*Desalination and Water Treatment*
www.deswater.com

12 (2009) 256–261

1944-3994 / 1944-3986 
doi: 10.5004/dwt.2009.938

# A novel approach for treatment of a typical perfumery chemical wastewater for possible reuse

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Received 21 November 2008; Accepted in revised form 8 October 2009

**ABSTRACT**

Heptaldehyde is a very important castor oil based perfumery chemical. This is produced by pyrolyzing castor methyl esters (CME). In this process large volumes of water are required and the wastewater produced is contaminated with heptaldehyde and other byproducts. The presence of heptaldehyde — a malodorous compound, causes serious problems to the nearby locality if the contaminated water is discharged without proper treatment. In the present investigation, a process was developed for the treatment of aldehyde contaminated perfumery chemicals wastewater. As the common coagulants such as alum, ferric chloride, alginic acid and chitosan either alone or in combination with powdered activated charcoal (PAC) as adsorbent did not have any desired effect, a novel pretreatment process was developed using sodium borohydride as reducing agent. This was followed by membrane processing. The process parameters for using both the reducing agent and PAC as adsorbent were optimized keeping in mind the removal of mal-odor of the wastewater samples. The pretreated water was first filtered using a micron filter and then processed through a reverse osmosis membrane. The final treated water was clear, odorless and the quality of the water was found to be suitable for reuse.

*Keywords:* Wastewater; Perfumery chemicals; Heptaldehyde; Sodium borohydride; Reducing agent; Powdered activated charcoal (PAC); Reverse osmosis (RO)

## 1. Introduction

In the last few decades, the whole world has witnessed unprecedented growth in industrialization. As a result, the total populace residing in urban areas has grown at a very fast pace and the requirement of fresh water has increased tremendously. Reducing number of fresh water resources and poor planning by governmental agencies as well as industrial bodies have worsened the situation over the period. However, in recent times various environmental protection agencies and regulatory authorities have taken an account of the present situation and tightened their norms of minimum discharge standards of the effluent of different grades of industries. As a result, industries are spending a considerable part of their resources to meet the discharge norms. Reuse of treated water has, therefore, become one of the main agenda of present day industries — particularly where the amount of water usage is high. Application of membrane separation techniques has contributed significantly in develop-

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ing some processes for reuse of wastewater coming out of various chemical, pharmaceutical, food processing and other industries [1–3]. With the use of newer membranes the possibility of commercial exploitation of these processes has become more viable.

In the present investigation, attempts were made to treat the wastewater from a perfumery chemicals industry for possible reuse. Heptaldehyde is produced by pyrolysis of castor oil methyl esters (CME). Water requirement in this process is high and considerable amount of wastewater is generated during the process. The wastewater produced is contaminated mainly with heptaldehyde which has pungent and irritating odor. This creates tremendous problems to the nearby habitats and also to the aquatic population if discharged to the sewage directly without any treatment. Because of higher demand of heptaldehyde and other byproducts, the production capacities of most of the plants are enhanced and new plants are being established. However, there was no report found in the literature for treating the wastewater coming out from this particular perfumery chemical industry. It was, therefore, decided to study the feasibility of treating this wastewater for possible reuse or recycling.

The wastewater sample was subjected to pretreatment with various known coagulants [4–8] and adsorbent treatments [8–10] as reported in the literature. However, the heptaldehyde odor could not be reduced or removed completely by the use of these coagulants like alum, ferric chloride, alginic acid and chitosan even with higher dosages. It was, therefore, decided to carry out a reaction of heptaldehyde present in the wastewater to get a new compound having no odor or less odor. Heptaldehyde — the major pollutant in the wastewater sample — can either be oxidized to heptanoic acid or reduced to heptanol. Oxidation of heptaldehyde produces heptanoic acid which also has a characteristic pungent smell. Moreover, these acids are corrosive in nature [11]. On the other hand, a reduction reaction of heptaldehyde produces heptanol that is a non-hazardous chemical and has a typical sweet alcoholic odor. Apart from that, the alcohol produced can be adsorbed on PAC and may be removed easily [12,13]. It was therefore decided to do the reduction reaction to convert the aldehyde into alcohol. Commercially available reducing agents are sodium borohydride [14–18], lithium aluminumhydride [14,18], potassium borohydride [19] and sodium cyanoborohydride [20]. Amongst all, sodium borohydride is most suitable as it is more easily available, safe [14,21] and economic compared to the other reducing agents. It was therefore chosen as the reducing agent for the present study. The reduction reaction reduced the odor considerably and changed the odor from a pungent aldehydic odor to a milder alcoholic odor. After the reduction reaction, adsorbent treatment by PAC was carried out in order to adsorb the alcohols and remove the milder alcoholic odor. In the final stage of the process, membrane separation techniques were used to reduce the conductivity, total dissolved solids (TDS), biological oxygen demand (BOD), and chemical oxygen demand (COD), etc.

After the studies on optimization of various parameters, the treatment schedule was finalized as follows: skimming of composite wastewater after settling, reduction reaction with sodium borohydride at pH 12, adsorbent treatment using PAC at pH 7 followed by microfiltration and reverse osmosis. The quality of the treated water was analyzed and found to have better characteristics compared to the actual process water used.

## 2. Materials and methods

### 2.1. Wastewater sample

Wastewater samples were collected from the process of pyrolysis of castor oil methyl esters (CME) from a continuous pilot plant situated at IICT, Hyderabad and were mixed thoroughly to obtain a composite sample.

The composite wastewater sample was skimmed to remove the oily layer as much as possible and the resultant water was taken for the further studies. The resultant water had the following characteristics as represented in Table 1.

### 2.2. Reagents

Sodium borohydride [16940-66-2] and powdered activated charcoal (PAC) [7440-44-0] were procured from S.D. Fine Chem Ltd., Mumbai, India. Commonly used chemicals to maintain the pH of the medium were NaOH (LR grade) [1310-73-2] and HCl (LR grade) [7647-01-0] and were procured from S.D. Fine Chem Ltd., Mumbai, India and Ranbaxy Fine Chemicals Ltd, New Delhi, India.

### 2.3. Membranes

#### 2.3.1. For lab scale studies

Hydrophilic PVDF flat sheet membranes having 0.45 μm pore size (HLVP09050) was procured from Millipore Corporation, MA, USA. TW30-1812 flat sheet thin

Table 1
Characteristics of composite raw wastewater

| Properties | Range |
|---|---|
| pH | 4.35–4.92 |
| Conductivity, μS/cm | 325–590 |
| TDS, mg/L | 280–506 |
| FOG, mg/L | 115–130 |
| COD, mg/L | 6,073–7,296 |
| BOD, mg/L | 2,400–3,500 |
| Appearance | Turbid and oily in color |
| Odor | Strong heptaldehyde odor |

film composite polyamide RO membrane with the characteristic rejection of NaCl (98–99%) was procured from Dow Chemical Company, Michigan, USA.

*2.3.2. For pilot scale studies*

The ceramic microfiltration membrane having 0.45 μm pore size used in pilot scale studies was procured from Orelis, France. It is having a tubular configuration with 19 channels, having 800 mm length and 0.167 $m^2$ surface area. A spiral wound RO membrane with 2 $m^2$ surface area was procured from Osmonics, Minnesota, USA. The membrane is made of cellulose acetate and has more than 99% NaCl rejection characteristics.

*2.4. Pretreatments*

For the pretreatment studies a stainless steel stirred tank reactor having the capacity of 75 L fitted with an overhead mechanical stirrer was used.

*2.4.1. Reduction reaction*

The wastewater after settling and skimming was filtered through an ordinary filter paper. The pH of the filtered wastewater was adjusted to the desired value with dilute NaOH solution then the reduction reaction with sodium borohydride was performed using various dosages and varying stirring time. The reaction product was then neutralized with dilute HCl solution under stirring.

*2.4.2. Adsorbent treatment*

The neutralized reaction product was then subjected to adsorbent treatment with PAC as an adsorbent. After adsorbent treatment, the sample was filtered with an ordinary filter paper.

*2.5. Membrane separation studies*

The filtrate after the adsorbent treatment was passed through the micron filter in order to take care of minute charcoal particles and minimize the load on the reverse osmosis membrane and the permeate was then passed through the reverse osmosis membrane.

*2.5.1. For laboratory scale studies*

Microfiltration was performed in a dead-end glass test cell having maximum pressure limit of 6 bar supplied by Millipore Corporation, MA, USA. The reverse osmosis experiments were done in a stainless steel test cell of dead-end type having the maximum pressure limit of 50 bar and this was supplied by Snowtech Pvt. Ltd., Mumbai, India. Both test cells were fitted with a magnetic stirrer. The transmembrane pressure (TMP) was generated by nitrogen gas.

*2.5.2. For pilot scale studies*

Pilot scale studies were done in a cross flow membrane unit with a 50 l stainless steel feed tank. This was supplied by Nishotech Systems Pvt. Ltd., Mumbai, India.

*2.6. Analytical methods*

Wastewater samples and various water samples after treatment were analyzed for pH and conductivity with the help of the digital pH meter (Model: DI 707), supplied by Digisun Electronics, Secundrabad, India and digital conductivity meter (DCM 900) supplied by Global Electronics, Hyderabad, India, respectively. Total dissolved solids (TDS), fats, oils and grease (FOG) were determined according to the standard methods [22]. For the estimation of the chemical oxygen demand (COD) the digestion of the sample was done in a COD reactor Model 45600, supplied by HACH, Colorado, USA followed by titration with standard ferrous ammonium sulphate according to the APHA standard method [22]. For the estimation of 5 day biological oxygen demand $BOD_5$ (20°C) APHA standard method [22] was used using YSI-5100 dissolved oxygen meter, supplied by YSI Incorporated, Ohio, USA.

## 3. Results and discussion

The wastewater generated from the castor oil based perfumery chemical industry, where castor oil methyl esters are pyrolyzed to form heptaldehyde and other byproducts, was chosen for the study. In this industry, water requirement is high and the large amount of wastewater generated is contaminated mainly with heptaldehyde having irritating and pungent characteristic odor. This has to be treated before discharge as otherwise this creates serious problems to the nearby locality and also to the aquatic environment where it is discharged. In this investigation, attempts were made using a novel hybrid treatment method to treat this wastewater for possible reuse. After pretreatment, which includes the reduction reaction of heptaldehyde and adsorption on PAC, membrane separation techniques were used to get the quality of the water that can be reused. At the initial stage of this study, experiments were carried out on a laboratory scale to check the feasibility of the process. Once the feasibility was established, studies were performed on a larger scale taking around 40 l of wastewater.

During the feasibility studies, the initial emphasis was given to removal of odor. Coagulant treatment was carried out at a laboratory scale after adjusting the pH of the wastewater to 7 using various known coagulants like alum, ferric chloride, alginic acid and chitosan. The dosages were varied from 25 mg/L to even 1 g/L. However, no significant improvement was observed as far as odor reduction and coagulation were concerned. Powdered activated charcoal (PAC) was used as adsorbent either alone or in combination with the coagulants with varying dosages ranging from 0.5 to 5 g/L. However, very little improvement could be achieved as far as odor removal was concerned.

The conventional methods of coagulation/adsorption did not have any significant effect on reduction of odor. Therefore, an alternative methodology was tried. Since the major odor producing contaminant was heptaldehyde — an aldehyde compound, it was then decided to convert heptaldehyde to heptanol — a non-hazardous chemical by the reduction reaction [23]. Being an alcoholic compound, heptanol had sweet odor. Conversion of heptaldehyde to heptanoic acid by oxidation was not preferred as heptanoic acid — a hazardous chemical, also has a pungent odor and is corrosive in nature [11]. Reduction of aldehydes to alcohols can be achieved by using various reducing agents like sodium borohydride, lithium aluminium hydride, potassium borohydride, sodium cyanoborohydride, etc. However, sodium borohydride was chosen as the reducing agent for its easy availability, ease of handling and for economic advantages. According to the reports published [17,24], reduction reaction with sodium borohydride proceeds more effectively under basic conditions. It was, therefore, decided to study the effect of pH on dosages of sodium borohydride for complete reduction of the typical heptaldehyde odor. The studies were performed in the pH range of 8–13 and the results are shown in Fig. 1.

For complete removal of heptaldehyde odor and to have a sweet alcoholic odor, it was observed that 3 g/L of sodium borohydride was required at pH 8. For the same effect, only 25 mg/L of sodium borohydride was found to be sufficient at pH 12. No further reduction in dosages could be achieved by increasing the pH to 13. All the further studies were therefore carried out at pH 12.

The treated water obtained after the reduction reaction was found to have a mild alcoholic odor due the presence of heptanol. This was then subjected to adsorbent treatment for complete odor removal. PAC, the most common adsorbent, was chosen for the study. The pH of the water sample was changed from 12 to 7 before the adsorbent treatment for better adsorption characteristics as activated powdered carbon was used for adsorption. The dosages were varied from 0.5 g/L to 3.0 g/L. Complete removal of odor could be achieved at 2.5 g/L dosage of PAC. After the adsorption treatment and filtration, the treated water sample was initially passed through a PVDF microfiltration membrane as described in section 2.5.1. The permeate obtained after microfiltration was then passed through a thin film composite polyamide reverse osmosis membrane. The quality of final water obtained is presented in Table 2.

The laboratory scale experiments, thus, showed encouraging results as the final treated water was found to

Table 2
Quality of treated water after reverse osmosis at laboratory scale

| Properties | Reverse osmosis permeate |
|---|---|
| pH | 7 |
| Conductivity, μS/cm | 28 |
| TDS, mg/L | 20 |
| FOG, mg/L | nil |
| COD, mg/L | 300 |
| BOD, mg/L | 120 |
| Appearance | Colorless |
| Odor | Odorless |

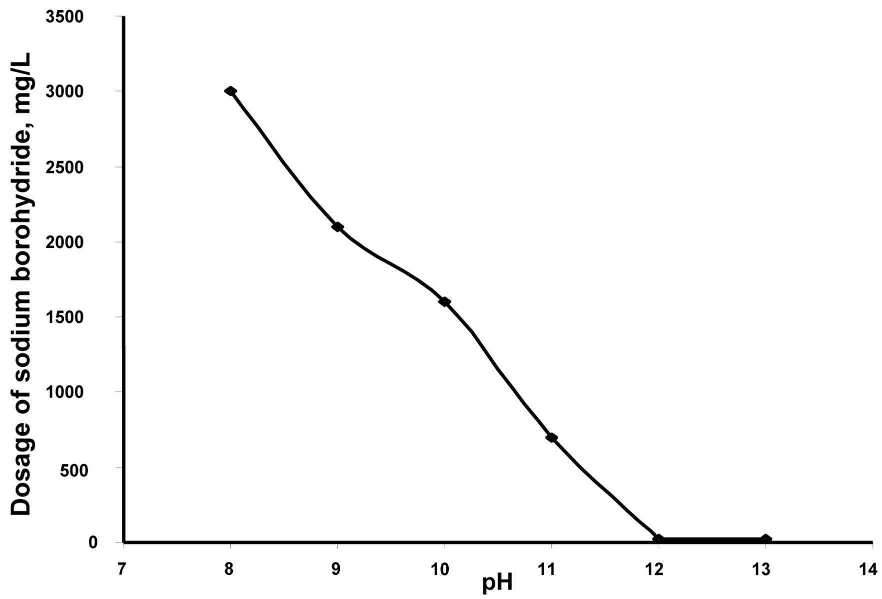

Fig. 1. Effect of pH on sodium borohydride dosage for the removal of heptaldehyde odor.

Table 3
Characteristics of raw wastewater sample taken for pilot scale studies

| Properties | Values |
|---|---|
| pH | 4.87 |
| Conductivity, μS/cm | 590 |
| TDS, mg/L | 498 |
| FOG, mg/L | 120 |
| COD, mg/L | 7,208 |
| BOD, mg/L | 3,250 |
| Appearance | Turbid |
| Odor | Strong heptaldehyde odor |

have much better quality and had absolutely no odor. The conductivity and TDS of the treated water were found to be very low, fats oils and grease (FOG) was completely removed and COD and BOD were also reduced significantly. This process was then repeated on larger scale taking around 40 l of wastewater sample. Three experiments were performed with the above mentioned wastewater samples. The results obtained with the wastewater sample having maximum amount of conductivity, COD, BOD etc are reported here. The characteristics of the wastewater sample taken are shown in Table 3.

As per the optimized conditions obtained in laboratory scale studies, the reduction reaction was carried out at pH 12 using sodium borohydride. The water was then treated with PAC for adsorption studies. It was observed that in the pilot scale experiments, with the wastewater sample having the above mentioned characteristics, the optimal dosages of sodium borohydride and PAC required to remove the odor completely were 60 mg/L and 3 g/L respectively. This showed that the dosages might be adjusted according to the quality of wastewater samples to be treated. After the adsorption treatment, the water was filtered through ordinary filter paper. The characteristics of water samples at various stages of reduction reaction and adsorption studies are presented in Table 4. The results showed reduction of FOG and it can be due to adsorption by activated carbon. The marginal increase in other parameters can be attributed to the addition of acids for adjustment of pH.

To reduce the fouling of the spiral wound reverse osmosis membrane and to remove larger particles, the treated water was passed through a microfiltration membrane using cross-flow ceramic membrane system as described in section 2.3.2. The flux obtained was 371 LMH at a transmembrane pressure of 2–2.5 kg/cm$^2$. The permeate of MF was then passed through a spiral wound cellulose acetate RO membrane. The flux obtained at 25 kg/cm$^2$ was around 52 LMH. The results obtained in various stages of membrane separations are presented in Table 5.

The conductivity, TDS, COD, BOD, etc. were reduced

Table 4
Characteristics of treated water at various stages of pretreatment at pilot scale studies

| Properties | After reduction reaction | After adjusting the pH to 7 | After adsorption treatment |
|---|---|---|---|
| pH | 11.7 | 7 | 6.97 |
| Conductivity, μS/cm | 3,800 | 3,950 | 3,950 |
| TDS, mg/L | 3,960 | 4,120 | 4,090 |
| FOG, mg/L | 56 | 56 | 20 |
| COD, mg/L | 10,427 | 10,662 | 10,741 |
| BOD, mg/L | 5,100 | 4,800 | 4,500 |
| Appearance | Dark yellowish | Light greenish | Colorless |
| Odor | Alcoholic odor | Alcoholic odor | Odorless |

Table 5
Characteristics of treated water samples at various stages of membrane separation at pilot scale studies

| Properties | Microfiltration permeate | Reverse osmosis permeate |
|---|---|---|
| pH | 7 | 7 |
| Conductivity, μS/cm | 3,480 | 6 |
| TDS, mg/L | 3,280 | nil |
| FOG, mg/L | nil | nil |
| COD, mg/L | 7,840 | 58.4 |
| BOD, mg/L | 3,600 | Nil |
| Appearance | Colorless | Colorless |
| Odor | Odorless | Odorless |

Table 6
Comparison of quality of final treated water with the actual process water

| Characteristics | Final treated water | Actual process water |
|---|---|---|
| pH | 7 | 7.62 |
| Conductivity, μS/cm | 6 | 1,187 |
| TDS, mg/L | nil | 300 |
| FOG, mg/L | nil | nil |
| COD, mg/L | 58.4 | 136.2 |
| BOD, mg/L | nil | nil |
| Appearance | Colorless | Colorless |
| Odor | Odorless | Odorless |

significantly. FOG was completely removed. The water sample was found to be clear, colorless and completely odorless. The quality of the final treated water, i.e., the RO permeate was then compared to that of the actual process water and the characteristics of the two water samples are tabulated in Table 6.

The results clearly indicated that the treated water had a much better quality compared to the actual process water as far as characteristics like conductivity, TDS, COD, BOD, etc. are concerned and hence, can be easily reused.

## 4. Conclusion

In this study, efforts were made to develop a process for treatment of wastewater generated in castor oil based perfumery chemical industry for possible reuse. A novel method was developed by using sodium borohydride as reducing agent to remove the irritating and pungent odor of the major contaminant — the heptaldehyde. Though, in this process, initially the conductivity, TDS, COD, BOD, etc. were increased, the pretreatment methodologies combined with membrane separation techniques could produce very good quality water that can be reused. This will have huge impact in treating the aldehyde –contaminated wastewater samples and will be of immense benefit to the nearby habitat of the particular perfumery chemical industry.

## Acknowledgements

N. Amarnath acknowledges the Council of Scientific and Industrial Research (CSIR), India for awarding junior research fellowship. The authors are thankful to Dow Chemical Company, Michigan, USA for giving an RO flat sheet membrane used in the study as a complimentary sample.

## References

[1] G. Capar, L. Yilmaz and U. Yetis, J. Membr. Sci., 281 (2006) 560–569.
[2] C.-Y. Chang, J.-S. Chang, S. Vigneswaran and J. Kandasamy, Desalination, 234 (2008) 393–401.
[3] B. Sarkar, P.P. Chakrabarti, A. Vijaykumar and V. Kale, Desalination, 195 (2006) 141–152.
[4] T.J. Brown and M.B. Emelko, Water Res., 43 (2009) 331–338.
[5] A.L. Ahmad, S. Sumathi and B.H. Hameed, Chem. Eng. J., 118 (2006) 99–105.
[6] A.C. Ridge and D.L. Sedlak, Water Res., 38 (2004) 921–932.
[7] E. Barbot, S. Moustier, J.Y. Bottero and P. Moulin, J. Membr. Sci., 325 (2008) 520–527.
[8] T. Hamada and Y. Miyazaki, Desalination, 169 (2004) 257–267.
[9] H.-S. Kim, S. Takizawa and S. Ohgaki, Desalination, 202 (2007) 271–277.
[10] C.-F. Lin, S.-H. Liu and O.J. Hao, Water Res., 35 (2001) 2395–2402.
[11] Heptanoic acid (Ar) 98%. MSDS according to Osha and Ansi, Health, Safety and Environmental Department, 2008, http://www.alfa.com/MSDSPDF/English_/A17704.pdf.
[12] R. Boussehain, M.L. Feidt and D. Balesdent, Thermochim. Acta, 103 (1986) 113–122.
[13] K. Hukao and Y. Takeda, Carbon, 29 (1991) 173–178.
[14] P.Y. Bruice, Organic Chemistry, 4th ed., Prentice Hall, New Jersey, 2003, pp. 842–847.
[15] S.W. Chaikin and W.G. Brown, J. Amer. Chem. Soc., 71 (1949) 122–125.
[16] R.D. Lillie and P. Pizzolato, Stain Technol., 47 (1972) 13–16.
[17] A.S. Craig, Histochem., 42 (1974) 141–144.
[18] M.B. Smith and J. March, eds., March's Advanced Organic Chemistry, 6th ed., John Wiley & Sons, New Jersey, 2007, pp. 1792–1794.
[19] J. Seyden Penne, Reductions by the Alumino and Borohydrides, 2nd ed., Wiley-VCH, New York, 1991, pp. 5–6.
[20] W. Carruthers and I. Coldham, Modern Methods of Organic Synthesis, 4th ed., Cambridge University, New York, 2004, pp. 446–447.
[21] M. Periasamy and M. Thrirumalaikumar, J. Organometal. Chem., 609 (2000) 137–151.
[22] APHA-AWWA-WEF, A.D. Eaton, L.S. Clesceri, E.W. Rice and A.E. Greenberg, eds., Standard Methods for the Examination of Water and Wastewater, American Public Health Association, American Water Works Association and Water Environment Federation, Washington, DC, 21st ed., 2005.
[23] Heptanol (AR) 98%. MSDS According to OSHA and ANSI, Health, Safety and Environmental Department, 2008. http://www.alfa.com/MSDSPDF/English_/A18391.pdf.
[24] O.B. Bayliss and C.W.M. Adams, Histochem. J., 11 (1979) 111–116.