TREATMENT OF CONCENTRATED PIMIENTO WASTES WITH POLYMERIC FLOCCULATING AGENTS

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Abstract

Chemical methods of treatment were investigated as a means to reduce the waste load of concentrated unit effluents from pimiento canning. Polymeric flocculating agents and inorganic salts were applied to unit effluents. Optimum laboratory conditions for suspended solids removal were then tested on a pilot plant scale. Turbidity of effluents from peel removal, core removal, and the total canning operation composite were reduced by 95, 93, and 74%, respectively. Corresponding values for suspended solids reduction were 95, 82, and 86%. Segregation and separate treatment of the peel removal effluent which contains 69% of the total load of suspended solids in only 18% of the waste water flow is recommended.

Many food processing industries are being required to adopt complex and costly provisions for handling of waste effluents. Difficulties are confounded by a number of factors, especially wide variations in volume and composition of the effluents on a seasonal and day-to-day basis. This is particularly true for fruit and vegetable canning operations where effluents from each commodity and each unit operation are unique in character whether alone or in combination. The variability and frequent high concentration of these effluents place severe limitations on the application of standard biological waste treatment practices. Reduction of specific effluent wastes by physical-chemical reactions such as coagulation of suspended solids and carbon adsorbtion of dissolved solids may offer more effective treatment. Chemical treatment with flocculating agents may be especially useful as a means to reduce the suspended solids load to meet pre-treatment discharge standards which are being developed by the Environmental Protection Agency.

Several workers have reported the wide variability of waste loads in canning effluents of different commodities and unit processes. Mercer et al. (8) have characterized the variations of in-plant waste streams from the canning of peaches and tomatoes. Splittstoesser and Downing (13) reported waste effluent data for factories processing apples, beets, carrots, cherries, corn, green beans, grape juice, peas, pumpkin, sauerkraut, and tomatoes. Shewfelt and Chipley (12) reported wide differences in the character of effluents from unit processes of a dry bean canning operation. In a subsequent report by Shewfelt (11), preliminary data were given on the use of polymetric flocculants and granular activated charcoal for the reduction of waste load in the processing effluents of leafy greens, pimientos, white potatoes, and poultry by-products.

Pimientos are canned mostly in California and in Georgia. It is estimated that more than 18,000 tons of pimientos were canned in 1972. The crop is of considerable economic importance because it provides income for a relatively large number of smallacreage growers and also for a significantly large number of cannery workers. Large volumes of water required for pimiento processing cause excessive dilution of the composite waste effluent and suggest consideration of separate physical-chemical treatment of certain unit process effluents (3). The present study was concerned with the application of chemical flocculation treatments to the waste effluents from commercially-canned pimientos.

Physical-chemical treatment techniques including flocculation and adsorption, have been successfully applied to municipal wastes (1, 2). These techniques are also applicable to food processing wastes which are often much more concentrated than municipal wastes and are often more variable due to processing schedules. Hopwood and Rosen (5) reduced the pollution load of concentrated slaughterhouse and poultry packing wastes by treatment with sodium lignosulfonate. A review by the National Canners Association (9) of liquid processing wastes indicated that inorganic salts such as lime, alum, or iron sulfates were the most common coagulating agents applied to liquid vegetable wastes. The efficiency of removal of suspended material by coagulation and settling ranged from 50 to 90% for pea, beet, corn, bean, tomato, and carrot wastes. No studies involving polymeric flocculating agents were reported.

A mechanism of action of polymeric flocculating agents is described by LaMer and Healy (6) in which the polymer destabilizes a collodial suspension by adsorption of particles and subsequent formation of particle-polymer-particle bridges. This is generally true for anionic and nonionic polyelectrolytes which are used to coagulate negative colloids. Cationic

TABLE 1. LABORATORY STUDY OF THE EFFECT OF POLYMER CONCENTRATION ON SUSPENDED SOLIDS REMOVAL FROM PIMIENTO PEEL REMOVAL EFFLUENT AT PH 4.0^1

Natron 86, mg/l	Suspended solids in settled supernatant, mg/i
0	45
5	49
10	56
20	52
30	52
50	16
70	82
100	116

¹The concentration of suspended solids in the raw waste was 230 mg/l.

polymers which are positively charged can destabilize a negative collodial suspension by charge neutralization as well as bridge formation according to O'Melia (10).

The objective of this study was to investigate the effects of treatment with polymeric flocculating agents on reduction of waste loads of pimiento canning effluents with particular emphasis on in-plant streams of relatively high concentration.

MATERIALS AND METHODS

Effluent samples

Samples of concentrated processing effluents were collected from a large-scale pimiento canning operation at the following plant locations: peel removal operation, effluent A; core removal operation, effluent B; citric acid dip, packing, and closing area, effluent E; and the sewer line carrying the total plant composite effluent, effluent F (3). All samples were screened at the plant through a 20-mesh screen. Each sample consisted of a 10 to 20-gal portion which was stored at 3 C within 15 min of collection and treated within 2 days. No significant changes in the concentration of suspended solids or COD were observed during this storage period.

Effluents C and D from the hand grading and cleaning areas were not tested in these treatment studies due to their dilute nature (3).

Laboratory studies

The effects of various combinations and concentrations of flocculating agents on reduction of waste load of the four effluents were investigated on a laboratory scale. Of eight polymers tested, two cationic polymers (Natron 86 and WT-2660) and one anionic polymer (WT-3000) were particularly effective in removing suspended solids from pimiento waste effluents. These polymers were tested separately and in combination with each other and with inorganic salts including ferric chloride (FeCl₃) and alum (Al₂(SO₄)₃). Effectiveness of polymer treatments was evaluated over a polymer concentration range of 0 to 100 mg/l. The effect of pH on flocculation treatments was also examined.

A laboratory stirrer with four stirring paddles (2.6×8.6 cm) and rotating at a variable controlled speed was used to mix 500-ml volumes of waste effluent contained in 800-ml beakers. Upon addition of the desired chemical agents, the contents of each beaker were mixed at 125 rpm for 4 min and then allowed to settle for 60 min. These conditions resulted in lower suspended solids and turbidity values in the supernatant than when chemicals were mixed at 100-200 rpm for 1 min and at 30 rpm for 4-5 min followed by settling. The supernatant liquid was decanted with care to prevent disturbing the settled materials and analyzed for suspended solids (7) and turbidity (4). A Hach Laboratory Turbidimeter, Model 2100A, was used for turbidity measurements.

Those sets of conditions in laboratory studies which resulted in greatest reductions in the concentration of suspended solids and turbidity were selected for further study on a pilotplant scale.

Pilot-scale studies

The pilot-scale unit illustrated in Fig. 1 was employed for the larger scale flocculation studies. While the charcoal adsoption column of the unit was used with selected effluent samples, the limited data obtained were not included in this paper. The top mixing tank was charged with 37.85 liters (10 gal) of waste effluent. A variable-speed stirring paddle was rotated in this tank at approximately 125 rpm. The chemical flocculating agents contained in 500 ml water were added to the mixing tank at a rate of 25 ml/min. Concentrations of polymer and salt added were those determined to be optimum in laboratory studies on the different unit effluents. The mixture was then transferred by gravity to the settling tank and allowed to settle while being stirred slowly with a rotating baffle at 6 rpm. Samples were decanted

Treatment	Chemicals added	cals added Samples			Turbidity, FTU	Suspended solids, mg/l		COD, mg/l	
no.	(final concn.)	рН	taken	Time (h)	Trial 1	Trial 1	Trial 2	Trial 1	Trial 2
1	Natron 86 (50 mg/l)	4.0	Raw	0	20	230	214	1940	1882
	Alum (40 mg/l)		Decanted	0.5	1.1	17	1	-	1419
	• • •		Decanted	1	1.0	11	1	1533	1419
			Decanted	2			2		1407
2	Natron 86 (5 mg/l)	4.0	Raw	0	8	209		2009	
	WT-3000 (5 mg/1) Alum (40 mg/l)		Decanted	2		33		1581	
3	Natron 86 (25 mg/1)	4.0	Raw	0		221			
	Alum (40 mg/l)		Decanted	0.5		112			
			Decanted	1		85			

TABLE 2. PILOT-SCALE STUDIES OF THE EFFECTS OF CHEMICAL TREATMENTS ON THE TURBIDITY, SUSPENDED SOLIDS, AND COD OF PIMIENTO ROASTER WASHER (PEEL REMOVAL) EFFLUENTS

*Not determined



Figure 1. A pilot-scale unit for physical-chemical treatment studies.

every 30 min from the lowest sampling port on the side of the settling tank.

Since suspended solids accounted for most of the turbidity of these wastewaters, the assay of turbidity was used to monitor the course of settling of flocculated solids. The concentrations of suspended solids and COD in the samples taken were determined later. Since both soluble and suspended solids contribute to the COD, no attempt was made to correlate COD with turbidity.

The	pilot-scale	treatments	applied	were	as	follows:
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Effluent	Treatment no.	рН	Chemical agents
Peel removal	1	4.0	Natron 86 (50 mg/l), alum (40 mg/l)
	2	4.0	Natron 86 (5 mg/1), WT-3000 (5 mg/1),
÷	3	4.0	alum (40 mg/1) Natron 86 (25 mg/l), alum (40 mg/1)
Composite	1	4.6	Natron 86 (30 mg/l), FeCl ₃ (40 mg/l)
	2	5.1	WT-2660 (2 mg/1)
Core removal	1	6 .0	Natron 86 (60 mg/l), alum (80 mg/l)
	2	6.1	Natron 86 (60 mg/l), FeCl ₃ (10 mg/l)
Citric acid dip	1	3.8	None

RESULTS AND DISCUSSION

Effluent from peel removal operation

Removal of the waxy peel from pimientos by roasting resulted in a considerable amount of charred material which was subsequently washed into the peel removal effluent. The suspended solids load of this unit effluent was 2.2 lb per ton of raw material processed (3). This accounted for 69% of the total load of suspended solids from all processing operations yet was contained on only 18% of the waste volume. Thus, segregation and separate treatment of this concentrated effluent would significantly reduce the total load of suspended solids.

The natural pH of the peel removal effluent was 6.0 ± 0.2 (3). In laboratory studies, lowering the pH to 4.0 followed by stirring for 4 min and settling for 60 min resulted in a 44% decrease in the suspended solids concentration over that of the raw settled effluent. The effect of varying the polymer concentration to determine the optimum amount for effective treatment (Table 1) indicated that the lowest suspended solids concentration in the settled supernatant was obtained with a polymer concentration of 50 mg/1. Further increases in the polymer concentration caused restabilization of the flocculated solids due to overdosing (10). Treatment No. 1 of Table 2 shows the results obtained from pilot-scale treatment of the pimiento peeling effluent.

As shown in Table 2, chemical treatment (No. 1, trial 1) with Natron 86 (50 mg/l) and alum (40 mg/l) at pH 4.0 followed by primary settling resulted in a 95% reduction in the turbidity from 20 to 1.0 Formazin Turbidity Units (FTU) and a 95% reduction in the suspended solids concentration, from 230 to approximately 11 mg/l. Removal of this suspended material accounted for a reduction of approximately 21% in the COD of the decanted supernatant from 1940 to 1533 mg/l. The values shown under trial 2 are from a replicate of Treatment No. 1 applied to a different batch of effluent.

Treatment No's. 2 and 3 applied to the peel removal effluent proved to be less effective than the conditions employed in Treatment No. 1. The combination of a cationic polymer, Natron 86, and an anionic polymer, WT-3000, in Treatment No. 2 resulted in an 84% reduction in the suspended solids concentration from 209 to 33 mg/l. Treatment No. 3 which employed half the concentration of Natron 86 (25 mg/l) as compared to Treatment No. 1, resulted in a 62% reduction in the concentration of suspended solids from 221 to 85 mg/l.

Composite effluent

The combined unit effluents resulted in a composite effluent which contained 3.2 lb. suspended

Table 3. Laboratory study of the effect of polymer and ferric chloride concentrations on suspended solids removal from the composite pimiento effluent at pH 4.6^4

Natron 86, mg/l	pН	FeCl _g , mg/l	Suspended solids in settled supernatant, mg/l
10	4.6	0	40
10	4.6	40	27
30	4.6	0	44
30	4.6	40	17
50	4.6	0	53
50	4.6	40	36
0	4.6	40	42
30	6.0	40	57
30	8.0	40	78

^aThe concentration of suspended solids in the raw waste was 100 mg/l.

solids/ton and 60.2 lb. COD/ton of raw material processed. The total flow of 849 gal/min corresponded to 4,840 gal waste water per ton (3). Treatment of this relatively dilute effluent with different concentrations of flocculant showed that 30 mg/l Natron 86 and 40 mg/l FeCl₈ (Table 3) resulted in reduction of the suspended solids concentration by approximately 83%. Without polymer treatment, a reduction of approximately 58% was obtained by settling.

Results of chemical treatment of the composite effluent on a pilot-scale with Natron 86 (30 mg/l) and FeCl^s (40 mg/l) at the natural pH of raw composite effluent (4.6-5.1) are shown in Table 4. Flocculation of suspended materials resulted in a 74% reduction in the turbidity from 17 to 4.4 FTU, and an 86% reduction in the concentration of suspended solids from 100 to 14 mg/l. Removal of this material accounted for a reduction of approximately 19% in the COD of the decanted supernatant from 970 to 790 mg/l. Replicate values are shown under trial 2.

Treatment No. 2 with WT-2660 (2 mg/l) resulted in little decrease in the turbidity, but effected a 57% decrease in the concentration of suspended solids from 67 to 29 mg/l.

Effluent from core removal operation

The core removal operation produced an effluent which contained a high proportion of soluble organic components as shown by a COD load of 13.8 lb./ton and a much lower suspended solids load of 0.4 lb./ton (3). Laboratory-scale studies on this effluent (Tables 5 and 6) indicated that treatment with 60 mg/l of the cationic polymer Natron 86 plus either 80 mg/l alum or 10 mg/l ferric chloride effectively reduced the turbidity and suspended solids concentration.

The results of pilot-scale chemical treatments on the core removal effluent are shown in Table 7. Treatment No. 1 with Natron 86 (60 mg/l) and alum (80 mg/l) at the natural pH of the raw unit effluent (6.0) caused a 93% reduction in turbidity, from 17 to 1.2 FTU. In addition, the concentration of suspended solids was reduced by 82%, from 76 to 14 mg/l. Removal of this suspended material accounted for a reduction in the COD of only 8.4%. Replicate values for suspended solids and COD are shown under trial 2.

The conditions of Treatment No. 2, Natron 86 (60 mg/l) and FeCl₃ (10 mg/l) at the natural pH of the raw effluent, were almost as effective as those of Treatment No. 1. The turbidity was reduced from 18 to 2.2 FTU, the suspended solids from 36 to 16 mg/l, and the COD from 1510 to 1469 mg/l. Effluent from the citric acid dip, packing, and

closing area

The suspended and dissolved solids concentrations of this effluent were 34 and 5,057 mg/l, respectively. The pH was 3.8 due to the citric acid dip. None of the chemical agents nor the different pH conditions tested were as effective as simply allowing the effluent to coagulate and settle for 1 h without further addition of chemicals. This simple procedure reduced the suspended solids concentration by 91% from 34 to 3 mg/l.

CONCLUSIONS

Advantages of physical-chemical treatment

Chemical flocculation of concentrated pimiento effluents was effective in reducing the turbidity and suspended solids when the appropriate conditions were determined. These techniques should be widely applicable in the food processing industry for reducing the waste load and treatment charges due to concentrated unit effluents. Also, by-products may be developed from the flocculated solids.

The major anticipated benefits of flocculation and other physical-chemical treatment systems to the food processor are: (a) ease of start-up and shut-down; (b) flexibility to handle shock loads; (c) specific treatment for different products; (d) small land area; (e) design flexibility for desired treatment efficiency; and (f) possibility for recovery of by-products from chemical treatment stage.

Separate treatment of concentrated effluents

The determination of optimum conditions and the effectiveness of chemical flocculation is a function of the chemical composition, pH, and concentration of the different effluents. The concentrated effluent from the peel removal operation which contained over 200 mg/l suspended solids was treated to remove 95% of the suspended solids and turbidity by a combination of Natron 86 cationic polymer (50 mg/l) and alum (40 mg/l) at a pH of 4.0. The effluent from the core removal operation which contained 76 mg/l

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Treatment	Chemicals added	Chemicals added Samples			Turbidity, FTU	Suspended solids, mg/l		COD, mg/l	
no.	(final concn.)	рН	taken	Time (h)	Trial 1	Trial 1	Trial 2	Trial 1	Trial 2
1	Natron 86 (30 mg/l)	4.6	Raw	0	17	100	100	970	882
	FeCl ₃ (40 mg/l)		Decanted	0.5	6.5	31	32	*****	
			Decanted	1	3.9	16	14		
			Decanted	1.5	3.8	12	10		
			Decanted	2	4,4	14	14	790	686
2	WT-2660 (2 mg/l)	5.1	Raw	0	18	67		972	
			Decanted	0.5	18	37			
			Decanted	1.0	18	a		-	
			Decanted	1.5	17	_			
			Decanted	2.0	17.5	30		-	
			Decanted	2.75	17	29		744	

TABLE 4. PILOT-SCALE STUDIES OF THE EFFECTS OF CHEMICAL TREATMENTS ON THE TURBIDITY, SUSPENDED SOLIDS, AND COD OF COMPOSITE PIMIENTO EFFLUENTS

"Not determined

suspended solids was treated optimally with Natron 86 (60 mg/l) and alum (80 mg/l) at pH 6.0 which removed 82% of the suspended solids and 93% of the turbidity. Thus, larger amounts of polymer and alum were required to treat the effluent having the lower concentration of suspended solids. Chemical flocculation with polymers was completely ineffective in the case of the effluent from the citric acid dip, packing, and closing area which contained only 34 mg/l suspended solids.

The concentration of suspended solids in the composite effluent was 100 mg/l which was sufficiently concentrated to respond to chemical flocculation. Treatment with Natron 86 (30 mg/l) and FeCl_s (40 mg/l) at pH 4.6 reduced the suspended solids by 86% and the turbidity by 74%.

These results show that chemical flocculation could be used to treat the total composite waste from a pimiento canning operation, but a preferred approach is suggested by the results obtained on separate treatment of concentrated effluents from unit operations. For example, the peel removal operation has been shown to contribute 69% of the load of suspended solids from the total pimiento canning operation, but this effluent accounts for only 18% of the total flow of waste water (3). This suggests that a more efficient means of reducing the pollution load of this effluent would be to treat it while still a concentrated stream, rather than after it has been diluted with weaker wash waters. The experimental results obtained in this study are in agreement with this hypothesis and suggest that segregation and separate treatment of concentrated unit effluents should be considered as a viable option in the planning of pollution control procedures and facilities.

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TABLE 5.	LABORATORY	SCALE	TREATMI	ENT (OF	PIMIENTO	CORE
REMOVAL	EFFLUENT	WITH	VARYING	CON	CEN	TRATIONS	OF
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Natron 86, mg/l	Alum mg/l	Suspended solids, mg/l	Turbidity, FTU
50	0		15
50	10	-	3.4
50	40	22	2.8
50	80	18	2.3
50	120	12	2.2
0	0		14
40	80		3.7
50	80		3.3
60	80	20	3.1
70	80		3.1

TABLE 6. LABORARORY-SCALE TREATMENT OF PIMIENTO CORE REMOVAL EFFLUENT WITH VARYING CONCENTRATIONS OF POLYMER AND FERRIC CHLORIDE AT PH 6.0

Natron 86, mg/l	FeCl ₃ mg/l	Suspended solids, mg/l	Turbidity, FTU
50	0	26	4.7
50	4	28	4.2
50	10	20	3.7
50	20	26	4.1
50	30	24	5.6
50	40	45	17
0	0	-	14
40	10	-	4,2
50	10		4.0
60	10		3.7
70	10		4.2

Treatment	Chemicals added		Samples	-	Turbidity, FTU	Susp solids	ended , mg/l		COD, mg/l
no.	(final concn.)	\mathbf{pH}	taken	Time (h)	Trial 1	Trial 1	Trial 2	Trial 1	Trial 2
1	Natron 86 (60 mg/1)	6.0	Raw	0	· 17	76	44	1615	1298
	Alum (80 mg/l)		Decanted	0.5	1.2	14	16	1498	^a
			Decanted	1	1.2	14	16	1479	1232
2	Natron 86 (60 mg/1)	6.1	Raw	0	18	39		1510	
	FeCl ₃ (10 mg/l)		Decanted	0,5	2.2	16		1437	
			Decanted	1	2.2	16		1469	

TABLE 7. PILOT-SCALE STUDIES OF THE EFFECTS OF CHEMICAL TREATMENTS ON THE TURBIDITY, SUSPENDED SOLIDS, AND COD OF EFFLUENTS FROM A PIMIENTO CORE REMOVAL OPERATION

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