeolite, $q_{e}$ (mol/kg), as a function of toluene concentration at the equilibrium, $C_{e}$ (mol/m³), as follows:

Langmuir equation:

$$q_{e} = \frac{q_{m} b C_{e}}{1 + b C_{e}}$$

where $q_{m}$ (mol/kg) is the maximum adsorption capacity and $b$ (m³/mol) is the adsorption equilibrium constant or Langmuir coefficient.

Freundlich equation:

$$q_{e} = k C_{e}^{1/n}$$

where $k$ (mol⁻¹·m³⁻¹·mol⁻¹/kg) stands for the adsorption equilibrium constant and $n$ is the empirical constant of the Freundlich model.

Toth equation:

Toth isotherm is a semi-empirical expression, normally used to describe a monolayer adsorption. Parameters given in this equation are used to characterise surface heterogeneity and interactions of adsorbed molecules. It is a three-parameter model usually written as follows:

$$q_{e} = \frac{q_{m} \cdot b^t \cdot C_{e}}{[b^t + C_{e}]^{1/t}}$$

where $q_{m}$ (mol/kg) is the maximum monolayer adsorption capacity parameter, $b^t$ ((mol/m³)²) is the Toth isotherm constant, and $t$ is a dimensionless constant, usually less than unity. Parameters $b^t$ and $t$ are specific for the adsorbate-adsorbent systems. The more the parameter $t$ is away from unity, the more heterogeneous is the system. Parameters $q_{m}$, $b^t$, and $t$ in Eq. (8) were determined numerically.

Adsorption equilibrium data of toluene are shown in Fig. 2. As can be observed, at low concentration of toluene a sharp initial increase on the adsorption capacity was observed that could correspond to micropore filling. At a relatively high concentration, a flat plateau region was registered, characteristic of monolayer adsorption on microporous adsorbents. A solid line in Fig. 2 shows that experimental data fit very well the Langmuir adsorption model. Additionally, experimental data were also fitted to other common isotherm models, such as: Freundlich and Toth equations. Although these isotherm equations showed good predictive capabilities; however, they appeared less compatible, with large errors (up to 5%) between the measured and modelled values (Table 2 and Fig. 2).

As can be seen in Fig. 2, the amount of toluene adsorbed on ZSM-5 at 300 K reached a plateau of 0.93 mmol/g. Micropore fillings were calculated using the assumption that the adsorbed phase was comparable to liquid state, highlighting the steric exclusion of toluene on ZSM-5 (58%). This value corresponded to an adsorption of about five toluene molecules per unit of zeolite cell. This result was in agreement with those reported by Weinmann and Prins (2000) who observed an adsorption capacity of 4.6 molecules per unit cell for HZSM-5/180 and NaA-ZSM-5 (with a framework Si/Al ratio of 180) and 7–7.5 molecules per unit cell for MFI type zeolites reported by Lee and Chiang (1996), Song and Rees (2000), and Song et al. (2007). As a way of comparison, Table 3 lists the amount of adsorbed toluene at the equilibrium on ZSM-5 (obtained in this work) and from literature references, using different adsorbents under similar conditions. As can be seen, the adsorption capacity of ZSM-5 toward toluene was in excellent agreement with the observed values using other porous adsorbents such as NaA-ZSM-5, HMOR (Serra et al., 2012), NaY (Jin and Zhu, 2000), and some activated carbons EA95,
CVD80 (Agnihotri et al., 2005). A more detailed comparison with the adsorption capacities of other volatile organic compounds and zeolites reported in the literature is not helpful. Adsorption capacities are dependent on the Si/Al ratio. Channel intersections (four per cell) have been claimed as preferential adsorption sites for cyclic hydrocarbons (Song et al., 2007). Toluene adsorption could be due to strong interactions between the methyl group of the toluene molecule and acidic surface groups of ZSM-5 zeolite. Similar adsorption mechanism has been proposed for toluene adsorption onto MCM-41, NaY and SiO2 (Zhang et al., 2012).

2.2. Toluene removal by the adsorption–ozonation process

The treatment of a simulated polluted air with toluene vapours was carried out at bench scale by a sequential process: adsorption followed by ozonation. The typical course of an experiment is represented in Fig. 3 for one cycle of adsorption–ozonation of toluene at room temperature.

Fig. 3a shows the evolution of the ratio of the concentration of toluene at the outlet and inlet of the reactor \((C_{out}/C_{in})\) as a function of time, during the adsorption step at 300 K (using 150 g of ZSM-5, 50 ppmV or 0.205 g\(_{CH\_4}/m^3\), and 5 m\(^3/h\)). Experimental results of the ozonation step are depicted in Fig. 3b, using 18 g\(_{O_3}/m^2\) and a flow rate of 0.25 m\(^3/h\). A classical breakthrough adsorption curve was observed. During the first 20 min of adsorption, toluene was not detected at the reactor outlet stream. Then, it started to increase progressively as a function of time, reaching a 30% of the saturation value \((C_{sat}/C_{in} = 0.3)\) after around 120 min. The weak slope of the breakthrough dynamic adsorption curve of ZSM-5 can be explained by a wide mass transfer zone, probably limited by internal mass transfer resistances inside the zeolite pellets. When a 30% of the saturation was reached, 0.012 g\(_{CH\_4}/g_{ZSM-5}\) is adsorbed (or 0.132 mmol\(_{CH\_4}/g_{ZSM-5}\)), corresponding to 1.83 g of toluene for the whole zeolite bed. This value was in agreement with the static adsorption equilibrium value (Fig. 2, 0.3 mmol\(_{CH\_4}/g_{ZSM-5}\)) and indicated that only 17.6% of the maximum adsorption capacity of the zeolite bed was used at this moment. After such condition, the inlet of polluted air was stopped and the ozonation of adsorbed toluene was carried out, switching the feeding to the O\(_3\)/air stream (18 g\(_{O_3}/m^2\) and 0.25 m\(^3/h\)). A very high peak in the concentration of toluene at the reactor outlet stream was observed (Fig. 3b) as soon as the ozonation step began, indicating a high release of toluene by thermal desorption. During this phase, the temperature in the zeolite bed increased, reaching around 372 K. Such results were evidences that a fraction of the adsorbed toluene desorbed from the ZSM-5 surface due to local heating generated by toluene oxidation reactions with ozone.

After 60 min of ozonation the amount of desorbed toluene was about 5.34 × 10\(^{-3}\) mmol/g\(_{ZSM-5}\), corresponding to 0.074 g

| Table 2 – Langmuir, Freundlich and Toth parameters for toluene adsorption on ZSM-5 zeolite. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| Langmuir parameters            | Toth parameters  | Freundlich parameters |
| \(q_m\) (mol/kg)                | \(q_m'\) (mol/kg) | \(k\) (mol\(^1\) / h\(^{-1}\) m\(^3\) - 1/m\(^2\)) | 1.10            |
| \(b\) (m\(^2\)/mol)             | \(b'\) ((mol/m\(^3\)/h)) | \(n\)                       | 7.5             |
| \(R^2\)                         | \(R^2\)          | \(t'\)                  | 0.71            |
|                                 |                 | 0.96                    | 0.96            |

\(q_m\): maximum adsorption capacity; \(b\): adsorption equilibrium constant or Langmuir coefficient; \(q_m'\): maximum monolayer adsorption capacity parameter, \(b'\): Toth isotherm constant, \(t'\): dimensionless constant; \(k\): adsorption equilibrium constant; and \(n\): empirical constant of the Freundlich model.
of toluene for the whole bed, which accounted for 4.05% of the initially quantity of adsorbed toluene. It is important to note that in a normal industrial operation, the adsorption step would be stopped before the zeolite adsorption bed reached 30% of saturation. Under such condition, thermally desorbed VOCs could be trapped in the zeolite bed zone free of adsorbate or could be recycled.

When the first cycle of adsorption–oxidation finished, a new polluted air stream was sent again over the zeolite bed at the same conditions as been applied during the first adsorption step. As can be seen in Fig. 3, during the first 20 min of the second adsorption step, toluene was not detected. The breakthrough curve was quite the same, indicating that a regeneration of the zeolite bed had occurred.

### Table 3 – Comparison of maximum adsorption capacities toward toluene of ZSM-5 and some other adsorbents reported in the literature.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Temperature (K)</th>
<th>Maximum adsorption capacity (mmol/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5</td>
<td>298</td>
<td>0.93</td>
<td>3.01</td>
</tr>
<tr>
<td>NaZSM-5</td>
<td>473</td>
<td>0.92</td>
<td>2.5</td>
</tr>
<tr>
<td>HMROR (Si/Al = 10)</td>
<td>473</td>
<td>1.07</td>
<td>2.2</td>
</tr>
<tr>
<td>EA95</td>
<td>298</td>
<td>1.7</td>
<td>3.4</td>
</tr>
<tr>
<td>CVD80</td>
<td>298</td>
<td>1.6</td>
<td>2.6</td>
</tr>
<tr>
<td>MCM-41</td>
<td>298</td>
<td>4.98</td>
<td>3.3</td>
</tr>
<tr>
<td>S-MCM</td>
<td>298</td>
<td>2.49</td>
<td>2</td>
</tr>
<tr>
<td>MOF-177</td>
<td>298</td>
<td>6.06</td>
<td>2</td>
</tr>
<tr>
<td>MCM-48</td>
<td>300.15</td>
<td>=1.08-3.45</td>
<td>2.3–2.2</td>
</tr>
<tr>
<td>Silica–alumina</td>
<td>300</td>
<td>0.085</td>
<td>0.13</td>
</tr>
<tr>
<td>DAY zeolite</td>
<td>298</td>
<td>=1.8</td>
<td>2.5</td>
</tr>
<tr>
<td>318</td>
<td></td>
<td>≈1.5</td>
<td>2.1</td>
</tr>
<tr>
<td>Na-Y/H-Y/USY/ZSM-5</td>
<td>298</td>
<td>≈2–2.5 or 3–4</td>
<td>3.3–4.1</td>
</tr>
</tbody>
</table>

EA95 and CVD80 refer to single-wall carbon nanotubes manufactured by electric arc and the HiPco by chemical vapor deposition; DAY zeolite represents a dealuminated Y-zeolite.

### 2.3. Successive cycles of adsorption–ozonation treatments

Figs. 4, 5 and 6 depict the experimental results of four adsorption–oxidation (AD–OZ) cycles performed over the same zeolite sample, using the same operating conditions as described before. Fig. 4 displays the evolution of the ratio of the concentration of toluene at the outlet and inlet of the reactor during four consecutive adsorption–ozonation cycles, as a function of processed bed volumes of contaminated stream per mass of ZSM-5 zeolite.

As can be noticed in Fig. 4, during the four adsorption steps, breakthrough curves A, C, E, G, and I had the same appearances. In all cases, the adsorption time remained unchanged after the four consecutive adsorption–ozonation cycles (around 20 min, corresponding to a ratio of $V_{\text{gas}}/V_{\text{cat}}$...
k_{ZSM-5} = 8.20 m^3/kg with C_{out}/C_{in} = 0). The comparison of the breakthrough time before and after the ozonation could be used as an estimate whether the adsorption capacity is recovered. Additionally, an increase in the concentration of toluene in the reactor outlet stream was also observed in Fig. 4, when the regeneration step using ozone was initiated (see curves B, D, F and H). These results were related to the registered increase of the temperature inside the reactor due to ozone reaction with adsorbed toluene, leading to a physical desorption of a fraction of the retained toluene.

Fig. 5 compares the results of five adsorption steps after different operating cycles of adsorption–ozonation. As can be seen, the adsorption breakthrough curves had the same appearance. The slopes had almost the same rate (3 × 10^{-4} m^3 min^{-1} for the 1st and 2nd cycle, 7 × 10^{-4} min^{-1} for the 3rd and 10^{-3} min^{-1} for the 4th cycle). Moreover, the same breakthrough time was found for each adsorption step, being around 57 min at C_{out}/C_{in} = 0.3. The results of the adsorption capacity recovery for each cycle are presented in Table 4 and are determined using the following equation:

\[
\text{RE} = \frac{Q_{\text{ads}}^{A}}{Q_{\text{cycle}}^{A}} \times 100\% \tag{9}
\]

where, RE (%) stands for the adsorption capacity recovery, \(Q_{\text{cycle}}^{A}\) \(\left( g_{C_{6}H_{6}}/g_{ZSM-5}\right)\) represents the amount of adsorbed toluene in the first adsorption step and \(Q_{\text{ads}}^{A}\) \(\left( g_{C_{6}H_{6}}/g_{ZSM-5}\right)\) is the amount of adsorbed toluene in the specified cycle number (nc). The adsorption capacity recovery of ZSM-5 was very good (92%–99%). This high capacity recovery level is not only related to the regeneration of the sites, but also to the fact that adsorption sites are not totally saturated at the end of adsorption step. In addition, breakthrough time remained constant, and the amount of adsorbed toluene after each ozonation step was around 0.012 \( g_{C_{6}H_{6}}/g_{ZSM-5}\).

Table 4 also lists the values of toluene mineralisation factor (MIN). These observed mineralisation values were determined by taking into consideration the stoichiometric ratios in the gaseous reaction between toluene and ozone (see Eq. (10)) and using registered experimental results. Eq. (11) was applied in the estimation of process mineralisation capacity.

\[
6O_3 + C_6H_6 \rightarrow 7CO_2 + 4H_2O \tag{10}
\]

\[
\text{MIN} = \frac{Q_{CO_2}}{Q_{C_6H_6}} \times \frac{1}{7} \times 100\% \tag{11}
\]

where \(Q_{CO_2}\) (mol CO_2/kg ZSM-5) is the amount of CO_2 generated per mass of zeolite and \(Q_{C_6H_6}\) (mol C_6H_6/kg ZSM-5) is the adsorbed amount of toluene after the thermal desorption step. As is shown in Table 4, the process mineralisation capacity was very high, reaching values between 75% and 85%. These results could be related to the three-dimensional structure of zeolite framework with interconnected channels and the proximity between the pores, which allows surface interactions between toluene and ozone (Alejandro et al., 2014; Brodu et al., 2013). ZSM-5 could confine and increases the surface contact between ozone and toluene. Thus, in the presence of ZSM-5 zeolite, adsorbed toluene could be eliminated by a surface reaction mechanism that might include direct interaction with gaseous ozone and indirect reactions with surface radicals generated after ozone adsorption and decomposition at active surface sites of ZSM-5 zeolite.

Fig. 6 shows the evolution in the concentration of CO_2, ozone and toluene at the reactor outlet stream as a function of time during different cycles of AD–OZ treatments. Additionally, the temperature variation of ZSM-5 bed was also presented. During the ozonation steps, the profiles of the outlet concentration of ozone had a form of “S”. The breakthrough time of ozone over the ZSM-5 bed was around 40 min for the four AD–OZ cycles. After that, the outlet concentration of ozone increased rapidly. At the end of the oxidation step, it was found that the outlet concentration of ozone tended to reach the inlet concentration as soon as the concentration of CO_2 decreased and became zero. A peak in the concentration of toluene was registered (3.6 to 4.6 times...
the value of the initial concentration) at the beginning of the experiment. This result could be related to toluene desorption due to the increase on temperature during the oxidation reactions.

The number of mol of ozone consumed per mol of toluene oxidised \((Y_{\text{O}_3/\text{C}_6\text{H}_5})\) and the number of mol of \(\text{CO}_2\) generated per mol of toluene oxidised \((Y_{\text{CO}_2/\text{C}_6\text{H}_5})\) are listed in Table 4. In the 1st cycle, a total amount of 0.133 mol\(\text{C}_6\text{H}_5\text{OH}/\text{kg} \text{ZSM-5}\) were adsorbed on ZSM-5 and only 0.005 mol\(\text{C}_6\text{H}_5\text{OH}/\text{kg} \text{ZSM-5}\) were desorbed. The amount of oxidised toluene was around 0.127 mol\(\text{C}_6\text{H}_5\text{OH}/\text{kg} \text{ZSM-5}\), which was about 97% of the total toluene removed in the AD–OZ system. Similar ratios (92–93%) were obtained in the 2nd, 3rd and 4th cycles. In the 1st, 2nd, 3rd, and 4th AD–OZ cycles, 5.46, 6.12, 6.00 and 5.30 mol of ozone were consumed per mol of toluene oxidised, respectively, indicating that ozone was effectively used in toluene oxidation. These values were comparable to the stoichiometric ratio given by Eq. (10) \((\text{O}_3/\text{C}_6\text{H}_5 = 6/1)\), showing that a significant amount of ozone was necessary for toluene oxidation. The amount of \(\text{CO}_2\) generated per oxidised toluene during the AD–OZ treatment cycles was also investigated. Experimental ratios of 5.5/1, 5.9/1; 5.9/1 and 5.2/1 were found for the 1st, 2nd, 3rd and 4th cycles, respectively. These values were close to the stoichiometric ratio given by Eq. (10) \((\text{CO}_2/\text{C}_6\text{H}_5 = 6/1)\).

![Graph](image)

**Table 4 – Mass balance of toluene ozonation over ZSM-5 zeolite.**

<table>
<thead>
<tr>
<th>Cycles</th>
<th>(Q_{\text{C}_6\text{H}_5}^\text{A}) (mol/kg)</th>
<th>(Q_{\text{C}_6\text{H}_5}^\text{D}) (mol/kg)</th>
<th>(Q_{\text{CO}_2}^\text{D}) (mol/kg)</th>
<th>(Q_{\text{CO}_2}^\text{A}) (mol/kg)</th>
<th>(Q_{\text{C}_6\text{H}_5}^\text{K}) (mol/kg)</th>
<th>(Q_{\text{O}_3}^\text{K}) (mol/kg)</th>
<th>RE (%)</th>
<th>MIN (%)</th>
<th>(Y_{\text{O}_3/\text{C}_6\text{H}_5}) (mol/mol)</th>
<th>(Y_{\text{CO}_2/\text{C}_6\text{H}_5}) (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st cycle</td>
<td>0.133</td>
<td>1.083</td>
<td>0.005</td>
<td>0.700</td>
<td>0.694</td>
<td>0.127</td>
<td>–</td>
<td>79</td>
<td>5.5</td>
<td>5.468</td>
</tr>
<tr>
<td>2nd cycle</td>
<td>0.132</td>
<td>1.444</td>
<td>0.009</td>
<td>0.720</td>
<td>0.75</td>
<td>0.122</td>
<td>99</td>
<td>84</td>
<td>5.9</td>
<td>6.148</td>
</tr>
<tr>
<td>3rd cycle</td>
<td>0.128</td>
<td>1.111</td>
<td>0.010</td>
<td>0.702</td>
<td>0.708</td>
<td>0.118</td>
<td>96</td>
<td>85</td>
<td>5.9</td>
<td>6.003</td>
</tr>
<tr>
<td>4th cycle</td>
<td>0.132</td>
<td>1.028</td>
<td>0.006</td>
<td>0.662</td>
<td>0.667</td>
<td>0.126</td>
<td>99</td>
<td>75</td>
<td>5.2</td>
<td>5.291</td>
</tr>
<tr>
<td>5th cycle</td>
<td>0.123</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>93</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Residence time and the inlet concentration of toluene were 0.16 sec and 0.205 g/m³, respectively.

RE: the adsorption capacity recovery; MIN: mineralisation factor; \(Q_{\text{CO}_2}\): the amount of \(\text{CO}_2\) generated per mass of zeolite; \(Q_{\text{C}_6\text{H}_5}^\text{A}\): the adsorbed amount of toluene per mass of zeolite; \(Q_{\text{C}_6\text{H}_5}^\text{D}\): the total amount of desorbed toluene per mass of zeolite; \(Q_{\text{C}_6\text{H}_5}^\text{K}\): the total applied load of ozone per mass of zeolite; \(Y_{\text{O}_3/\text{C}_6\text{H}_5}\): the number of moles of ozone consumed per mole of toluene oxidised, calculated by the equation \(Y_{\text{O}_3/\text{C}_6\text{H}_5} = \frac{Q_{\text{O}_3}}{Q_{\text{C}_6\text{H}_5}}\).

\(Y_{\text{CO}_2/\text{C}_6\text{H}_5}\): the number of moles of \(\text{CO}_2\) generated per mole of toluene oxidised, calculated by the equation \(Y_{\text{CO}_2/\text{C}_6\text{H}_5} = \frac{Q_{\text{CO}_2}}{Q_{\text{C}_6\text{H}_5}}\);

\(Q_{\text{O}_3}\): the amount of ozone consumed per mass of zeolite, calculated by \(Q_{\text{O}_3} = \int_0^t \frac{\text{C}_{\text{O}_3}}{\text{C}_{\text{O}_3}} \text{d}t\);

\(Q_{\text{C}_6\text{H}_5}^\text{D}\): the amount of oxidised toluene per mass of zeolite, calculated by \(Q_{\text{C}_6\text{H}_5}^\text{D} = Q_{\text{C}_6\text{H}_5}^\text{A} - Q_{\text{C}_6\text{H}_5}^\text{D}\).
C$_2$H$_6$ = 7/1). The strong CO$_2$ production and ozone consumption were indicative of toluene oxidation. Indeed, the formation of trace oxidation by-products such as acetic acid and acetaldehyde was also detected by GC-MS analysis. Their concentrations were much lower than toluene and CO$_2$. These intermediate by-products remained adsorbed on zeolite surface and they could be only indentified after methanol extraction. Such intermediate by-products were also detected by Brodú et al. (2012) after the ozonation of methyl ethyl ketone adsorbed on ZSM-5.

Three main mechanisms have been proposed to describe catalytic ozonation of VOCs (Oyama, 2000; Kasprzyk-Horden et al., 2003). One mechanism indicates that the adsorbed VOC (chemisorbed or physisorbed) could react directly with gaseous oxygen (O$_2$) (after diffusion through the gas film to the zeolite surface). This type of interaction has been proposed for the catalytic ozonation of ethanol over SiO$_2$ (Kastner et al., 2005). Another mechanism suggests that ozone could be adsorbed on the catalyst surface and converted into radicals for subsequent VOC oxidation reactions (Jans and Hoigné, 1998). This reaction mechanism has been also used to describe the interaction of aqueous ozone and activated carbon during the oxidation of organic pollutants in waters during a kind of advanced oxidation process (Jans and Hoigné, 1998; Kasprzyk-Horden et al., 2003). Other research groups suggest that both the VOC and O$_2$ could be adsorbed on the catalyst surface, promoting a surface reaction between the two chemisorbed substances, where O$_2$ decomposes catalytically into surface active oxygen species and subsequently reacts with the chemisorbed VOC (Roscoe and Abbott, 2005; Chao et al., 2007; Brodú et al., 2013; Alejandro et al., 2014; Valdés et al., 2014). Hence, the fact that the observed number of mol of ozone consumed per mol of toluene oxidised was close to the theoretical stoichiometric ratio of O$_2$/C$_2$H$_6$ in the gaseous reaction (6/1), suggests that a surface interaction would mainly occur in the vicinity of the zeolite surface. Ozone in the gas phase could move down into the atmosphere close to the zeolite surface and react with adsorbed toluene molecules, leading to toluene oxidation.

3. Conclusions

In this research, a new process technology that combines adsorption followed by ozone oxidation was studied for controlling toluene emissions from industrial processes and indoor environments. Results obtained in this work showed that toluene adsorption onto ZSM-5 zeolite followed by ozone oxidation could be used as a hybrid process for the control of low levels of VOCs in gaseous streams. Experimental results indicated that the destructive efficiency of toluene vapours was greater than 95% at room temperature. The major oxidation by-products of toluene detected in this study were CO$_2$ and H$_2$O, and no significant secondary products were observed. After five cycles of AD-OZ treatment, there was no evidence of catalytic deactivation of ZSM-5. Hence, the AD-OZ process using ZSM-5 could be effectively applied as an alternative low cost treatment to destroy toxic organic pollutants from industrial emissions.

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