Colour removal of pulp and paper effluents

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The paper industry requires large volumes of process water of high purity and generate equally large volumes of waste water from digestion process, which is highly coloured. The removal of colour from paper mill waste water is one of the major environmental problems, because of the difficulty of treating such water by conventional methods. The present study was undertaken for removal of colour from paper mill effluents using waste sludge from ETP as an adsorbent, with heat treatment. The operating variables studied were effluent concentration, adsorbent dosage and contact time.

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The demand of water requirements for basic needs increases with increase in population and industrialization. The biggest consumers of water are textile, tannery, pulp and paper and electroplating industries and perhaps these are the most serious polluters of environment. These industries generate equally large volumes of coloured waste water, in which colour is contributed by colloidal or suspended material. Such coloured waste water are unfit for recycling without proper treatment. Thus, colour is removed to make the water suitable for general or industrial applications.

The pollutants in the paper mill effluents are mostly organic in nature and contain lignin and its derivatives, in addition to other colour imparting phenolic and resinous compounds. Lignin is the main constituent responsible for colour in the pulp and paper industry. Lignin is the principal constituent of woody structure of higher plants. Spent liquors from the wood pulp industry are the principal commercial sources of lignin available in the free or acid form as sodium lignate and as various metal salts of lignin sulphonic acid. These products are available in a wide range of grades as brown powders or aqueous solutions.

Lignin is a class of complex high molecular weight polymers whose exact structure varies. It is an amorphous polymer that acts as binding agent to hold cells together. Like cellulose and hemicellulose lignin is made from carbon, oxygen and hydrogen. However, these elements are arranged differently so that they are not classified as carbohydrate. They are instead classified as phenolics, and the polymer is based on the phenyl propane unit.

Upon discharge, these effluents are very harmful to agricultural crops, aquatic life and human being. Various techniques are used to decolorize the paper mill effluents and simultaneously bringing down the level of other pollutants within permissible limits for their safe disposal.

In this paper, an attempt has been made to study the adsorption characteristics of wood based material generated, for colour removal of effluent of the same industry.

Experimental Procedure
Materials and Methods
Waste Water

The waste water used for these studies was collected from one of the largest integrated pulp and paper mill in India. The mill produces about 225 MT/day of writing and printing paper using bamboo eucalyptus and hardwood as raw material by kraft sulfate pulping technique. The mill has constructed the Effluent Treatment Plants (ETP’s) to treat around 22000 m³/d of effluents generated from various process units of the plant. The effluent is dark brown in colour due to presence of lignin compounds which are biologically non-degradable. This effluent basically consists of wash liquor from pulp mill, brown stock washers, black liquor spill leakage from digester house and caustic extraction effluent from
pulp mill. The total quantity of coloured effluent is about 4.0 to 4.5 MGD. The physicochemical characteristics of coloured effluent were given in Table 1.

**Waste sludge (as adsorbent)**

The pulp and paper mill treats the coloured and organic wastewater in a ETP consisting of clarifier, settling tank and activated sludge process. The suspended matter and other solid material is settled in a settling tank in the form of sludge. The sludge mainly consists of unused wood based material generated during the digestion process. The sludge from the settling tank is removed and dried in sludge drying beds. As the sludge is mainly of wood based material, the same can be processed to generate micro porous nature similar to activated carbon or charcoal with heat treatment and can be used as adsorbent. Physico-chemical characteristics of waste sludge is given in Tables 2 and 3.

Waste sludge is heated in absence of air in furnace in the range of 100 to 900°C for generating the adsorbent for colour removal. The carbon present in it gets activated at a definite temperature of 300 to 400°C and an enormous number of pores in 100 Å diameter range (decolourizing carbons) are opened. After activation, the carbon has large surface area (500-1500 m²/g) which is responsible for adsorption phenomenon.

**Method**

The method adopted here for colour removal is adsorption which is one of the most effective and economical method.

The work is based on positive adsorption in which solute alone is adsorbed and the concentration of solution gets decreased. This type of adsorption follows Freundlich’s equation.

**Freundlich’s adsorption isotherm**

\[ \frac{x}{m} = K C^{1/n} \]  

\[ x = \text{amount of adsorbate}, \quad m = \text{amount of adsorbent}, \quad C = \text{concentration of solute in g mol/L}, \quad k \text{ and } n \text{ are constants depending on nature of } x \text{ and } m, \quad n \text{ is less than unity.} \]

Equation (1) predicts the effect of concentration on the adsorption of solution at constant temperature. Taking log of Eq. (1)

\[ \log\frac{x}{m} = \log k + \frac{1}{n} \log C \]

If \( \log x/m \) is plotted against \( \log C \) straight line should be obtained. The slope of the line will give the value of \( 1/n \) and intercept on y axis gives the value of \( \log k \) i.e. \( \text{intercept} = \log k \)

Slope = \( b/a = 1/n \)

by Eq. (2) values of \( k \) and \( n \) can be calculated from graph.

**Analytical methods for colour detection**

**Apparatus**

The hach model DR/2010 spectrophotometer, microprocessor controlled, single beam instrument for

**Table 1 — Characteristics of coloured effluent**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.1-8.4</td>
</tr>
<tr>
<td>Colour (Pt-Co unit)</td>
<td>8000-12000</td>
</tr>
<tr>
<td>T. H</td>
<td>995-1089</td>
</tr>
<tr>
<td>Cal. H</td>
<td>150-198</td>
</tr>
<tr>
<td>Mg H</td>
<td>720-891</td>
</tr>
<tr>
<td>S. S</td>
<td>316-544</td>
</tr>
<tr>
<td>T.D.S</td>
<td>800-1100</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>142-330</td>
</tr>
<tr>
<td>BOD</td>
<td>96-158</td>
</tr>
<tr>
<td>COD</td>
<td>800-984</td>
</tr>
<tr>
<td>SO(_4)(^{2-})</td>
<td>125-220</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>100-250</td>
</tr>
<tr>
<td>PO(_4)(^{3-})</td>
<td>13-20</td>
</tr>
</tbody>
</table>

All values except pH and colour are in mg/L.

**Table 2—Physical properties of waste sludge**

<table>
<thead>
<tr>
<th></th>
<th>Bulk density g/cc</th>
<th>Particle density g/cc</th>
<th>Porosity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste sludge (Raw)</td>
<td>0.82</td>
<td>1.42</td>
<td>42</td>
</tr>
<tr>
<td>Burn at (300°C)</td>
<td>0.84</td>
<td>2.26</td>
<td>63</td>
</tr>
<tr>
<td>Burn at (400°C)</td>
<td>0.81</td>
<td>1.70</td>
<td>52</td>
</tr>
</tbody>
</table>

**Table 3—Chemical properties of waste sludge**

| Parameters | Silica | Total carbon | Al\(_2\)O\(_3\) | Cu | Cr | Pb | Ni | Co | Zn | Fe | Cd | Ca | Mg |
|------------|--------|--------------|-----------------|----|----|----|----|----|----|----|----|----|----|----|
| Sludge     | 13.1   | 31           | 20              | 0.70 | ND | ND | 0.11 | 0.01 | 0.55 | 1.94 | 0.06 | 9.60 | 19.1 |

All values in %

ND – Not detected
colorimetric testing, Digital pH meter, filtration assembly and shaker.

**Reagents**

Standard solution of 500 PtCo unit is prepared by dissolving 1.246 g of K₂PtCl₆ and 1 g of crystallized CoCl₂·6H₂O with 100 mL concentrated HCl in 1 L. From this stock solution different colour standards are prepared.

**Procedure**

The study has been carried out by collecting the coloured effluent from the source of process. Physico-chemical analysis of both the effluent and waste sludge were carried out with determination of adsorption capacity of wood waste by burning it at various temperature ranges. The weight loss of the waste sludge is observed at different temperatures to determine the evaporation losses of organic material and optimize the temperature to which the waste material has to be subjected to maximize the pore structure for adsorption. The behaviour of the waste material at different temperatures is given in Fig. 1. The waste material follows a linear equation up to a temperature of 300°C with a slope of 0.12 and beyond 300°C the weight loss is marginal as shown in Fig. 1.

Batch adsorption experiments were carried out by fixing a constant volume of effluent as well as constant contact time between the waste sludge and coloured sample. After this, effluent is filtered through filtration assembly to remove the suspended matter.

The percentage adsorption is estimated spectrophotometrically at the wavelength of 465 nm, then at this wavelength standard samples of known concentrations are used to obtain the calibration chart from which future sample readings are read off.

Colour is pH dependent and invariably increases as pH of sample increases, thus, pH of each sample was measured.

**Results and Discussion**

Waste sludge is used for removal of highly coloured effluent of paper mill and nearly 95% removal of colour was observed.

Removal of colour depends on,

1. *Turbidity*—Turbidity is removed before estimating the colour because it affects the colour reading.
2. *pH*—Because pH is invariably related to colour, thus pH is maintained at 7.6 before estimating the colour.
3. *Effect of contact time*—Figure 2 shows the effect of contact time on percentage removal of colour. It is observed from the figure that colour removal is maximum at a contact time of 15 min and as the contact time is increased the efficiency of colour removal is reduced. Efficiency of colour removal with time is given in Table 4.

![Weight loss versus temperature of waste sludge](image1)

![Variation of colour removal with time](image2)

<table>
<thead>
<tr>
<th>Table 4 — Efficiency of colour removal with time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shaking time (min)</td>
</tr>
<tr>
<td>5 g wood waste + 50 mL coloured effluent</td>
</tr>
<tr>
<td>10 g wood waste + 50 mL coloured effluent</td>
</tr>
<tr>
<td>15 g wood waste + 50 mL coloured effluent</td>
</tr>
<tr>
<td>20 g wood waste + 50 mL coloured effluent</td>
</tr>
</tbody>
</table>

Colour unit : Pt Co
4. **Effect of effluent concentration** — Figure 3 shows the effect of effluent concentration in percentage removal of colour. It is seen from the figure that percentage removal of colour reduces with increase in effluent concentration. Efficiency of colour removal with effluent volume is given in Table 5.

5. **Effect of dosage of adsorbent** — Figure 4 shows the effect of dosage of adsorbent on percentage removal of colour. It is seen from the figure that rate of adsorption increases with increase of dosage of adsorbent at definite contact time of 15 min.

![Fig. 3—Variation of colour removal with effluent volume](image1)

![Fig. 4—Reduction of colour with adsorbent dosage](image2)

**Table 5 — Efficiency of colour removal**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Effluent colour</th>
<th>% Colour removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 g waste + 50 mL Effluent</td>
<td>487</td>
<td>95.9</td>
</tr>
<tr>
<td>5 g waste + 100 mL Effluent</td>
<td>1965</td>
<td>83.6</td>
</tr>
<tr>
<td>5 g waste + 150 mL Effluent</td>
<td>4370</td>
<td>63.6</td>
</tr>
<tr>
<td>5g waste + 200 mL Effluent</td>
<td>5450</td>
<td>54.6</td>
</tr>
</tbody>
</table>

Original colour concentration : 12000 Pt Co unit
Contact time : 15 min

![Fig. 5—Relationship between log x/m and log c](image3)

Figure 5 shows the Freundlich’s adsorption isotherm for colour removal from the effluent at various contact time. At a contact period of 15 min the colour removal efficiency is the maximum and as time increases beyond 15 min, the removal efficiency is marginally decreased. Thus, the 15 min shaking time is sufficient to obtain the maximum colour removal from the effluent.

### Conclusion

The conclusion drawn from the experiment is, that, lignin is responsible for colour in pulp and paper industry and the most economical and effective technique of adsorption by the waste sludge of same
industry has been adopted here. 95% removal of
colour is observed by increasing the surface area of
waste sludge at 300°C for one hour.

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