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STARTING-UP OF A FULL-SCALE TWO-PHASE CONTACT PROCESS TREATING CITRIC ACID WASTEWATER

I. E. Gönenç* and M. Kerestecioğlu**

**ITU Inşaat Fak., Çevre Müh. Böl., 80626 Maslak-Istanbul, Turkey*
***Sistem Planlama Ltd. Şti., Barbaros Bulvari, Bahar Sok. 4, Kişlaönü-Istanbul, Turkey*

ABSTRACT

The results of three years' starting-up period of the phased-recycled flocs system (contact process) treating citric acid factory wastewater are presented in the light of the process characterization approach. After the description of the system and starting-up studies, the reasons of and remedies for the problems of starting-up are discussed with emphasis laid on the biochemistry and microbiology, design and operation parameters, and environmental factors of the anaerobic process.

KEYWORDS

Starting-up of anaerobic system; phased anaerobic recycled flocs system; anaerobic process kinetic.

INTRODUCTION

FÜRSAN is one of the important agro-industries of Turkey. Citric acid is produced mainly by fermentation of sugar-beet molasses at the industry. Lime treatment, sedimentation, filtration, acidification, rotary filtration, active carbon adsorption, ion-exchange, evaporation, crystallization, centrifugation and drying are other processes used for the production of solid citric acid.

The most important wastewater derives from the calcium citrate filtration with a flow rate of up to 200 m^3/d. It is hot (45-60 ^oC), high strength (COD (avg) = 35,000 mg/l, BOD (avg) = 25000 mg/l) acidic (pH= 5.5 - 7.0) wastewater and contains considerable amount of sulphate (SO_4=1300 mg/l), calcium (Ca^{+2} =1000 mg/l) and nitrogen (TKN(avg)=1800 mg/l). Other wastewaters are fermentation chambers wash water, anion and cation exchangers regeneration waters, evaporator condensate and sewage. The flow rate of these wastewaters is 150 m^3/d and the average BOD concentration is 1000 mg/l.

After a long discussion, it was decided that the filtration wastewaters alone should be anaerobically treated and then the effluent and all other wastewaters should be mixed and treated aerobically. Due to this decision the competition was made and the phased-recycled flocs system (contact process) was selected as the most attractive system by the industry. This system consists of a reactor followed by a sedimentation tank. In the reactor the microorganisms have to form flocs and these flocs are kept suspended by mechanical and gas stirring. In the sedimentation tank, separation of flocs and wastewater is performed and suspended settled flocs are recycled to the reactor. Excess sludge can be drawn from the recycle pipe, accordingly. When they are compared, the recycled floc reactor and the sludge blanket reactor resemble each other to a high degree, the main difference being an external sludge separation device instead of an internal one (Pol and Lettinga, 1986). On the other hand, phasing can be used for all reactor types, and might result in reduced total reactor volume and better operational control since anaerobic treatment is mainly mediated by two distinct microbial groups, and since these groups are significantly different with respect to physiology, growth and metabolic characteristics, and sensitivity to environmental stresses (Ghosh and Klass, 1978; Henze and Harremoës, 1983).

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The phased-recycled flocs system was planned and constructed by the Turkish firm SİSTEM YAPI under supervision of a Belgium firm, BIOTIM. In this paper, results of three years starting-up period (or it may be called operational period) of the system are presented and discussed in the light of the process characterization approach.

DESCRIPTION OF THE SYSTEM AND STARTING-UP STUDIES

Description of the System

For phase separation, the kinetic control technique was used to design the system. By this technique, hydrolysis/acidification and methanogenic phases can be kinetically controlled by adjustment of residence time and biomass recycling in each of the reactors of a two-phase system. Accordingly, the first reactor is called conditioning reactor (CR) and the second reactor is called methane reactor (MUR)

The design parameters of the system are summarized in Table 1. As it can be seen, the reactors were designed in two-steps considering the future expansion of the industry. On the other hand, the cylindrical steel reactors were constructed for the final volume need, but they have been operated using the present volume need.

TABLE 1 Design Data of the System

REACTOR	Flow rate (m^3/d)	Influent Load (tCOD/d)	Reactor Volume (m^3)	Height/ Diameter (m)	Biogas (65%CH4) (m^3/h)	Sludge Recycle (m^3/h)	Excess sludge (m^3/h)
1.reactor (CR) present	173	6.0	300	5/8.80	4	2.0	0.5
final	420	14.7	730	12/8.80	10	4.0	1.5
2.reactor (MUR) present	160	5.0	913	5/15.25	70	2.0	0.4
Final	394	12.4	2192	12/15.25	170*	4.0	1.5

* gas production is approximately 4000 m^3/d and equivalent to 2.5 tons of fuel/d.

Starting-up Studies:

In the recycled flocs reactors, the biomass is found in suspended flocs. For optimal operation of the reactor, suspended solids concentration should be as high as possible. Thus, the separation of wastewater and flocs is the critical part of the system and the development of stable grown and well settling flocs is a prerequisite for stable operation. The period preceding this steady-state situation is called the starting-up. Starting-up of an anaerobic reactor is more time-consuming and subject to disturbances than is the start-up of this reactor (Salkinoja-Salonen et al., 1983; Dolfing, 1986; Henze and Harremoës, 1983).

Within this context, the term 'starting up' has been used to describe the studies during the three-year operation period instead of 'start-up'. These studies may be separated in three periods as below:

- first starting-up period in which start-up procedure was applied to reach the designed value of the volumetric load and starting-up was considered as an experimental procedure rather than scientific. Since inoculation could be done with manure and septic sludge-the right microbial culture was not at hand-it took up to a year before the system was in operation, although not at the guaranteed values. At the end of the period, the sedimentation tank of the CR was taken off due to the results of rule-of-thumb experiments. During the period, wash-out of the organisms occurred many times due to organic overloading resulting from the low and uncontrolled suspended growth of biomass within two reactors.

- second starting-up period in which the studies were devoted to process characterization both from a fundamental and practical standpoint. In this respect, quality of waste, compounds which cause inhibition, nutrients and trace elements need all the necessary environmental conditions to improve efficiency, and biochemistry/microbiology were carefully analysed. At the beginning of this period, the applied operation parameters during first starting-up period were reviewed in the light of the process characterization approach and instead of volumetric loading, organic loading rate parameters were initiated to control the system operation. Figure 1 shows the results of this period.

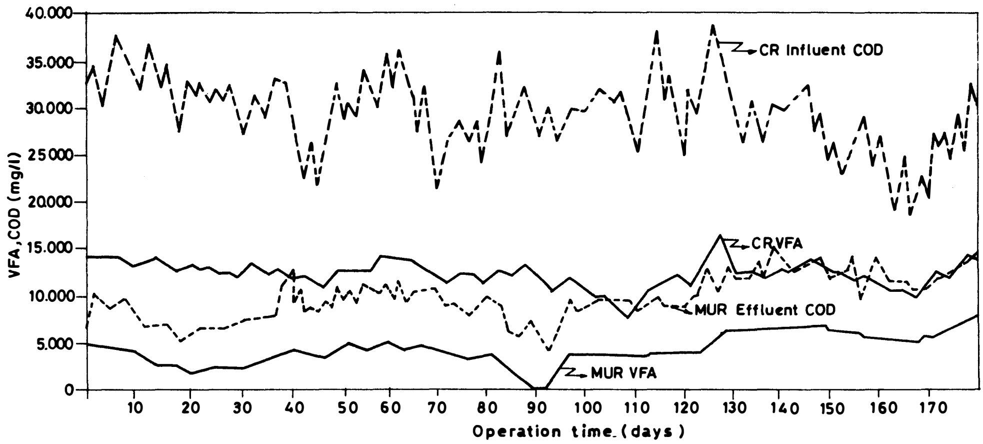

Fig. 1 Influent and effluent COD and VFA concentration during second starting-up period.

- third starting-up period in which stable grown and highly concentrated suspended flocs were obtained by constructing a new separator which has improved settling efficiency and prevented wash out of the flocs by effective recycle. Eventually, microbial steady-state or stable operational conditions were reached and guaranteed effluent COD concentrations were obtained (Figure 2).

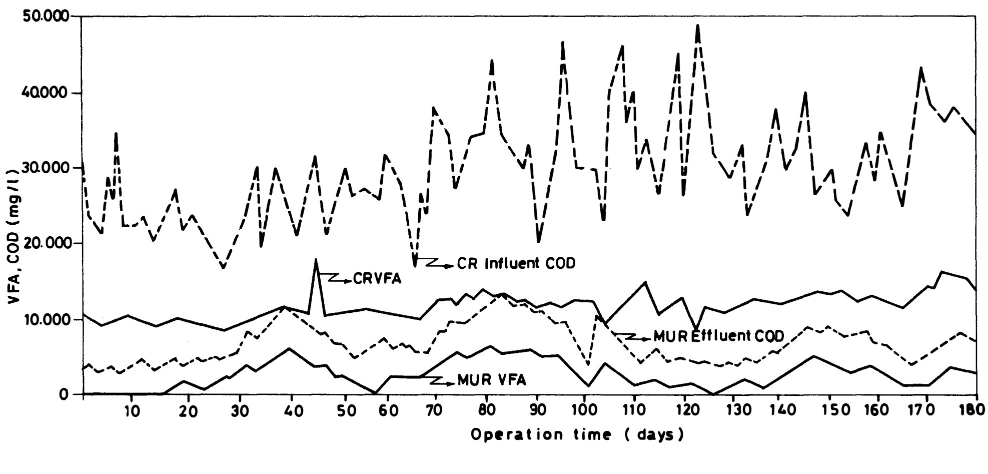

Figure 2: Influent and effluent COD and VFA concentration during third starting-up period.

RESULTS and DISCUSSION

This section deals with the reasons of and remedies for the starting-up problems. The major idea has been to discuss the results within the framework of the process characterization approach.

Remedies Obtained by the Review of Biochemistry and Microbiology

During the first and second starting-up period, it was observed that the concentrations of propionic and butyric acid, and hydrogen in the CR increased and subsequent accumulation of these acids in the MUR inhibited the acetic acid formation and then, methane production. Figure 3 shows the VFA concentration against COD concentration of the CR and MUR effluent, and diversion of metabolism towards propionic and butyric acid from the first to the last period may easily seen,

Many researchers have indicated that mainly four groups of bacteria, namely acid-forming, acetogenic, acetoclastic and hydrogenophilic, are involved in the anaerobic metabolism (Henze and Harremoes, 1983; Gujer and Zehnder, 1983; Mosey, 1983; Novaes, 1986). The acid-forming bacteria formed in the CR are fast-growing bacteria and responsible for the production of acetic, propionic, butyric acids and ethanol from the hydrolysis and fermentation of complex organic compounds. Mosey (1983) has suggested that the pathway chosen and their final products is directly related to the hydrogen concentration. At low partial pressure of H_2 (less than 10^{-6} atm) the formation of H_2, CO_2 and acetate is favored since this reaction provides the bacteria with the biggest energy yield for growth . At higher pressures, fermentation of pyruvic acid to ethanol, propionic and butyric acid occurs (Novaes, 1986; Harper and Pohland, 1988) and these reactions are the bacteria's response to accumulations of hydrogen during varying load conditions (Mosey, 1983). This fits well into the general picture, and can also explain the increased propionic/butyric acid concentrations in the CR operating at very short solids retention time and varying load conditions.

Once formed, propionic and butyric acids must be degraded to acetic acid by acetogenic bacteria and this process is also influenced by hydrogen. Since less than 10^{-4} atm H_2 is required for the oxidation and the growth of the acetogenic bacteria (minimum doubling times of 1.5 to 4.0 days (Mosey, 1983), their performance in the CR has been easily stopped due to high H_2 pressure and they could only grow in the MUR, accordingly. On the other hand, the situation has pushed the reaction into propionic acid overload in the CR with no COD reduction. During the first starting-up period, the residence time of the MUR was limited for acetogenic bacteria and thus, butyric/propionic acid could not be completely degraded to acetic acid. For the second starting-up period, the residence time was increased to allow acetogenic bacteria growth.

Hydrogenophilic bacteria produce methane from hydrogen and carbon dioxide, and obtain energy for growth from this reaction. They grow quite quickly with minimum doubling times around six hours and control the redox potential of the process (Mosey, 1983) . As a result, it can be concluded that these bacteria have grown in both CR and MUR, and they have caused the certain methane production in the CR. However, a stable enrichment of acetogenic bacteria as a result of continuous production of butyric and propionic acid in the CR could be maintained together with the associated hydrogenophilic methanogens in the MUR during the second starting-up period. Accordingly, methane production of the MUR increased and diversion of metabolism towards acetic acid could be achieved as can be seen in Figure 3. On the other hand, the highly enriched bacteria concentration of the third starting-up period strongly promoted this situation.

Acetoclastic bacteria produce methane from acetic acid and grow slowly. They are strictly unable to metabolise propionic/butyric acids as it was observed during the first starting-up period. These bacteria are not greatly affected by the hydrogen concentration and they can even control the pH value of the system by removal of acetic acid and production of carbon dioxide . It may be concluded that they have been present in the MUR during the whole starting-up period, but mostly during the third period.

Remedies Obtained by the Review of Design and Operation Parameters

Table 2 shows the design values by which the system was constructed and operated during the first starting-up period, and the predicted values of performance parameters by which the relevant features of the anaerobic process may be taken into account. The frequently used literature ranges are also given in Table 2. By this means it has been attempted to identify the reasons of operational failures. The result is that these values are more or less within the literature ranges. But the problem is that they could not properly be applied during most of the time of operation. This is very understandable because of the difficulty in obtaining sufficient suspended flocs in the CR and MUR and because of the volumetric loading used without considering the concept of solid retention time, as discussed below.

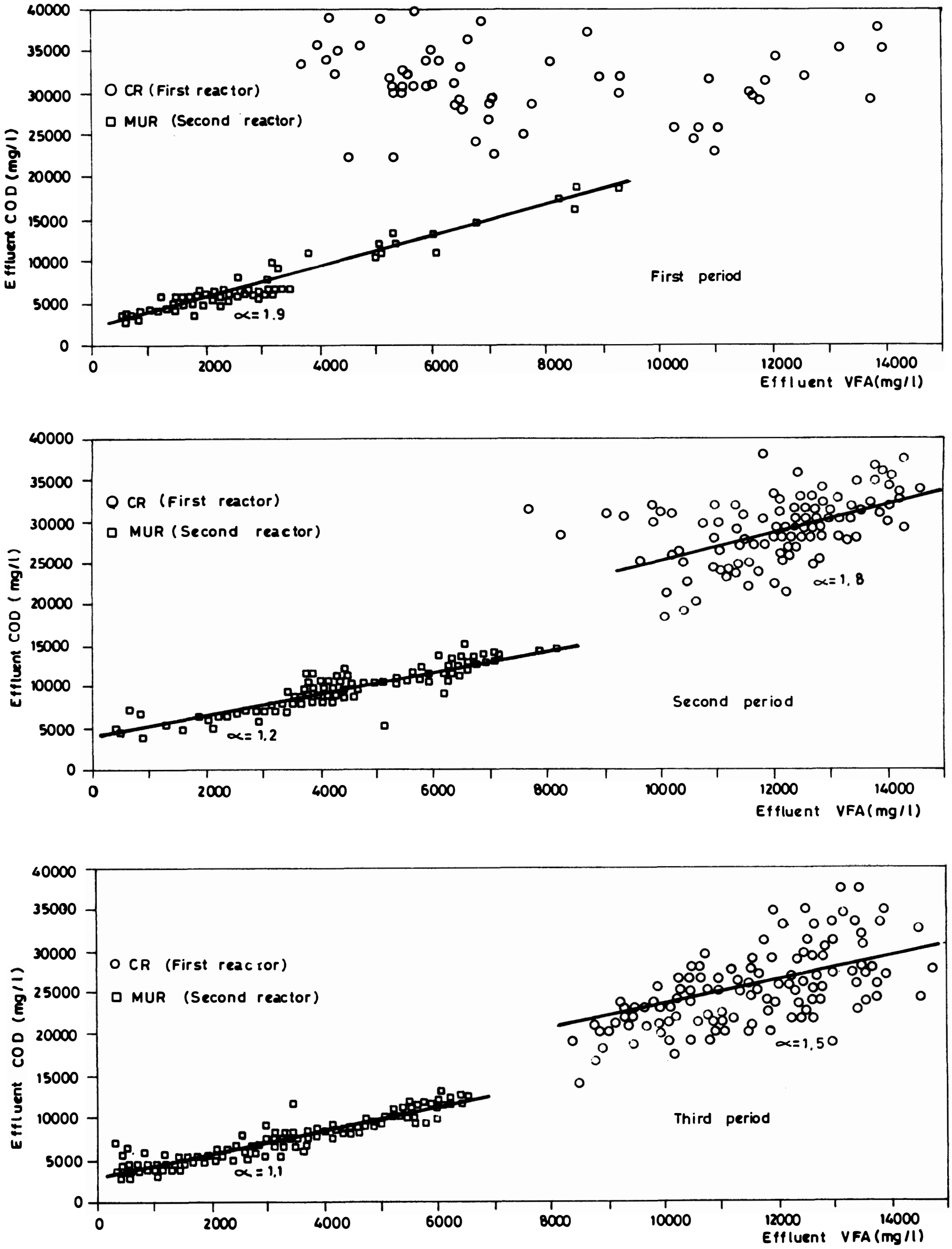

FIG.3 Effluent COD and VFA correlation for the phased reactors

Table 2 Design and Performance Parameters

REACTOR	Design Parameters: Residence time (day)	Design Parameters: Volumetric loading ($kgCOD/m^3$*d)	Performance Parameters: Solids retention time (day)	Performance Parameters: Organic loading kgCOD / kgVSS*d	Performance Parameters: Observed yield kgVSS / kgCOD	Performance Parameters: Removal rate kgCOD / kgVSS*d
1. reactor (CR)	1.7	21	3 (1-4)	5.0 (4.0-10)	0.07(0.15)	4 (7-13)
2. reactor (MUR)	5.3	6 (2-6)	9 (7-20)	1.3(0.8-1.5)	0.12(0.18)	1 (1-2)

* figures in parenthesis show literature values

Henze and Harremoës (1983) indicated that volumetric load parameter (B_v) could be established as a function of solids retention time (θ_x), reactor suspended flocs concentration (X_2) and yield coefficient (Y) as below:

$$B_v = \frac{X_2}{\theta_x Y} \qquad \text{where } B_x = \frac{B_v}{X_2}$$

It is well known that the maximum organic loading (B_x) is 1-1.5 kg COD/kg VSS d at which the yield will be near maximum. Whereas a reactor with a small suspended flocs concentration, only a small volumetric loading should be allowed (Gönenç et al , 1988).

This means that loading higher than this will result in significant VFA build-up and inhibition of the methane production. This can explain why the system failed whenever the volumetric loading increased during the first starting-up period. Due to this conclusion, organic loading was decreased by increasing the volume of the CR and MUR using the final capacity at the beginning of the second starting-up period. For balancing the probable shock loading and minimizing flocs wash-out, the MUR effluent was recycled during this period. However the settling characteristics of the suspended flocs could not be sufficiently improved and thus the parallel plate settling tank of the MUR was replaced by more efficient 'sepafloc' separator and the third starting-up period has been started. When the MUR suspended flocs concentration could be increased by a factor of 2, (from 5 to 10 kg/m^3), then the volumetric loading was increased by decreasing the volume of both reactors almost by the same factor. Figure 4 and Figure 5 show the removal rate of the system against the volumetric and organic loading rate for all starting-up periods, respectively.

Remedies Obtained by the Review of Environmental Factors

Due to their primary importance, temperature and pH have been strictly controlled within the range of 38-41°C, and 5-6 in the CR, and 35-38°C and 7-8 in the MUR, respectively.
Thus, their possible effects were eliminated during all periods.

According to literature, the theoretical minimum nutrient requirement in terms of COD/N/P ratio may be considered to be 350/7/1. From this, only the phosphorus deficiency was estimated and phosphoric acid has been continuously added into both reactors during all periods.

Nutrients other than N and P essential for the bacterial growth have been reviewed after the first period, and iron and nickel salts have been added to maintain stimulatory concentration during the second and third periods.

It was considered that sulphate could be converted to the toxic free hydrogen sulphide due to low pH in the CR. To overcome this problem, addition of iron salts, decreasing the loading rates and recycle could be useful due to dilution effect. However, it was observed that the system itself could tolerate the possible sulphide inhibition after a period of acclimation. On the other hand, propionic acid has been found to be responsible for partial toxicity to methanogenic bacteria and furthermore it appeared to retard acetogenic bacteria in the MUR. It was overcome by decreasing the loading rate and establishing balance between acetogenic and methanogenic bacteria at increased suspended flocs medium.

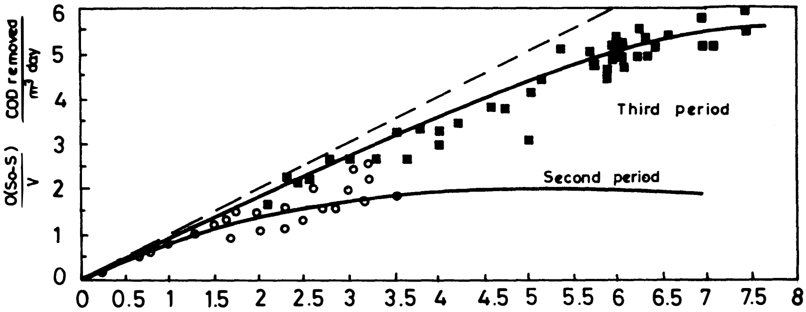

FIG.4 COD removal rate versus volumetric loading.

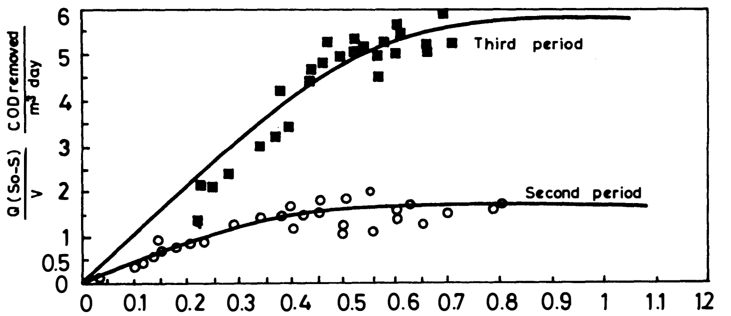

FIG.5 COD removal rate versus organic loading.

CONCLUSION

It may be concluded that the acid-forming bacteria and their final products are responsible for unstable operation and low removal rates of the anaerobic systems. In the light of the process characterization approach the organic loading used with the volumetric loading the yield coefficient and the biomass concentration is found as the most significant design and operation parameter of the recycled flocs system. Accordingly, the solids-liquid separation equipment becomes an extremely important part of the system .

On the other hand, the microbial steady state or stable operation conditions can only be established after stably grown and sufficiently concentrated suspended flocs are obtained .

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