Immobilized reactor for rapid destruction of recalcitrant organics and inorganics in tannery wastewater

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Abstract: The wastewater discharged from tanneries lack biodegradability due to the presence of recalcitrant compounds at significant concentration. The focal theme of the present investigation was to use chemo-autotrophic activated carbon oxidation (CAACO) reactor, an immobilized cell reactor using chemoaotrophs for the treatment of tannery wastewater. The treatment scheme comprised of anaerobic treatment, sand filtration and CAACO reactor, which remove COD, BOD, TOC, VFA and sulphides respectively by 86%, 95%, 81%, 71% and 100%. Rice bran mesoporous activated carbon prepared indigenously and was used for immobilization of chemoaotrophs. The degradation of xenobiotic compounds by CAACO was confirmed through HPLC and FT-IR techniques.

Keywords: chemo-autotrophic activated carbon oxidation (CAACO); mesoporous rice bran activated carbon; xenobiotic

Introduction

The anthropogenic compounds used in tanning and retanning processes impart the leather resistance to microbial attack and to withstand thermal shock. Despite they are classified under organic compounds they lack biodegradability due to their toxic nature to biodiversity distributed in anaerobic/aerobic reactors of wastewater treatment facilities (Locher, 1991). The synthetic organic chemicals used during tanning such as sulphonated mono, di- and tri-nuclear aromatics, sulphonated azaaromatics, sulphated or sulphited long chain fatty acids etc. in wastewater escaped in the primary chemical treatment and the secondary biological treatment unit operations (Reemtsma, 1993; 1995). Most of these compounds resist biodegradation, as metabolites of these compounds or their derivatives are toxic to the microorganism (Okada, 2000). These compounds are mostly carcinogenic, mutagenic and teratogenic in nature. The toxic nature of the organics was due to their tendency to inactive the organisms through adsorption on cellular membrane (Hugo, 1977), which prevents the synthesis of exo-cellular polymer or induce cell wall rupture.

The compounds that resist microbial degradation are considered to be bio-refractory or xenobiotic compounds. The solubility of xenobiotic compounds tends to increase on substitution of sulphonic acid group to the aromatic nuclei of the molecule. Hence, such compounds escape anaerobic/aerobic biological treatment units employing bacterial culture in suspension. However, organisms immobilized in suitable matrixes have demonstrated several advantages in degrading the refractory organics over those in suspended state.

The process used in the study consists of immobilization of chemoaotrophs mainly Bacillus sp., in mesoporous activated carbon, packed in a reactor known as chemo autotrophic activated carbon oxidation (CAACO). Activated carbon have been selected as bedding material in reactor due to its great adsorptive surface and its structure opted as suitable supporting material for microorganisms, and also provides high adsorption capacity for organic compounds. The activated carbon contains rough fissured surface and pores on which the microorganisms can settle and colonize easily (Morsen, 1990).

The activated carbon, packed bed reactor has got the ability to efficiently degrade high strength wastewater (Lorenzo, 2004). Thus the prime objective of present investigation was to study the efficacy of chemoaotrophs immobilized in rice bran activated carbon for rapid and complete removal of recalcitrant or xenobiotic compounds from tannery wastewater.

1 Materials and methods

The samples of wastewater discharged from tanneries are treated through CAACO reactor after passing through primary clarification and anaerobic treatment system.

1.1 Activated carbon preparation and characteristics

The selected rice husk material was precarbonized at 400°C for 4 h at the rate of 10°C /min under reduced atmosphere. The precarbonized carbon was then subjected to chemical activation using H₂SO₄ as the activating agent. The ratio of chemical activating agent per precarbonized carbon was fixed at 4.2. The resulting mixture were activated in a vertical cylindrical furnace at 800°C under controlled atmosphere.

1.2 Chemoautotrophic activated carbon oxidation (CAACO) reactor

The CAACO reactor has replaced conventional biological wastewater treatment system, due to its higher treatment efficiency and eco-friendliness. The prepared mesoporous activated carbon of height 9.26 cm was filled over the coarse strainer of height 5 cm. The oxygen required for the oxidation of organics in wastewater was supplied in the form of air at a pressure of 5 kg/cm² through air diffuser placed over the bed of the coarse strainer. The CAACO reactor of volume 720 cm³ having internal diameter 5.5 cm and effective carbon bed volume of 220 cm³ was used in this study. The schematic flow diagram consists of the unit operations anaerobic digester, sand filtration and CAACO used for the treatment of tannery wastewater is shown in Fig. 1. Both anaerobic digestion and sand filtration are considered to be pretreatment steps for CAACO process. The anaerobic digester improves both the physical removal of suspended solids and improves the biological conversion. The sand filtration removes the suspended solid particles in the wastewater. The effluent after sand filtration was tested in CAACO reactor. These digestion and filtration processes helps in transformation of organic or inorganic contaminants to environmentally acceptable oxidation/reduction process. After
pretreatment steps the tannery effluent was feed into the CAACO in downward flow. The oxygen/COD ratio of the inlet in CAACO was maintained at 1.0.

![Diagram](image)

**Fig. 1 Schematic flow diagram for CAACO system for the treatment of tannery wastewater**

1.3 Chemical analysis

The tannery effluent treated through from primary clarifier, anaerobic treatment, CAACO, was analyzed for chemical oxidation demand (COD), total organic carbon (TOC), biological oxidation demand (BOD), volatile fatty acids (VFA), pH using standard methods (Clesceri, 1989). The pollutants breakdown was confirmed through high performance liquid chromatography (HPLC) and fourier transform infrared spectroscopy (FT-IR).

1.4 Surface morphology

Surface morphology was carried out at the samples of mesoporous activated carbon and chemoeconomats immobilized mesoporous carbon using Leo-155 scanning electron microscope after it was coated with gold by a gold sputtering device.

1.5 Fourier transforms infrared spectroscopy (FTIR)

The effluent samples before and after CAACO treatment were dried under vacuum and the residue was pelletized at a pressure of about 1 MPa of spectroscopic grade with KBr. The surface functional groups were analyzed to determine changes using Perking Elmer infrared spectrometer.

1.6 High performance liquid chromatography (HPLC)

The effluent sample of volume 50 ml before and after CAACO treatment was centrifuged to remove coarse solids and dried in glass crucible under vacuum. After complete drying, the moisture free samples were then extracted in methanol and filtered. The filtered samples were injected into shim pack C18 column using methanol; water (50:50) as mobile phase with a flow rate of 1 ml/min in a Perkin Elmer HPLC and detected.

2 Results and discussion

2.1 Characteristics of carbon

The characteristics of carbon are presented in Table 1. It shows that the carbon percentage is 48.45 and it has the decolorizing power of 22 mg/g. This carbon has got low surface area of 220 m²/g and pores are in the mesoporous range.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Carbon, %</td>
<td>48.45</td>
</tr>
<tr>
<td>2</td>
<td>Hydrogen, %</td>
<td>0.7</td>
</tr>
<tr>
<td>3</td>
<td>Nitrogen, %</td>
<td>0.1</td>
</tr>
<tr>
<td>4</td>
<td>Ash content, %</td>
<td>51.8</td>
</tr>
<tr>
<td>5</td>
<td>Bulk density, g/ml</td>
<td>0.405</td>
</tr>
<tr>
<td>6</td>
<td>Moisture content, %</td>
<td>3.8</td>
</tr>
<tr>
<td>7</td>
<td>Ash content, % by mass</td>
<td>40</td>
</tr>
<tr>
<td>8</td>
<td>Matter soluble in water, %</td>
<td>0.428</td>
</tr>
<tr>
<td>9</td>
<td>Matter soluble in acid, %</td>
<td>3.908</td>
</tr>
<tr>
<td>10</td>
<td>pH</td>
<td>6.66</td>
</tr>
<tr>
<td>11</td>
<td>Decolorizing power, mg/g</td>
<td>22</td>
</tr>
<tr>
<td>12</td>
<td>Phenol number, mg/g</td>
<td>3.18</td>
</tr>
<tr>
<td>13</td>
<td>Ion exchange capacity, meq/g</td>
<td>0.015</td>
</tr>
<tr>
<td>14</td>
<td>Surface area (BET), m²/g</td>
<td>220</td>
</tr>
<tr>
<td>15</td>
<td>Pore size, μm</td>
<td>20 x 10⁻⁹...50 x 10⁻¹⁰</td>
</tr>
</tbody>
</table>

2.2 Catalytic oxidation of tannery effluent

The wastewater after primary treatment, anaerobic treatment and CAACO treatment were analyzed for chemical pollution parameters (Table 2). The BOD/COD ratio of untreated wastewater index which measures biodegradability of wastewater was 0.31 suggesting that the wastewater is less amenable to biological wastewater treatment. The poor biodegradability of wastewater is due to the presence of mono-, di- and tri-nuclear sulphonated aromatic compounds in wastewater. The COD/SO₄²⁻ ratio of wastewater was in the range of 2.0—2.7, such a high ratio does not favor methanogens to survive instead sulphate reducing bacteria (SRB) are more favored in anaerobic environments (Elke, 1996; Lens, 1998). Free energy from fermentation of organic compounds using sulphate as electron acceptor to form sulphides instead of methane, as the end product is much more favored (Kjeld, 2003). This is evident from the characteristics of wastewater discharged from upflow anaerobic lagoon of detention time 2.8 d, presented in Table 2. Table 2 reveals that the sulphide content of anaerobic wastewater was increased by 188 ± 47 mg/L over the primary treated wastewater and sulphate content of anaerobic wastewater was decreased from 1113 ± 199 mg/L to 965 ± 190 mg/L. The same kind of result was also observed by Matthais, showing organic and inorganic sulphur compounds conversion to sulphides during anaerobic treatment of wastewater (Matthais, 1998). During anaerobic digestion of sulphate, rich sulphide wastewater are produced (Brandis, 1981; Ingvorsen, 1984) and a fraction (f) of total sulphide produced is retained in aqueous phase in the soluble form and remaining sulphide(1-f) occupies the gaseous phase in the form of hydrogen sulphide. The fraction of sulphides, which exists in the aqueous phase as a function of pH is determined by the expression

\[ f = 1 - \exp(-k \cdot \text{pH}) \]
The anaerobic treated wastewater was further treated in CAACO reactor. The concepts reinforced in the technology are: (1) Immobilization of organisms in the carrier matrix will allow a high cell density to be maintained in a bioreactor and thus rate of reaction is increased; (2) Reducing the mean free path of the biocatalyst to the substrate increases accessibility of enzymes to the substrate; (3) Reduce the cellular synthesis by using the organisms (chemoautotrophs) with low yield co-efficient.

Fig. 2 and 3 illustrate the scanning electron micrographs of mesoporous carbon. In Fig. 2 the morphology of pore arrays and fissures are clearly viewed. In Fig. 3 the presence of mesopores are evident. Fig. 4 is a clear evident for the immobilized bacillus sp. in mesoporous carbon. The degradation of organics by immobilized bacterial cultures on activated carbon occurs as a combination of physical adsorption and biological degradation (Ehrhardt, 1989).

The bacteria immobilized in anoxic zone can fragment the organics into simpler compounds and the bacteria in oxic zone perform oxidation of organics. In addition to bacterial oxidation, catalytic oxidation is also facilitated at the active sites of the carbon matrix. The activated carbon protects the organisms from the toxic effects of the organics (Morsen, 1990).

The adsorbed organics desorb, diffuse out of the carbon and can then be metabolized. The rate of desorption depends on the culture conditions, fluid dynamics, metabolic activity of the organism, and density of the particles (Fan, 1990).
cross over the activation energy barrier, which normally determines the rate of any chemical reaction (John, 2004).

The freedom of movement of molecules is also restricted at the surface of adsorbent as they are anchored at the sites and thus energy expenditure towards transnational motion, which is considered to be the major component in the orientation of molecule, is lowered to maximum extent. The partially oxidized organic molecule is aerobically oxidized with low heat of combustion by aerobic organisms immobilized at the mouth of the pores and thus energy available for cellular synthesis is decreased and consequently the biomass production is decreased. Since, the organisms are in immobilized state the expenditure of energy towards diffusion of organic molecules, and oxygen from the bulk liquid to cellular matrix is minimum compared to that in suspended growth system. Further activated carbon contributes to the buffering capacity of the immobilized microbial system by adsorbing acid and alkaline compounds, as well as enriching dissolved oxygen (Baldanf, 1993).

Hence, the conservation of energy in the immobilized state enhances the rate of degradation of organics in wastewater is much greater than in suspended growth system. Therefore, the number of active sites available for oxidation of organic compounds remains a constant and thus the rate of removal of dissolved pollutants in wastewater is nearly constant.

The characteristics of the wastewater discharged from CAACO reactor are shown in Table 2. The BOD of the treated wastewater was 52 ± 18 mg/L and COD was 471 ± 99 mg/L. It was interesting to observe that sulphate content of CAACO treated effluent compared with the anaerobic treatment was reduced from 960 ± 190 mg/L to 728 ± 90 mg/L. Volatile fatty acid content was reduced from 609 ± 202 mg/L to 338 ± 98 mg/L. Secondary biological treatment of wastewater removed major concentration of chemical pollutants expressed in terms of COD, BOD and TOC.

2.3 Instrumental confirmation

Fig. 5 shows the IR spectra before and after CAACO treatment of effluent. The FTIR analysis of the dried tannery effluent was carried out between 400—4000 cm⁻¹. There is a broad envelope in the higher energy region 2900 and 3900 cm⁻¹, which is assigned to -OH stretch of H₂O, -COOH and -NH stretch. The presence of alkyl groups in the effluent constituents is confirmed by the symmetric and asymmetric stretching modes of -CH₂ groups below 3000 cm⁻¹. The C—O stretch, -NH bend, C—N vibrations and -CH₂ bending also produced broad band between 1200 and 1800 cm⁻¹. The intense band lying just above 1000 cm⁻¹ is due to -COO⁻ and alkoxy C—O vibrations. The alkyl, carbonyl and amino groups seemed to be reduced to a greater extent after CAACO treatment.

Fig. 6 shows the HPLC chromatogram before and after CAACO treatment. It shows the removal of high molecular weight compounds corresponding to retention time 2.02 and 3.68 min. The disappearance of the above peaks and the appearance of new peak at retention time 1.93 min in the HPLC chromatogram suggest that high molecular weight organic compounds in wastewater might have been bio-transformed into smaller compounds by chemoautotrophs.
3 Conclusions

The wastewater discharged from tanning industries lack biodegradability due to the presence of xenobiotic compounds at considerable concentration. The effluent after treatment through primary clarifier, anaerobic reactors and chemoaotrophs immobilized cell reactor known as CAACO reactor removed all pollution parameters like COD, BOD, TOC, VFA and sulphide respectively by 86%, 95%, 81%, 71% and 100%.

From the above results the following conclusions were achieved:

- The chemoaotrophs immobilized cell reactor was highly efficient in COD, BOD, TOC, VFA and sulphides removal within short retention period.

- The degradation efficiency of immobilized cell reactor was not altered invariably of wastewater strength.

- The organics removal rate is mainly due to immobilization of chemoaotrophic bacteria's in mesoporous rice bran activated carbon rather than in suspended form.

- The removal efficiency also proved the intrinsic relationship between the activated carbon and bacteria, and also highlight the applicability of rice bran activated carbon to achieve a steady state and higher efficiency in continuous mode tannery wastewater treatment process.

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References:


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