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# Simultaneous removal of ethyl acetate and ethanol in air streams using a gas–liquid–solid three-phase flow airlift loop bioreactor

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**Abstract**

A gas–liquid–solid three-phase flow airlift loop bioreactor was applied to treat air streams containing a mixture of ethyl acetate and ethanol. The activated sludge was replaced by biological membrane in the experiment. The influences of pH and jet waste gas influx on the removal efficiency and outlet ethyl acetate and ethanol mixture concentration were investigated. The optimum pH and jet waste gas influx were 6.0 and 4.4 m/s, respectively. Under the optimum operation conditions, the average removal efficiencies of ethyl acetate and ethanol in the mixture were higher than 98%, and accordingly, the outlet concentrations of ethyl acetate and ethanol were lower than 150 mg/m$^3$. The elimination capacities of ethyl acetate (504 g/m$^3$/h) or ethanol (685 g/m$^3$/h) in the mixture as two mixture pollutants, which were higher than those in biofilters (ethyl acetate 400 g/m$^3$/h and ethanol 195 g/m$^3$/h) reported in the literatures [Y.H. Liu, X. Quan, Y.M. Sun, J.W. Chen, D.M. Xue, J.S. Chung, Simultaneous removal of ethyl acetate and toluene in air stream using compost-bases biofilters, J. Hazard. Mater. B 95 (2002) 199–213; D. Arulneyam, T. Swaminathan, Biodegradation of ethanol vapour in a biofilter, Bioprocess Eng. 22 (2000) 63–67], were also higher than those of pure ethyl acetate (480 g/m$^3$/h) or ethanol (671 g/m$^3$/h) as single pollutant in gas–liquid–solid three-phase flow airlift loop bioreactor.


*Keywords:* Gas–liquid–solid three-phase flow; Airlift loop bioreactor; Ethyl acetate; Ethanol; Volatile organic compounds (VOCs)

## 1. Introduction

Volatile organic compounds (VOCs) are common pollutants produced by a variety of industries and their emissions are facing increasingly stringent environmental regulations [1]. There are mainly three methods of VOCs treatment, biochemical method (biofilters, bioscrubbers, activated sludge), chemical method (chemical scrubbers, thermal oxidation, catalytic oxidation, ozonation) and physical method (condensation, adsorption of activated carbon, absorption such as clean water scrubbers). VOCs from industry have traditionally been treated using physical or chemical processes, including scrubbing, adsorption, condensation, oxidation and so on. Biological treatment of VOCs has only gained support as an effective and economical option in the past few decades. Biological methods of VOCs treatment were paid much attention in Europe in the 1990s owing to their efficiency, cost-effectiveness, and environmental acceptability, and by 1994 accounted for 78% of odour treatment in Germany [2].

In all types of bioreactors for waste gas treatment, the pollutants diffuse into the liquid phase where microorganisms degrade them into products, such as $CO_2$, $H_2O$, and minerals [2]. The two most promising biorectors for air pollution control are biofilters and biotrickling filters. Biofilters are essentially compost beds through which the contaminated air is passed [3–6]. The contaminants are absorbed and degraded by naturally occurring mixed cultures immobilized on the packing. Biotrickling filters work in a similar manner to biofilters, except that an aqueous phase is trickled over the packing, and that the packing is usually made of some

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**Nomenclature**

| | |
|---|---|
| $C_{in}$ | the inlet concentration (mg/m$^3$) |
| $C_{out}$ | the outlet concentration (mg/m$^3$) |
| EBRT | the empty bed retention time (s) |
| EC | elimination capacity of ethyl acetate (g/m$^3$/h) |
| $L$ | bulk load (g/m$^3$/h) |
| $Q_g$ | flow rate of waste gas stream (m$^3$/h) |
| RE | removal efficiency (dimensionless) |
| $V_e$ | the effective volume of the bioreactor (m$^3$) |

synthetic or inert material, like plastic rings, open pore foam, or lava rock. The trickling solution contains essential inorganic nutrients such as nitrogen, phosphorous, and potassium, and is usually recycled [7–9]. Recently, airlift bioreactors with microorganisms suspended in the liquid phase indicated their great potential for biopurification of VOCs [10]. None is known, however, about the research on treating missions containing ethyl acetate and ethanol in gas–liquid–solid three-phase flow airlift loop bioreactor containing immobilized cells, characterized by higher operational flexibility, shorter reaction time and greater processing capability.

Cell immobilization is an attractive technique to fix and retain biomass on suitable natural or synthetic materials support for biopurification of waste water or waste gas [11–13]. Despite the fact that the suspended-cell system allows better contact with the substrates, the cell immobilization technique has many advantages including biomass retention within the working environment, less environmental impact, relatively high vitality and local cell density and process efficiency. Due to its advantages of ease of preparation, biocompatibility and capability to retain cells by entrapment in its fine pores, activated charcoal has been used extensively in cell immobilization for biotreatment of waste water and waste gas.

The purpose of this study is to investigate the capability of gas–liquid–solid three-phase flow airlift loop bioreactor containing immobilized-cells on treating gas stream containing a mixture of ethyl acetate and ethanol. In addition, the elimination capacity of two-composition in-gas system was compared with sole-composition in-gas system.

## 2. Materials and methods

### 2.1. Airlift loop bioreactor

The schematic diagram of the airlift loop bioreactor was shown in Fig. 1. A 400 mm high Perspex draft tube (9) of 25 mm in diameter was fixed concentrically inside the main 650 mm high Perspex reactor tube of 55 mm in diameter. Accordingly, the ratio of the cross-sectional area of the riser to the reactor is 0.2066. A concentric jet nozzle (10) of 2 mm was designed and located in the bottom of the riser. The growing medium, stored in reservoir (17), was pumped into the

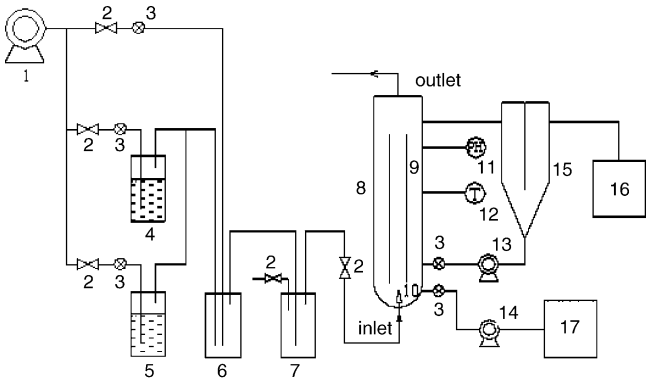


Fig. 1. Schematic diagram of the apparatus.

downcomer of the reactor using a micropump (13). During the experiment, the airlift loop bioreactor was operated with a liquid flow rate of 100 ml/h, correspondingly 0.091 h$^{-1}$ of dilution rate. All the experiments were performed at atmospheric pressure and the temperature of the liquid was maintained around 30 ± 0.1 °C by the temperature controlled system (12) consisted of a coil with cold water and an electric heater coupled with a constant thermometer. The pH was adjusted by a controlled system (11), consisting of a pH-meter and micropumps supplying base or acid as required. The liquid flow rate was controlled by the micropump (14). The role of baffle plate separator (15) was to separate the carriers from the liquid in the effluent leaving the reactor and then the carriers were sent back to the reactor by the micropump (13). The waste gas stream with the mixture of ethyl acetate with initial concentration of 8000 mg/m$^3$ and ethanol with initial concentration of 8000 mg/m$^3$, simulated the waste gas exhausted by pesticide industry, was produced by blowing air through two water-bathed vessels containing liquid ethyl acetate (4) and liquid ethanol (5), respectively. The concentration of the waste gas was controlled by the flux of air stream and the temperature of the water bath. Air was mixed with the air streams carrying ethyl acetate and ethanol in the mixer (6) then in the buffer (7) which could mix the air streams better and keep the concentrations of the waste gases unchanging when the gas influx was changed. Then the air stream was fed to the bioreactor through the jet nozzle (10).

### 2.2. Culture medium

The composition of the nutrients used for microbial cultivation was given in Table 1 [14].

### 2.3. Adaptations and immobilization

For the adaptation, a 1000 ml flask containing culture medium was seeded with activated sludge obtained from a local municipal wastewater treatment plant. The pH varied

Table 1
Nutrients used for microbial cultivation [14]

| Compound | Concentration (mg/l) | Compound | Concentration (mg/l) |
|---|---|---|---|
| $(NH_4)_2SO_4$ | 2500 | $CuSO_4{\cdot}5H_2O$ | 2.5 |
| $KH_2PO_4$ | 2500 | $NaMoO_4{\cdot}2H_2O$ | 0.4 |
| $CaCl_2{\cdot}2H_2O$ | 58.8 | $MnCl_2{\cdot}4H_2O$ | 4 |
| $MgSO_4$ | 240 | $H_3BO_4$ | 1.5 |
| $FeCl_3{\cdot}6H_2O$ | 27 | $CoCl_3{\cdot}6H_2O$ | 0.4 |
| $ZnSO_4{\cdot}7H_2O$ | 25 | $FeSO_4{\cdot}7H_2O$ | 7.6 |

in the range of 6.5–7.0 and the temperature was maintained between 25 and 30 °C. The mixture of waste gas stream was introduced into the flask. After 10–15 days, the quantity of the activated sludge increased obviously, and the removal efficiencies of the flask for both ethyl acetate and ethanol reached 99%, in contrast to the initial removal efficiencies, below 5%. In the following 2 days, no obvious decrease in removal efficiency of ethyl acetate or ethanol was observed, and then the adaptation was completed. Then 100 g activated charcoal with the average diameter of 0.2 mm was put into the flask for film-forming culture. The culturing was continued until the steady-state biomass loading on the activated charcoal was achieved. After 10 days, most free bacteria film was clung to the activated charcoal. At last, the activated charcoal was moved out and put into the airlift loop bioreactor described earlier.

### 2.4. Analytical method

Both ethyl acetate concentration and ethanol concentration in the air streams were examined using a gas chromatograph (GC9800, Shanghai, China) equipped with a flame ionization detector (FID). The inlet and outlet gases were sampled through a six-path valve connected with the gasification chamber. Oven temperature was 60 °C, while the injector and FID detector temperatures were 130 and 200 °C, respectively.

COD was analyzed by dichromate method according to GB 11914-89 of PR China. Nitrate and nitrite were measured using the ion chromatography method by selecting Shimpack IC-A3 as chromatographic column, 8.0 mM *p*-hydroxy benzoic acid and 3.2 mM bis-Tris as mobile phase, and CDD-6A, 3.2 mS/cm FS as conductivity detector.

## 3. Results and discussion

Bulk VOCs elimination capacities of the gas–liquid–solid three-phase flow airlift loop bioreactor were measured as a function of VOCs influent concentrations and loads. Bulk load ($L$), elimination capacities (EC), and removal efficiencies (RE) of ethyl acetate were calculated as follows:

$$L = \frac{3.6C_{\text{in}}}{\text{EBRT}}$$

$$\text{EC} = \frac{3.6(C_{\text{in}} - C_{\text{out}})}{\text{EBRT}}$$

$$\text{RE} = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\%$$

where 3.6 was a conversion factor that converted mg to g and s to h. Therefore, EC and $L$ were in unit of g of the pollutant per $m^3$ of medium and per h ($g/m^3/h$). The inlet and outlet concentrations, $C_{\text{in}}$ and $C_{\text{out}}$, were measured in $mg/m^3$. The empty bed retention time (EBRT) was

$$\text{EBRT} = \frac{3600V_{\text{e}}}{Q_{\text{g}}}$$

and the unit of EBRT was s.

### 3.1. Effect of pH

pH is an important effect factor in the biological air pollution control technology. Fig. 2 illustrated the influences of different pH on the removal efficiency and the outlet concentrations of ethyl acetate and ethanol at the same of waste gas jet waste gas influx of 4.4 m/s. It could be observed that the removal efficiency of ethyl acetate increased remarkably and the removal efficiency of ethanol decreased slightly with the increase in pH for pH lower than 6.0. However, the removal efficiency of ethanol decreased remarkably, and the removal efficiency of ethyl acetate decreased slightly with the increase in pH for pH higher than 6.0. Therefore, the optimum pH was selected as 6.0.

### 3.2. Effect of jet waste gas influx

The typical results of the removal efficiency and the outlet concentration of ethyl acetate and ethanol as a function of the jet waste gas influx at the given pH value of 6.0 were illustrated in Fig. 3. It was seen that the jet waste gas in-

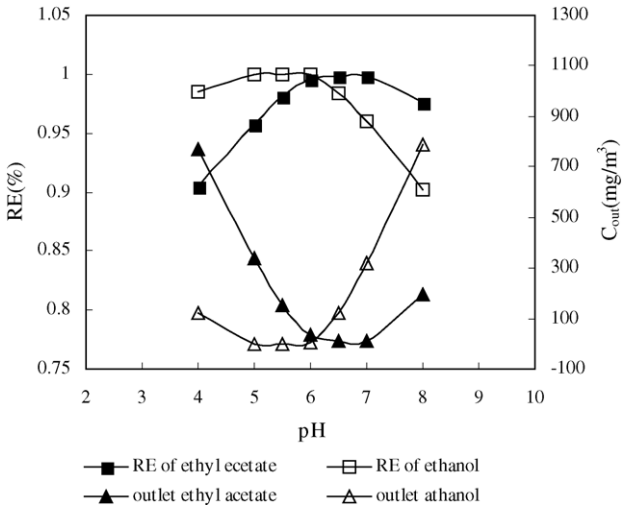


Fig. 2. Effect of pH values.

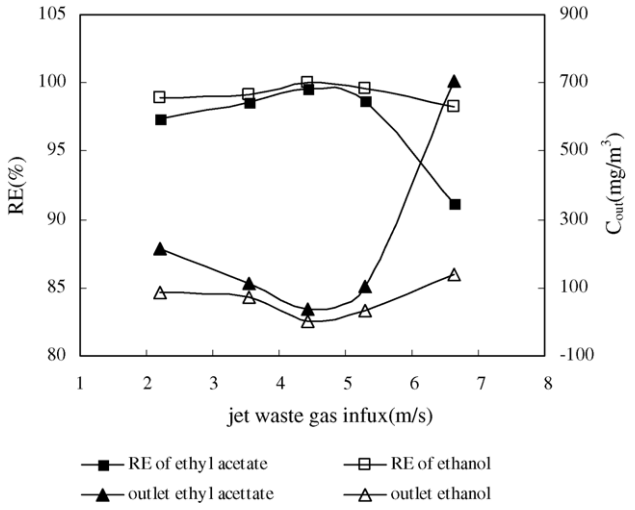


Fig. 3. Effect of jet waste gas influx.

flux had great effects on the removal efficiency and the outlet concentrations of ethyl acetate and ethanol. When the jet waste gas influx was smaller than 4.4 m/s, the carriers inside this bioreactor were fluidized and suspended (called stationary fluidization region). The profiles of the carriers inside bioreactor were gradually improved with increase in the jet waste gas influx, resulting in the increase in the removal efficiency and the decrease in the outlet concentrations of ethyl acetate and ethanol. When the jet waste gas influx reached the value of 4.4 m/s, the carriers inside this bioreactor were completely fluidized (called completely fluidization region). Here the distribution of the carriers inside the bioreactor was completely uniform, and the bulk load achieved the maximum elimination capacity, leading to the maximum in the removal efficiency and the minimum in the outlet concentrations of ethyl acetate and ethanol. With further increase in the jet waste gas influx, the bulk load increased and was larger than the maximum elimination capacity. Thus the outlet concentrations of ethyl acetate and ethanol increased as calculated from Eqs. (2) and (4), resulting in the decrease in the removal efficiency. Therefore the optimum jet waste gas influx was selected as 4.4 m/s.

### *3.3. The continuous bioprocess under the optimum operation conditions*

Experiment was carried out at the pH value of 6.0 and jet waste gas influx of 4.4 m/s. As could be seen from Fig. 4, under above optimum operation conditions the average removal efficiencies of ethyl acetate and ethanol were higher than 98% for more than 30 days, corresponding to the outlet concentration of ethyl acetate and ethanol lower than 150 mg/m$^3$. Furthermore, the COD and $NH_4^+$–N of the effluent, shown in Fig. 5, were below 100 and 15 mg/l during the 30 days, which were completely satisfied the primary discharge standard in China: COD < 150 mg/l and $NH_4^+$–N <60 mg/l (GB 8978-1996).

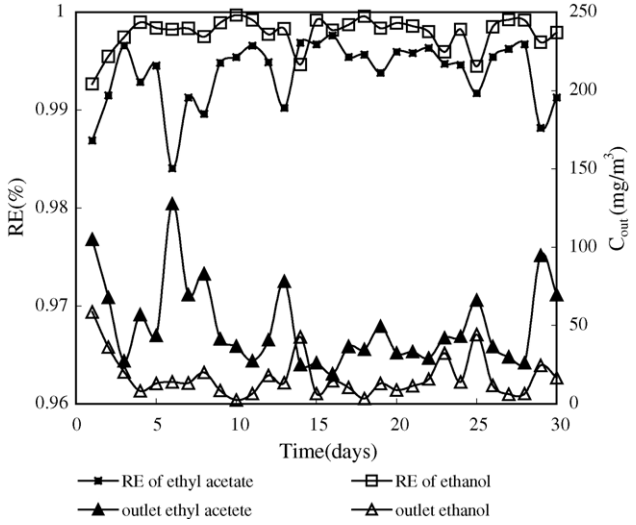


Fig. 4. The continuous bioprocess under the optimum operation conditions.

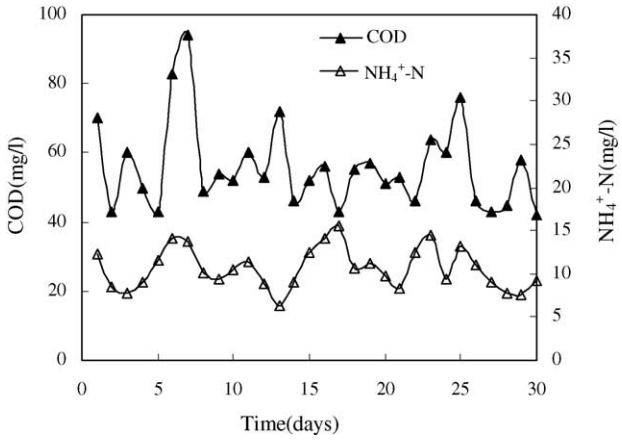


Fig. 5. The COD of the effluent during the continuous bioprocess.

### *3.4. Elimination capacity (EC)*

Fig. 6 showed the comparison of the elimination capacities of ethyl acetate and ethanol in the mixture as two mixture pollutants to those of pure ethyl acetate or ethanol as single pollutants in the gas–liquid–solid three-phase flow airlift loop bioreactors under the optimum operation conditions. The maximum elimination capacities of ethyl acetate and ethanol in the mixture were about 504 and 685 g/m$^3$/h, respectively. When ethyl acetate load was beyond 504 g/m$^3$/h and ethanol load was beyond 685 g/m$^3$/h, the elimination capacities of ethyl acetate and ethanol did not increase obviously with the increase of the loads, indicating that this biopurification followed zero-order kinetics in this concentration range, in agreement with "the reaction limited" scenario [15]. In addition, it was observed that the elimination capacities of ethyl acetate or ethanol in the mixture as two mixture pollutants were higher than those of pure ethyl acetate (480 g/m$^3$/h) or ethanol (671 g/m$^3$/h) as single pollutants. This might be due

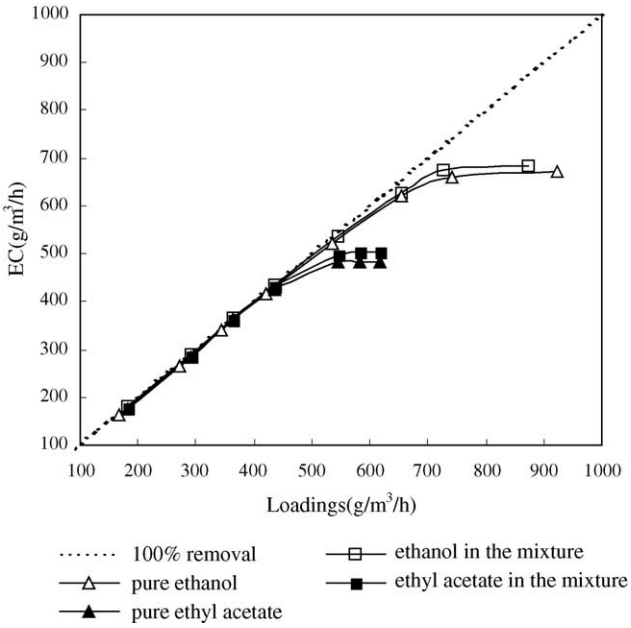


Fig. 6. The comparison of the elimination capacities of ethyl acetate and ethanol.

to the common-metabolic effects of microorganisms. And as reported in the literature, in the biofilters the elimination capacities of ethyl acetate and ethanol were 400 and 195 g/m$^3$/h, respectively. Thus the elimination capacities of both ethyl acetate and ethanol in gas–liquid–solid three-phase flow airlift loop bioreactor were higher than those in the biofilters as reported in the literatures [3,6].

## 4. Conclusions

In the present study, the gas–liquid–solid three-phase flow airlift loop bioreactor could be successfully applied to treat air streams containing a mixture of ethyl acetate and ethanol. In the bioreactor the optimum pH value and jet waste gas influx were 6.0 and 4.4 m/s. Under the optimum operation conditions, the average removal efficiencies of ethyl acetate and ethanol in the mixture were higher than 98%, and accordingly, the outlet concentrations of ethyl acetate and ethanol were lower than 150 mg/m$^3$. The elimination capacities of ethyl acetate (504 g/m$^3$/h) or ethanol (685 g/m$^3$/h) in the mixture as two mixture pollutants were higher than those of pure ethyl acetate (480 g/m$^3$/h) or ethanol (671 g/m$^3$/h) as single pollutants in gas–liquid–solid three-phase flow airlift loop bioreactor. And also, the elimination capacities of ethyl acetate or ethanol in the mixture as two mixture pollutants were higher than those in biofilters (ethyl acetate 400 g/m$^3$/h and ethanol 195 g/m$^3$/h as reported in the literature).

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