A method for treating wastewater containing formaldehyde

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Abstract

Many industrial activities utilise formaldehyde as a key chemical in organic synthesis including: synthesis of special chemicals such as pentaerythritol and ethylene glycol, synthetic resins, paper products, medicinal products and drugs and others, too numerous to mention. Therefore, effluents arising from these applications may contain significant amounts of formaldehyde. In a biodegradation experiments of a wastewater sample containing formaldehyde ranging from 31.5 to 125 mg/l, residual formalin (a solution of formaldehyde gas in water) ranging from 40% to 85%, respectively, was found at the end of the run (16 d) showing the inhibition effect of formalin which increased with the increase in formalin concentration. The biodegradation of formalin decreased significantly at concentrations higher than 300 mg/l. A method to convert formaldehyde to an easily biodegradable substance is herein described. In the commercial manufacture of resins from phenol and formalin the reaction is never completely quantitative. As a result during the dehydration stage phenol and formalin are distilled from the wastewater. Phenol is toxic to several biochemical reactions. However, biological transformation of phenol to a non-toxic entity is possible through specialized microbes. Transformation of phenol is inhibited by the presence of formaldehyde. Biotransformation of phenol in a wastewater containing high concentrations of formaldehyde started shortly after treating the wastewater with calculated amounts of sodium sulphite. Sodium sulphite is believed to react with formaldehyde forming sodium formaldehyde bisulphite, which is not only non-toxic to microorganisms but also a biodegradable substance. From the DO measurements before and after the addition of sodium sulphite, the authors noticed that the dissolved oxygen in a wastewater containing formaldehyde is not affected by the addition of the calculated amount of sodium sulphite, which is just enough to consume the measured amount of formaldehyde in that wastewater. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Phenol; Formaldehyde; Biodegradability; Industrial wastewater; BOD

1. Introduction

Formaldehyde and phenol are key precursors in the industrial manufacture of resins. Formaldehyde finds many varieties of usage due to its high reactivity, colourless nature, stability, purity in commercial form and low cost. It serves as a resinifier, curing agent, synthetic agent, disinfectant, fungicide, and preservative. In chemical synthesis, it acts as a sort of chemical “button” by means of which similar and dissimilar radicals and molecules may be linked together with methylene group. Formalin is reported to react with sodium sulphite to give sodium formaldehyde-bisulphite [1].

The origin of phenols in the environment [2] is both anthropogenic as well as man-made. Anthropogenic sources are from forest fire, natural run-offs from urban areas where asphalt is used as the binding material and natural decay of lignocellulosic materials. Man-made sources are industrial wastes derived from fossil fuel extraction and beneficiation processes, chemical manufacturing processes such as phenol manufacturing plants, pharmaceutical industry, wood processing...
industry and pesticide manufacturing plants. Phenol is reported to be toxic to most microorganisms [3–5]. Microbial degradation of phenolic wastewater has been documented by several authors [6–10]. It has been reported that chlorine can react with phenols to produce mono-, di-, or trichlorophenols, which impart tastes and odours to waters [11]. Chlorinated phenols have often been detected in treated wastewaters [12,13]. These compounds have been identified in fish [14] and are readily bioaccumulated.

The main goal of this study was to evaluate the use of sodium sulphite for treating high strength formaldehyde wastewater. The biodegradations of both synthetic and industrial wastewaters containing phenol, formaldehyde and mixtures of formaldehyde and phenol are herein described.

2. Materials and methods

2.1. Reagents and chemicals

Phenol and formalin are commercially available solvents and other chemicals used were all reagent-grade.

2.2. Analytical determinations

2.2.1. Determination of phenol

The brominating mixture method [15] for phenol determination was slightly modified by the author in order to make it capable of detecting phenol at lower concentrations (standard 0.5 mg/l phenol solution was accurately detected). The modified method is as follows: In a 250 ml conical flask, pipette out 25 ml brominating mixture and add 25 ml water, 5 ml conc. hydrochloric acid and 5 ml potassium iodide solution. The solution will become dark brown due to liberation of iodine. Titrate this with sodium thiosulphate solution until the solution is light yellow in colour and then add few drops of starch solution. Add the sodium thiosulphate very carefully and note the volume of sodium thiosulphate at the end point marked by the disappearance of the blue colour, this blank titration is used to determine the volume of brominating mixture equivalent to 1 ml of sodium thiosulphate solution. Then take 25 ml of standard phenol for titration, add 50 ml water and 5 ml conc. hydrochloric acid. To this add brominating mixture from a burette until the solution is light yellow and no more precipitate of tribromophenol separates out. Add 2 ml more of the brominating mixture and note the volume added, then add 2 ml potassium iodide and titrate the liberated iodine against sodium thiosulphate using starch as the indicator as described under blank experiment above. Since for lower phenol concentrations the resulting tribromophenol will be a small amount and then the residual bromine would be too high to be consumed by 2 ml KI. It has been found that it is more convenient to add 3 ml of KI instead of 2 ml. Reproducible results have been obtained. Repeat the titration with 25 ml of the unknown phenol solution in the same manner as with the standard phenol solution described above. Use the same volume of brominating mixture for the unknown phenol solution.

Calculations:

\[ \text{Mass of phenol in the unknown solution} = 4W\left( {V'' - \left[ {25\ V_2/V} \right]} \right)/\left[ {25\ V_1/V} \right] \ g/l, \]  

where \( W \) is the weight of phenol in the standard solution, \( g \), \( V \) the volume of sodium thiosulphate used in blank experiment against 25 ml brominating mixture, ml, \( V' \) the volume of brominating mixture added to 25 ml standard phenol solution, ml, \( V_1 \) the volume of sodium thiosulphate used for known phenol solution, ml, and \( V_2 \) the volume of sodium thiosulphate used for unknown phenol solution, ml.

\[ V \text{ ml sodium thiosulphate solution} = 25\text{ ml brominating mixture}, \]

hence,

\[ 1\text{ ml of sodium thiosulphate solution} = 25/V' \text{ ml brominating mixture}. \]

Therefore,

\[ V_1 \text{ ml of sodium thiosulphate solution} = (25/V') \times V_1 \text{ ml of brominating mixture}. \]

Volume of brominating mixture used for 25 ml of standard phenol solution = \( V' - [25\ V_1/V] \) ml. Similarly volume of brominating mixture used for 25 ml of unknown phenol solution = \( V' - [25\ V_2/V] \).

2.3. Determination of formaldehyde

Formalin was determined quantitatively by using the iodometric method [15].

2.4. Biodegradation studies

The biodegradation studies included two phases. The first phase was based on using synthetic wastewater seeded with 10% municipal wastewater and dosed with either phenol, formalin or both of them. Controls were prepared in the same way but without the addition of phenol or formalin. The biodegradability, at 25°C and in the dark, was followed using a respirometric BOD controller and a continuous measurement of the substrate concentrations. The second phase included the investigation of the biodegradability of an industrial effluent emanating from an industry using both phenol and formalin as major raw materials.
2.5. Synthetic wastewater composition

The BOD of the seed (municipal wastewater) alone was measured under the same experimental conditions in each run, for seed-corrected data calculations. Experiments were done in duplicate at 25 °C, magnetic stirring and in dark. After the appropriate time of incubation the supernatant was separated to determine the final phenol and formalin concentrations. Seed acclimation was ensured by comparing the BOD of the samples with that of the corresponding controls.

3. Results and discussion

In the first run, synthetic wastewater with the composition shown in Table 1 was used. Phenol was added in concentrations ranging from 11.8 to 146.7 mg/l, and experiments and controls were done under the same experimental conditions. Seed-corrected data were obtained in all cases. Results are shown in Fig. 1.

Theoretical BOD calculations for the above phenol concentrations were in good agreement with the measured ultimate carbonaceous BOD (Table 2), indicating complete utilisation of phenol in 9 d.

The ultimate BOD of a wastewater can be determined by adding the plateau BOD and the theoretical BOD of the cells produced up to the plateau:

\[ \text{BOD}_{\text{ult}} = \text{BOD}_{\text{plateau}} + \text{BOD}_{\text{cell}}. \]  

(2)

Table 1

<table>
<thead>
<tr>
<th>Constitute</th>
<th>Stock concentration (g/l)</th>
<th>Quantity used (ml/5 l)</th>
<th>Final concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bacto-peptone</td>
<td>32.25</td>
<td>27.3</td>
<td>352.73</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>10.00</td>
<td>25.0</td>
<td>50.00</td>
</tr>
<tr>
<td>MnSO₄·H₂O</td>
<td>1.00</td>
<td>25.0</td>
<td>5.00</td>
</tr>
<tr>
<td>FeCl₃·6H₂O</td>
<td>0.175</td>
<td>25.0</td>
<td>1.00</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>100.00</td>
<td>25.0</td>
<td>3.75</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>52.25</td>
<td>33.4</td>
<td>349.4</td>
</tr>
<tr>
<td>K₂HPO₄</td>
<td>107.00</td>
<td>33.4</td>
<td>715.56</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Initial phenol conc. (mg/l)</th>
<th>Phenolic carbon content (mg/l)</th>
<th>Calculated biomass (mg/l)</th>
<th>BODcell (mg/l)</th>
<th>Plateau BOD value (mg/l)</th>
<th>Ultimate BOD (mg/l)</th>
<th>Theoretical BOD (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.8</td>
<td>9.04</td>
<td>5.82</td>
<td>8.26</td>
<td>20</td>
<td>28.26</td>
<td>28.1</td>
</tr>
<tr>
<td>29.5</td>
<td>22.59</td>
<td>14.55</td>
<td>20.66</td>
<td>52</td>
<td>72.66</td>
<td>70.25</td>
</tr>
<tr>
<td>59</td>
<td>45.16</td>
<td>29.08</td>
<td>41.29</td>
<td>100</td>
<td>141.29</td>
<td>140.44</td>
</tr>
<tr>
<td>88.3</td>
<td>67.63</td>
<td>43.56</td>
<td>61.85</td>
<td>150</td>
<td>211.85</td>
<td>210.3</td>
</tr>
<tr>
<td>146.7</td>
<td>112.36</td>
<td>72.36</td>
<td>102.75</td>
<td>248</td>
<td>350.75</td>
<td>349.4</td>
</tr>
</tbody>
</table>

An empirical cell formulation, C₆H₅O₂N with a theoretical BOD of 1.42 O₂/g cells, was used in the ultimate BOD estimation. For theoretical BOD calculations, complete oxidation of phenol requires 3.11 g of oxygen per gram of carbon according to the following equation:

\[ C₆H₅OH + 7O₂ \rightarrow 6CO₂ + 3H₂O. \]  

(3)

Our analytical measurements also proved 100% biodegradation of phenol in these first studies after 9 d. In another set of experiments, with the same phenol concentrations but with increased volume of the seed (municipal wastewater), phenol removal was faster indicating that the biodegradability is highly dependent on microorganism concentration.

In case of formalin as a pure substrate, the bacterial activities were very slow at the beginning of the run and started to increase after a few days. The ultimate BOD (Fig. 2) in each case was found to be not consistent with the theoretical BOD associated with the complete consumption of the formalin dosed, that is due to the inhibition effect of the toxic formalin. Residual formalin was detected in most of the cases at the end of each run (16 d).

From the continuous measurements of the BOD of the control sample and the samples dosed with formalin,
it was clear that formalin is causing inhibition to the microbial activities. For higher formalin concentrations (above 300 mg/l) degradation percentages decreased as the formalin concentration increased.

In another set of duplicated experiments, the existence of phenol as a pure substrate in high concentrations (930 and 1140 mg/l) caused a temporary inhibition to the bacterial activities for a period of 3–5 d after which the activities increased significantly, residual phenol (320 and 600 mg/l respectively) was detected in each case at the end of the run (30 d). In case of phenol experiments we observed both inhibition at higher phenol concentrations and a complete removal at lower concentrations. In a separate run, under the same experimental conditions and with the same phenol concentrations (930 and 1140 mg/l), addition of formalin (415 and 207 mg/l, respectively) caused almost complete inhibition (Fig. 3). Phenol was almost completely recovered at the end of the run.

The BOD measurements of a synthetic wastewater sample containing 300 mg/l formalin before and after treatment with sodium sulphite are shown in Fig. 4.

In all our repeated experiments, under the same experimental conditions, biological activities started immediately in the formalin-dosed samples treated with sodium sulphite.

In similar formalin-dosed samples, without treatment with sodium sulphite, the bacterial activities took long lag periods (3–7 d) to start in case of relatively diluted samples and it was inactive in the concentrated ones (more than 300 mg/l).

Two different industrial wastewater samples (Table 3) were examined, before and after treatment with sodium sulphite. As indicated in Fig. 5, the biological activities in the treated samples are much higher than those in the untreated samples. The authors decided to try using powdered activated carbon (PAC) with untreated wastewater samples (synthetic and industrial) containing formalin (300 and 203 mg/l, respectively), the purpose of adding the PAC was to improve the biodegradation by reducing the concentration of formalin through adsorption and to help increasing the rate of multi-

![Fig. 2. BOD values for different formalin.](image)

![Fig. 3. Inhibition effect of formalin on the biodegradation of phenol.](image)

![Fig. 4. BOD values for a 300 mg/l formalin solution before and after treatment with sodium sulphite.](image)

**Table 3**

<table>
<thead>
<tr>
<th>Analysis of the two industrial wastewater samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test sample no.</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Total dissolved salts (mg/l)</td>
</tr>
<tr>
<td>Suspended solids (mg/l)</td>
</tr>
<tr>
<td>Ammonia nitrogen (mg/l)</td>
</tr>
<tr>
<td>Nitrate nitrogen (mg/l)</td>
</tr>
<tr>
<td>Phosphates (mg/l)</td>
</tr>
<tr>
<td>Sulphates (mg/l)</td>
</tr>
<tr>
<td>Chlorides (mg/l)</td>
</tr>
<tr>
<td>COD (mg/l)</td>
</tr>
<tr>
<td>BOD₅ (mg/l)</td>
</tr>
<tr>
<td>Formalin (mg/l)</td>
</tr>
<tr>
<td>Phenol (mg/l)</td>
</tr>
</tbody>
</table>
plication of the micro-organisms by increasing the surface area, we noticed no improvement in the biodegradation of formalin. The BOD values were even lower in cases where PAC was added, that might be attributed to the adsorption of some other nutrients by the PAC, but that is not thoroughly confirmed in this study.

4. Conclusions

In case of effluents containing phenol, biodegradation seems to be a reasonable way of treatment. Both inhibition at higher concentrations and complete removal at lower concentrations were observed. It appears that 9 d is a convenient time to reach satisfactory biodegradation.

In case of formalin as an effluent, both temporary inhibition at lower concentrations and almost complete inactivation at higher concentrations were observed. Addition of calculated amounts (to avoid any consumption of the dissolved oxygen in the effluent, nevertheless aeration afterwards is recommended) of sodium sulphite (reaction ratio is 1:1, sodium sulphite:formalin) to the effluent, allowed the microbial biodegradation to take place without any noticeable inhibition. The use of PAC did not cause any improvement in the biodegradation of effluents containing formalin.

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References