TREATMENT OF TOMATO LYE PEELING WASTEWATER BY FERRIC CHLORIDE COAGULATION AND FILTRATION

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ABSTRACT

The suspended solids, soluble and insoluble COD, and particle size were measured for lye peeling wastewater from the tomato industry. The wastewater was treated by conventional coagulation techniques using ferric chloride as a coagulant. Acidification and carbonation were compared as methods to lower the pH. Jar testing was done using a pH level of 9-13 and coagulant levels of 8.6-51 mg/L. The most effective coagulation was achieved at a coagulant dose of 26 mg/L at a pH level of 9 resulting in an average residual turbidity reduction of 92%. Coagulation significantly reduced the insoluble solids (60%), but had no significant effect on dissolved organic matter, thus total COD was only decreased by 14.5%. Filtration had no effect on the suspended or dissolved solids in wastewater.

INTRODUCTION

Wastewater from industries is usually biologically treated at neutral pH and the sludges produced are aerobically or anaerobically digested. These sludges are also dewatered and landfilled, incinerated or recycled (Luonsi et al. 1986). The increasing costs of waste disposal and more stringent regulations on what can be disposed of from food plants, has increased the pressure to find alternate treatment methods of wastewater treatment. Many food-processing facilities are being forced to pretreat their high strength wastewaters. New techniques such as membrane filtration are needed for the removal of suspended and dissolved matter (Anon. 1993). Since most treatments work efficiently at neutral pH, alkaline pH of wastewater restricts the method of treatment unless the pH is sufficiently reduced. Conventional methods such as coagulation and new techniques such as filtration can be used for treatment of high pH wastewater. However, there are certain constraints
For coagulation the pH of the solution was found to be the determining factor for maximum organic matter removal (Crozes et al. 1995). Coagulation outside the optimum pH zone would involve a waste of chemicals. Though alum is the most commonly used coagulant, iron salts are known to have greater pH range. Iron salts form insoluble hydroxides at alkaline pH and hence are more effective than aluminum salts, which form soluble aluminates at the same pH levels (Cohen and Hannan 1971). Though several membranes are available only a few of them are suitable for filtering high pH wastewater and the major problems associated with membrane filtration are compaction, concentration polarization and fouling (Cheryan 1998).

In the tomato processing industry water from tomato washing and trimming, effluent from scalding and peeling, which contains peel, suspended and dissolved solids, canning water (also called red water) and concentrator flows from tomato paste production constitute the wastewater (Napoli 1979). The current project defines wastewater as the high pH material coming directly from the lye peeler, as this is the most difficult to treat.

Wastewater from the tomato industry is characterized by a high amount of suspended solids from various stages of processing and consequently high BOD, COD and chemicals, whenever chemical peeling methods are used. Previous work done by Napoli (1979) on tomato wastewater suggested the use of a primary treatment of clariflocculation in combination with a special bio oxidative technique. However, this method was costly and problems were encountered with the disposal of clariflocculation sludge.

In potato peeling wastewater, Karim and Sistrunk (1985) found that coagulation with ferric chloride was effective, and reduced total COD by over 90%. Filtration and flocculation was used to recover waste material, reduce COD and save energy in potato and wheat starch processing (Meuser and Kohler 1983). Filtration has been successfully used by other food industries such as dairy (Yip et al. 1996) and starch fermentation processing (Canepa et al. 1993) for effluent treatment. It has been proposed that caustic peeling solutions from fruits and vegetables could be recovered using membrane filtration (Merlo et al. 1993). The objective of this study is to use coagulation and filtration to treat tomato lye peeling wastewater.

METHODS

Lye peeling wastewater was obtained from a commercial tomato cannery at the end of the tomato peeling season for two consecutive years (Hirzel Canning Co., Toledo, OH). The tomatoes were peeled in 12% lye at 82-88°C with a dwell time of 30-40 s and had approximately 10-12% peel loss. The wastewater characteristics were measured to determine the nature of the waste. The suspended solids were measured by standard method 2540D, Total suspended solids dried at 103-105°C.
COAGULATION OF TOMATO LYE WASTE

The sample was dried at 103-105°C but only 5 mL of wastewater was used for measurement to prevent the suspended matter from clogging the filter. The soluble and total COD were measured by standard method 5220B, Open Reflux Method (APHA 1989). Only 1 mL of the filtrate was used for measurement because of high COD values. The volatile and fixed solids were measured by method 2540E, fixed and volatile solids ignited at 550°C (APHA 1989). All measurements were made in triplicate for accuracy.

The pH was measured using Accumet 1000 Series portable pH meter (Fisher Scientific, Pittsburgh, PA). Viscosities were measured with the Contraves rheomat (115, Rheometric Scientific, Piscataway, NJ). Turbidities were measured using Ratio X/R turbidimeter (Hach Co., Loveland, CO). Buffer capacity was measured by titrating the wastewater against 2N HCl and 2N NaOH. It was expressed as the volume of acid or base needed (in mL) for a unit change in pH. Particle size analysis was done using Malvern Mastersizer (Malvern Instruments Inc., Southborough, MA).

The pH was reduced in steps of 1 by carbonation. Approximately 10 L of wastewater was placed in a glass tank (1' x 1' x 2') and continuously mixed using a motorized stirring rod at 20 rpm. Carbon dioxide was introduced into the system, at an inlet pressure of 20 psi, through a sparger of 5 microns. The pH was monitored using a pH meter. When the desired pH level was reached, the wastewater was allowed to stand for 2-3 h to stabilize the pH. The wastewater was then dispensed into beakers and ferric chloride (Fisher Scientific) at the desired dosage was pipetted into the beakers.

Jar tests were done at several pH levels and coagulant doses to determine the extent of coagulation. The pH levels were varied between 9-13 and the coagulant doses between 8.6 - 51 mg/L. Residual turbidity was used as a measure of the effectiveness of coagulation.

Jar tests on the wastewater were done using the method of USEPA (1975) modified with the following mixing speeds and times. Wastewater samples at a given pH were placed in 1 L glass beakers and the coagulant at various levels was added. The contents were rapidly mixed with a six-paddled mechanical stirrer at 100 rpm for 30 s, followed by slow mixing at 20 rpm for 30 min. After slow mixing the paddles were turned off for a half hour settling period. The supernatant after coagulation was collected and the residual turbidity measured. The percent reduction in turbidity compared to the original value after carbonation was computed. Triplicate measurements were made. The reduction in the dissolved organic matter was measured at the optimum pH in terms of reduction in COD of the filtrate from suspended solids measurement. This constituted the soluble COD. COD measurements were made on the wastewater before and after carbonation to determine the effect of carbonation on the total and dissolved organic matter. Statistical differences were computed using a two-sample t-test assuming equal variances.
For membrane filtration, a total of 7 membranes made of high pH resistant material were obtained (Membrane Development Specialists, CA). Of the seven, three membranes DS-12, PW-PR and PW-PP were in the nanofiltration range. The DS-12 was 1 nm. The PW membranes were 3-5 nm in size. The other pore sizes used were 0.1, 0.2, 0.45 and 1.0 microns. Since the organic load of material was very high a lower pore size was presumed to be better.

The filtration unit (NIRO Inc., Hudson WI) used was equipped with two modules, plate and frame and spiral, which were interchangeable. The plate and frame module was used for this experiment so that several membranes could be tested at the same time.

The system used circular flat sheet membranes cast on a support paper. Two membranes were mounted on either side of a membrane support plate and held in place by neck rings. The support plates also served as outlets for permeate. They were alternated with peripherally perforated spacers. The assembly of membranes on the support plates and spacers was stacked on a central tie-rod with a spacer at each end and hydraulically compressed between two end plates. The feed was pumped from the feed tank, up through the bottom end plate and traveled through the pores in the spacer. The feed moves radially across the membrane and through the annulus around the tie-rod and reaches the next spacer. It goes up the plates and the retentate gets pumped out through the retentate tube connected to the upper end plate. An inlet valve and a backpressure valve controlled the flow rate. The retentate was recycled into the tank and the permeate was collected through the permeate tubes. The permeate flow rate was measured after 10 min when the flow stabilized.

Initial flow rates of the membranes were measured by pumping distilled water through the system. The COD of the permeate samples from different membranes was measured.

RESULTS AND DISCUSSION

Wastewater Characteristics

The lye peeling wastewater from tomato processing was characterized in order to determine the best method of treatment. Coagulation with salts and ultrafiltration were possible options. The wastewater has a very high pH, approximately 14 (Table 1). Because of this high pH, the waste is not microbiologically degradable. This pH would also make it difficult to use most coagulants or membranes successfully. Among the coagulants, the iron salts are effective up to a pH of 8.8, while the salts of alum are only effective up to a pH of 7.5 (Packham 1963). For ultrafiltration membranes, the cellulose acetate membranes function in the pH range of 2-8, the polyamides up to pH 11, and while the polysulfones (PS) and polyether sulphones (PES) can be used between pH 1-13, they cannot withstand high pressures and are prone to fouling (Cheryan 1998.)
The wastewater also has a high suspended solids content. Approximately 25% of the suspended solids are volatile in nature. If the sample is acid treated to alter the pH, there will be a loss of the volatile component of the suspended solids. The suspended solids consist of carotenoids, proteins and cellulosic cell walls. The high turbidity values indicate a high suspended solids content and deep color. The suspended solids are probably the particles arising from the breakdown of the peel itself, while the soluble solids are probably from the tissue beneath the peel.

The lye waste has a high concentration of soluble organic solids oxidizable by COD. Soluble COD formed 75-89% of the total organic solids oxidizable by COD. The cell walls of tomato consist of pectins and other polysaccharides (Seymour et al. 1990), cutin acids, waxes and organic compounds (Baker et al. 1982), some of which may contribute to soluble COD. The rheological behavior of the waste is Newtonian with a low viscosity and a negligible yield stress.

The dissolved solids measurement by the standard method 2540C Total dissolved solids dried at 180C (ALPHA 1989) was not feasible for this study. The process involves drying the filtrate obtained from the suspended solids measurement. This precipitated sodium hydroxide, which had to be accounted for by titration to determine the amount present. The only alternative to this method was to measure the COD of the filtrate obtained from suspended solids measurement (soluble COD). Comparison of the standard method after making the correction for sodium hydroxide with the COD measurements gave no statistically significant difference between the two methods (Table 2).

The Standard method is more cumbersome than COD and involves more measurements that may lead to propagation of error. Moreover, when the feed was carbonated it was not possible to account for the sodium carbonate or bicarbonate formed. Hence COD was used instead of the Standard Method.

<table>
<thead>
<tr>
<th>Wastewater characteristic</th>
<th>Year 1</th>
<th>Year 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>13.80 ± 0.08</td>
<td>14.02 ± 0.02</td>
</tr>
<tr>
<td>Suspended solids (g/L):</td>
<td>5.624 ± 3.591</td>
<td>2.8 ± 0.84</td>
</tr>
<tr>
<td>Volatile solids (g/L)</td>
<td>1.340 ± 0.741</td>
<td>*</td>
</tr>
<tr>
<td>Fixed solids (g/L)</td>
<td>4.284 ± 2.598</td>
<td>*</td>
</tr>
<tr>
<td>Total COD (g/L)</td>
<td>35.2 ± 1.1</td>
<td>44.5 ± 0.6</td>
</tr>
<tr>
<td>Soluble COD (g/L)</td>
<td>31.4 ± 2.5 (88.99%)</td>
<td>33.2 ± 2.1 (74.5%)</td>
</tr>
<tr>
<td>Insoluble COD by difference (g/L)</td>
<td>3.8 (11.01%)</td>
<td>11.3 (25.5%)</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>330</td>
<td>1689</td>
</tr>
<tr>
<td>Viscosity (Pa-Sec)</td>
<td>0.012</td>
<td>*</td>
</tr>
</tbody>
</table>

*Not measured
Effect of Acidification Versus Carbonation to Lower the pH

To reduce the pH of the feed, two methods were compared. One was to acidify the feed using sulfuric acid and the other was to carbonate it by pumping in carbon dioxide to convert the sodium hydroxide to sodium carbonate or bicarbonate, lowering and buffering the pH. To accurately predict the effectiveness of the coagulation treatment at reducing the load of organic matter, the effect of pretreatment by acidification or carbonation was compared for suspended and dissolved solids.

The concentration of suspended solids and soluble COD was decreased by acidification but carbonation had no effect (Table 3). The difference is statistically significant at 95% level of confidence using a t-test. During the acidification process, the heat of neutralization produced by the reaction of the strong acid (H$_2$SO$_4$) with the strong base (NaOH) may have volatilized the suspended and dissolved solids thus decreasing the suspended solids content and soluble COD. Carbonation was used for the rest of the experiment since the total COD were not affected by this treatment (Table 3).

### TABLE 2.

COMPARISON OF STANDARD METHOD AND COD

<table>
<thead>
<tr>
<th>Standard Method</th>
<th>Measured value</th>
<th>% of total solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Solids (g/L)</td>
<td>46.53 ± 6.23</td>
<td>100.00</td>
</tr>
<tr>
<td>Dissolved solids (g/L)</td>
<td>41.29 ± 10.18</td>
<td>88.73$^a$</td>
</tr>
<tr>
<td>Suspended Solids (g/L)</td>
<td>5.24</td>
<td>11.27$^b$</td>
</tr>
<tr>
<td>COD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total COD (g/L)</td>
<td>35.2 ± 1.1</td>
<td>100.00</td>
</tr>
<tr>
<td>Soluble COD (g/L)</td>
<td>31.4 ± 2.5</td>
<td>88.99$^*$</td>
</tr>
<tr>
<td>Insoluble COD (g/L)</td>
<td>3.8</td>
<td>11.01$^b$</td>
</tr>
</tbody>
</table>

$^a$ values with different letters were significantly different at 95% confidence level.

### TABLE 3.

EFFECT OF ACIDIFICATION AND CARBONATION ON WASTEWATER CHARACTERISTICS

<table>
<thead>
<tr>
<th>Wastewater characteristic</th>
<th>Total COD (g/L)</th>
<th>Soluble COD (g/L)</th>
<th>Suspended solids (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
<td>44.5 ± 0.6$^a$</td>
<td>29.2 ± 0.6$^b$</td>
<td>2.05 ± 1.06$^d$</td>
</tr>
<tr>
<td>After acidification</td>
<td>*</td>
<td>27.6 ± 0.2$^c$</td>
<td>0.625 ± 0.16$^e$</td>
</tr>
<tr>
<td>After carbonation</td>
<td>44.4 ± 1.5$^a$</td>
<td>29.0 ± 1.1$^b$</td>
<td>2.11 ± 0.79$^d$</td>
</tr>
</tbody>
</table>

* not measured

** values with different letters were significantly different at 95% confidence level.
Buffer Capacity

The buffer capacity of the lye waste decreased from 250 at pH 14 to 3.57 at pH 12. From pH 12 to 7 the buffer capacity decreased slightly from 3.57 to 0.56. The solution resists pH changes at high pH levels which makes it difficult to neutralize. Once the pH is below 12 there is a marked decrease in buffer capacity, thus the wastewater is easier to neutralize.

Coagulation by Jar Test

Most industrial wastewaters, at neutral or acidic pH, can be treated with alum or ferric chloride to remove the organic matter (Lind 1995). This experiment was conducted using ferric chloride as it is effective as a coagulant at a broader and higher pH range than alum (Cohen and Hannah 1971). The main aim was to determine the optimum pH and the coagulant dose that produces maximum reduction in the organic matter.

The pH of the lye peeling wastewater was lowered by bubbling carbon dioxide through the wastewater. Carbonation of the lye peeling wastewater decreased the pH by neutralizing the hydroxyl ions of the lye (Eq. 1). This reaction leads to the formation of sodium carbonate and bicarbonate, which are weak bases in solution. Sodium carbonate also acts as a buffer stabilizing the pH.

\[ \text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{NaHCO}_3 \]  

Carbonation lowered the pH, but as it approached neutrality further reduction was not possible. The carbonate species saturates the solution buffering the pH and resisting further changes. The lowest pH achieved was 9.

When ferric chloride was added to the wastewater under mildly alkaline conditions, a series of hydrolysis reactions occurred. They have been expressed by Le Prince et al. (1984) with the following equation:

\[ x\text{Fe}^{3+} + y\text{H}_2\text{O} = \text{Fe}_x\text{(OH)}_{(3x-y)+} + y\text{H}^+ \]  

The monomeric and polymeric iron hydroxide species formed are the active coagulant species. The weakly alkaline conditions enhanced the formation of species with a range of charges. Having species with a range of charges increases the coagulation effectiveness.

All combinations of pH levels 9-13 and coagulant doses 8.6-51 mg/L were tested (Fig. 1). The same trends were seen both years thus data from the first year is presented. The turbidity measurements were plotted against the coagulant doses for various pHs. At pH 13 the maximum reduction of turbidity was observed at the highest dosage level (51 mg/L). At high pH levels the range of charged monomeric to polymeric species formed is considerably reduced hence higher dosages are required to generate the active coagulant species. Since pH is the limiting factor,
the maximum reduction observed was only 25% of the turbidity values. At pH 9 the maximum reduction in turbidity was 83%, occurred at dosage levels of 26-43 mg/L. For economical reasons the lowest dosage that produces maximum reduction in turbidity is preferred. Hence pH 9 and dosage of 26 mg/L were the apparent optimum for maximum reduction.

In jar tests floc formation is used as an indicator to determine whether the dosage used is optimum for the sample being treated. When insufficient dosages are used small flocs are formed and at higher than optimum dosages the flocs redisperse, increasing the turbidity values. Since the sample being treated is colored red because of tomato pigments, floc formation was not visible. The increase in turbidity values observed in some samples at coagulant dosages of 51 mg/L is likely due to the redispersion of flocs.

The lower the pH, the more effectively the ferric chloride reduced the turbidity. At the coagulant dosage of 26 mg/L the turbidity was reduced from 84.3% at pH 13 to 17.8% at pH 9. The ferric chloride works more effectively at pH 9 because a mildly alkaline pH promotes a wide range of charges on the more active coagulant species.

The total reduction in the organic load was recorded not only in terms of turbidity but also in terms of COD. Coagulation significantly reduced the turbidity
COAGULATION OF TOMATO LYE WASTE

of the original wastewater, which measures the suspended solids content or insoluble COD. However, coagulation did not reduce the dissolved organic matter, or soluble COD (Table 4). The reduction in turbidity occurred due to the precipitation of insoluble solids. Since the insoluble solids are only 25.5% of the total solids, and only 60% of the insoluble solids are removed by coagulation, the use of ferric chloride produced only 14.5% reduction in the total solids of the system. It was expected from previous work on natural organic matter with ferric chloride that the coagulant would have also removed the dissolved solids (AWWA Coagulation Committee 1989). In potato peeling wastewater, Karim and Sistrunk (1985) found that coagulation with ferric chloride was effective, and reduced total COD by over 90%. This may have been due to a lower dissolved solids content in potato peeling wastewater than in tomato peeling wastewater.

<table>
<thead>
<tr>
<th>Total COD</th>
<th>Measured Value</th>
<th>% of COD in untreated sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated sample (g/L)</td>
<td>44.5 ± 0.6 a</td>
<td>100</td>
</tr>
<tr>
<td>Treated sample (g/L)</td>
<td>38.1 ± 0.6 b</td>
<td>85.53</td>
</tr>
<tr>
<td>Soluble COD</td>
<td>33.2 ± 0.2 c</td>
<td>74.46</td>
</tr>
<tr>
<td>Treated sample (g/L)</td>
<td>33.6 ± 0.6 d</td>
<td>75.38</td>
</tr>
<tr>
<td>Insoluble COD by difference</td>
<td>11.4 d</td>
<td>25.54</td>
</tr>
<tr>
<td>Treated sample</td>
<td>4.5 e</td>
<td>10.15</td>
</tr>
</tbody>
</table>

**values with different letters are significantly different at 95% confidence level

Particle Size Analysis of Wastewater

The particle size analysis of the original feed, acidified feed, carbonated and coagulated feed, shows how treating the carbonated feed with ferric chloride greatly reduces the particle size (Fig. 2). Acidification and carbonation also reduce the particle size to some extent.

The mode and median particle size in the original wastewater is 105 μm. After acidification, there is a reduction in the number of large particles (greater than 105 μm). This is due to the heat generated by the neutralization reaction between sulfuric acid and sodium hydroxide in the wastewater, which breaks down the larger particles.
Carbonation also reduced the particle size significantly. This is because the carbonation process involved agitation due to the bubbling of carbon dioxide and continuous mixing which may have broken down the flocs and the larger particles, thereby reducing the particle size with no immediate effect on the COD of the sample.

The particle size of the coagulant treated wastewater is smaller than the other samples, with 90% of the particles less than 2 μm. The ferric chloride enmeshed all of the large particles (> 10 μm) and coagulated them, removing them from solution.

Membrane Filtration

The membranes in the nanofiltration range are not useful since the pores are too small to allow a measurable permeate flux rate. The highly fouling nature of the feed clogged the membrane preventing proper filtration in the nanofiltration range. The membranes in the ultrafiltration range had a low but measurable flux rate. There was no significant difference between the COD of any of the filtrates of the original feed. Since the plate and frame module operates under high shear conditions, the shear may have decreased the particle size of the solids so that they all passed through the membranes in the UF range. This would explain why there
is no difference between the COD measurements of the feed and filtered permeate. From this experiment it can be concluded that filtration is not a feasible alternative.

CONCLUSIONS

It may be possible to use gases produced as a by-product of the boiler room as a cheap source of CO₂. Due to high sewage charges, it may be cost effective to remove the suspended solids and dispose of them on the fields here they would act as fertilizer. Carbonation reduces the pH of the waste considerably. Use of coagulant for pretreatment after carbonation may be helpful but it only removes 15% of the total solids. Biological treatment may be used after mixing the carbonated lye peeling wastewater with wash and rinse water for an additional two-fold dilution to bring it close to neutrality.

REFERENCES


