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TREATABILITY OF RICE STARCH WASTEWATER

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INTRODUCTION

Production of starch in Egypt starts from low grade rice as a basic raw material. A major rice starch processing plant is located in Alexandria and is considered one of the major polluting industries at Moharram Bey Industrial Complex (MBIC). This complex discharges all its wastes into the massively polluted Lake Mariut at the entrance to the city.

The wastewater generated at this plant originates mainly from two manufacturing processes, namely, the steeping process in which clean broken rice seeds are macerated in caustic soda solution for dissolution of proteinaceous matter, and the primary concentration process involving centrifugation of the milk of starch. The plant discharges 800 cu meter/day of concentrated organic waste.

Although biological treatment has been successfully applied to potato starch wastes (2) and corn starch wastes (3), Brehon et al. (4) noted markedly detrimental effect of potato starch wastes on a municipal (trickling filter) treatment plant. This contradiction in results could be attributed to the different loading conditions used by various investigators.

Chemical coagulation of potato processing wastes using iron and calcium salts has been found effective in reducing the polluitional content of this waste (5). Protein recovery from potato starch wastes by multi-stage evaporation was emphasized by Stabile et al. (6), who recommended the use of recovered protein as animal feed.

This study was conducted in order to evaluate the potential for acidification, biological treatment and filtration of rice starch wastewater to reduce its polluitional content and recover reusable constituents for animal feed.

MATERIALS AND METHODS

Treatability experiments were conducted at room temperature (18-22°C) using a multiple treatment system consisting of two pH adjustment-sedimentation units, an activated sludge unit, and two filtration columns. The system was operated at different treatment conditions and its performance was evaluated based on solids and organic removal. The parameters measured daily included pH, electric conductivity, solids, turbidity, biochemical oxygen demand, chemical oxygen demand, and sludge volume index. Some other parameters were determined occasionally such as sulfates, nitrates, phosphates and dissolved oxygen.

The experimental program comprised three series of experiments as shown in Figure 1. Basically, each series of experiments involved four consecutive treatment stages, namely: acidification to pH 3 and sedimentation; pH adjustment to 6.5-7 with sedimentation; activated sludge treatment; and filtration. This scheme was typically followed in series I, but in series II different doses (1, 2, 5 mg/l) of a non-ionic polymer (Hercules 824,3) were added in the first treatment step, whereas in series III different doses (50, 100, 150 mg/l) of powdered activated carbon were added in the activated sludge aeration tank.

The experimental units used for pH adjustment and sedimentation consisted of two polyethylene tanks of 200 liters each. In the first tank, the wastewater was poured and acid 10% H$_2$SO$_4$ solution was added to adjust the pH at 3, stirred for one minute at 120 r.p.m. to achieve rapid mixing and for 10 minutes at 20 r.p.m. to promote flocculation. The tank contents were left to settle quiescantly for one hour after which the supernatant was discharged to the second tank whereas the precipitated starch was withdrawn at the bottom of the tank. To allow for further precipitation of starch and to render the supernatant suitable for biological treatment, the pH of the supernatant from the first tank was adjusted in the second tank at 6.5-7 while stirring as followed in the first tank.

**Fig(1): SCHEMATIC OF EXPERIMENTAL MULTIPLE TREATMENT SYSTEM**
The activated sludge unit consisted of a plexiglass rectangular tank of 120 cm length, 25 cm width, and 30 cm liquid depth. This unit was divided into an aeration compartment of 72 liters volume and a clarification compartment of 14.4 liters at the effluent end of the unit. The two compartments were separated by a sliding baffle adjusted to leave a slot opening at the bottom for the back flow of the settled return sludge. Intentional wasting of excess sludge was made to attain MLSS of 2000-3000 mg/l in the aeration compartment. The air flow rate was controlled to maintain 3-4 mg/l of dissolved oxygen in the aeration compartment.

Two filtration columns made of plexiglass were connected in series and used for final polishing of the activated sludge process effluent. The first column was packed with dual media of charcoal (1.1 mm particle size) and sand (0.45 mm particle size). The second column was filled with sand only (0.45 mm particle size). Each column had a total median depth of one meter.

Chemical and physical analyses were performed according to the Standard Methods for the Examination of Water and Wastewater (7).

RESULTS AND DISCUSSION

1. Wastewater Characteristics

Table 1 summarizes the average characteristics of the raw wastewater. In general, these characteristics varied slightly during the phases of study and daily variations were moderate. The raw waste is highly organic with a considerably high percentage of solids (about 02 percent) in the volatile form. The COD/BOD ratio of the raw waste averages 1.3 indicating that the waste is fairly biodegradable. This ratio was reduced during treatment especially after acidification which shows that the majority of the organics in the colloidal form were removed.

The raw wastewater was relatively low in phosphate (1.8 mg/l of P<sub>2</sub>O<sub>5</sub>) and nitrate (2.3 mg/l of NO<sub>3</sub>) content. These nutrient deficiencies of the waste were compensated for by the addition of phosphoric acid and ammonia solution prior to activated sludge treatment to attain the BOD:N:P ratio of 100:5:1 required for successful treatment.

2. Process Performance

Acidification to a pH value of 3 proved to be effective in solids and organic removals (Table 2). This particular pH value was adopted based on the results of a previous study(1) which showed best removals at pH 3. The results summarized in Table 2 also indicate that subsequent adjustment of the pH of the acidified waste to 6.5-7 achieved further removals of solids and organics.

Considering the nature of colloids (quasi-hydrophobic-hydrophilic) present in the starch waste, it is postulated that acidification resulted in lowering the zeta potential and, to a certain extent, enhanced coagulation of the colloid. Presumably, the magnitude of the zeta potential of the hydrophobic colloid was reduced so that repulsive forces between particles are less than the Vander Waals attractive force. Thus coalescence of colloidal particles would occur and coagulation could be accomplished. This caused the destruction of dispersed colloids in the wastewater and led to their settling and reduction of suspended solids and organics in the suspended form.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Raw Wastewater Characteristics (Average Values During Experiments)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PP</td>
</tr>
<tr>
<td>Experiment</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>9.3</td>
</tr>
<tr>
<td>2</td>
<td>9.7</td>
</tr>
<tr>
<td>3</td>
<td>8.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Summary of Results of Acidification and pH Adjustment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T.S.</td>
</tr>
<tr>
<td>Acidification to pH 3</td>
<td>16.0</td>
</tr>
<tr>
<td>Overall Percentage Reduction</td>
<td>22.0</td>
</tr>
<tr>
<td>Adjusted Effluent Quality (mg/l)</td>
<td>1553</td>
</tr>
<tr>
<td>Overall Percentage Reduction</td>
<td>97.0</td>
</tr>
</tbody>
</table>

The additional reduction of these parameters through the readjustment of pH to 6.5-7 was probably dependent upon the isoelectric point of the hydrophilic colloids (e.g., proteins) at which minimum solubility occurs being in the range of pH 4.0 to 6.5 for the majority.

Addition of different doses of the monomeric poly electrolyte after acidification (series II experiments) improved the percentage removal of solids and organics (Figure 2) but a polymer dose of 1 mg/l gave the best results. However, addition of a higher dose of the poly electrolyte than the indicated optimum (1 mg/l) did not bring better coagulation, this is probably due to re-stabilization or deflocculation of the colloid when excess polymer doses are used(1). In general, the high polymer cost does not justify the slight improvement in solids and organic removals achieved by polymer addition after acidification. Moreover, addition of polymer or other coagulants may alter the nature of the precipitate to be recovered as an animal feed.

![Fig(2): EFFECT OF POLYMER ADDITION ON ACIDIFIED WASTE CHARACTERISTICS](image)

The performance of the activated sludge process was evaluated at different hydraulic detention times in the range of 8 to 15 hours which correspond to organic loadings in the range of 0.18 to 1.2 kg BOD<sub>5</sub>/kg MLSS-day. The results
obtained (Table 3) indicated that a significant portion of the organic constituents in the wastewater were removed during biological treatment. Approximately 85 percent of the BOD and 95 percent of the COD were removed during the best operating periods.

![Graph](image)

**Table 3**

<table>
<thead>
<tr>
<th>Operating Parameters</th>
<th>0.18</th>
<th>0.6</th>
<th>0.9</th>
<th>1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>kg BOD/kg MLSS-day</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrotic detention time, hours</td>
<td>15</td>
<td>12</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>SVI, ml/g</td>
<td>44</td>
<td>90</td>
<td>120</td>
<td>175</td>
</tr>
</tbody>
</table>

**Percentage removal of the successive treatments**

1. Activated sludge system
   - BOD: 83.0%
   - COD: 70.3%
2. Multi-media filter
   - S.S: 82.0%
   - BOD: 68.5%
3. Sand filter
   - S.S: 63.0%
   - BOD: 35.0%

The BOD results fitted fairly well (Figure 3) the kinetic model suggested by Eckenfelder(B) which relates the removal rate of BOD to the effluent BOD concentration as follows:

\[
\frac{S_x}{S_e} = K_e X \frac{1}{t}
\]

Where:
- \(S_x\) = influent BOD concentration, mg/l
- \(S_e\) = effluent BOD concentration, mg/l
- \(X\) = mixed liquor volatile suspended solids concentration (MLVSS) mg/l
- \(t\) = hydraulic detention time, days
- \(K_e\) = BOD removal rate coefficient, L/mg/day.

![Graph](image)

**Figure 3:** BOD REMOVAL KINETICS

The BOD removal rate coefficient \(k\) obtained is 0.0046 at a temperature of about 20°C ± 2°C. This coefficient is comparable to values reported for sewage(11) indicating that the waste was fairly biodegradable.

The BOD removal percentages were plotted against the parameter \(X \frac{1}{t}\), as shown in Figure 4. Detention time \(t\) was corrected by MLVSS in the aeration tank during different experimentations. Figure 4 clearly indicates that higher organic removals were obtained at longer detention times.

![Graph](image)

**Figure 4:** BOD REMOVAL CHARACTERISTICS

Acidification, in addition to its effect on starch precipitation, could have resulted in partial solubilization by hydrolysis of the colloid remaining in the acidified effluent fed to the activated sludge process. The hydraulized substrate was presumably more readily uptaken by the process microorganisms.

Figure 5 shows the effect of organic loading (F/M ratio) on BOD removal efficiency and on sludge settleability as indicated by SVI. Lower organic loadings resulted in higher BOD removals and better settling characteristics in the range of loadings studied. As expected, the higher loaded systems bulked and developed dispersed organisms that did not settle well. As the loadings were increased higher than 0.6 kg BOD/kg MLSS-day the system performance deteriorated drastically. This corresponded to hydraulic detention times of less than 12 hours in this study.

![Graph](image)

**Figure 5:** PARAMETER RESPONSE TO ORGANIC LOADING

In a trial to improve the activated sludge system performance operated at a high organic loading of 1.2 kg BOD/kg MLSS-day, PAC was added to the aeration tank at doses of 50, 100 and 150 mg/l. Addition of PAC improved the system performance considerably as shown in Figure 6. The organic removal efficiency was increased with the increase in PAC dose in the studied range. Also, the sludge recovered its good settleability. Figure 6 shows that percentage COD removals were higher than dose for BOD removals, indicating better removal of non-biodegradable organic matter after PAC addition.

![Graph](image)

**Figure 6:** EFFECT OF POWDERED ACTIVATED CARBON ON ORGANIC REMOVAL IN THE ACTIVATED SLUDGE PROCESS
The use of filtration for polishing of the activated sludge process effluent proved to be effective (Table 3). The first dual-media filter column adsorbed and retained most of the remaining organics and solids escaping the activated sludge process through adsorption/filtration. The second sand filter retained further suspended solids escaping the first filter. Up to 100 percent reductions in turbidity were achieved after filtration. However, in field applications, the problem of filter back-washing must be considered.

3. By-Product Recovery

One of the objectives of this research was to recover a saleable by-product from the starch wastewater to be used as an animal feed. The solids precipitated by acidification and pH adjustment can be further dried and processed for a cheap animal feed. Experiments conducted in this study showed that about 70 grams of dry solids were recovered per liter of acidified waste. This means that the rice starch processing plant under study would produce about 56 tons of dry solids daily.

CONCLUSIONS

Based on the results of this study the following conclusions can be made:

1. Acidification of the rice starch waste to pH3 effectively reduced the solids and organic content of the waste. Further adjustment of the pH to near neutralization achieved additional solids and organic removals and rendered the waste suitable for activated sludge treatment. Overall removals of SS, BOD and COD were 87%, 78% and 80% respectively.

2. The rice starch waste is amenable to activated sludge treatment. However loadings higher than 0.6 kg BODs/kg MLSS-day resulted in drastic reductions in process performance and led to sludge bulking. Up to 96 percent of the BOD and 95 percent of the COD were removed at optimum loading conditions of 0.2 kg BODs/kg MLSS-day.

3. Reasonable activated sludge system performance attained at higher organic loadings when PAC doses in the range of 50-150 mg/l were added to the aeration tank.

4. Double stage filtration, using charcoal sand and sand filters, proved to be an effective polishing treatment for the activated sludge process effluent. Total removals of 98 percent each of SS, BOD and COD can be achieved through this multiple treatment system.

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1. Saad, S.G. "Case-Study of Rice Starch Waste Treatment". In "Treatment and Disposal of Liquid and Solid Industrial Wastes". 3rd Turkish-German Environmental Engineering Symposium, Bogazici University, Istanbul, Turkey, Vol.3; L57 (1973).


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