Evaluation of Dairy Waste Treatability by Gel-Chromatography

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Abstract

Effluents from dairy processing create some of the most difficult industrial pollution problems. To minimize water usage and waste load it is often worthwhile to renovate and recycle the waste water.

A serious obstacle in selecting the proper renovation technique is the lack of information concerning the treatability of the constituents of dairy waste by biological and/or physicochemical methods. Thus in the present paper a gel chromatographic technique was applied to evaluate the treatability of the dairy effluents according to their elution characteristics.

The elution characteristics of the water fraction evinces effective removal by biological treatment. Compounds which absorb in UV are selectively removed by coagulation and adsorption. In the case of concentrated effluents, it is proposed that biological treatment in combination with coagulation and adsorption is reguired for effective waste renovation. However, for dilute effluents coagulation and adsorption are sufficient to produce water with an acceptable quality for reuse in dairy processing.

Introduction

The increased awarenss of the need to halt the progressive deterioration of the environment has spawned the rebirth of interest in advanced treatment of industrial wastes as an important water conservation measure.

The dairy industry uses vast quantities of water in all processing operations. The effluents contain dilutions of whole milk, separated milk and whey; in addition to the sanitizers used for the cleaning operations. The waste contains colloidal matter as well as dissolved organics.

Numerous papers concerning the treatment of dairy waste have been published recently. Bebin and Renaudin[1] suggested that dairy waste can be purified by means of highly loaded activated sludge process with pure oxygen supply. Sullins et al.[2] proposed a multi-biological system for treatment of dairy wastes. Tanaka[3] reported on a 2-stage aerated lagoon which achieved substantial reduction in BOD_5 and NH_3-N. The results of Tuwiner[4] indicated that electrolysis can be used to reduce the COD of cheese whey wastewater. Anderson[5] discussed coagulation with $Al_2(SO_4)_3$, $FeCl_3$ and $Ca(OH)_2$. Coagulation of effluents having

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BOD_5 of 800–970 mg/l was not effective except in combination with biological treatment.

An approach to the evalution of soluble organics removal from wastewater based on molecular size distribution was recently suggested by Tambo[6]. He proposed the use of TOC and UV-absorbance at 260 and 220 nm in connection with Gel Chromatography [GC] for the evalution of the treatability of domestic wastes.

Gel chromatography has long been recognized as a valuable technique for fractionation of materials that differ from each other in molecular size. Usually, the first substances to pass through the GC column are those having a molecular size which prevent them from entering into the gel micropores. Smaller molecules penetrate the gel particles to a varying extent dependig upon their size and shape. They are eluted in the sequence of their decreasing molecular size. In some instances, substances with a strong affinity to the gel are not eluted easily with water. In interpreting the GC data both molecular size and affinity to the gel must be considered.

This investigation was stimulated by the interest in applying the GC techniques for assessing the treatability of dairy wastes.

Materials and Methods

DAIRY EFFLUENTS: Samples were collected from Snow Brand Dairy Plant [SBDP] in Sapporo, Japan; during a period from Nov. 1976 to March 1977. The plant generates 2,000 cubic meters of wastewater during a daily operation period of 10 hours. Wastewater pretreatment at SBDP is limited to simple aeration which reduces the COD and BOD_5 by 40–50%. The samples selected for the study were; butter processing waste, yogurt processing waste, clean-up waste, and the final effluent (Dairy Waste).

PREPARATION OF SAMPLES FOR THE GC STUDY: All samples were filtered through a 0.45 μm membrane filter. Samples having less than 200 mg/l dissolved organic carbon [DOC], were concentrated by rotary evaporators at 30°C. The samples were refiltered to remove any precipitates formed during the concentration process.

PROCEDURE OF GEL CHROMATOGRAPHY: Sephadex G-15 (Pharmacia, Uppasala, Sweden) was used as molecular size exclusion material in the study. The gel was prepared by equilibrating 145 g of the dry Sephadex G-15 in water for 24 hrs., then applied to 2.5×90 cm column. The samples were placed at the top of the column in 10 m*l* portions. The retained substances were eluted by a two-stage process. In the first stage, distilled water was passed through the column at a constant rate of 1.2 m*l*/min. and the effluent was collected in 10 m*l* fractions by an automatic fraction collector. In the second stage, 0.1N-NH_4OH was added for the elution of the constituents which possess a high affinity to the gel. A preliminary investigation indicated that elution with 400 m*l* distilled water and 500 m*l* of 0.1N-NH_4OH were necessary to recover all retentates.

The DOC of the collected fractions was measured by a TOC analyzer (Beckman-

Toshiba Model 102) according to the procedure of the Standard Methods[7]. The UV absorbance were measured at 260 and 220 nm using 1 cm cell (E_{260} and E_{220}). In a previous study by Dobbs et al.[7], they indicated that inorganics are generally absorbed at wave lengths below 235 nm, while organics are absorbed in 254 nm.

THE COAGULATION STUDY : Treatment of the final efflent was performed by coagulation using 100 to 600 mg/l $Al_2(SO_4)\cdot 18HO_2$ at pH 3 to 8. All experiments were carried out by using a standard jar test in 1 *l*-beakers. The pH of the samples was adjusted by 0.5 N HCl or 0.5 N NaOH. Alum was then added and the suspensions were stirred for 5 min at 150 rpm and 15 min at 40 rpm. After a sedimentation period of 30 min the supernatant was homogenized and the following parameters were measured : Residual turbidity by a photoelectric turbidemeter (Nihon Seimitsu Kogaku Co.), colloid charge according to the method developed by Kawamura and Tanaka[8], pH, DOC, E_{260} and E_{220}.

THE ADSORPTION STUDY : Samples of the final effluent were pretreated by coagulation before their use in the adsorption study. Adsorption was performed at 12°C in a non-flow system with constant agitation at 120 rpm. A 100-150 mesh activated carbon (Grade S. S., Taiyo Koken Co.) was added in doses from 100-1,000 mg/l to 1 *l* samples. After a contact period of 2 hours, the filtered samples were tested for their DOC, E_{260} and E_{220}. Another series of samples were treated for various contact periods using 1000 mg/l activated carbon. The GC patterns after adsorption for 1, 3, 8 and 24 hours were investigated to evaluate the effect of adsorption on the removal of soluble organics of the dairy waste.

Discussion of Results

TYPICAL CHROMATOGRAMS OF DAIRY EFFLUENTS : Chromatograms of the dairy effluents are shown in Figures 1, 2, 3 and 4. The elution patterns indicate the presence of two groups, namely, the water eluted group [Group I] and the NH_4OH eluted group [Group II].

Numerical evalution of the GC data was based on the determination of the following parameters :

1) the peak ratio of DOC to E_{260} [R].
2) the DOC content in Group II to total DOC [r].
3) the volume required for elution of pollutants in maximum concentration [V_e].
4) the exclusion parameters K_d and K_{av}.

The parameter K_d is defined as the fraction of the inner volume of the gel available for diffusion, whereas K_{av} is defined by Laurent and Killander[9] as the fraction of the total gel available for diffusion.

$$K_d=\frac{V_e-V_0}{V_i} \qquad \text{and} \quad K_{av}=\frac{V_e-V_0}{V_t-V_0}$$

where, V_0 = void volume between gel grains (1.1 m*l*/g for Sephadex G-15).
V_i = inner volume of the gel bed (3.0 m*l*/g for Sephadex G-15).
V_t = total volum of the gel bed.
V_e = elution volume.

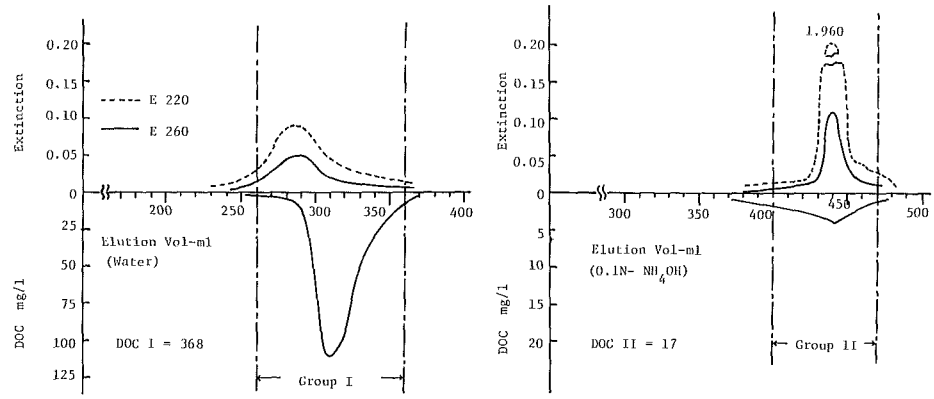

Figure 1 GC pattern of the dairy wast
[conc ×5, DOC=370 mg/l, GC recovery=105%]

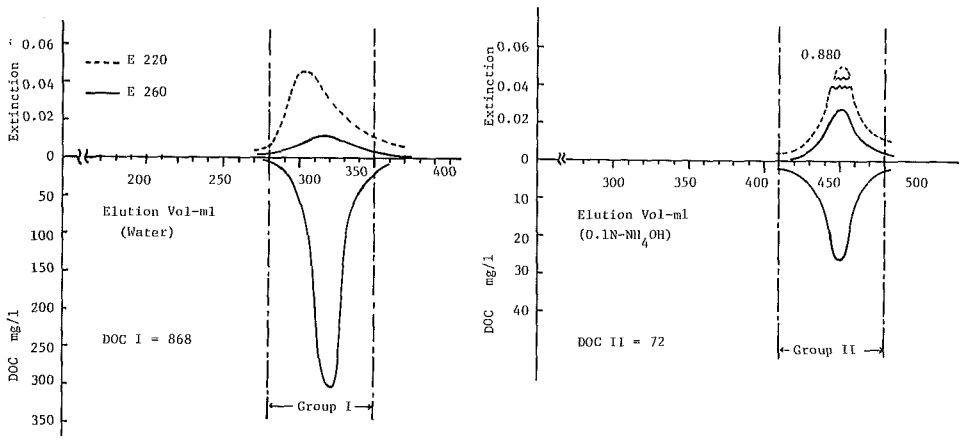

Figure 2 GC pattern of yogurt processing waste
[Conc ×5, DOC=900mg/l, GC recovery=104%]

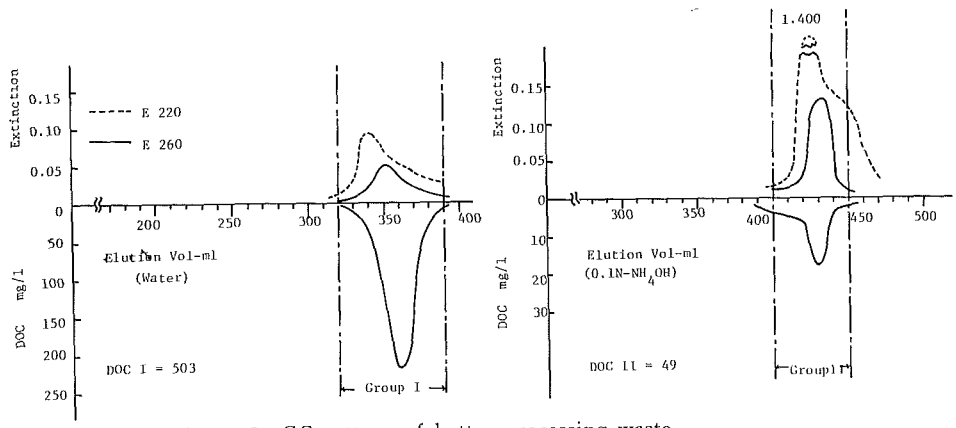

Figure 3 GC pattern of butter processing waste
[Conc ×1, DOC=506 mg/l, GC recovery=109%]

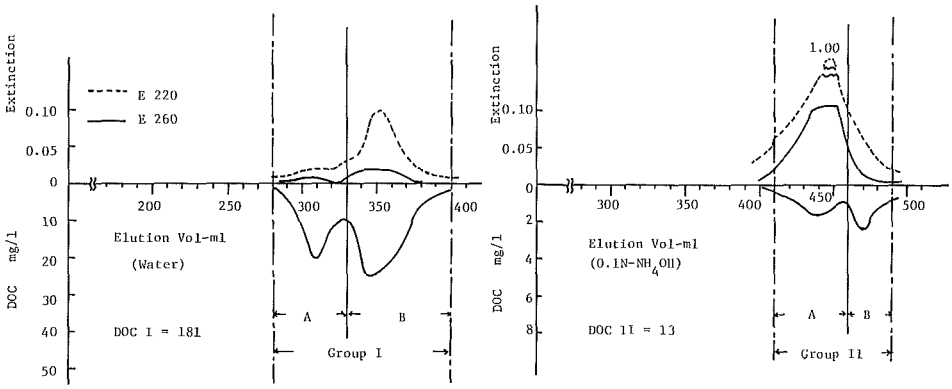

Figure 4 GC pattern of clean-up waste
[Conc ×1, DOC=204 mg/l, GC recovery=95%]

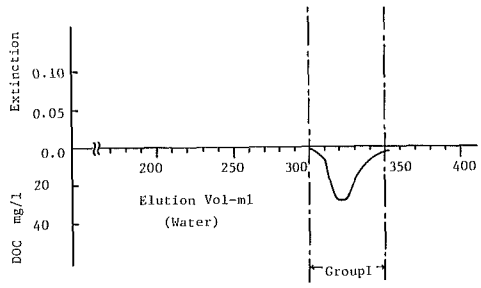

Figure 5 GC pattern of lactic ACID

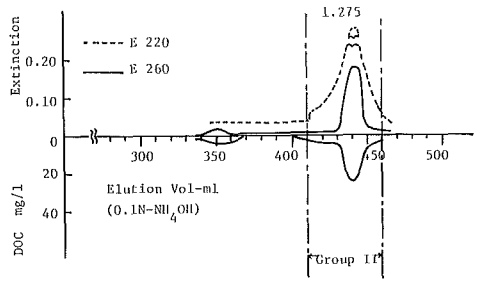

Figure 6 GC pattern of SBDP sanitizer

Table 1 Elution parameters of the Dairy effluents

Source	Parameter	Group I		Group II
Dairy waste	R	2200	4.4%	36
	r			
	Ve ml	310[1]		440
	K_d	0.354		0.644
	K_{av}	0.533		0.993
Butter Waste	R	4630	8.9%	138
	r			
	Ve ml	360[1]		430
	K_d	0.471		0.662
	K_{av}	0.711		0.958
Yogurt waste	R	EH	7.6%	860
	r			
	Ve ml	320		450
	K_d	0.378		0.684
	K_{av}	0.561		1.028
Clean-up waste	R	2200[2]/2000[3]	6.7%	19[4]/300[5]
	r			
	Ve ml	310/340		430/470
	K_d	0.355/0.408		0.662/0.714
	K_{av}	0.533/0.638		0.958/1.099

1) DOC peak 2) Group I-A 3) Group I-B
4) Group II-A 5) Group II-B EH=Extremly High

The numerical values of R, r, V_e, K_d and K_{av} obtained for the dairy effluents are shown in Table (1).

Two postulated approaches are developed to assess the treatability of the dairy effluents:

1) Both K_d and K_{av} possess a negative relationship to the molecular radius r as stated by Determann[10].

$$K_d^{1/3} = \text{const.} - \text{const.} \times r \qquad \text{and} \quad (-K_{av})^{1/2} = \text{const.} + \text{const} \times r$$

Therefore, the greater the K_d and K_{av} values, the smaller the molecular size of the pollutants and the easier the assimilation of these pollutants by biological treatment.

2) Most complex organics have an absorbance in wave lengths near 254 nm. However, sugars, simple aliphatic and amino acids together with alcohols are not absorb in UV. These simple organics are readily assimilated through the bacterial cell walls during biological treatment processes. Therefore, as the R values of the wastewater increase, soluble organics become amenable to biological treatment due to the predominancy of simple compounds. According to the same hypothesis, low R-values indicate less amenability to biological treatment. For fractions with low R-values, it is postulated, that their removal would be achieved effectively by physico-chemical treatment processes.

Unfortunately, the elution parameters can not be used as absolute measures of treatability since their values depend on the type of eluant, gel material, affinity of the constituents to the gel and instrumental accuracy.

Despite these restrictive factors, elution parameters, and in particular the R value can offer valuable information concerning the treatability of dairy effluents.

As shown in Table 1, the constituents of Group I for all wastes are expected to be easily removed by biological treatment, due to their very high R values ($R \geq 2000$). It is interesting to note that all parameters are consistently higher for butter waste in comparison with other effluents. The R value for the yogurt waste should be excluded from this comparison due to the inaccuracy involved in its estimation at DOC < 300 mg/l and $E_{200} < 0.015$.

Constituents of Group II for dairy and butter wastes possess low R, K_d and K_{av} values, in comparison with the yogurt waste. They are expected to respond poorly to biological treatment. In this case, complete treatment can be achieved by biological treatment for the removal of soluble organics in Group I and physico-chemical treatment for the removal of organic constituents in Group II.

The gel chromatograms of the dairy effluents shown in Figures 1, 2, 3 and 4 reveal some interesting characteristics:

1) Compared to the complex GC patterns of sewage[4] and leachate[11], dairy effluents have simple elution patterns, which indicate a fair homogeneity of the constituents, except for that of the clean-up waste.

2) The percentages of the compounds with high affinity to the gel are relatively low.

3) All chromatograms of Group II possess unusually high E_{220} peaks. This high peak was also identified for the sanitizer used at SBDP as shown in Figure

6. Since cleaning operations are continuously carried out during processing, it may be expected to find the sanitizing materials to be a common constituent of all processing effluents.

Typical chromatogram of the yogurt waste is illustrated in Figure 2. Both Group I and II of this waste showed minute adsorption in E_{260}, due to the predominancy of the non UV-absorbing compounds in this waste. Group I of the yogurt waste resemble the GC pattern of lactic acide shown in Figure 5, while Group II is similar in its pattern to that of the sanitizer used at SBDP. The high elution parameters for both groups indicate the amenability of the yogurte waste to biological treatment processes.

The chromatogram shown in Figure 4, illustrates an example of the GC pattern of the clean-up waste. Two different regions were identified in the water and NH_4OH elution groups. Group I-A of Figure 4 is similar to Group I of the yogurt waste, while Group I-B has a relatively similar pattern to that of Group I of the butter waste. On the other hand, the pattern of Group II-A resembles the GC pattern of the sanitizer. Group II-B of the clean-up waste has a large portion of non-UV absorbing soluble organics. The observed heterogeneity of the clean-up pattern is typical of the cleaning wastes due to the great variations in the type and concentration of their constituents.

DAIRY WASTE TREATMENT BY COAGULATION: The effect of alum dosage and pH on residual turbidity is shown in Figure 7. The formation of soluble species of alum $[Al(OH)_2^+]$ at pH 3 to 4 have an insignificant destablizing effect on the colloidal and suspended particles of the dairy waste. The noticeable

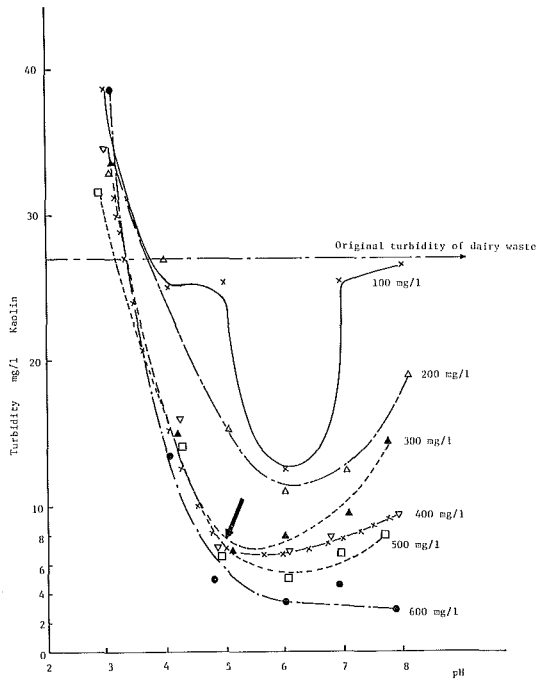

Figure 7 Residual turbidity of dairy waste after coagulation

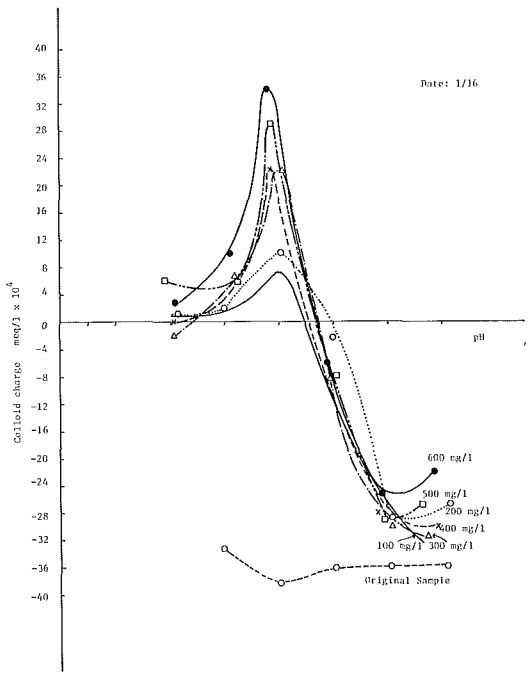

Figure 8 Effect of coagulation on colloid charge of dairy waste

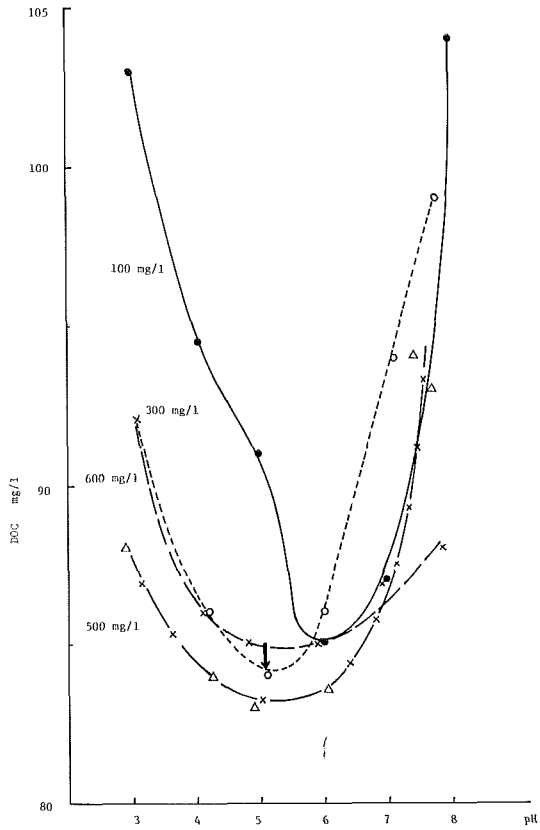

Figure 9 Residual DOC after coagulation
[DOC of the dairy waste=108.5 mg/l]

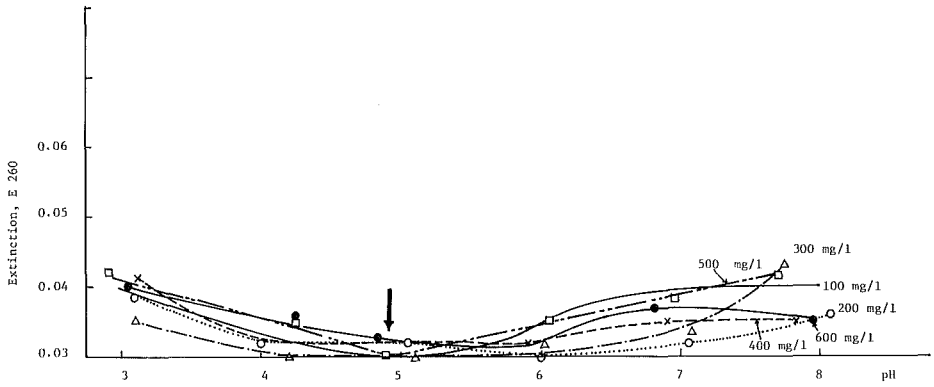

Figure 10 Effect of coagulation on UV absorbance
[E_{260} of the dairy waste=0.110]

increase in the turbidity at pH 3 was contributed by the partial precipitation of dissolved organics at this low pH. The polymeric species of $Al_8(OH)_{20}^{+4}$ formed at pH 4 to 6[11], resulted in neutralization of the negatively charged colloids and their coagulation. At pH 7 to 8 neutral complexes of $Al(OH)_3$ were predominant[12]. These complexes are generally ineffective for charge neutralization.

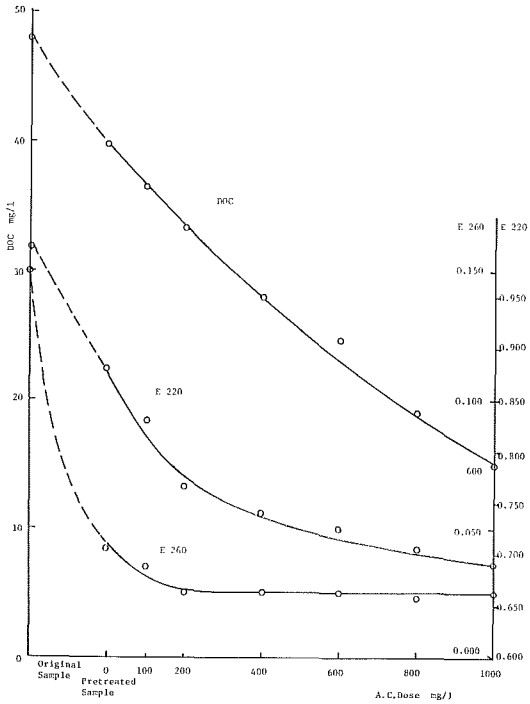

Figure 11 Removal of dissolved organics by coagulation and adsorption [contact time=2hr]

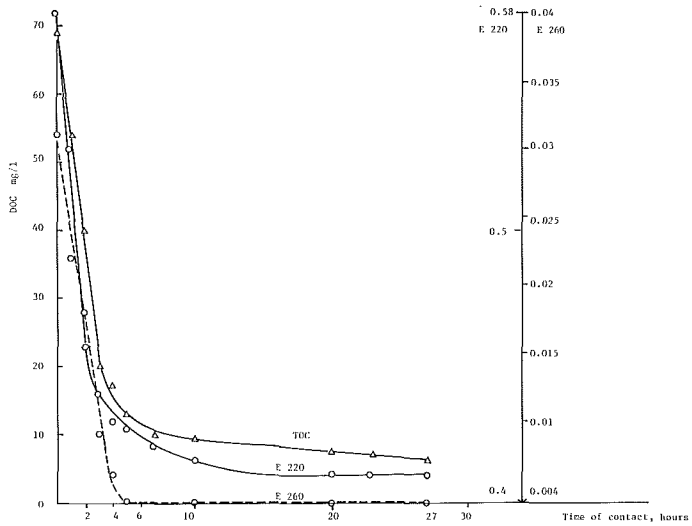

Figure 12 Effect of adsorption time of removal of dissolved organics in dairy waste [Dairy waste DOC=84 mg/l, E 260=0.133]

The change of colloid charge at different pH and alum dosage is demonstrated in Figure 8. Initial charge of the dairy waste was about -35 meq/$1 \cdot 10^{-4}$. Addition of alum reversed the charge at pH 3 to 5. The highest increase in the charge was associated with the highest alum dosage. The zone of positive charge was expanded with the increasing alum dosage due to the existance of excess

aluminum complex ions. Significant drop in the positive charge was observed at pH higher than 5. The charge was changed to negative at pH 5.5 to 6.

Figure 9 shows the effect of coagulation at different pH and alum dosages on the residual DOC. In general, coagulation resulted in some but not significant reduction in the DOC of dairy waste. The increase of alum dosage from 100 to 600 mg/l did not bring a noticeable decrease in the DOC. An interesting effect of the alum dosage on the UV-absorbance is shown in Figure 10. Within the range of the experimented pH and alum dosage, coagulation produced an excellent removal of the UV absorbing compounds. This led to the conclusion that soluble organics removed by coagulations were generally of high molecular weight compounds which absorb in E_{260}. The finding by Brodsky and Procházka[19], agrees with the above conclusion. They reported that coagulation is a highly selective process for removal of large molecular weight organics from river waters. The results of Figures 7, 8, 9 and 10 concurrently suggest optimum coagulation of dairy waste with 300 mg/l alum at pH 5.

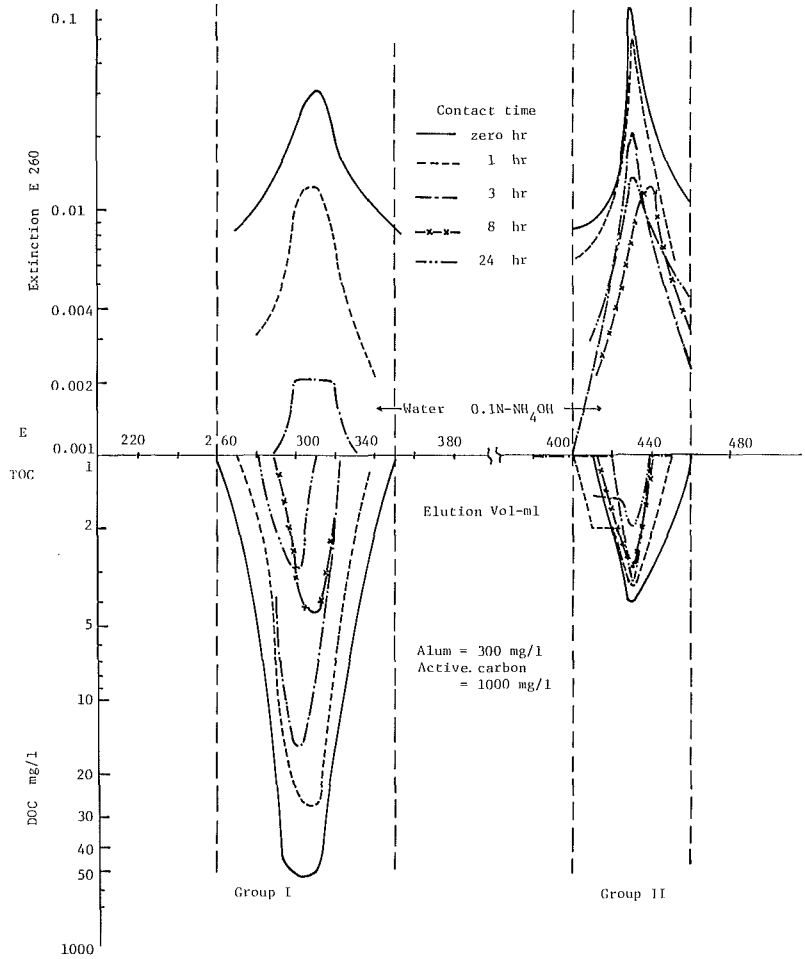

Figure 13 Schematic GPC patterns of dairy wastes after adsorption for different contact periods [Conc.×5]

CARBON ADSORPTION OF DAIRY WASTE : The surpernatant formed by coagulation with 300 mg/l alum at pH 5 was subjected to adsorption in a non-flow system. As seen in Figure 11, the residual DOC continuously decreassed by increasing the carbon dosage from 100 to 1000 mg/l. The UV-absorbing compounds remained after coagulation were removed by adsorption using 100 mg/l activated carbon. Higher carbon dosage removed the non UV-absorbing costituents. The study by Tambo et al.[14], supports this finding. They reported that trisaccharides and disaccharides are preferentially removed by adsorption with a small carbon dosage. Smaller molecular weight compounds which do not absorb in UV are removed by a much larger carbon dosage.

The residual DOC and UV-absorbance as functions of adsorption contact time are shown in Figure 12. Here again, a major portion of the UV-absorbing organics was removed effectively in a short time. The results suggest that an alternative to the removal of non UV-absorbing organics by biological treatment would be adsorption using a high carbon dosage.

Schematic GC patterns of the dairy waste after adsorption for different contact periods are shown in Figure 13. All UV-absorbing compounds were removed by adsorption for 3 hrs using 1000 mg/l activated carbon. The non UV-absorbing compounds in Group I as well as the constituents of Group II were successively removed by increasing the contact time to 24 hours. As seen in Figure 14, most of the DOC removal by adsorption for periods longer than 8 hours was mostly contributed by the constituents of Group II. Almost complete removal of DOC was attained by prolonged adsorption up to 72 hrs using 3,000 mg/l activated cabon. In case of water renovation and recycling in dairy processing, prolonged adsorption using a large dosage of carbon is not necessary since traces of DOC are acceptable in process water as well as drinking water supplies.

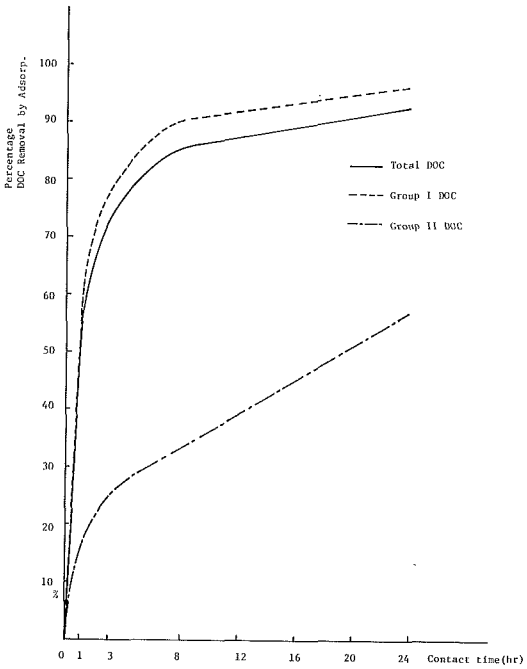

Figure 14 Removal of DOC from Group I and II by adsorption

Conclusions

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

1) Gel chromatography offers a reliable technique for evaluating the treatability of soluble organics in dairy wastes. Most of the organic constituents can be easily eluted by water. The chromatographic pattern of these constituents evinces their amenability to biological treatment. A minor portion of the organic

constituents possess a high affinity to the gel. This portion can be eluted by NH_4OH. The chromatographic pattern of this portion in dairy and butter wastes reveal a predicted low response for removal by biological processes. A combination of biological treatment and activated carbon adsorption is needed for effective treatment in this case. This would be particularly essential in the case of renovating wastewater for the purpose of recycling.

2) Coagulation preteatment of dairy wastes 300 mg/l alum at pH 5 is suggested to enhance the efficiency of the final treatment by adsoption. Coagulation is selective towards the removal of soluble organics with high molecular weights.

3) Coagulation and adsorption with 100 mg/l activated carbon is sufficient for the removal of organics which absorb in UV. The non UV absorbing costituents in the water elution fraction as well as the constituents of the NH_4OH elution fraction require a carbon dosage of 1,000 mg/l and extended contact periods for their removal.

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References

1) Bebin, J. and Renaudin, K.: Dairy wastes purification by means of highly loaded activated sludge process with pure oxygen, Prog. Wat. Tech., Vol. 8, 1976, No. 2/3, pp. 301–311.
2) Sullins, J. K., Arldege, W. L. and Ricci, E. V.: Treatment of raw milk waste by multistage biological system, Jour. Milk Food Tech., Vol. 38, 1975, pp. 232–236.
3) Tanaka, T. Use of aerated lagoons for dairy effluent treatment, Ann. Bull. Intl. Dairy Fed. (G, B), 1974, No. 77, 93.
4) Tuwiner, S. B.: Improvement of treatment of food processing wastes, EPA Technol. Ser. Rept., EPA, 1974, 660/2-24-035.
5) Anderson, N.: Treatment of dairy effluents by chemical precipition, Ann. Bull. Intl. Dairy Fed. (G. B), 1974, No. 77, 131.
6) Tambo, N.: Application of gel chromatography to the evaluation of removal efficiency of organic impurities in wastewater treatment processes, Japan Research Group of Water Pollution International Seminar, Tokyo, Oct., 1976.
7) Standard methods for the examination of water and wastewater, APHA-AWWA-WPCF, N. Y. 14th cd., 512, 1975.
8) Kawamura, S. and Tanaka, Y.: Applying colloid titration techniques to coagulant dosage control, J. Water & Sewage Works, Vol. 113, 1966, No. 9, 348.
9) Laurent, T. C. and Killander, J.: A theory of gel filtration and its experimental verification, J. Chromatog., Vol. 14, 1964, pp. 317–330.
10) Determann, H.: Gel chromatography, From the German by Gross, E. and Harkin, H., 2ed cd., Berlin, Springer, 78, 1969.
11) Matijevic, G. E. and Kerker, M.: Reversal of charge of lypohobic colloids by hydrolyzed metal ions in aluminum nitrate, Jour. of Colloid Sci., Vol. 19, 1964, pp. 333–346.

12) Tambo, N. and Ito, H.: Electrophretic studies of natural colloid coagulation with alum, Jour. of Japan Water Works Assoc., Vol. 508, 1977, pp. 38–50.
13) Brodsky, A. and Procházka, J.: Water treatment analysis by gel chromatography, Jour. of Amer. Water Works Assoc. Vol. 67, 1975, No. 1, pp. 23–26.
14) Tambo, N., Kamei, T., Nishimura, T. and Fukushi, K.: Adsorption chracteristics of organics in sewage, Proceedings of the 12th Sanitary Eng. Seminar, Japan Soc. of Civil Eng., 1–6, 1976.