Modeling of Air Stripping-Vapor Permeation Hybrid Process for Removal of Vocs from Wastewater and VOCs Recovery

F. Zareei and A.A. Ghoreyshi

Faculty of Chemical Engineering, Noshirvani University of Technology, Babol, Iran

Abstract: This study deals with modeling of air stripping-vapor permeation hybrid process for removal of VOCs from wastewater. The hybrid process allows desorbed VOCs from air stripping process to be subsequently recovered using a membrane based vapor permeation process. A mathematical model was developed to describe the mass transfer in both processes based on the resistance in series model. The model parameters which give the individual resistance against mass transport were found by the fit of experimental flux data available in literature with the model equations. The separate evaluation of feed bulk phase and membrane phase resistances were carried out in using at different feed hydrodynamic condition in a constant membrane thickness. A sensitivity analysis was carried out using the developed model to investigate the effect of operational factors such as temperature, pressure, feed concentration, gas and liquid flow rate on separation performance of the process. As typical cases, the removal four VOCs, i.e. 1,2-dichloroethane (DCE), 1,1,2-Trichloroethane (TCE), Chloroform and Dichloromethane from water was investigated in a hybrid process consist of a stripping column of 90 cm height and vapor permeation unit employing PDMS membrane with an effective area of 1.47 cm². The results indicated while the gas phase resistance is negligible in air stripping process, but it plays a significant role in vapor permeation process, especially in feed side. The modeling results demonstrated that the air/water ratio has a great impact on the removal efficiency of air stripping process, but it use is limited to flooding ratio. The examination of the hybrid model has shown that the hybrid process is appropriate for high concentration and high gas flow rate and optimal temperature.

Keywords: Water treatment • Air stripping • Vapor permeation • Hybrid system • Volatile organic compounds

INTRODUCTION

The removal of volatile organic compound (VOC’s) from wastewater or contaminated groundwater is a major problem [1]. The treatment methods for removing VOCs include air stripping, adsorption, advanced oxidation, distillation, anaerobic/aerobic biological treatment, bioreactor and membrane technology [2]. These methods have some shortcomings and limitations. Air stripping is conventionally used for this purpose due to its simplicity and low cost of operation. However, it is effective for high volatility compounds (high Henry’s constants). Besides it shifts the water pollution to air pollution. Adsorption is economic only at low VOC levels due to the high cost of the adsorbents and the need for its frequent regeneration. Biological treatment is a clean method, but it is time consuming and also effective only at low VOC levels. Advanced oxidation is efficient for specific compound but it maybe forms new products that are more harmful than the original ones [2]. Pervaporation is membrane process that has a potential of providing a better alternative to the above conventional process. In addition pervaporation can remove semi-volatile and non-volatile organic compounds at the same time [3]. However, the high cost of membrane materials has avoided its application and development for bulk application.

A hybrid process consist of an air stripping process in packed column and membrane based vapor permeation process can combine the advantage of simple operation in air stripper and high efficiency of vapor permeation process for VOCs recovery from air stream exiting stripper [3]. This can avoid a water pollution problem becomes an air pollution problem. Vapor permeation through membranes offers significant opportunities of energy saving and reuse of VOC’s as compared to the conventional VOC control process, particularly if the VOC concentration is high [4]. The driving force in this process is a chemical potential gradient generated by partial
pressure reduction on the permeate side, which can be accomplished either by applying vacuum or blowing a seep inert gas [5]. The purpose of hybrid process follows several goals. First, decreasing of pollution from wastewater that is the main subject. The second aim is decreasing of air pollution that is important for environment and returning clean air to process too. The third and final goal is recovery of VOC that is important of economic viewpoint [6].

The application of air stripping- vapor permeation process requires a deep knowledge regarding both processes and the affecting parameters on their performance. In one hand, the optimum design of an air stripping process in a packed column for the removal of a given VOC depends on the proper understanding and use of mass transfer coefficients, vapor-liquid equilibria and other physicochemical properties. On the other hand, the separation performance of vapor permeation process depends on the characteristics of the membrane as the selective separation barrier and also hydrodynamic condition in gas bulk phase. The main purpose of this study was to develop a mathematical model based on the resistance-in-series to describe the separation performance of the system by individual resistance in each phase (gas-liquid phase in air stripping and gas-membrane phase in vapor permeation). The data available in literature for different VOCs such as Chloroform (CHCl3), 1,1,2-Trichloroethane (C2H3Cl3), Dichloroethene (C2H4Cl2) and Dichloromethane (CH2Cl2) were used to verify the model efficiency. The predominant resistance for each process was identified and effects of operating conditions were analyzed.

**Model Development:** The overall concept of the hybrid process was illustrated schematically in Fig. 1. Wastewater enters the top of an air stripper and flows down to the sump. The strip gas enters the bottom of the tower and flows countercurrent to the liquid phase. The VOC-rich gas leaving the stripper is fed membrane system, where the membrane modules separate the strip-gas stream into a VOC-rich and a VOC-depleted residue, which is fed back to the stripper. The VOC-rich permeate is cooled and the VOC is condensed out and recovered as a liquid. In the membrane separation step, VOC-laden air contacts one side of a membrane that is permeable to organic vapors but relatively impermeable to air. A pressure difference across the membrane causes the organic vapor to preferentially permeate the membrane; the permeate vapor is then condensed to recover the organic fraction.

![Schematic Diagram](image)

**Fig. 1:** The schematic diagram of hybrid air stripping/membrane separation process.

**Air Stripping:** The following assumptions were made in the model description:

- Heat of solution is negligible because the solution is too dilute. Therefore the enthalpy balance can be decoupled from the set of describing equations and the temperature can reasonably be assumed constant throughout the column.
- Pressure drop throughout the column is negligible.
- A linear vapor-liquid equilibria (Henry's law) is assumed.

Axial mixing is assumed to be negligible due to the high flow rate of stripping air.

In this study the removal of volatile organic compounds in packed towers was modeled based on differential mass transfer equation for liquid and gas phase, separately:

Differential mass transfer equation for liquid phase:

\[ L \frac{dx}{dz} = k_x a (X_i - X_i^v) \]  

(1)

Differential mass transfer equation for gas phase:

\[ G \frac{dy}{dz} = k_y a (Y_i^v - Y_i) \]  

(2)

Differential mass balance in steady state:

\[ L \frac{dx}{dz} = G \frac{dy}{dz} \]  

(3)

Equilibrium relationship (Henry's law):
\[ \frac{Y}{1+Y} = \left( \frac{H_y}{P} \right) \frac{X^*}{1+X^*} \]  

(4)

Assuming that the number of component to be \( n \), we have \( 4n \) equations which should be solved simultaneously for \( 4n \) unknown variables \( (X_i, Y_i, X^*_i, Y^*_i) \). A further simplification can be made by combining individual mass transfer resistances in liquid and gas phases and using the overall mass transfer coefficient based on resistance in series model in the following form:

\[ \frac{1}{K_X} = \frac{1}{(H_X)k_{xi}} + \frac{1}{k_{xi}} \]  

(5)

\( H_x \) is Henry's law coefficient which is affected by temperature and type of material, is obtained from literature. Using \( k_{xi} \) instead of \( k_{xi} \) in Equation (1), it is possible to eliminate differential mass transfer equation in gas phase (Equation 2).

**Estimating Model Parameters:** Equilibrium coefficients in the form of Henry's constants as a function of temperature were obtained from the literature [10]. Mass transfer coefficients were estimated from Onda et al. [11] correlations. Other physicochemical properties such as diffusion coefficients, viscosity and density required in the model were calculated by the best well-known available correlations in the literature [12].

**Algorithm of Solution:** The process governing equations (1-4) were solved numerically to determine the height of the tower, concentration profile of organic contaminants and the removal efficiency. To start the solution, we know the composition and flow rate of liquid entering at the top of the column and the flow rate and composition of gas phase entering at the bottom of the column. To start the integration, the flow rate and the composition should be estimated at the bottom of the column. With the above estimated values, the set of described equations were integrated by fourth order Runge-Kutta method up to the top of the column. A comparison was made at the top between the calculated and the actual values of composition. A further iteration was followed until the required convergence is achieved. Fig. 2 shows the flowchart of simulation program.

**Vapor Permeation:** Driving force in vapor permeation process can be pressure gradient or concentration gradient. The process generally uses a homogeneous dense membrane such as PDMS which favors VOCs permeation. The pressure is kept as low as possible in the permeate side. Individual transport steps including

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Fig. 2: Flowchart of simulation program
Where $t$ is the thickness of membrane, $PV$ the permeability coefficient of VOC component. For dilute systems, the relationship between the partial pressure and concentration of a permeant on membrane surface is expressed in terms of solubility coefficient, $S_m$ [8]:

$$\frac{C_{m,f}}{P_{m,f}} = \frac{C_{m,p}}{P_{m,p}} = S_m$$

(10)

The concentration $C_{m,f}$ is related to $C_b^*$ by the distribution coefficient $K_{dis}$ as follows:

$$C_{m,f} = K_{dis} C_b^*$$

(11)

Equation (9) can be rewritten as follows:

$$J_{m} = \frac{P_{m,f} K_{dis} C_b^*}{t} - \frac{D_m K_{dis} C_b^*}{t}$$

$$P_{m,f} = D_m S_m$$

(12)

$$\frac{1}{K_{ij}} = \frac{1}{K_b} + \frac{1}{D_m K_{dis}}$$

(13)

In general mass transfer resistance in each step can be expressed in term of each reciprocal mass transfer coefficient, respectively. Overall mass transfer coefficient, that is the reciprocal of overall mass transfer resistance is given as the sum of a membrane resistance $1/(D_m K_{dis})$ and the boundary layer resistance $1/K_b$. This equation describes a connection of the resistance in series, that is, a so-called resistance-in-series concept [6].

The boundary layer mass transfer coefficient is sometimes given by the ratio of diffusion coefficient $D_b$ and the boundary layer thickness $\Delta$. Also, the thickness of boundary layer determined by the hydrodynamic of feed flow field, expressed as a function of the feed velocity [5]; thus the term can be given as

$$K_b = \frac{D_b}{\delta} = K_b u^{-n}$$

(14)

Where $u$ is the feed flow rate in the membrane cell, $K_0$ and $n$ are the constants with feed flow rate but dependent on other operating conditions, such as temperature, feed composition and the kind of VOC in feed mixture. Equation (13) can then be rewritten as [1].
\[ \frac{1}{K_f} = \alpha \ a^n + R_m \]  

(15)

Where \( R_m \) denotes the membrane resistance and \( \alpha \) refers to \( 1/K_0 \). The membrane resistance is also considered to be constant with feed flow rate for the permeation of a given mixture at a certain temperature. The overall mass transfer coefficient, \( K_f \), can simply be determined from the experimental fluxes of the VOC component in mixtures. Then by fitting of overall mass transfer resistances, \( K_f \) values against equation (11) at various feed flow rates, constants such as \( \alpha, n \) and \( R_m \) can be evaluated and then \( K_b \) is determined by equation (14).

**RESULT AND DISCUSSION**

The efficiency of the model described above for air stripping tower and vapor permeation is now examined by experimental data available in the literature. Stripping tower was with height and diameter 90, 19.5 cm respectively [5]. For permeation process, permeation of VOC/N2 mixtures through homogeneous PDMS membrane have been given at different operating conditions [1]. Feed pressure was kept at 1.5 bar and feed flew through the membrane cell at different rates of 0-600 cm³/min. Also the resistance in permeate adjacent to the membrane surface, was prevented by keeping the permeate pressure be low 2 torr. The thickness of membrane was 130-160 μm. The VOC’s which have been considered for the assessment of separation performance were: Chloroform, 1,1,2-Trichloroethane, Dichloroethane and Dichloromethane. Table 1 Exhibits overall mass transfer coefficient at various feed flow rate for the above mentioned VOCs.

To calculate the hybrid process efficiency, we need to know the composition of retentate and permeate products which can be determined using a material balance for the overall process as follows:

\[ N_i = J_i \times A_m \]  

(16)

\[ N_t = N_p + N_r \]  

(17)

\[ N_p Y_f = N_p Y_{f} + N_r Y_r \]  

(18)

Where \( N_F, N_P \) and \( N_R \) are mole flow rate at feed, permeate and retentate, respectively. \( Y_F, Y_P \) and \( Y_R \) are mole fraction of feed, permeate and retentate, respectively.

Knowing that \( Y_{Out} = Y_{Retentate} + Y_{Gasout} \), the overall efficiency for hybrid process can be given as:

![Graph showing the influence of inlet concentration in removing three VOC compounds](image)

**Fig. 4:** Influence of inlet concentration in removing three VOC compounds; Gas flow rate 40 (l/h), Temperature and pressure 45°C and 1 atm respectively

\[ \text{Removal} = \frac{Y_{Feed} - Y_{Out}}{Y_{Feed}} \]  

(19)

**Influence of Input Concentration:** To check the potential ability of hybrid process in reducing contaminant concentration in water from a given inlet concentration, the model equations were solved under condition of atmospheric pressure, temperature (\( T=45°C \)) and air/water ratio (\( G/L = 5 \)).

Fig. 4 shows that the removal efficiency increases with the feed concentration. This can be attributed to the increase in equilibrium concentration of VOC in water which causes an increase in driving force for mass transfer. In air stripping system, reduce the concentration of some more volatile organics to the permissible limit in a packed tower with height. However, the generalization of these results to high solubility compound is not plausible and in these cases the operation and tower dimensions will become uneconomical. In membrane system, as the VOC concentration in the feed increased, both the VOC flux and VOC concentration in the permeate increase as well. In hybrid process, the overall VOC removal decreases with decreasing VOC concentration because the ability of membrane system to recover VOC from the recirculating air stream is reduced as the VOC concentration in that stream decreases. However, at concentration higher than 500 ppm, an increase in the VOC concentration of water entering to the column have a little effect on removal efficiency.

According to the solution-diffusion model, three steps are involved in the permeation through the membrane: sorption, diffusion and desorption. Since the
permeate side was exposed to vacuum, desorption is normally not a controlling factor and membrane permeability is primarily determined by the solubility and diffusivity of the penetrant. Smaller molecules tend to have a greater diffusivity. So based on higher selectivity for Dichloromethane and Chloroform over Trichloroethane, their removal efficiency are more than Trichloroethane.

**Influence of Inlet Flow Rate:** In this part the effect of inlet gas flow evaluated at constant concentration of 175 ppm for three VOCs. Fig. 5 and Fig. 6 shows the result of model and experimental values for, methylene chloride and 1,1,2-trichloroethane, chloroform, respectively. In general, in air stripping process an increase in air/water ratio enhances the effective contact between liquid and gas phases and reduces the gas phase resistance. On the other hand, it causes a decrease in partial pressure of the solute in the gas phase, decreases its solubility and improves its removal efficiency. These results show the balance between the efficiencies of the stripper and the membrane unit. If the air-to-water ratio is very large, then the stripper performance will be good provided the membrane unit removes the VOC from the stripper discharge air. The efficiency of the membrane VOC-removal step then becomes very important. So, if the air-to-water ratio is low the performance of the system is controlled by the stripper even if the membrane system achieves high removals.

From Fig. 5 it can be observed that as the gas flow of dichloromethane is increased, the removal efficiency increases. Comparing the result of model with the experimental data in published article by Roizard [5], shows the separation behavior is well predicted by model.

Fig. 6 shows that with an increase in flow rate at constant concentration, removal efficiency of hybrid process increases. That is because with increasing gas flow rate mass transfer resistance decreases in gas phase resulting higher efficiency in air stripping tower. But in membrane process with increasing gas flow rate at constant VOC concentration, a reduction in efficiency is expected due to decreasing of molar flow rate of VOC component in gas phase,. However, in high concentration, removal efficiency the efficiency remains constant. Therefore, hybrid process has potential to increase the removal efficiency over stripping tower at high gas flow content.

**Influence of Temperature:** Dependence of the removal efficiency on temperature has been examined by the developed model in the temperature range of 35-65°C.

![Fig. 5: Influence of inlet flow rate in removal of methylene chloride; Liquid flow rate 40 (l/h), Temperature 45°C, Input concentration 175 ppm](image)

![Fig. 6: Influence of inlet flow rate in removal of Chloroform and Trichloroethane; Liquid flow rate 40 (l/h), Temperature pressure 45°C, Input concentration 175 ppm](image)

![Fig. 7: Influence of temperature in removal of Trichloroethane in three process; Gas flow rate 40 (l/h), Liquid flow rate 8 (l/h), Input concentration 175 ppm](image)

Fig. 7 shows the removal percent of pollutant in three process as hybrid process, air stripping process and membrane process versus temperature. Since an increase
in the column temperature, decreases the solubility of organic compounds in water and increases Henry’s law coefficient hence improves the efficiency. This effect is more significant for more volatile compounds, thus An ascending trend in Fig. 7 can be seen for air stripping process.

But at same time in membrane system, temperature dependency can be explained qualitatively from the solubility and diffusivity aspects. In general, the sorption process is exothermic and the solubility coefficient tends to decrease with an increase in temperature. On the other hand, an increase in temperature will increase the thermal motion of the segments of the polymer backbone, thereby enhancing the diffusion of the permeant through the membrane. In case of VOC permeation, however, the solubility is high due to the strong permeant-membrane affinity. When the temperature is low, the sorption aspect dominates the permeation and thus the VOC permeability decreases with an increase in temperature. When temperature is high enough, both the diffusion and sorption become significant for VOC permeation. While the diffusivity tends to increase with an increase in temperature, the solubility decreases. As a result, the temperature dependency of the VOC permeability is less significant at relatively high temperatures, as shown in Fig. 7. Obviously, a low operating temperature is favorable for the separation of organic vapors from air and it is therefore desirable to operate the membrane system at ambient temperature from an application point of view.

Therefore at higher temperature removal efficiency is less for vapor permeation process and a descending trend is obvious in Fig. 7. Removal efficiency in hybrid process is mainly affected by the yield of column and ascends with the slope lower than air stripping process as is visible in Fig. 7. So it is recommended the choice of an optimal temperature.

**CONCLUSION**

In this study, a mathematical was developed for air stripping-vapor permeation hybrid process based on resistances-in-series theory. The ability of stripping column and vapor permeation process for removal of a number of VOCs were individually tested by the model. Derivation of the model parameters using the experimental data was described. The results obtained by the examination of air stripping model shows that the air/water ratio is the most important factor affecting the removal efficiency in the stripping tower, in special for compounds with higher volatility. The vapor permeation of was investigated at various feed flow rate. The results obtained by the examination of vapor permeation model using the data available for VOC’s/N2 mixtures through PDMS membrane revealed that the feed flow rate has a major effect in process performance. At low flow rate the resistance in boundary layer may become significant. Since the main advantage of hybrid process is preventing air pollution by the recovery of desorbed VOCs from air stripping tower, the overall efficiency of the VOCs recovery was tested by the hybrid model. The results have shown that this process is appropriate for high concentration and high gas flow rate.

**Nomenclature:**

- $a$: Surface area of packing (m$^2$/m$^3$)
- $N_h$: Mole flow rate (mol/s)
- $A_m$: Effective area of membrane (m$^2$)
- $P_0$, $P_s$: VOC vapor pressure in feed and permeate, respectively (atm)
- $C_{in}$, $C_{out}$: VOC concentration in feed adjacent membrane surface and feed bulk,
- $P_v$: permeability coeficient of VOC (cm$^2$/(STP)) cm/(cm$^3$ cmHg)
- $C_{in}$, $C_{out}$: VOC concentration at the feed-side surface and permeate-side surface of
- $R_m$: Membrane resistance (s/cm)
- $D$, $D_h$, $D_e$: Diffusion coefficient of permeant and VOC in boundary layer and VOC in
- $S_m$: Solubility coefficient of VOC (cm$^3$/(STP))/(cm$^3$ cmHg)
- $L_m$, $G_t$: Mass transfer flux (kg/m2 s)
- $t$: Membrane thickness (cm)
- $H$: Henry law coefficient (atm cm$^3$/mol)
- $U$: Feed flow rate (cm$^3$/min)
- $J_v$: Permeation rate (cm$^3$/(STP))/(cm$^2$/s)
- $x$, $y$: Liquid and gas composition(-)
- $K_{d}$: Distribution coefficient (cm/s)
- $Y_{out}$: Total output mole fraction, output mole fraction from membrane and output mole fraction from column
- $K_0$, $K_{r}$: Overall mass transfer coefficient and mass transfer coefficient of VOC in boundary layer respectively (cm/s)
- $z$: Height of stripping column (m)
- $k_r$, $k_{r}$: Mass transfer coefficient in liquid and gas phase (m/s)
- $\Delta$: Boundary layer thickness (cm)
- $K_{r}$: Total mass transfer coefficient in liquid phase (m/s)
REFERENCES