Removal of hydrophobic volatile organic compounds with sodium hypochlorite and surfactant in a co-current rotating packed bed

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ABSTRACT

A co-current flow rotating packed bed was applied to remove volatile organic compounds (VOCs) by sodium hypochlorite (NaClO) and surfactant (sodium dodecyl benzene sulfonate, SDBS) from air stream. Xylene was used as a model VOC herein. The effect of pH, concentration of NaClO and SDBS solution, liquid flow rate, gas flow rate and rotational speed on xylene removal efficiency and overall mass transfer coefficient ($K_{Ga}$) were discussed. Then, a correlation for $K_{Ga}$ of the co-current rotating packed bed was proposed by fitting the experimental data of $K_{Ga}$ and independent variables of liquid/gas ratio, rotational speed, pH, NaClO concentration and treatment time, which was in good agreement with the experimental data (the deviation ≤ ±30%).

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Introduction

Volatile organic compounds (VOCs) emitted from chemical process industries (CPI), automobile exhaust and cooking oil fumes (COFs) have caused serious environmental problems and health concerns, such as photochemical smog, ozone generation, and carcinogenesis. (Atkinson and Arey, 2003; Schauer et al., 2002; Selke et al., 1977; Wei et al., 2014). Many methods (e.g., condensation, membrane separation, catalytic oxidation, absorption and adsorption) have been used for VOC treatment. Among them, absorption has been considered to be a safe, effective and economical method (Chen and Liu, 2002; Li et al., 2015; Parthasarathy and El-Halwagi, 2000; Yang et al., 2011; Yeom et al., 2002). Traditional packed beds are widely used in VOC absorption, however, their poor mass transfer efficiency and large occupied area lead to high cost in operating, thus the development of the traditional packed beds is largely restricted (Murugesan and Sivakumar, 2002; Silverberg, 1996). As a result, to design a device with high mass transfer, small occupied area and low gas pressure drop are of great importance to response to “process intensification”.

A rotating packed bed (RPB), which was first invented by Ramshaw and Mallinson (Ramshaw and Mallinson, 1981), could enhance the efficiency of mass transfer through tearing liquids into smaller droplets, and thinner films with a centrifugal force to decrease mass transfer resistance and increase gas–liquid interfacial area. RPBs have already been applied to several fields of chemical industry, such as absorption (Lin et al., 2003; Qian et al., 2012; Zhang et al., 2011), distillation (Lin et al., 2002; Wang et al., 2008), stripping...
(Chen et al., 2005; Singh et al., 1992), ozone oxidation (Ko et al., 2011; Zeng et al., 2012), and synthesis of nano-materials (Lin et al., 2012; Sun et al., 2011).

Pressure drop is one of the most important parameters to evaluate the performance of a RPB. Liu et al. (1996) used water–air system to study the pressure drop of a counter-current flow RPB, whose results indicated that the pressure drop in dry bed increased with the rotational speed, but decreased with the rotational speed when liquid was introduced to the rotor. It has been reported by Guo et al. (1997) that the gas pressure drop of a cross-flow RPB in the dry bed was not influenced by the rotational speed, and was proportional to the liquid flow rate, proportional to the square of gas flow rate and also inversely proportional to centrifugal acceleration in wet bed. The study by Li and Hao (2013) indicated that gas pressure drop of a co-current flow RPB increased with the increase of gas flow rate, decreased with the increase of liquid flow rate and rotational speed, it had much lower gas pressure drop when compared with counter-current flow RPB. Therefore, co-current flow RPBs are suitable for treating VOC-containing waste gas with low pressure drop in restaurant cooking fume exhaust and roof exhaust of painting workshop.

Among numerous reports of RPBs, counter-current flow and cross-flow RPBs have been widely applied for VOC absorption (Chen et al., 2008; Chiang et al., 2012; Hsu and Lin, 2011, 2012; Lin and Chien, 2008; Lin et al., 2006, 2009). However, co-current flow RPBs were rarely reported for VOC absorption despite its obvious merit that low pressure drop is demanded. Moreover, the fresh absorption liquid in the reported RPB-systems was exhausted after gas-liquid mass transfer and no more recycling, resulting in a huge equipment with at least two liquid tanks and not full utilizing of absorption liquid. Accordingly, in the view of process intensification and cost-effect, design of a co-current RPB with recycling of absorption liquid in a circulating liquid tank can simplify the equipment and reduce energy consumption, which may be more suitable for industrial application.

In this work, a novel co-current flow RPB with a circulating liquid tank was designed and applied for xylene absorption. Sodium hypochlorite (NaClO) and surfactant (sodium dodecyl benzene sulfonate, SDBS) were used as oxidant and absorbent (Cheng and Hsieh, 2010). Xylene removal efficiency ($E$) and overall mass transfer coefficient ($K_{G,a}$) were discussed with the effect of pH, concentration of NaClO and SDBS solution, liquid flow rate, gas flow rate and rotational speed. In addition, a correlation for $K_{G,a}$ of the co-current RPB was proposed by fitting the experimental data of $K_{G,a}$ and independent variables of liquid/gas ratio, rotational speed, pH, NaClO concentration and treatment time. The results in this paper casted some light on applying co-current RPB for waste gas treatment which demands low pressure resistance.

1. Materials and methods

1.1. Chemicals

The pH was adjusted by sulfuric acid ($H_2SO_4$, 96%) purchased from Beijing Chemical Works. NaClO (10%) was obtained from Tianjin Guangfu Fine Chemical Research Institute. SDBS ($C_{12}H_{25}SO_3Na$, SDBS) was purchased from Tianjin Fuchen Chemical Reagents Factory.

1.2. Reactor

In this work, the co-current flow RPB equipped with random stainless steel wire mesh packing has an inner radius of 3.2 cm, an outer radius of 11.0 cm, and an axial height of 6.5 cm. The rotor is fixed into a cylindrical circulated liquid tank, which has a diameter of 36 cm, a height of 25 cm and a total volume of 25 L. The liquid distributor consists of a tube which contains four set of holes, and each set has three holes of 0.4 cm diameter with 0.6 cm distance between holes in a vertical direction. A baffle is introduced near the rotor to make the liquid which came out from rotor fall into the bottom of the liquid tank and mix with fresh liquid, then pump into the rotor again.

1.3. Experimental section

Fig. 1 briefly describes the experimental process of xylene treatment. A high purity nitrogen stream (99.99%) of a low flow rate passed through a bubbler containing xylene, which was diluted to a desired concentration (120 ppmv) by compressed air. The xylene solution was added to a gas inlet and then gasified in a gas bubbler. The gas stream containing xylene was introduced into a gas inlet of the RPB. The rotating speed of the rotor was set up to 250 rpm. The gas and liquid flow rates were controlled by rotameters. The gas outlet was connected to a rotameter and vacuum pump. The outlet gas stream containing xylene was collected and measured for xylene concentration. The liquid outlet was connected to a liquid distributor and recycled back into the reactor. The experiments were conducted at different pH values, NaClO concentrations, SDBS concentrations, liquid flow rates, gas flow rates and treatment times.

![Fig. 1 – Schematic diagram of a co-current RPB for VOC treatment. RPB: rotating packed bed; VOC: volatile organic compound.](image-url)
air. The xylene-air stream of desired concentration from gas inlet was introduced into the RPB, and then traveled through the inner edge to the outer edge of the packed bed. The absorption liquid was sprayed into the packing through the liquid distributor, then xylene-air stream and liquid stream contacted co-currently with mass transfer in the RPB. Finally, the liquid containing xylene was threw toward the baffle and fell into the circulating liquid tank. The rotational speed varied from 500 to 1100 r/min, providing 21–105 times gravitational acceleration based on the arithmetic mean radius. The gas flow rate was 0.8, 1.0 and 1.2 m3/hr, and the liquid flow rate was 250, 500 and 650 mL/min. The volume of circulated fluid was maintained 3 L. The controlled pH in NaClO solution were 4.5, 5.5, 6.5, 7.5 and 8.5. The concentrations of SDBS surfactant were 0, 5 and 10 mmol/L. The xylene concentration in xylene-air stream was detected by an on-line spectrometry, SPIMS-1000).

2. Result and discussion

2.1. Removal efficiency and overall volumetric gas-side mass transfer coefficient

The removal efficiency of xylene in a co-current flow RPB is defined as follows:

\[ E = \frac{C_{g0} - C_{gi}}{C_{g0}} \times 100\% \]  

(1)

where \( E \) is the removal efficiency of xylene, \( C_{gi} \) and \( C_{g0} \) are the xylene concentration in inlet and outlet xylene-air stream (ppmv), respectively. The value of \( E \) was obtained under different operating conditions, including pH of the solution, gas flow rate, liquid flow rate, rotational speed, concentration of NaClO and SDBS.

Based on mass balances, the overall volumetric gas-side mass transfer coefficient \((K_{Ga})\) of the co-current flow RPB for xylene absorption can be determined by the following equation (the detailed explanation to obtain the \( K_{Ga} \) in Eq. (2) is given in the Appendix):

\[ K_{Ga} = \frac{G}{\pi (R_{i}^2 - R_{o}^2)Z_{0}} \frac{1}{1 + \frac{1}{A}} \ln \frac{C_{g0} - C_{gi} - HC_{li}}{C_{g0} - C_{gl} - HC_{li}} \]  

(2)

where \( C_{li} \) (ppm) is the hydrophilic organic compounds’ concentration in inlet liquid phase. \( Z_{0}(m) \) is the axial length of the RPB, \( R_{i} \) (M) and \( R_{o} \) (m) are the inner and outer radius of the RPB. The absorption factor \( A \) is defined as \( L/HG \) (dimensionless), where \( L \) (m/sec) is the volumetric flow rate of liquid, \( G \) (m³/sec) is the volumetric flow rate of gas, \( H \) is the Henry’s law constants, which value is 0.25 for xylene (Noonan and Curtis, 1990). To evaluate the mass transfer performance of the co-current RPB for VOC-removal, the value of \( K_{Ga} \) was calculated by Eq. (2) at various values of \( C_{g0}, C_{go}, C_{li}, L \) and \( G \).

2.1.1. Effect of the solution pH

Fig. 2 shows the value of \( E \) and \( K_{Ga} \) at different pH ranged from 4.5 to 8.5. The results indicate that the xylene removal efficiency and overall volumetric gas-side mass transfer coefficient increase with lower pH, but the distinction of \( E \) and \( K_{Ga} \) around pH 6.5 is not obvious. These phenomena ascribe that HClO is easier to form at low value of pH, which has high oxidation ability. Therefore, the aqueous chlorine solution that contained strong oxidant HClO could react with xylene, which transforms into water soluble organic compounds afterwards. The value of \( E \) and \( K_{Ga} \) decreases as time goes on, because of the consumption of NaClO in the circulated liquid. Obviously, lower pH is conducive to removal efficiency and gas-liquid mass transfer, but has corrosive effect to the RPB equipment. As shown in Fig. 2, to keep higher removal efficiency and gas-liquid mass transfer and lower corrosion, pH 6.5 is suitable for the following experiment, which is also in agreement with Cheng’s report (Cheng and Hsieh, 2010).

2.1.2. Effect of liquid flow rate

Effect of liquid flow rate on xylene removal efficiency and overall volumetric gas-side mass transfer coefficient is shown in Fig. 3, respectively. At fixed gas flow rate of 1.0 m³/hr and rotational speed of 500 r/min, the removal efficiency increases along with the increase of liquid flow rate, the same result is observed on \( K_{Ga} \). This ascribes to the fact that the increasing liquid flow rate wets steel wire mesh packing effectively, and enlarges the contact interface of gas-liquid, as shown in the dashed box of Fig. 3a, which are in favor of the gas-liquid mass transfer and removal efficiency.
2.1.3. Effect of gas flow rate
Fig. 4 shows the value of removal efficiency and overall volumetric gas-side mass transfer coefficient as a function of treatment time with different gas flow rate of 0.8, 1.0 and 1.2 m³/hr. It is obvious that the removal efficiency decreases with the increasing of gas flow rate. This ascribes that an increasing gas flow rate reduces the contact time of gas and liquid, so gas-liquid two-phase does not react adequately and leaves the packing zone quickly.

The tendency of $K_Ga$ at different gas flow rate can be observed in Fig. 4b. Before the treatment time of the second minute, the value of $K_Ga$ increased along with the increase of gas flow rate. On the contrary, after the second minute, the value of $K_Ga$ decreased with the increase of gas flow rate. The gas-liquid mass transfer efficiency is the result of the interaction of mass transfer rate combined with contact time. When fresh liquid absorbed xylene, mass transfer rate was predominant, so higher gas flow rate was in favor of gas-liquid mass transfer, it was in agreement with counter-current flow RPB (Lin et al., 2010). As treatment time went on, the absorption liquid was close to saturation, mass transfer rate decreased and contact time was predominant, the larger gas flow rate, the shorter gas-liquid contact time, which went against mass transfer, thus the value of $K_Ga$ decreased with the increase of gas flow rate as time went on.

2.1.4. Effect of NaClO concentration
Effect of various NaClO concentrations on xylene removal at pH 6.5 is shown in Fig. 5. It is clear that the duration on xylene removal of 500 ppm NaClO concentration is twice than the blank experiment, which is without adding NaClO. The aqueous solution of NaClO could react with xylene (Chakraba and Kretschm, 1974). The first step was that NaClO directly oxidized xylene, and the second step was that NaClO formed strong oxidizing HClO in acid condition, xylene could also be oxidized by HClO. Therefore, the removal efficiency and overall volumetric gas-side mass transfer coefficient increased with higher concentration of NaClO.

2.1.5. Effect of SDBS concentration
Surfactants lower the surface tension of NaClO aqueous solution and enhance the ability of removing organic compounds (Cameron, 1986; Clarkson et al., 2006). Therefore, the presence of SDBS increases the solubility of xylene, and the oxidation reaction carries out simultaneously. The value of removal efficiency and overall volumetric gas-side mass transfer coefficient as a function of treatment time with different concentration of SDBS is shown in Fig. 6. The value of $E$ and $K_Ga$ does not exhibit a significant difference among 5 and 10 mmol/L concentrations of SDBS. That is because the surface of solution has already reached the saturation state.
when SDBS concentration surpasses the critical micelle concentration (CMC, 1.5 mmol/L) (Ni et al., 2014), and forms hydrophilic micelle, which has no surface activity.

2.1.6. Effect of rotational speed

As shown in Fig. 7, the xylene removal efficiency and overall volumetric gas-side mass transfer coefficient improve along with the increase of rotational speed ranged from 500 to 900 r/min. However, after reaching 1100 r/min, the value of \( E \) and \( K_{Ga} \) decreases significantly when compared with lower rotational speed. In the range of 500 to 900 r/min, increasing the rotational speed offered a higher centrifugal force which resulted in thinner liquid film and smaller droplets, and reduced the mass transfer resistance. The surface renewal rate accelerated, and thus enhanced the gas–liquid mass transfer. After 1100 r/min gas–liquid contact time affected the mass transfer tremendously. Basing on the co-current flow, gas and liquid are along the same direction into the stainless steel wire mesh packing. When a high rotational speed was introduced, liquid stream left the packing more quickly compared with low rotational speed, this meant the drop-tear effect of packing was underutilization, thus the shorter contact time from high rotational speed resulted in lower value of \( E \) and \( K_{Ga} \).

Therefore, from the above results, the removal efficiency is related with mass transfer and contact time. Actually, the higher mass transfer coefficient means lower mass transfer resistance for VOC absorption process, resulting in higher removal efficiency. However, the shorter contact time goes against the full contact between VOCs and absorbent, resulting in lower removal efficiency.

2.2. \( K_{Ga} \) correlation in the RPB

A correlation for \( K_{Ga} \) of the co-current RPB was proposed. The dependent variable of \( K_{Ga} \) is related to the independent variables of liquid/gas ratio, rotational speed, pH, NaClO concentration and treatment time. The correlation of \( K_{Ga} \) was obtained from the linear regression of experimental data of \( K_{Ga} \) and independent variables, as shown in Eq. (3).

\[
K_G^\alpha = 8.5173 \left( \frac{L}{G} \right)^{1.2357} \cdot N^{-0.2783} \cdot t^{1.2783} \cdot pH^{-0.2351} \cdot C_{NaClO}^{0.0346} \tag{3}
\]

Fig. 8 shows the experimental values of \( K_{Ga} \) lie within ±30% of the values estimated by Eq. (3). From Eq. (3), the values of \( K_{Ga} \) are proportional to \( L/G \) ratio and \( C_{NaClO} \), inversely proportional to rotational speed (greater than 900 r/min), treatment time and pH, which are in accordance with the experimental results.
3. Conclusions

This study has examined the performance of co-current RPB for xylene treatment. Xylene removal efficiency (E) and overall mass transfer coefficient ($K_{Ga}$) were discussed under different conditions by using NaClO and surfactant (SDBS) as absorption liquid. As expected, pH, NaClO concentration, liquid flow rate, gas flow rate, rotational speed and treatment time can affect the overall mass transfer coefficient ($K_{Ga}$) obviously. Moreover, the values of $K_{Ga}$ are the result of the interaction between different variables and residence time of xylene-air stream. Also, a correlation for $K_{Ga}$ of the co-current RPB was developed by fitting the experimental data of $K_{Ga}$ and independent variables of liquid/gas ratio, rotational speed, pH, NaClO concentration and treatment time, which coincided with the experimental data well, and the deviation lay within ±30%.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2016.12.009.

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