Continuous Photocatalytic Oxidation for Toluene Vapours in a Multi-stage Fluidised Bed

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Abstract
Continuous deduction of toluene vapours in a three-stage gas fluidised bed photoreactor was studied using TiO$_2$ coated activated carbon (AC/TiO$_2$) particles as the fluidising media. The toluene vapour concentration deducted in this work was as high as 1000 ppm. Experimental results showed that when the toluene photocatalytic reaction was diffusion-limited when the gas flow rate was below 10 l/min. The diffusion-limited toluene photocatalytic reaction could double its toluene removal efficiency by coating the photocatalysts on the active carbons. The effectively usage of the UV light in the three-stage system can further improve the toluene removal efficiency for 50%. The usage of a silver reflector outside the reactor column can furthermore increase the toluene removal efficiency for about 10%.

1. Introduction
The fluidised bed reactor provides the photocatalyst with uniform UV light exposure and good contacts to the reactant gas. It also allows good penetration of the UV light into the bed and is therefore a good candidate for the photocatalyst reactions to take place. Although the deduction of volatile organic compounds (VOCs) in a photocatalytic fluidised bed reactor was proposed as early as 1980s, this application suffered from the problem of the slow VOC-photocatalyst mass transferring and hence most operations were low concentration (say few ppb) VOC deductions. The combination of the active carbons with the photocatalysts can effectively increase the local VOC concentration gradients and avoid the excited electron-hole pair recombination. Ao and Lee successfully purified 200 ppb NO stream at high level relative humidity over TiO$_2$ photocatalyst immobilized on active carbon filters. Kuo and Wu studied toluene deduction in a single-stage continuous fluidised bed photo-reactor using TiO$_2$ coated active carbons as the fluidising media. They continuously deduced 200 ppm toluene vapours to meet the toluene emission standards (100 ppm) in Taiwan.

The idea of using “multi-stage” in a fluidised bed reactor design not only has the advantages of uniform inlet gas stream distribution, avoiding particle and gas back mixing, adjusting the gas retention time easily and loading more catalytic particles in a given reactor, but also improves the catalysts light exposure efficiency. It is expected that the combination of the merit of the effective light usage in a multi-stage reactor design and the merits of the effective local mass transfer and electron-hole pair recombination avoidance by TiO$_2$ coated active carbons can significantly improve the continuous VOC degradation. In this work, toluene in the gas stream degraded in a three-stage fluidised bed photo-reactor using TiO$_2$ coated active carbons as the fluidised media was studied.

2. Experimental
The sketch of the experimental system is shown in Fig. 1. The reactor was a quartz glass cylinder of 50 mm internal diameter and 320 mm in length. A 15 W UV lamp was installed at the centre of the reactor with the light wavelength 254 nm. The reactor can be operated in a single-stage mode or in a three-stage mode by inserting stage(s) in the reactor column. In the single-stage experiments, the stage was located 4 cm above the gas distributor. In the three-stage experiments, each stage was 7 cm in height and the lowest stage was also 4 cm above
the gas distributor. The stage sector was a stainless mesh support covered with a screen printing cloth. The image of the three-stage reactor design is shown in Fig. 2.

![Image of reactor design](image)

Fig. 2 The image of the three-stage fluidised bed photo-reactor system.

The experimental method and method for the preparation of the titanium dioxide coated activated carbon (TiO₂/AC) as fluidising media were the same as those in the work of Kuo and Wu. The toluene removal efficiency was defined as,

\[
toluene \text{ removal (\%)} = \frac{\text{inlet toluene concentration} - \text{outlet toluene concentration}}{\text{inlet toluene concentration}}
\]

3. Results and Discussions

Table 1 shows the toluene removal efficiencies at different gas flow rates in the single-stage reactors using TiO₂ coated 150 μm glass bead particles as the fluidising media at 25°C with the inlet toluene concentration 1000ppm and relative humidity 30%. The toluene removal efficiency decreased when the gas flow rate increased from 3 L/min to 20 L/min. The reactor system was assumed to be a perfect mixed reactor and the dimensionless overall toluene deduction rate in Table 1 was estimated by the reduction of the toluene concentration before and after the reactor times the gas volumetric flow rate.

<table>
<thead>
<tr>
<th>Gas volumetric flow rate ((V_0)) [L/min]</th>
<th>3</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene removal efficiency [%]</td>
<td>8</td>
<td>7</td>
<td>5</td>
<td>3</td>
<td>1.5</td>
</tr>
<tr>
<td>Dimensionless overall toluene deduction rate ((-r_A')) [-]</td>
<td>240</td>
<td>350</td>
<td>500</td>
<td>450</td>
<td>300</td>
</tr>
</tbody>
</table>

The catalytic toluene degradation reaction is a catalytic reaction in nature and may be a diffusion-limited reaction or a reaction-limited reaction. We proposed that the surface reaction is so rapid that the rate of diffusion of the reactant to the catalyst surface limits the overall...
reaction rate. Under this circumstance, the overall toluene deduction rate \((-r_A)\) is controlled by the toluene mass transferring from the bulk to the catalyst surface,

\[ -r_A \approx k_c C_A \]  

(2)

where \(C_A\) is the toluene concentration in the bulk (ppm) and \(k_c\) is the mass transfer coefficient (cm/s) and may be estimated by the high Reynolds number Frössling correlations\(^8\),

\[
\frac{k_c d}{D_{AB}} = 0.6 \left( \frac{dU}{v} \right)^{1/2} \left( \frac{v}{D_{AB}} \right)^{1/3}
\]  

(3)

where \(d\) is the particle diameter (cm); \(D_{AB}\) is the gas diffusivity (cm\(^2\)/s); \(U\) is the superficial gas velocity (cm/s); \(v\) is the kinematic viscosity (cm\(^2\)/s).

Combining equations of (2) and (3), we obtain

\[ -r_A \approx \frac{D_{AB}}{d} 0.6 \left( \frac{dU}{v} \right)^{1/2} \left( \frac{v}{D_{AB}} \right)^{1/3} C_A \propto \left( \frac{U}{d} \right)^{0.5} C_A \]  

(4)

With the same inlet toluene concentration and photocatalyst sizes, the diffusion-limited toluene degradation reaction should show that the overall toluene deduction rate being proportional to square root of the superficial gas velocity.

Fig. 3 shows the relation between the dimensionless overall toluene deduction rate and the square root of the gas volumetric flow rate. The result indicated that the catalytic toluene degradation reaction in our system was diffusion-limited when the gas volumetric flow rate was below 10 l/min. Hence, if one wants to improve the toluene removal efficiency, one may intend to increase the local concentration gradient from the bulk to photocatalyst surface when the gas volumetric flow rate is below 10 l/min.

The proposed toluene degradation reaction mechanism is schematically shown in Fig. 4.

Toluene vapour is firstly adsorbed on the AC particles quickly and then being mass transferring to the photocatalyst TiO\(_2\) active sites, conducting the photocatalytic degradation reaction rapidly. Therefore, the better performance of AC/TiO\(_2\) than AC or TiO\(_2\) in the photocatalytic
reaction was attributed to the increasing of the local toluene concentration gradient during the mass transferring to photocatalyst TiO₂ active sites step.

Fig. 5 shows the measured toluene removal efficiencies in the single-stage system with different toluene inlet concentrations using active carbons (AC) or titanium dioxide coated active carbons (AC/TiO₂) as the fluidising media. The effective operating time (i.e., degraded toluene concentration was less then 100 ppm) was improved for approximately 130-137% using AC/TiO₂ particles compared to using AC particles in the single-stage fluidised bed photo-reactor in the toluene concentration range between 250 ppm and 1000 ppm. The toluene removal efficiency improved to approximately 15% when the volumetric gas flow rate 10 l/min.

The toluene removal efficiency was doubled when comparing to the similar condition in Table 1. The improvement in the toluene local toluene concentration gradient was from the adsorption saturated active carbons, which leaded to a much higher toluene concentration than that in the bulk. Coating TiO₂ on active carbons can effectively increase the toluene removal efficiency due to the increasing in the toluene local concentration gradient.

When AC/TiO₂ (20g/3g) particles fluidised in the single-stage reactor column, the bed height was only 1/3 length of the UV-lamp and 2/3 of the ultraviolet light exposure region was not effectively used. In order to effectively use the light exposure in the reactor, the three-stage fluidised bed photo-reactor system was used. The toluene removal efficiencies in a three-stage fluidised bed system with different amount of AC/TiO₂ loadings are shown in Fig. 6.

Compared to the steady state toluene removal efficiency obtained in the single-stage system (~15% toluene removal efficiency in Fig. 6), the steady state toluene removal efficiency in the three-stage systems improved the toluene removal efficiency to 22% when loading the same amount of catalysts on each stage. The efficiency improved only 50% when loading three times of AC/TiO₂ particles in the system. This is not as good as expected. This was probably due to the fact that adding too many particles in a stage leads to the “light blockage” and prevented the light further penetrating into the fluidised bed. The results in Fig. 6 show that loading AC/TiO₂ (15g/2.25g) at each stage could reach the best toluene removal efficiency in the experimental conditions tested. The steady state toluene removal efficiency could reach 26%.

In Figs. 3 and 5, we have demonstrated that the diffusion-limited toluene photocatalytic reaction could double its toluene removal efficiency by coating the photocatalysts on the
active carbons. In Fig. 6, we also showed that the effectively usage of the UV light can further improve the toluene removal efficiency 50%.

To further improve the light usage efficiency, the white reflector and silver reflector used in a typical LCD backlight unit were applied to the reactor wall. The silver reflector covered outside the reactor column, avoided light leakage from the system, and increased the toluene removal efficiency about 10% in both single-stage system and three-stage system as shown in Fig. 7. Using the silver reflector improved the toluene removal efficiency about 5% higher than the improvement using the white reflector.

4. Conclusions
Continuous deduction of toluene vapours in a three-stage gas fluidised bed photoreactor was studied using TiO$_2$ coated activated carbon (AC/TiO$_2$) particles as the fluidising media. The effective toluene deduction duration (according to the Environment Pollution Regulation in Taiwan) was improved for approximately 130-137% using AC/TiO$_2$ particles as the fluidising media compared to that using AC particles as the fluidising media in the single-stage fluidised bed photoreactor with the gas flow rate between 3 and 15 L/min and the toluene vapour concentration between 250 ppm and 1000 ppm.

Experimental results showed that when the toluene photocatalytic reaction was diffusion-limited when the gas flow rate was below 10 l/min. The deducting mechanisms were proposed. The diffusion-limited toluene photocatalytic reaction could double its toluene removal efficiency by coating the photocatalyst on the active carbons. The better performance of using AC/TiO$_2$ as the fluidising media than using TiO$_2$ as the fluidising media was attributed to the increasing of the local toluene concentration gradient.

The effectively usage of the UV light in the three-stage system improved the toluene removal efficiency for only 50%. It was probably to due the fact that adding too many particles in a stage blocked the light penetration into the bed. Adding AC/TiO$_2$ (15g/2.25g) at each stage could reach the steady state toluene removal efficiency to 26% with 1000 ppm inlet toluene concentration. The usage of a silver reflector outside the reactor column can furthermore increase the toluene removal efficiency for about 10%.

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References

