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Physical treatments of food processing waste waters

by G. D. Saravacos and H. D. Iredale

INTRODUCTION

The preservation of the natural environment from industrial and municipal pollution is currently receiving much attention. In the food industry, the most important problem is the treatment and disposal of large quantities of waste-water, a by-product of various processing operations. Of less importance is the disposal of solid wastes and air pollution.

Wastewaters from food plants contain variable amounts of suspended and soluble solids, which must be reduced to an acceptable level before disposal into natural bodies of water (1). Suspended solids are removed readily by a *primary treatment* method, such as screening, filtration, sedimentation, or centrifugation. A variety of equipment is available for solids/liquid separation, and its selection depends on the economics and size of the operation (2).

Soluble solids in wastewater include inorganic ions and relatively small organic molecules. In food wastewaters, the soluble organic substances are the most important group from the pollution standpoint. These substances include sugars, organic acids, and alcohols, at typical concentrations of 1,000 to 5,000 ppm expressed as chemical oxygen demand (C.O.D.) or biological oxygen demand (B.O.D.). The soluble organic substances (C.O.D. and B.O.D.) must be reduced to a low value (less than 100 ppm) before the effluent is discharged. This reduction is usually accomplished by a *secondary treatment* method, which is essentially a biological oxidation process, utilizing natural microorganisms and atmospheric oxygen.

In the treatment of food processing wastewaters, lagooning is used extensively. This method requires minimum equipment and attention, but it has some serious disadvantages: Large areas of land are needed, and the process of oxidation is too slow because of the inefficient transfer of atmospheric oxygen. Undesirable odors may be produced by anaerobic fermentation in the lagoons. The activated sludge process utilizes mechanical aeration resulting in faster oxidation and less land requirement. Liquid oxygen has been suggested recently as a new method of accelerating the biological oxidation.

The effluent from the biological oxidation treatment may contain considerable amounts of inorganic ions, such as phosphates and nitrates, which have a pollution potential. It may also contain some esthetically undesirable minor compounds, as, for example, color and odor. These compounds can be reduced significantly by *tertiary treatment*, a process receiving increased attention recently. This treatment involves usually physical separation processes such as carbon adsorption, reverse osmosis, ion exchange, and stripping of dissolved gases. Chemical processes may also be applied in special cases, such as oxidation (chlorine, ozone) and chemical precipitation.

Physical separation methods are used extensively in the process industries to recover various products from dilute solutions. They require rather elaborate equipment, which, in most cases, is expensive for the treatment of wastewater. However, when a by-product can be recovered, or when the pollution problem cannot be solved by other methods, physical processes can be used effectively. In

some cases, a physical process may complement or replace the biological treatment entirely (for example, reverse osmosis or carbon adsorption).

This report describes some experimental work and results obtained on the physical treatments of food processing wastewaters at the Geneva Food Research Laboratory during the period 1969-1971. Typical wastewaters from local fruit and vegetable processing industries were used, and the methods investigated were: evaporation, distillation, reverse osmosis, and carbon adsorption.

EVAPORATION AND DISTILLATION

Evaporation of industrial wastewaters for the recovery of fresh water is usually not economical because of the cost of equipment and the heat energy required. When a by-product can be recovered, evaporation can be profitable. A typical example is the concentration of citrus wastewater into citrus molasses.

Some experiments were made on the concentration and distillation of a cherry brine, obtained from a local processor. The brine was a by-product of processing cherries with SO₂. It contained 9.8 per cent soluble solids (mainly sugars) and 4,500 ppm total SO₂, and it had a pH of 4.0. The total and free SO₂ (2,800 ppm) were analyzed by the oxidation with iodine method (3).

A pilot-scale falling film evaporator was used for flash-evaporation and concentration of the brine. The main evaporator body consists of a vertical tube 2-in. O.D. and 10 ft. long, and it can evaporate up to 150 lb. of water per hour (4). Using a brine feed rate of 1 gpm and a steam jacket pressure of 28 psig, 8.3 per cent of the liquid was flash-evaporated at atmospheric pressure in one pass through the evaporator. Under these conditions, the brine was concentrated from 9.8° to 10.6° Brix, and the total SO₂ content was reduced from 4,500 to 3,900 ppm. The distillate contained 2,400 ppm of SO₂. The brine was concentrated further in vacuum (100° F) and the concentrate (20.4° Brix) contained 4,300 ppm SO₂.

It was evident that evaporation of the cherry brine removed only the free SO₂, while the bound SO₂ was retained in the concentrate. SO₂ is known to combine with sugars in various fruit juices, but most of it can be removed during evaporation of the juices. In cherry brine, SO₂ is combined, in addition to sugars, with the cherry pigments, and this binding appears too strong to be broken by evaporation or distillation.

Steam-stripping of the cherry brine in a distillation column removed most of the free SO₂, confirming the evaporation experiments. A 2-in. glass

column (Oldershaw-type) containing 20 plates was operated at atmospheric pressure with a feed rate of 1.4 liters/hr. and a countercurrent flow of live steam (5). Using a 12.6 per cent stripping (amount of distillate as a percentage of feed rate), the free SO₂ in the brine was reduced from 2,800 to 220 ppm (92%), while the total SO₂ was reduced from 4,500 to 1,120 ppm. By increasing the stripping rate to 30.8 per cent, the removal of free SO₂ was raised to 95 per cent, but the total SO₂ remained the same. A higher removal of the free SO₂ can be accomplished by using more distillation plates.

In a related experiment, a 10 per cent glucose solution, containing 5,000 ppm of total SO₂, was stripped in the same Oldershaw column using 12.5 per cent stripping rate. The total SO₂ was recovered almost quantitatively (99%), indicating that sugars alone are not responsible for the strong binding of SO₂ in the cherry brine. In a similar stripping experiment, 99 per cent of the total SO₂ was removed from Concord grape juice containing 1,000 ppm SO₂.

Addition of strong mineral acids (hydrochloric or sulfuric) to the cherry brine released the bound SO₂, and the red color reappeared. It was found necessary to bring the pH to 1.25 for the complete release of SO₂. The acidified brine was flash-evaporated in a laboratory glass apparatus resulting in an almost complete removal of the SO₂. Thus, by 20 per cent flash evaporation, more than 97 per cent of the total SO₂ was removed from the brine. A more thorough removal of the total SO₂ was achieved using the glass distillation column. The stripped brine was decolorized readily with activated carbon, as discussed later. In applying the acidification process to industrial equipment, the corrosion problems posed by the strong acids should be considered.

During flash-evaporation or steam-stripping of the cherry brine, the distillates contained a high concentration of SO₂ (10,000 to 20,000 ppm). These strong SO₂ solutions can be reused in food processing, eliminating, at the same time, a serious source of pollution.

REVERSE OSMOSIS

Reverse osmosis is a new physical method of separation of salts and organic substances from dilute aqueous solutions. Initially proposed for desalting brackish and sea water, reverse osmosis has potential applications in the concentration of fruit juices and the treatment of wastewater (6). The aqueous solution is forced through a semi-permeable membrane (cellulose acetate or nylon), which allows the passage of water and retains most of the other molecules and ions. The applied

mechanical pressure must exceed the osmotic pressure of the solution, which depends directly on the concentration of the soluble solids.

A typical cellulose acetate membrane (7) consists of a thin, dense surface layer (0.25 micron) backed by a thicker porous layer (100 microns). Various configurations have been suggested for membrane equipment, including the tube, the plate and frame, the spiral-wound, and the capillary systems.

Industrial and municipal wastewaters, containing relatively high concentrations of organic soluble solids (about 2,000 ppm C.O.D.), require tight membranes and pressures of about 500 psig. Reverse osmosis should be distinguished from ultrafiltration, which is used to remove rather large molecules, such as proteins and polysaccharides, from aqueous solutions. Ultrafiltration requires a porous membrane and a relatively low pressure (about 50 psig).

A preliminary evaluation of the reverse osmosis process can be made with a test cell. An Abcor 3-in. cell (8) was used in our experiments, and it was operated batchwise. The stainless steel cell contained a porous disc and a perforated plate, which supported the 3-in. (diameter) membrane.

After assembling the cell with the appropriate membrane, 100 ml of the test solution was added to the high-pressure chamber. To minimize concentration polarization at the membrane surface, the solution was mixed continuously with a magnetic stirrer bar in the cell. Nitrogen pressure (500-600 psig) was applied from a gas cylinder. It was necessary to use a high-pressure reducing valve and a stainless steel tube connection (Vi in. O.D.). The cell was operated until 90 ml of permeate was collected.

The initial solution, the permeate, and the concentrate were analyzed for soluble solids ($^{\circ}$ Brix), SO₂ (3), color, and C.O.D. (by the dichromate oxidation method [9]). It was found that a tight membrane is necessary for a significant reduction of the C.O.D. and color of the wastewater. Porous membranes, used in ultrafiltration, were ineffective for this application. The most effective membrane was Eastman RO-97, which is a tight membrane yielding 97 per cent rejection of sodium chloride from an aqueous solution. This membrane, used in the test cell, removed 95-98 per cent of the C.O.D. from three different wastewaters (Table 1).

The color was also removed effectively from the beet wastewater and the cherry brine. All the bound and 90 per cent of the free SO₂ was removed from the cherry brine. The concentrate resulting from the cherry brine contained, therefore, most of the color and SO₂, together with the sugars. If the brine concentrate is to be reused, it is

Table 1. Reverse osmosis of food processing wastewaters.

Sample	Feed	Permeate	% Rejection
1. Blanch water from cut-beans C.O.D.	2,184 ppm	100 ppm	95.4
2. Canned beets wastewater C.O.D.	2,500 ppm	100 ppm	96.0
Color	red	colorless	100.0
3. Cherry brine C.O.D.	98,000 ppm	2,000 ppm	98.0
Free SO ₂	2,800 ppm	280 ppm	90.0
Bound SO ₂	1,700 ppm	0	100.0
Color	yellow	Colorless	100.0

necessary to remove the SO₂ and the color by steam stripping and carbon decolorization. An attempt was made to separate the sugars from the SO₂ and the pigments by a semi-permeable membrane, but all the membranes tested were ineffective for this purpose.

The permeate rates in the test cell varied with the type of membrane, the concentration of soluble solids in the wastewater, and the applied pressure. For a typical C.O.D. of 2,500 ppm and a pressure of 600 psig, the permeate rate of the RO-97 membrane in the 3-in. cell was 120 ml/hr., corresponding to 22.5 gal./day sq. ft. of membrane surface. The permeation rate along with the membrane life are important parameters in cost estimations.

A two-stage reverse osmosis treatment or tighter membranes may be necessary when the original wastewater is too high in C.O.D. content, or when the C.O.D. of the final effluent must be below a maximum allowable level.

ACTIVATED CARBON TREATMENT

Activated carbon is a very porous solid, in powder or granular form, which can remove various organic substances from aqueous solution by physical adsorption. It is used commercially for decolorizing sugar solutions and for removing various organic vapors from the air. Its adsorptive capacity is attributed to the high surface area of the pores, which varies from 500 to 1,400 square meters per gram (10).

In the industrial treatment of liquids, powdered carbon is used as a slurry and the liquid is separated by filtration. Granular carbon is used usually in percolation columns through which the liquid

flows continuously. The granular form is preferred because dusting is eliminated and pressure drop in packed columns is minimized. The spent carbon can be regenerated by heating in a slightly oxidizing atmosphere.

Activated carbon adsorption has been proposed recently as a method of removing residual C.O.D. in the treatment of wastewater (1). Dissolved and colloidal organic substances, present in the effluent of biological oxidation, can be removed thoroughly by passing through a bed of granular carbon. Recent experimental work in California has shown that activated carbon can be used for reconditioning of olive brines (11). Treatment in carbon columns removes most of the dark color and other undesirable substances, leaving a light-colored brine (sodium chloride) which can be reused in olive processing.

For laboratory evaluation of the carbon adsorption process, batch tests were made with Pittsburgh CAL 12 x 40 granular carbon (12). One hundred ml samples of the liquid were mixed with 2-10 per cent activated carbon and shaken mechanically in 500 ml Erlenmeyer flasks for 30 minutes. The mixture was filtered through No. 5 Whatman paper, and the filtrate was analyzed for color, C.O.D., or SO₂. These tests showed the amount of carbon required for the removal of the undesirable substances. The data obtained in the batch tests can be used for the construction of adsorption isotherms (11), which are useful for scale-up calculations.

Wastewater from canned beets was decolorized very effectively using 3-4 per cent of activated carbon. The color was measured with a Bausch and Lomb Spectronic 20 colorimeter (520 mu). At the same time, the C.O.D. of the beet wastewater was reduced from 4,760 to 1,680 ppm (65% removal). It is obvious that carbon treatment cannot replace the secondary treatment (biological oxidation) entirely. It can, however, be used effectively for the treatment of the effluent from the secondary treatment by removing the residual C.O.D. and color.

Carbon treatment was partially effective in decolorizing the cherry brine. It was found necessary to increase the carbon dosage to 10 per cent in order to achieve a significant reduction in the yellow color of the brine. This difficulty in decolorization may be due to the presence of large amounts of SO₂ in the cherry brine.

Carbon treatment removed significant amounts of free SO₂ from the brine, while the bound SO₂ content was unchanged. Thus, treatment of the brine with 10 per cent carbon reduced the free SO₂ from 2,800 to 1,600 ppm. The adsorption of SO₂ on the active carbon sites may have prevented

the effective adsorption of the larger pigment molecules. It is also possible that the pigments in the brine are in some bound form, and they cannot be adsorbed readily.

As discussed in the evaporation experiments, addition of strong acids to bring the pH to about 1.2 resulted in a release of the pigments and the bound SO₂. The SO₂ was stripped readily by either flash evaporation or, more thoroughly, by steam distillation. The stripped pink brine was decolorized very effectively with 3-4 per cent activated carbon. The colorless sugar solution was adjusted to pH 4.0 before reuse.

CONCLUSIONS

Our preliminary experiments have shown the possibilities and the limitations of physical separation methods in the treatment of food processing wastewaters.

Established processes, such as evaporation, distillation, and carbon adsorption, can be applied successfully when the economics of the process are favorable. Thus, evaporation and carbon decolorization can be used in the treatment of cherry brine, if the recovered sugar concentrate can be utilized as a syrup, or for fermentation. Stripping and recovery of SO₂ from wastewater in a column may be justified if there is no other acceptable alternative.

Reverse osmosis is a promising new method of wastewater treatment, either as a replacement or in combination with the established biological oxidation processes. Commercial application requires more operational and economic data on the membranes and the utilization or disposal of the concentrated by-product. Reverse osmosis could also be used for the decolorization of wastewater, competing with the established carbon adsorption process.

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