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# Removal of Methylene Chloride from Paint Stripping Wastewater by Air Stripping Process

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## ABSTRAK

Eksperimen skala makmal pelucutan udara telah dijalankan pada beberapa kadar aliran udara unit (Q) untuk menyingkirkan metilena klorida dari air buangan pelucutan cat. Keputusan kajian menunjukkan bahawa penyingkiran metilena klorida melalui proses pelucutan udara tersebar mengikut kinetik tertib pertama dan metilena klorida dapat dikurangkan ke kepekatan yang kurang dari 0.1 mg $l^{-1}$ dalam tempoh kurang dari 120 minit pada kadar aliran udara unit 0.833 l $min^{-1}$ $l^{-1}$. Pemalar kadar pelucutan $k_v$ yang mengukur kadar pelucutan udara dapat diramalkan dari persamaan $k_v = (H/RT)Q$, di mana H adalah pemalar hukum Henry, R pemalar universal dan T suhu asalkan nilai Q adalah di dalam lingkungan atau kurang dari 0.833 l $min^{-1}$. Nilai $k_v$ masing-masing adalah 0.028, 0.056, 0.088 dan 0.087 $min^{-1}$ pada nilai 0.286, 0.571, 0.833 dan 1.33 l $min^{-1}$ $l^{-1}$ bagi *Q*.

## ABSTRACT

Laboratory-scale air stripping experiments were conducted at various unit air flow rates (Q) to remove methylene chloride from paint stripping wastewater. The results showed that the removal of methylene chloride by batch diffused air stripping process follows first-order kinetics and that the concentration of methylene chloride could be reduced to less than 0.1 mg $l^{-1}$ within 120 min at a unit air flow rate of 0.833 l $min^{-1}$ $l^{-1}$. The stripping rate constant $k_v$, which quantifies the rate of air stripping, can be predicted from the equation $k_v = (H/RT)$ Q, where H is the Henry's law constant, R a universal constant and T temperature, provided that Q is kept within 0.833 l $min^{-1}$ $l^{-1}$. The values of $k_v$ were found to be 0.028, 0.056, 0.088 and 0.087 $min^{-1}$ at Q of 0.286, 0.571, 0.833 and 1.33 l min $l^{-1}$, respectively.

**Keywords: methylene chloride, air stripping process**

## INTRODUCTION

Air stripping has been acknowledged as a highly effective and relatively inexpensive process for the removal of volatile organic compounds from wastewater (Pekin and Moore 1982; Riznychok *et al.* 1983; Whittaker and

Moore 1983). It is, however, recognized that the transfer of organic materials from water to the atmosphere is not a treatment *per se* and may even contravene the air quality regulations. Nevertheless, where the impact on air quality level is insignificant, an air stripping process remains the preferred treatment choice; alternative methods can be costly and are not always effective.

The Henry's law constant (H), which is defined as the ratio of the compound's vapour pressure divided by its solubility, generally provides a good indication of the suitability of air stripping for the removal of the organic compounds. McCarty (1980) as well as Strier and Gallup (1982) noted that compounds removed in air stripping in general have Henry's law constants above $10^{-3}$ atm $m^3$ $mol^{-1}$. Based on this criterion, organic compounds such as toluene ($5.7 \times 10^{-3}$), benzene ($4.6 \times 10^{-3}$), 1,1,1-trichloroethane ($3.6 \times 10^{-3}$) and methylene chloride ($2.5 \times 10^{-3}$) are all good candidates for removal by air stripping process.

Batch air stripping of volatile compounds dissolved in water can be expressed as a first-order kinetic process and written in the following mathematical form:

$$-\frac{dc}{dt} = k_v c \tag{1}$$

where c is the concentration of the compound in the aqueous phase, t is the time of stripping and $k_v$ is the stripping rate constant. Equation (1) can be integrated to give

$$\ln (C/C_o) = -k_v t \tag{2}$$

where $c_o$ is the initial concentration of the compound. By employing Equation (2), the stripping rate constant $k_v$ can be determined experimentally by monitoring the change of compound concentration with time. However, it is more useful to link $k_v$ to the operating parameters of the stripping process such as the air flow rate and the physical properties of the compound being stripped. Mackay *et al.* (1979) proposed the following equation:

$$\ln (C/C_o) = -(HG/VRT)t \tag{3}$$

where G is the air flow rate ($m^3$ $min^{-1}$), V is the volume of liquid ($m^3$), R is the universal gas constant ($m^3$ atm $mol^{-1}$ $K^{-1}$), H is the Henry's law constant (atm $m^3$ $mol^{-1}$), T is the system temperature (K) and t is the time (min). The assumptions are:

(i) the system is isothermal,
(ii) the liquid phase is well mixed,

(iii) the vapour behaves ideally,
(iv) Henry's law is obeyed over the relevant concentration range,
(v) the volume of liquid remains constant,
(vi) the partial pressure of solute is small compared to the total pressure,
(vii) the organic compound in the gas bubbles is in equilibrium with the surrounding liquid before leaving the liquid surface.

The objectives of this bench-scale study were:

(1) to investigate the feasibility of methylene chloride removal from paint stripping wastewater by batch air stripping;
(2) to determine the stripping rate constant $k_v$ under different air flow rates and pH values;
(3) to test the validity of the model (Equation (3)) proposed by Mackay *et al.* (1979) under various operating conditions.

## MATERIALS AND METHODS

Air was passed through a Matheson flowmeter and then bubbled through water contained in a gas washing bottle with a fritted cylinder in order to saturate it and reduce water loss from the stripping vessel to a minimum. The water-saturated air was then introduced to the bottom of the stripping vessel, which was a 4-litre beaker, through a fritted glass disk.

The synthetic paint stripping wastewater to be stripped was prepared by diluting a commercially available paint stripper with deionized water in the ratio 1:125, the typical resulting composition of which is shown in Table 1. Batch diffused air stripping of the synthetic paint stripping waste was conducted at pH 2.85, 7.60 and 9.65 at an air flow rate of 2.5 l min$^{-1}$ for waste volume of 3l. With the pH of waste fixed at 7.60, air stripping was carried out at the air flow rates of 1 l min$^{-1}$ and 2l min$^{-1}$ for a waste volume of 3.5 l and 4 l min$^{-1}$ for a waste volume of 3l. The operating conditions of the six runs are summarized in Table 2.

TABLE 1
Synthetic waste composition

| Parameter | Concentration (mg/l) |
|---|---|
| Methylene chloride | 5,016 |
| Phenol | 1,824 |
| Sodium chromate | 91 |
| Paraffin<br>Cellulose derivative<br>Rosin soap<br>Petroleum sulphonates | 2,189 |
| Naphthalene | 29 |
| COD | 6,500 |

TABLE 2
Operating conditions of air stripping experiments

| Experiment No. | Air flow rate (1 min$^{-1}$) | Wastewater volume (1) | pH | Temperature (°C) |
|---|---|---|---|---|
| AS-1 | 2.5 | 3.0 | 2.85 | 21.5 |
| AS-2 | 2.5 | 3.0 | 7.60* | 21.5 |
| AS-3 | 2.5 | 3.0 | 9.65 | 21.5 |
| AS-4 | 1.0 | 3.5 | 7.60* | 21.5 |
| AS-5 | 2.0 | 3.5 | 7.60* | 21.5 |
| AS-6 | 4.0 | 3.0 | 7.60* | 21.5 |

* without pH adjustment

At specified times, liquid samples were taken from the centre of the stripping vessel using a pipette and stored in 25-ml vials closed with a screw cap lined with teflon. The head space in the vial was minimized as far as possible to reduce possible loss of methylene chloride due to volatilization. In a typical run, about eight samples were collected. Consequently, the decrease in volume of waste due to sampling constituted less than 7% of the initial volume. The samples were analysed for phenol and methylene chloride. Phenol was analysed colorimetrically using the CHEMETRICS evacuated glass ampoule based on the 4-aminoantipyrine method (510 C) in the APHA standard methods (APHA 1985). Methylene chloride was determined according to EPA Method 601 using a Hewlett Packard Series 5880A gas chromatograph and a HP 7675A purge and trap system.

## RESULTS AND DISCUSSION

### *Feasibility of Methylene Chloride Removal by Air Stripping*

The results of Experiment No. AS-1 are shown in Table 3. As there was no

TABLE 3
Variations of concentrations of methylene chloride and phenol with time in Experiment AS-1

| Time (min) | Methylene chloride (mg 1$^{-1}$) | Phenol (mg 1$^{-1}$) |
|---|---|---|
| 0 | 2370 | 1500-1800 |
| 15 | 583 | 1200-1500 |
| 30 | 152 | - |
| 45 | 41 | 1500-1800 |
| 60 | 9.1 | 1200-1500 |
| 90 | 0.67 | 1500-1800 |
| 120 | 0.071 | 1500-1800 |

detectable decrease in phenol concentration during air stripping, phenol determination was discontinued after AS-1. Although the methylene chloride concentration was expected to be in the region of 5000 mg $l^{-1}$ (Table 1), the actual initial methylene chloride concentration was found to be considerably less.

Owing to the volatility of the compound, a significant amount of it was lost during the preparation of the synthetic wastewater. In order to assess quantitatively the feasibility of methylene chloride removal by air stripping, Equation (2) was employed to determine the stripping rate constant $k_V$. Thus, the logarithm of methylene chloride concentration was plotted against time for all six runs; some of the results are shown in *Fig. 1.* All the plots can be fitted very well with a straight line, indicating that the batch air stripping of methylene chloride follows first-order kinetics closely within the range of operating conditions adopted in this study. Least square fitting of the straight lines yields the best values of $k_V$, which are presented in Table 4.

Once the stripping rate constant $k_V$ was known, estimates were made on the time periods required for the methylene chloride concentration to decrease to half its initial value (half-life, $\tau_{50}$) and also to 10% of its initial

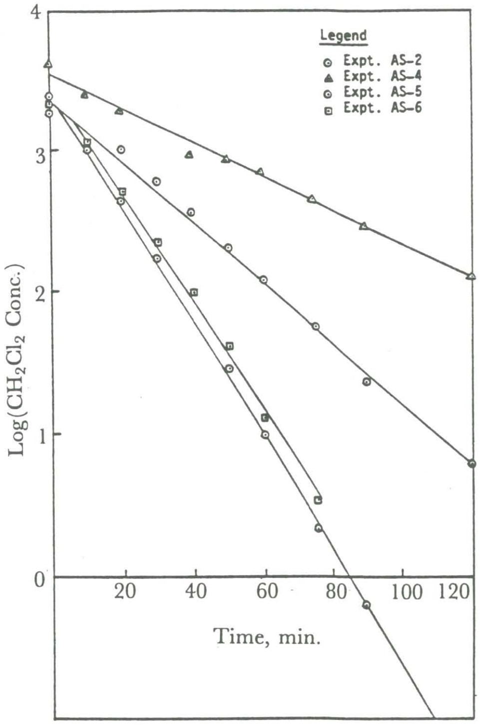

*Fig. 1. Plots of log (methylene chloride conc.) versus time for Exp. AS-2, AS-4, AS-5 and AS-6*

TABLE 4
Calculated ($k_v$) and predicted ($k_v^M$) rate constants

| Experiment No. | Air flow rate (G) (1 min$^{-1}$) | Waste volume (V) (1) | Unit air flow rate (Q) × $10^3$ (1 min$^{-1}$ 1$^{-1}$) | $k_v \times 10^2$ (min$^{-1}$) | $k_v^M \times 10^2$ (min$^{-1}$) |
|---|---|---|---|---|---|
| AS-1 | 2.5 | 3.0 | 833 | 8.8 | 8.35 |
| AS-2 | 2.5 | 3.0 | 833 | 9.2 | 8.35 |
| AS-3 | 2.5 | 3.0 | 833 | 8.5 | 8.35 |
| AS-4 | 1.0 | 3.5 | 286 | 2.8 | 2.86 |
| AS-5 | 2.0 | 3.5 | 571 | 5.6 | 5.73 |
| AS-6 | 4.0 | 3.0 | 1333 | 8.7 | 13.4 |

TABLE 5
Air stripping rates of methylene chloride and phenol from paint stripping waste

| Compound | $k_v \times 10^2$ (min$^{-1}$) | $\tau_{50}$ (min) | $\tau_{10}$ (min) |
|---|---|---|---|
| Methylene chloride | 8.8 | 8 | 26 |
| Methylene chloride | 2.8 | 25 | 82 |
| Methylene chloride | 5.6 | 12 | 41 |
| Phenol | 1.35 × $10^{-4}$* | 357** | - |

*From Truong and Blackburn (1984)
**In days

value ($\tau_{10}$) by employing Equation (2). The corresponding time periods for phenol were also computed by making use of the stripping rate constant data from Truong and Blackburn (1984) for comparison. The calculated results are shown in Table 5. It is obvious that phenol cannot be removed by air stripping. To reduce methylene chloride from 5000 mg $1^{-1}$ (its expected concentration in synthetic waste) to, e.g., 0.1 mg $1^{-1}$, the time period was found to be 6.4 hours if the lowest stripping rate constant, i.e. 2.8 × $10^{-2}$ min$^{-1}$, is used. The stripping time period is shortened to 2.0 hours if $k_v = 8.8 \times 10^{-2}$ min$^{-1}$ is used.

*Effect of pH on* $k_v$

Although there is some variation in the values of $k_v$ for air stripping conducted at three different pH (Expt. AS-1, AS-2 and AS-3), the differences observed are considered to be mainly due to experimental variation in air flow rate and waste volume measurements. As a result, there is an estimated 10% error in the determination of $k_v$. Consequently, within experimental error, it can be stated that the change of pH has no observable effect on the air stripping rate.

### *Effect of Air Flow Rate (G) and Waste* Volume *(V) on* $k_v$

These two operational parameters can be combined to become a single parameter called unit air flow rate ($Q = G/V$). The model proposed by Mackay *et al.* (1979) (Equation (3)) has incorporated this parameter into the air stripping rate constant $k_v^M$ such that

$$k_v^M = (H/RT)Q \tag{4}$$

According to Equation (4), the air stripping rate constant $k_v^M$ is directly proportional to the unit air flow rate provided the temperature is constant. When the unit air flow rate Q in Table 4 was plotted against $k_v$, a linear relationship was observed at least up to unit air flow rate of 0.833 l min$^{-1}$ (*Fig. 2*). A similar kind of relationship between Q and $k_v$ have been proposed by other researchers based on purely empirical correlation. Engelbrecht *et al.* (1961) proposed the following linear relationship,

$$k_v = k_o + RQ \tag{5}$$

where $k_o$ and R are parameters to be fitted from the data. More recently, Truong and Blackburn (1984) suggested the following empirical relationship to correlate $k_v$ and H for diffused aeration system.

$$\frac{k_v}{Q} = b(H)^m \tag{6}$$

where b and m are power equation constants. For pure water, the value of m was found to be very close to 1, and this has made Equation (6) almost identical to Equation (4).

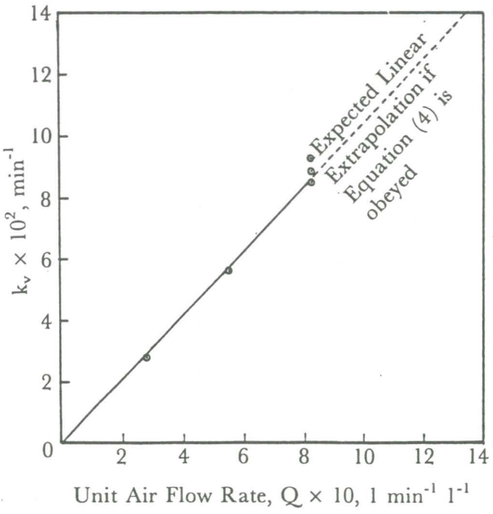

*Fig. 2. Effect of unit air flow rate, Q, on stripping rate constant* $k_v$

Based on this study and the results of earlier work, a linear relationship between $k_v$ and Q can be established for air stripping of methylene chloride from paint stripping wastewater provided Q does not exceed the value of 0.8333 l $min^{-1}$ $l^{-1}$.

*Equation (4) as the Predictor for Stripping Rate Constant*

The validity of the model proposed by Mackay *et al.* (1979) (Equation (3) can be tested by employing Equation (4) to calculate the stripping rate constant. The predicted $k_v$ ($k_v^M$) values are shown in the last column of Table 4. For unit air flow rates (Q) at 0.286, 0.571 and 0.833 l $min^{-1}$ $l^{-1}$, there is good agreement between $k_v$ and $k_v^M$, indicating that Equation (4) is a good predictor for $k_v$. This also means that the seven assumptions propounded by Mackay *et al.* (1979) for the application of Equation (3) are generally valid under these operating conditions. However, at the higher unit air flow rate of 1.333 l $min^{-1}$ $l^{-1}$, the predicted $k_v$ value is much higher than the experimentally-determined value. In other words, Equation (3) is no longer valid under these particular operating conditions.

Among the seven assumptions listed by Mackay *et al.* (1979), assumptions (ii) and (vii) are most difficult to satisfy. If the organic compound in the exit gas bubbles does not reach an equilibrium concentration, Mackay *et al.* (1979) and Matter-Muller *et al.* (1981) proposed that Equation (3) should be modified to include a term which is the fraction of equilibrium achieved. Thus, Equation (3) would become

$$\ln(C/C_o) = -(HG/VRT)[1 - \exp(1 - K_l AVRT/GH)]t \qquad (7)$$

where $K_l$ is the overall liquid phase mass transfer coefficient and A is the total interfacial area.

At the higher unit air flow rate of 1.333 l $min^{-1}$ $l^{-1}$, the exit gas is probably only partially saturated with methylene chloride, thus Equation (7) should be used to describe this situation. This is not pursued further due to lack of information on the magnitude of $K_l A$ for methylene chloride at this unit air flow rate.

## CONCLUSION

The conclusions which can be drawn from this study are:

1. Batch air stripping offers a feasible and simple process for removing methylene chloride from paint stripping wastewater.
2. First-order kinetics seems to hold for the stripping of methylene chloride at the range of unit air flow rates studied.
3. For the unit air flow rates up to 0.833 l $min^{-1}$ $l^{-1}$, the stripping rate constant $k_v$ can be predicted reasonably well using the model proposed by Mackay *et al.* (1979), namely, $k_v = (H/RT)\,Q$.

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