

# Recovery of 2,4-dichlorophenol from acidic aqueous streams by Membrane Aromatic Recovery System (MARS)

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**Abstract:** This study describes the successful recovery of 2,4-dichlorophenol (DCP) from wastewater using the Membrane Aromatic Recovery System (MARS). In the MARS process a non-porous membrane separates a wastewater stream and a stripping solution. DCP is extracted from the wastewater and concentrated in its ionic form in the stripping solution, with  $\text{pH} \gg \text{p}K_a$  DCP. The MARS extraction stage was operated in batch mode with the stripping solution placed inside, and the wastewater stream outside, the membrane tubes. Advantages of this configuration are avoidance of membrane blockage, reduction of stripping solution volume and operational flexibility. The stability and mass-transfer characteristics of two different membrane materials, poly(dimethylsiloxane) (PDMS) and ethylene-propylene diene terpolymer (EPDM), were tested in DCP solutions with different acidities in order to simulate real industrial waste streams. EPDM exhibits one order of magnitude lower mass-transfer rates than PDMS ( $1.4 \times 10^{-7} \text{ m s}^{-1}$  vs  $20 \times 10^{-7} \text{ m s}^{-1}$  at  $30^\circ\text{C}$  and  $2.4 \times 10^{-7} \text{ m s}^{-1}$  vs  $39 \times 10^{-7} \text{ m s}^{-1}$  at  $60^\circ\text{C}$ ), however its higher resistance to acid attack provides higher membrane lifetimes. This can be crucial for MARS processes treating real acidic industrial wastewater. A 97% recovery of DCP with a water content of 15 wt% was obtained upon neutralisation of the stripping solution.

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**Keywords:** dichlorophenol; membrane; wastewater detoxification; recovery; removal; aromatic

## NOTATION

$A$	Area of membrane ( $\text{m}^2$ )	$k_{\text{shell}}$	Shell side liquid film mass transfer coefficient ( $\text{m s}^{-1}$ )
$C_s$	Current stripping solution concentration of neutral DCP ( $\text{kg m}^{-3}$ )	$k_{\text{tube}}$	Tube side liquid film mass transfer coefficient ( $\text{m s}^{-1}$ )
$C_{\text{tot}}$	Total concentration of neutral and ionic dichlorophenol in the stripping solution ( $\text{kg m}^{-3}$ )	$K$	Partition coefficient (dimensionless)
$C_w$	Current wastewater solution concentration of DCP ( $\text{kg m}^{-3}$ )	$K_a$	Dissociation constant (M)
$C_{w_0}$	Initial DCP concentration at the wastewater side ( $\text{kg m}^{-3}$ )	$K_{\text{ov}}$	Overall mass transfer coefficient ( $\text{m s}^{-1}$ )
$D$	Diffusion coefficient ( $\text{m}^2 \text{ s}^{-1}$ )	$K_{\text{ov}}^{\text{STMEx}}$	Overall mass transfer coefficient in STMEx ( $\text{m s}^{-1}$ )
DCP	2,4-Dichlorophenol	$L$	Length of membrane tube (m)
DCPhO <sup>-</sup>	Ionic form of 2,4-dichlorophenol	$P_m$	Permeability of membrane ( $\text{m s}^{-1}$ )
DCPhOH	Neutral form of 2,4-dichlorophenol	PDMS	Poly(dimethylsiloxane)
$E$	Chemical reaction enhancement factor (dimensionless)	$r_i$	Internal radius of the tube (m)
EPDM	Ethylene-propylene-diene monomer	$r_o$	Outer radius of the tube (m)
$k_f$	Wastewater side liquid film mass transfer coefficient ( $\text{m s}^{-1}$ )	$Re$	Reynolds number, $Re = \rho v d / \mu$ (dimensionless)
$k_m$	Membrane mass transfer coefficient ( $\text{m s}^{-1}$ )	$t$	Time (s)
$k_s$	Stripping solution side liquid film mass transfer coefficient liquid ( $\text{m s}^{-1}$ )	$V$	Volume of the wastewater and stripping solution in STMEx ( $\text{m}^3$ )
		$V_w$	Volume of wastewater in the wastewater tank ( $\text{m}^3$ )
		$\eta_{\text{pro}}$	Process efficiency (%)

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$\eta_{\text{rec}}$	Recovery efficiency (%)
$\eta_{\text{rem}}$	Removal efficiency (%)
$\mu$	Viscosity (Pa s)
$\rho$	Density ( $\text{kg m}^{-3}$ )
$v$	Velocity ( $\text{m s}^{-1}$ )

## INTRODUCTION

The Membrane Aromatic Recovery System (MARS) was developed for the recovery of aromatic acids and bases from industrial aqueous wastewater streams and has been successfully applied for extraction and recovery of phenol<sup>1</sup> and aniline.<sup>2</sup> The MARS process (Fig 1) comprises two stages: in the first, extraction stage, a non-porous hydrophobic membrane is used to extract the aromatic acid (base) from the wastewater to a caustic (acidic) stripping solution, in which the aromatic is concentrated in its ionic form; in the second, recovery stage, the aromatic acid (base) is recovered as a final product by neutralisation of the stripping solution.

One major drawback of membrane technologies is membrane tube blockage<sup>3</sup> due to solid particles, resins or gum-like products in industrial wastewaters. In MARS, blockage can be avoided by placing the wastewater outside the membrane tube. This configuration has an added advantage in reducing the volume of the stripping solution. Moreover, it is more convenient in some industries to treat wastewater in batches, providing operational flexibility,<sup>4</sup> for instance in fine chemical manufacture wastewaters are often produced in batches. Industrial wastewater streams containing aromatic acids are often acidic in nature; for example, production of phenoxy herbicides generates a wastewater stream containing chlorophenols

and HCl. Recent studies conducted by Han *et al*<sup>5</sup> showed that silicone rubber (poly(dimethylsiloxane), PDMS<sup>6</sup>) has a poor acid resistance, while ethylene-propylene-diene terpolymer (EPDM) has a good resistance under acidic conditions.

Chlorophenols are toxic compounds<sup>7</sup> and are typically released into the environment from agro-industrial sources.<sup>8</sup> According to US EPA classification 2,4-DCP is a toxic, carcinogenic and hazardous compound, with maximum allowed concentrations of  $2.020 \text{ mg dm}^{-3}$  for surface water,<sup>9</sup> and  $0.9 \text{ mg dm}^{-3}$  for drinking water.<sup>10,11</sup> Chlorinated phenols are inhibitory to biodegradation<sup>12</sup> with maximum biodegradable concentrations<sup>13</sup> observed in the range of  $600 \text{ mg dm}^{-3}$ . Other destructive processes, such as chemical oxidation,<sup>14</sup> can be applied to chlorophenols, however they destroy the value in the chemical and can be responsible for secondary pollution of the environment. Recovery processes such as liquid membrane extraction, pervaporation and adsorption, have been proposed. Emulsion liquid membranes<sup>15</sup> are inherently unstable, and pervaporation processes<sup>16,17</sup> have not found broad technical-scale development for low volatility organics. Adsorption processes<sup>18</sup> have major drawbacks due to the regeneration stages. In a recent study conducted using the GlaxoSmithKline Green Technology Guide<sup>19</sup> it was concluded that MARS presents significant environmental, efficiency, and energy advantages compared with an alternative polymeric resin adsorption system.

In the present paper, 2,4-dichlorophenol was selected as a representative chlorinated phenol because of its hazardous nature, toxicity, and extensive industrial production (estimated worldwide production

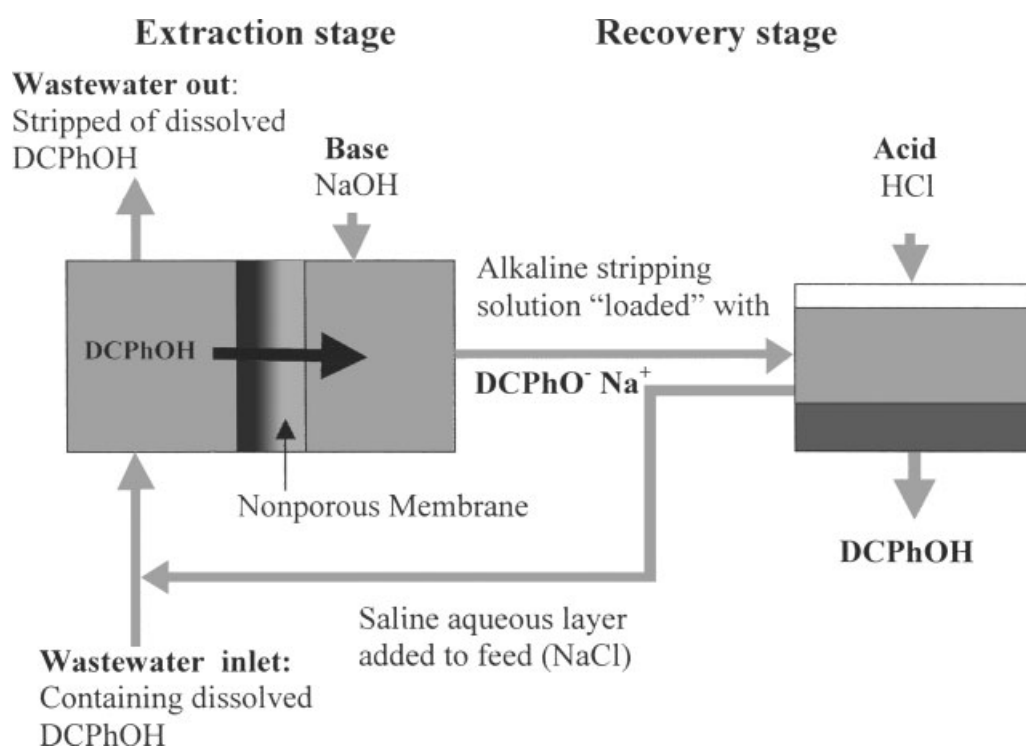


Figure 1. MARS process operating principle.

$\sim 40$  million  $\text{kg year}^{-1}$ ).<sup>20</sup> An acidic industrial wastewater was simulated by adding HCl to an aqueous DCP solution. The performance of the MARS process was investigated in batch mode using an EPDM membrane tube to overcome the foregoing practical challenges.

### MATHEMATICAL ANALYSIS

In this study, the rate of dichlorophenol permeation through PDMS and EPDM membranes is characterised by the overall mass transfer coefficient (OMTC) based on a concentration driving force, and the resistances in series concept. A detailed description of the resistances in series approach applied can be found elsewhere.<sup>1</sup>

For the MARS process employed here the following expression for the OMTC holds:

$$\frac{1}{K_{ov}} = \frac{1}{k_f} + \frac{r_o \cdot \ln \frac{r_o}{r_i}}{D \cdot K} + \frac{r_o}{E \cdot k_s} \quad (1)$$

where the membrane resistance is:

$$\frac{1}{k_m} = \frac{r_o \cdot \ln \frac{r_o}{r_i}}{D \cdot K} = \frac{r_o \cdot \ln \frac{r_o}{r_i}}{P_m}$$

The reaction taking place in the stripping solution falls into the instantaneous reversible category. The enhancement factor ( $E$ ) expression for such reactions was developed by Olander.<sup>21</sup> It follows from the numerical solution of the Olander model for the operating conditions in this work, the relatively high value of the 2,4 DCP equilibrium constant ( $10^{6.11}$ ),<sup>22</sup> and the high hydroxide concentrations employed, that  $E$  will be large in all cases, so the stripping solution resistance term can be neglected.

In order to make overall mass transfer coefficients comparable between runs, all the batches were performed at the same hydrodynamic conditions and with the stripping solution at steady state, i.e. stripping solution pH and DCP concentration were kept constant.

### Determination of $K_{ov}$

In batch mode, when the stripping solution circulates inside the tube and wastewater is placed outside the tube in a feed tank as in Fig 2, the mass balance can be written as:

$$V_w \cdot \frac{dC_w}{dt} = -K_{ov} \cdot A \cdot (C_w - C_s) \quad (2)$$

Integration of eqn (2) gives:

$$\ln(C_w - C_s) = -\frac{K_{ov} \cdot A}{V_w} \cdot t + \ln(C_{w0} - C_s) \quad (3)$$

DCP is a weak acid that dissociates into  $\text{DCPhO}^-$  and  $\text{H}^+$ , with a dissociation acid constant ( $K_a$ )<sup>22</sup> of  $10^{-7.89}$  at  $25^\circ\text{C}$ . For a given pH, the concentration of neutral dichlorophenol ( $C_s$ ) in the stripping solution can be expressed as follows:

$$C_s = \frac{C_{tot}}{1 + K_a/10^{-pH}} \quad (4)$$

The molar percentages of ionic and neutral dichlorophenol in the stripping solution as a function of pH can be calculated from eqn (4). The percentage of neutral DCP sharply decreases with increase in pH above pH 6, until it reaches nearly zero after pH 10. At high pH, 12–14, when  $C_s$  is negligible compared with  $C_w$ , eqn (3) can be simplified and  $K_{ov}$  can be estimated from the slope of the linear relationship between  $\ln(C_w)$  and time. This approach was used to calculate the OMTC values presented in this paper.

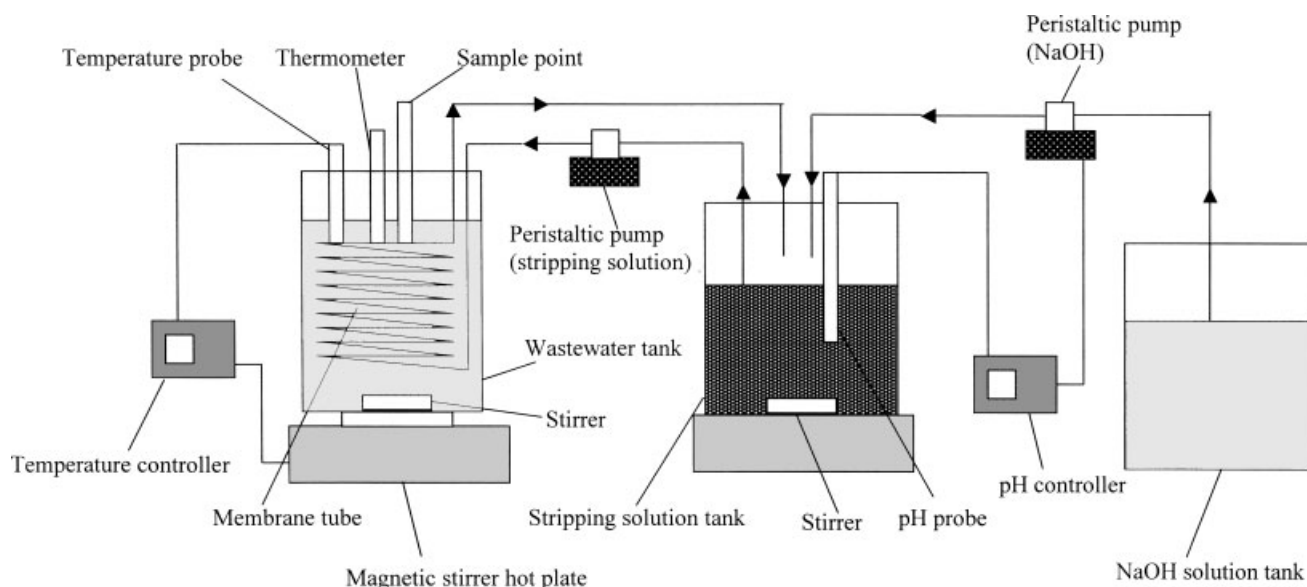


Figure 2. Experimental set up for batch extraction of DCP.

However, near the end of the batch, the concentration  $C_s$  becomes significant and for that reason only experimental points with  $20.C_s < C_w$  were used for  $K_{ov}$  estimation.

## MATERIALS AND METHODS

### Chemicals and membranes

2,4-Dichlorophenol (>98%) was supplied by Aldrich, UK. Sodium hydroxide (pellets, 99%) and HCl solution (35.4 wt%) were obtained from Merck, UK. All the solutions were prepared using deionised water. Two different membrane tubes were used in this study:

- Silicone rubber tube ( $3 \times 10^{-3}$  mid;  $0.5 \times 10^{-3}$  m wall thickness; 36 m length), obtained from Silex Ltd, UK, is composed of 30 wt% fumed silica and 70 wt% poly(dimethylsiloxane), PDMS;
- EPDM tube ( $3 \times 10^{-3}$  m id;  $1 \times 10^{-3}$  m wall thickness; 36 m length), supplied by Dunlop UK, is composed of ethylene-propylene-diene monomer or EPDM (a terpolymer made of ethylene, propylene and diene groups), 30–40 wt % carbon black, as filler, and zinc oxide, stearic acid and antioxidant so that the EPDM content is around 30 wt%.

### Analytical methods

Total organic carbon (TOC) was measured with the TOC-5050, Shimadzu (Japan) analyser. The machine repeats the assay on a sample until the coefficient of variation is less than 2%, 2,4-DCP content was determined either by spectrometric absorption (UV-2101PC, Shimadzu) at 285 nm wavelength or by gas chromatography. The coefficient of variation of the UV assay was 1% over five independent measurements of each sample at the concentration of  $100 \text{ mg dm}^{-3}$ . GC analyses were performed using a program of 2 min at  $50^\circ\text{C}$ , followed by an increase of the temperature to  $190^\circ\text{C}$  at a rate of  $20^\circ\text{C min}^{-1}$ . Details about the GC equipment and analyses can be found elsewhere.<sup>1</sup> The coefficient of variation from five independent measurements of this assay was 5% at  $500 \text{ mg dm}^{-3}$ .

### MARS batch configuration set-up

Figure 2 shows the experimental set up for batch extraction of DCP. Operating conditions are summarised in Table 1. The membrane tube coil was immersed into the wastewater feed tank, where the temperature was controlled by a magnetic stirrer hot plate. Stripping solution was circulated inside the membrane tube with a peristaltic pump at flow rate of  $1.5 \text{ dm}^3 \text{ h}^{-1}$ . The pH of the stripping solution tank was maintained at 12.5 by a feedback loop with a pH probe and a pump, adding 10 wt% NaOH solution when required. The starting stripping solution was also prepared by neutralising 10 wt% NaOH with DCP until pH 12.5, and in this way the  $C_s$  concentration and pH were kept constant into the stripping solution vessel through the whole batch. However,

inside the membrane lumen, the stripping solution pH was not controlled and it decreased alongside the membrane tube due to the neutralisation reaction. The wastewater tank was filled with  $5 \text{ dm}^3$  synthetic wastewater at the start of each batch and emptied at its completion. Wastewater samples were taken over time, while stripping solution samples were taken at the start and end of each batch.

## RESULTS AND DISCUSSION

This work summarises the results of 13 batch experiments. Removal, recovery and process efficiencies are defined as following:

$$\eta_{\text{rem}} = \left[ 1 - \frac{\text{Total DCP remaining after extraction}}{\text{Total DCP fed to extraction}} \right] \times 100 \quad (5)$$

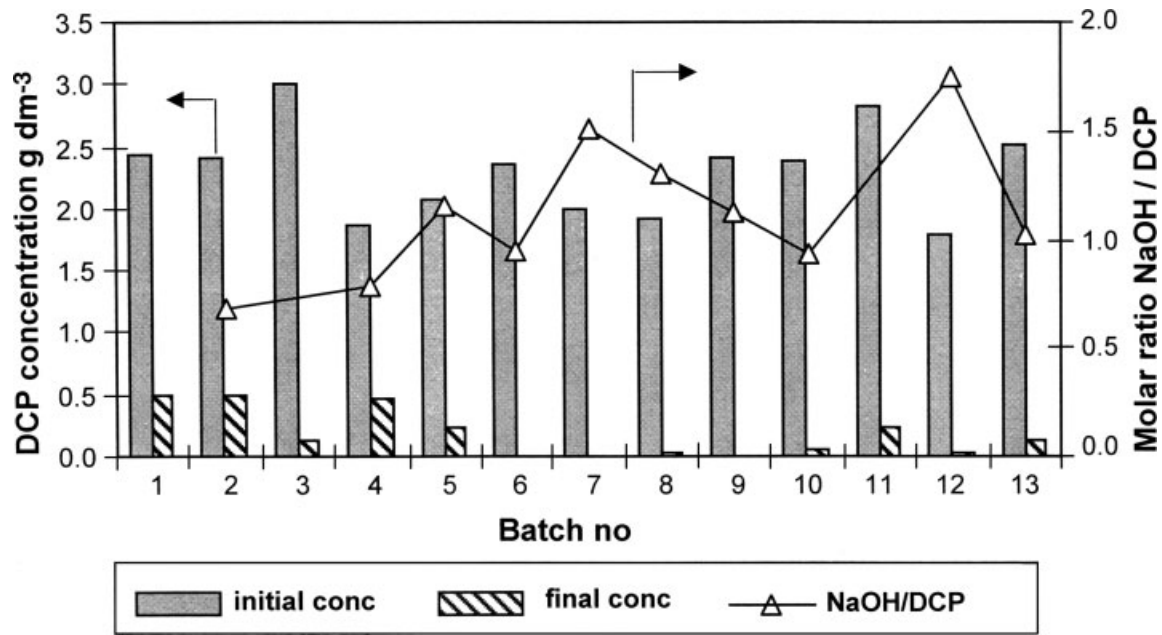
$$\eta_{\text{rec}} = \frac{\text{Total DCP recovered}}{\text{Total DCP into recovery}} \times 100 \quad (6)$$

$$\eta_{\text{pro}} = \frac{\text{Total DCP recovered}}{\text{Total DCP into process}} \times 100 \quad (7)$$

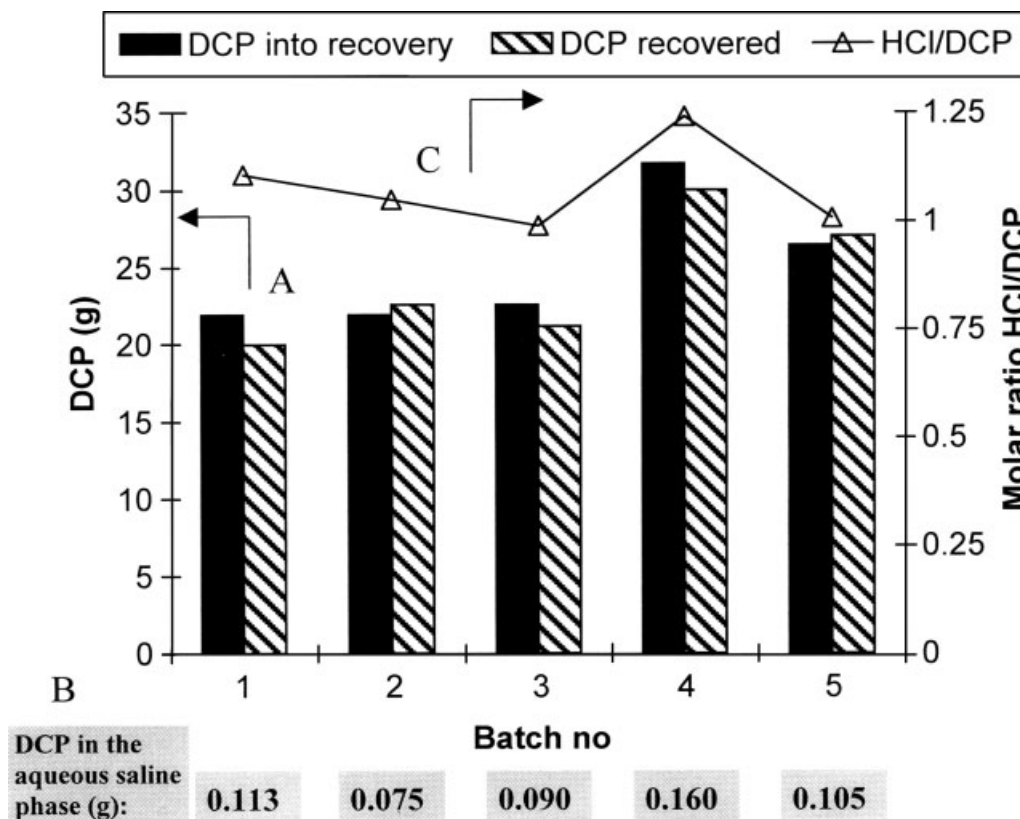
The total efficiencies for the whole 13 batches are, respectively,  $\eta_{\text{rem}} = 92\%$ ;  $\eta_{\text{rec}} = 97\%$  and  $\eta_{\text{pro}} = 80\%$ . On the wastewater side 150.1 g of DCP were subjected to extraction, and 11.4 g remained in the post-extraction wastewater; 124.6 g of DCP were extracted into the stripping solution and submitted to the recovery stage. The DCP mass balance on the extraction closed within 10.2%. Overall 120.8 g of DCP were recovered, representing losses of 3% during the recovery stage. No other compounds were detected by GC analyses of the organic phase and the stripping solution. Experimental parameters and results for each run are presented in Table 1 and in Figs 3 and 4.

**Table 1.** Parameters for different batches

Batch no	Membrane material	Temperature ( $^\circ\text{C}$ )	Batch operating (hs)	HCl (wt%) or pH	DCP removal (%) $\eta_{\text{rem}}$
1	EPDM	30	22	pH ~ 3	80.1
2	EPDM	30	30	pH ~ 3	79.3
3	EPDM	30	80	5 wt%	96.0
4	EPDM	30	46	5 wt%	74.4
5	EPDM	60	24	pH ~ 3	88.3
6	EPDM	60	72	pH ~ 3	99.8
7	PDMS	30	24	pH ~ 3	99.5
8	PDMS	30	20	pH ~ 3	98.7
9	PDMS	30	5	5 wt%	91.9
10	PDMS	60	26	pH ~ 3	99.6
11	PDMS	60	7	pH ~ 3	99.8
12	PDMS	60	72	5 wt%	99.2
13	PDMS	60	6	5 wt%	91.3



**Figure 3.** Initial and final concentrations of DCP in wastewater for each batch, and molar ratio (NaOH added to the stripping solution)/(DCP extracted).



**Figure 4.** Dichlorophenol recovery stage for recovery batches 1–5, including: (A) mass balance between stripping solution DCP into recovery and DCP recovered, (B) DCP content into the post-recovery aqueous phase and (C) HCl/DCP molar ratio at the stripping solution neutralisation stage.

### Extraction stage

#### Extraction stage removal efficiency

The removal efficiency for each batch, calculated from eqn (5), is presented in Table 1. A typical DCP removal efficiency over time curve (batch 10—Table 1) for the PDMS membrane is presented

in Fig 5(a). Within a batch, the removal efficiency increases with time and reaches its maximum value, when the wastewater DCP concentration becomes equal to the neutral DCP concentration in the stripping solution, due to the absence of any driving force for the mass transport. Most DCP (98%)

was extracted in the first 3 h of operation, and the respective wastewater concentration reached was  $0.025 \text{ g dm}^{-3}$ . Then, the removal efficiency increased at a much lower rate and reached its maximum value of 99.6% in 26 h at a wastewater concentration of  $0.0064 \text{ g dm}^{-3}$ . This value is in good agreement with a value of  $0.0063 \text{ g dm}^{-3}$  for the neutral DCP concentration in the stripping solution calculated theoretically from eqn (4). The DCP concentration can be further reduced below  $0.0064 \text{ g dm}^{-3}$  by increasing the pH of the stripping solution, or by replacing the steady state stripping solution with a fresh 10 wt% NaOH as a stripping solution. In this way, the concentration of neutral DCP in the stripping solution is drawn back to zero and the corresponding equilibrium concentration in the wastewater will also be reduced. However, this second extraction stage will be too slow and inefficient due to the low driving force. An attractive option could be the coupling of the MARS process with biological processes. MARS can reduce high DCP concentrations to levels which do not inhibit bacterial growth, and biological processes<sup>13</sup> then can be applied for further reduction of the DCP concentration in order to reach the discharge criterion.

*Extraction stage overall mass transfer coefficients*

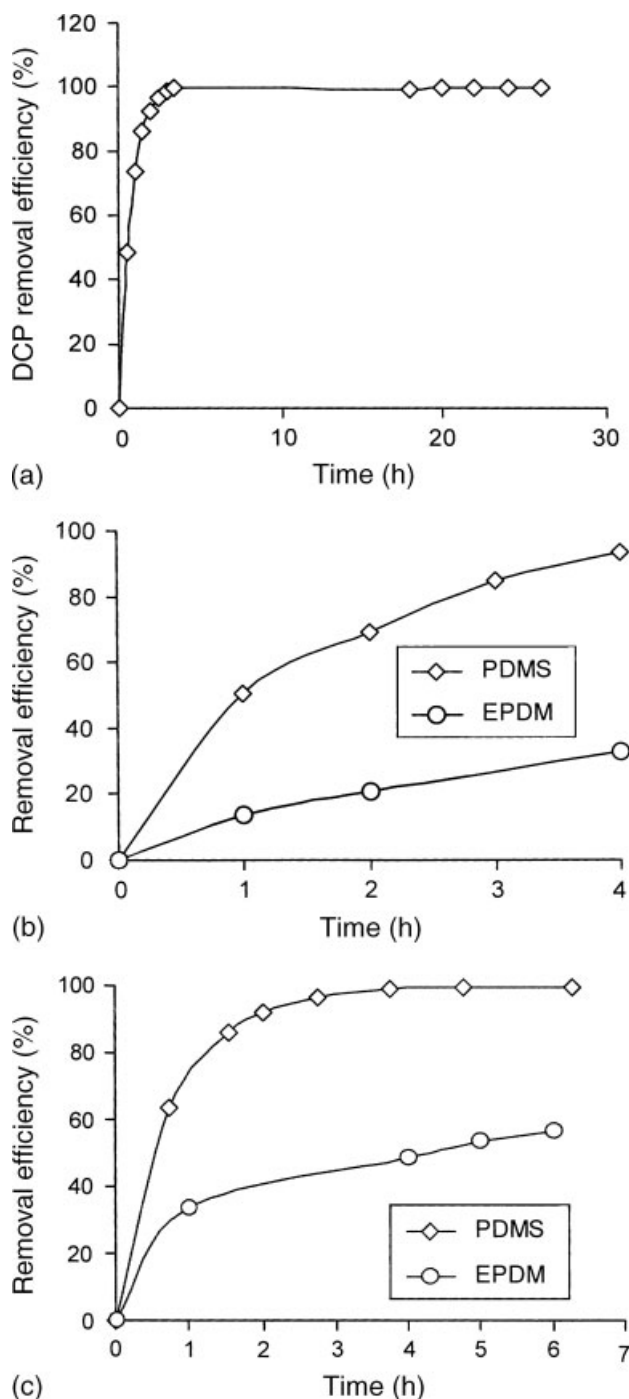
The overall mass transfer coefficients were calculated using eqn (3) in its simplified form as described in the mathematical analysis section. The average values of  $K_{ov}$  with their standard deviations are listed in Table 2. These values are one order of magnitude higher for DCP extraction through PDMS than those through EPDM. The differences in the transport rates of these two elastomers may be due to the differences in their polymeric structures, and this mainly affects the removal efficiency over time. For example, for a temperature of  $30^\circ\text{C}$  (Fig 5(b)), depending on the membrane material (either PDMS or EPDM) after 4 h of operation, removal efficiencies of 93% and 33% respectively could be achieved.

*Effect of temperature on the extraction stage*

To investigate the effect of temperature on the DCP overall mass transfer coefficient, experiments were performed with PDMS and EPDM at  $30^\circ\text{C}$  and  $60^\circ\text{C}$ , holding the rest of the parameters equal. The results are shown in Table 2. An increase

**Table 2.** Overall mass transfer coefficients at different temperatures and different HCl concentrations

Temperature (°C)	HCl (wt%)	PDMS		EPDM	
		OMTC ( $\text{m s}^{-1}$ ) $\times 10^7$	Standard deviation $\times 10^7$	OMTC ( $\text{m s}^{-1}$ ) $\times 10^7$	Standard deviation $\times 10^7$
30	~0 (pH = 3)	20	0.1	1.4	0.2
30	5	17	–	1.8	1.4
60	~0 (pH = 3)	39	2.2	2.4	0.2
60	5	28	2.4	–	–



**Figure 5.** Extraction efficiencies over time: (a) typical curve for PDMS membrane: batch 10; (b) Influence of the membrane material on the extraction efficiency at  $30^\circ\text{C}$ : batches 2 and 7; (c) influence of the membrane material on the extraction efficiency at  $60^\circ\text{C}$ : batches 6 and 11.

in overall mass transfer coefficients was observed with temperature in both membranes. The removal efficiency for PDMS after 2 h was already 92% for a temperature of  $60^\circ\text{C}$ , but only 69% at  $30^\circ\text{C}$ . The removal efficiencies through EPDM after 4 h are 33% and 49% at 30 and  $60^\circ\text{C}$ , respectively (see Fig 5(b and c)). This is in agreement with diffusion studies conducted at different temperatures in *n*-hexane and *n*-octane by George *et al*,<sup>23</sup> who found that both the diffusion rate and mole percent solvent uptake at

equilibrium increased with increasing temperature. These observations were attributed to the increase in free volume and polymer chain mobility with temperature, allowing easier penetrant diffusion.

#### Estimation of the extraction stage individual mass transfer resistances

**Estimation of membrane mass transfer resistance (permeability).** Figure 6 shows the single tube mass exchanger (STMEx) used to measure the membrane resistance. The length of the PDMS and EPDM tubes used were 525 mm and 550 mm, respectively, and the internal diameter of the glass shell was 14 mm. Temperature was controlled at 30 °C within a water bath. An aqueous solution with initial DCP concentration of 2.5 g dm<sup>-3</sup> and pH = 3 was circulated through the membrane shell side, and an aqueous solution with pH = 3 was circulated through the membrane tube. The pH value of 3 (adjusted with HCl) was used on both sides to keep DCP in a non-dissociated form.  $K_{ov}^{STMEx}$  was estimated separately from eqn (8)—for the wastewater side, and from eqn (9)—for the stripping solution side (note, that both equations are derived for the case when the stripping and wastewater solution volumes are equal). The final  $K_{ov}^{STMEx}$  value was taken as an average of these two values.

$$\frac{1}{2} \cdot [\ln C_{w_0} - \ln(2 \cdot C_w - C_{w_0})] = \frac{K_{ov}^{STMEx} \cdot A}{V} \cdot t \quad (8)$$

$$\frac{1}{2} \cdot [\ln C_{w_0} - \ln(C_{w_0} - 2C_s)] = \frac{K_{ov}^{STMEx} \cdot A}{V} \cdot t \quad (9)$$

High Reynolds numbers ( $Re_{tube} = 12\,087$  and  $Re_{shell} = 3022$ ) were used on both shell and tube sides to minimise the contribution of the liquid film resistances to the overall mass transfer resistance. However, the liquid film resistances were still taken into account and the liquid film mass transfer coefficients were calculated from eqns (10) and (11).<sup>24</sup>

$$k_{tube} = 1.36 \times 10^{-8} Re_{tube}^{0.8} \quad (Re_{tube} > 4800) \quad (10)$$

$$k_{shell} = 4.05 \times 10^{-8} Re_{shell}^{0.8} \quad (Re_{shell} > 2470) \quad (11)$$

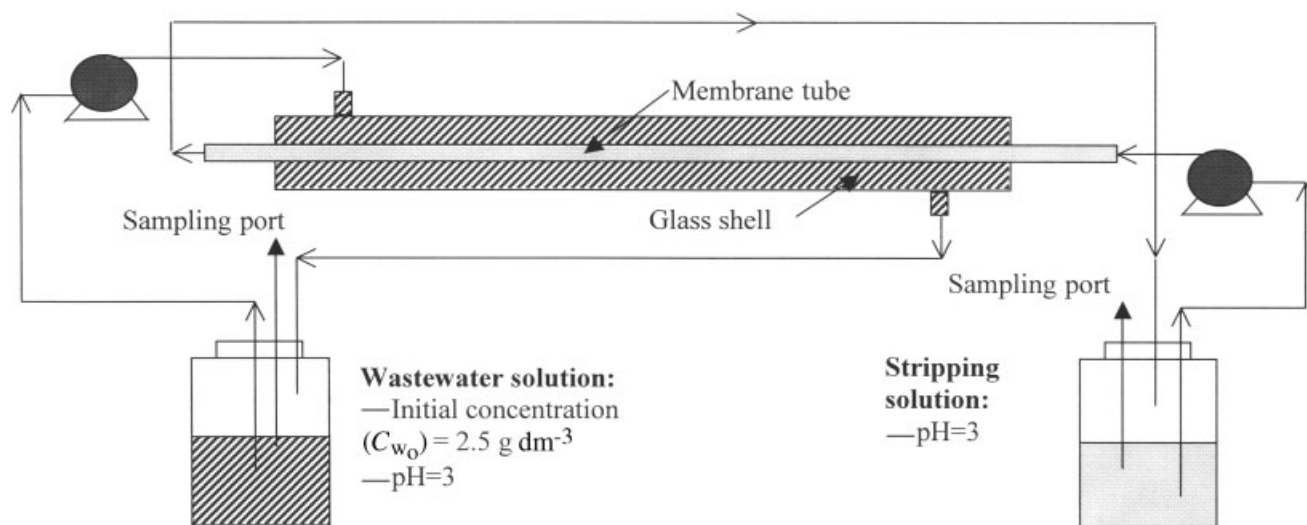


Figure 6. Schematics of the single tube mass exchanger (STMEx).

The membrane resistance was calculated from eqn (1) (for the case without chemical reaction, ie  $E = 1$ ) by subtracting the calculated liquid film resistances ( $1/k_{tube}$  and  $1/k_{shell}$ ) from the overall resistance ( $1/K_{ov}^{STMEx}$ ) measured using the STMEx.

The membranes mass transfer coefficients ( $k_m$ ) calculated in this way were  $5.3 \times 10^{-6} \text{ m s}^{-1}$  for PDMS and  $1.3 \times 10^{-7} \text{ m s}^{-1}$  for EPDM, respectively. The membrane tubes have different thicknesses, hence to assess which is the more permeable material, the corresponding permeability ( $P_m = D \cdot K$ ) was calculated, showing that the PDMS membrane is 9.2 times more permeable than the EPDM tube ( $30.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  against  $3.3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ , respectively).

Nijhuis *et al*<sup>25</sup> investigated a wide range of elastomers for pervaporation processes. According to their results, PDMS showed the highest permeability to organic compounds among the elastomers studied, while EPDM had an intermediate performance. They correlated the permeabilities of the organic components with structural parameters such as degree of unsaturation, and presence of steric side groups. The lower the glass-transition temperature (and the higher the chain flexibility), the higher is the permeability. The glass-transition temperature is an important parameter affecting the diffusion coefficient of a compound through a polymer. The reported values of the glass-transition temperatures of PDMS and EPDM are  $-132$  and  $-62$  °C, respectively.<sup>5</sup> The corresponding diffusion coefficients of toluene<sup>5</sup> in these two polymers were  $1.1 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$  and  $0.13 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ , eg a ratio of  $\sim 8.5$  was observed. This result is consistent with the permeability values ratio obtained in this study.

#### Estimation of liquid film mass transfer resistance

The wastewater side liquid film resistance for the MARS batch process ( $3.2 \times 10^{-6} \text{ m s}^{-1}$ ) was calculated from eqn (1), using the overall mass transfer coefficient ( $K_{ov} = 2.0 \times 10^{-6} \text{ m s}^{-1}$ ) at 30 °C

and the membrane mass transfer coefficients ( $k_m = 5.3 \times 10^{-6} \text{ m s}^{-1}$ ) for PDMS membrane at the same temperature.

The estimated value ( $3.2 \times 10^{-6} \text{ m s}^{-1}$ ) shows that the wastewater side liquid film resistance and the PDMS membrane resistance are comparable. Therefore, in this case improving the mixing on the wastewater side could increase the mass transfer rate. However, for the EPDM membrane, the membrane mass transfer coefficient ( $k_m = 1.3 \times 10^{-7} \text{ m s}^{-1}$ ) and the overall mass transfer coefficient ( $K_{ov} = 1.4 \times 10^{-7} \text{ m s}^{-1}$ ) have very similar values, which indicates that the membrane resistance dominates, and improving mixing in the feed tank will not further improve the mass transfer.

#### Membrane chemical stability

As expected, in terms of mass transfer the PDMS membrane performs better than EPDM but is not suitable for long-term operation under strong acid/base conditions. Pinholes in the membrane were observed after a few weeks' operation in 5 wt% HCl solutions. EPDM showed no obvious structural changes after a similar period of operation. The considerably lower OMTC of the EPDM membrane could be increased by reducing the membrane thickness  $\sim 40$  times. To achieve the same overall mass transfer coefficient of the 500  $\mu\text{m}$  PDMS membrane, using an EPDM membrane, the thickness of the EPDM membrane should not surpass 25  $\mu\text{m}$ . However, such a thin membrane, will lack mechanical strength and a support will be required, adding an extra resistance to the system. A composite membrane with a very thin non-porous layer of EPDM supported on a chemically-resistant porous material could be the solution for an ideal MARS membrane. However, this composite membrane will have the inherited disadvantage of a loss of effective area, since the contact of the active layer with the solution will be limited by the pore diameter and support porosity. A detailed study on the effect of the EPDM thickness and support resistance on organic fluxes across could be found elsewhere.<sup>26</sup> Another possible solution for a better membrane for the MARS process may be to sandwich the PDMS membrane between very thin EPDM layers. In this way, the material might be protected from the acid/base attack on both sides.

#### Stability of the extracted DCP

*From direct stripping solution sample analysis.* Stripping solution samples were analysed for total DCP (DCPOH plus  $\text{DCP}^-$ ) concentration by both GC and TOC methods at the start and end of each batch. Direct measurements of TOC should detect not only the organic carbon from DCP, but also from any other organic side product eventually formed and present in the solution. The DCP concentration values measured by GC analyses were converted into organic carbon concentrations, and these values were then compared with the ones measured directly by

the TOC method. The deviations between these two values were within  $\pm 12\%$  and were not systematic but random. This result suggests that all organic content in the stripping solution is DCP, and there are no side products formed.

*From the NaOH mass balance.* As dichlorophenol is extracted into the stripping solution it reacts with sodium hydroxide to form sodium dichlorophenate (eqn (12)). NaOH is added, as required to maintain a high stripping solution pH and draw the equilibrium reaction towards the sodium dichlorophenate formation:



The stoichiometry of this reaction requires that one mole of NaOH should be added to the stripping solution for each mole of DCP extracted from the wastewater. The experimental data were consistent with this stoichiometry (Fig 3) and most probably the only reaction occurring in the stripping solution is the formation of  $\text{Na}^+\text{DCPhO}^-$ .

#### Recovery stage

##### Recovery stage efficiency

The stripping solution overflow collected from several batches was titrated with 35.4 wt% HCl until a pH value of 1 was reached in the saline layer, to ensure that the system is well beyond the neutralisation point.



Since the solubility of neutral DCPhOH is much lower than that of sodium dichlorophenate, the resulting solution separates into two phases, the lower layer consisting of a DCP-rich organic phase and the upper layer consisting of aqueous solution containing sodium chloride and a small amount of DCP. Since the DCP is solid at room temperature (melting point  $45^\circ\text{C}$ <sup>27</sup>), neutralisation and phase separation were carried out at  $60^\circ\text{C}$ . The DCP in the saline upper layer phase became solid on cooling to  $4^\circ\text{C}$ , and an additional amount of DCP was recovered by filtration using a Whatman 50 filter paper. The masses and DCP concentrations of all the initial and final solutions/phases were measured for mass balance purposes.

Recovery efficiency (as defined in eqn (6)) of 97% was achieved for all the batches. This recovery efficiency is higher than that of phenol<sup>1</sup> and of aniline<sup>2</sup> (94% and 92%, respectively) and is due to the lower solubility of aqueous DCP and the use of an additional aqueous phase filtration step following the initial phase separation. It is clear from the stoichiometry of the base-acid reaction (eqn (13)) that one mole of HCl is required to neutralise one mole of  $\text{Na}^+\text{DCPhO}^-$ . The experimental data shown in Fig 4 are quite consistent with the theoretical HCl/DCP molar ratio of one. This



result could also be considered as partial evidence of the product's purity.

#### *Effect of NaCl on the solubility of DCP in aqueous phase*

As already mentioned, in the MARS process, the caustic stripping solution was maintained at pH 12.5 by adding a 10 wt% NaOH solution during DCP extraction. In the recovery stage this stripping solution was neutralised using a 35.4 wt% HCl solution. Ultimately the sodium ends up as NaCl in the saline aqueous upper layer with a concentration of 12.3 wt% NaCl. If the recovery is performed after each batch, and the saline layer generated is re-circulated back into the next batch of fresh wastewater effluent (see Fig 1), NaCl is released into the environment at a final concentration of 0.06 wt%, which, while undesirable, would be much more environmentally acceptable than the release of DCP streams. DCP concentration measured in the saline aqueous layer was typically  $1.0 \text{ g dm}^{-3}$ . The residual DCP concentration in the saline layer is expected to depend strongly on the NaCl concentration, due to the salting out effect.<sup>2</sup>

The effect of NaCl on the solubility of DCP in the aqueous phase was investigated at 30 °C. Sample solutions of 0, 10, 15, 20, 25 wt% NaCl in deionised water were prepared, and 1.5 g of DCP was added to 100 g of each solution, ensuring an excess of DCP above its solubility limit ( $\sim 5.5 \text{ g dm}^{-3}$ —measured in deionised water). The equilibrium DCP concentration in the saline phase was measured using GC analysis.

Results are presented in Fig 7, which shows that the salting out effect is considerable up to NaCl concentrations of 20 wt%. From Fig 7, a DCP solubility of about  $2 \text{ g dm}^{-3}$  for a 12.3 wt% NaCl concentration can be estimated. The difference between the value obtained in the MARS recovery stage and this one can be explained by the difference of temperatures at which the phase separation in the recovery stage and the experiments for the salting out effect (4 °C and 30 °C) were performed.

The salting out effect of DCP could be used to improve the recovery efficiency of the process. For example, a stripping solution with higher NaOH concentration will result in a higher NaCl concentration in the aqueous saline upper layer. Hence, due to the lower DCP solubility in the

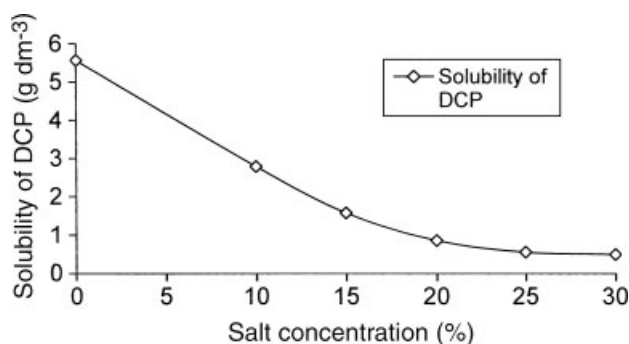


Figure 7. The effect of NaCl on solubility of DCP.

aqueous saline phase, the organic layer will be enriched in DCP, and the recovery efficiency will be improved. Furthermore, the higher the NaOH concentration is, the lower the volume of the aqueous saline layer generated will be, thus decreasing both DCP concentrations and volumes of aqueous saline solution re-circulated to the wastewater. However, an increased NaOH concentration leads to higher total DCP concentrations in the stripping solutions at steady state. This will increase the neutral DCP concentration in the stripping solution ( $C_s$  in eqn (4)), and consequently reduce the driving force and the removal efficiency. Therefore to reach the same process performance, some extra cost will be added in the form of membrane area requirement. A compromise value of 10 wt% NaOH was used in this study, in order to optimise removal and recovery efficiencies, however for scaled-up application a detailed economic analysis of each case is required.

## CONCLUSIONS

The MARS process can be successfully applied for the extraction and recovery of DCP. It can be operated in a batch mode, by placing the wastewater outside, and the stripping solution inside, the membrane tube, thus avoiding the problems of membrane blockage, and reducing the volume of the stripping solution used. The final DCP concentration achieved in the stripping solution was 56 times higher than its solubility in water, which shows the great potential of MARS as a concentrating process. High recovery efficiencies and sufficient purity of the final product is a promising indication for the commercial applicability of this technology. The process's mass transfer efficiency can be improved by increasing the operating temperature. The much better stability of EPDM under highly acidic conditions (5% HCl) makes it a preferred membrane choice for DCP recovery from real industrial wastes, although shows an order of magnitude lower mass transfer characteristics. Application of more stable polymeric membranes such as EPDM can improve significantly the stability and exploitation lifetime of the industrial MARS process.

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