CHEMICAL ENGINEERING TRANSACTIONS Volume 18, 2009
Editor Jiří Klemeš
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DOI: 10.3303/CET0918025

Hydrolysis of starch using Fenton's reagents as a key for waste integrated management in a potato processing industry

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A main characteristic of wastewater from a potato processing industry is its high concentration of starch. This wastewater requires special management due to the physical characteristics of starch. An alternative utilization method seems to be necessary. Utilization of the high energy content of starch through conventional anaerobic digestion may be applicable since anaerobic digestion is usually included in a typical potato processing industry wastewater treatment plant. The direct feed of starch in an anaerobic digester causes serious operational problems leading to system's failure. A hydrolysis step is thus necessary. In this paper a new approach in hydrolysis of starch waste was proposed. Chemical hydrolysis was performed by use of Fenton's reagents. The optimum operational conditions (temperature, concentrations of Fenton's reagents) and experimental procedure were determined in order to maximize the easy biodegradable soluble carbon concentration per gram of starch. The hydrolyzed effluent was then treated anaerobically and the energy content of the solution was converted successfully in methane. Applying this technique in a potato processing industry the estimated energy profit can be increased over 66%. Apart from the energy profit, the ratio of carbon to nitrogen is improved rendering the biological treatment of total wastewater stream efficient. Conclusively, this proposed hydrolysis technique could be the key factor for the integrated waste management in a potato processing industry regarding both the reduction of organic load as well as the energy production from biomass.

1. Introduction

The potato processing industries have high water consumption and thus produce large volumes of wastewater (Kárpáti and Schultheisz, 1984). The production process includes the stages presented in Figure 1. Wastewater is produced from all the potato washing processes as well as from the washing process of industrial floors and machines (Figure 1).

Please cite this article as: Vlyssides A., Barampouti E.M., Mai S., Stamatoglou E. and Rigaki K., (2009), Hydrolysis of starch using fenton's reagents as a key for waste integrated management in a potato processing industry, Chemical Engineering Transactions, 18, 165-170 DOI: 10.3303/CET0918025

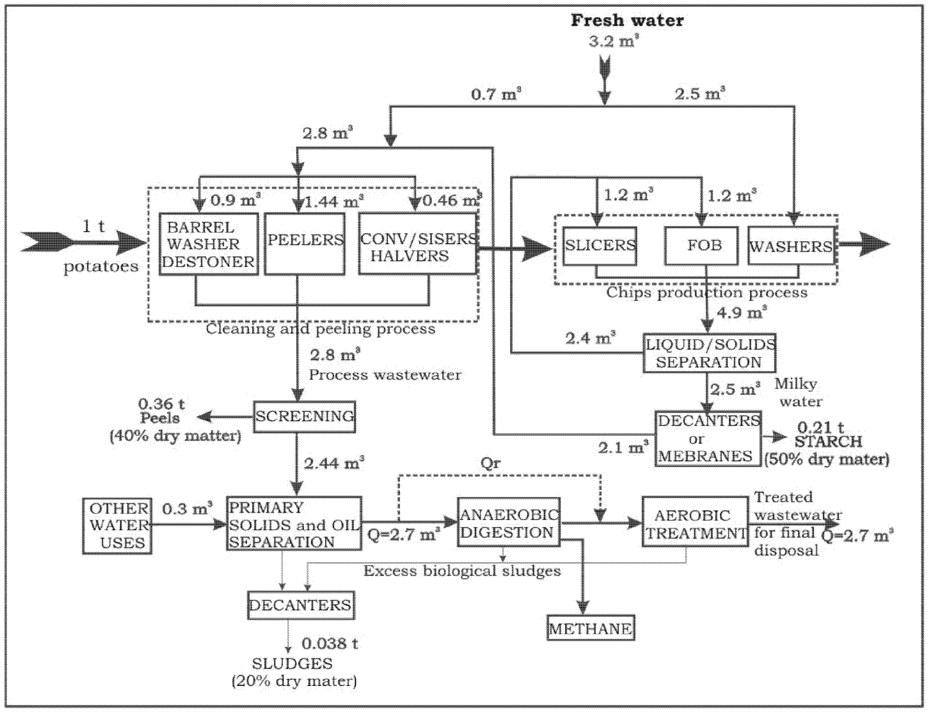

Figure 1: Chart flow of the production process and wastewater treatment plant of a potato processing industry

During the operation of potato processing industries (frozen fried potatoes, chips, dehydrated potatoes etc.), the water used coming from the production lines has a starch concentration of about 0.5%. This amount, although it seems low, needs special management due to the physical characteristics of starch.

Starch as a glucose polymer has a high organic load and thus cannot be disposed untreated in water resources. Starch granules are insoluble in cold water and they swell by absorbing water up to 25%. Under certain conditions they may create a colloidal solution (gelatination). These characteristics render the treatment of such waste difficult (Mitch, 1984). Thus, the current practice is to apply physical separation techniques in order to remove starch and treat the effluent with conventional biological methods. In a potato processing industry usually the wastewater is divided in two streams: the starchy stream and the main wastewater stream. The starchy stream is led to a decanter, where a starch fraction with 50% moisture is produced and the effluent is reused in the cleaning and peeling process. This starch fraction enters a second life cycle. It can be used either as animal food or as raw material for enzymatic hydrolysis and glucose production. These methods cannot be considered as feasible, taking into account the amounts and the production method of this starch waste. The selection of starch separation is necessary due to the problems caused in the operation of the biological treatment plant and not due to the market value of the starch as by-product. Nevertheless even the treatment scheme mentioned above encounters the problem of low carbon to nitrogen ratio in the aerobic process. The low C/N ratio inhibits the progress of nitrification and consequently the final effluent has high concentration of nitrogen. It is well established in literature that the minimum C/N ratio for efficient nitrification/ denitrification is 2,8 (Metcalf and Eddy, 1991). For this reason, a by-pass of untreated wastewater directly to the aerobic process is usually applied in such treatment plants in order to meet the needs of carbon and nitrogen. This solution even though it leads to a clear final effluent, has adverse effects on the energy efficiency of the system by reducing the biogas production.

This paper aims at presenting an integrated waste management scheme in a potato processing industry. The main goals are the final effluent to meet the disposal limits and the energy profit to be maximized. In this context, an alternative utilization method of starch seems to be necessary. Utilization of the high carbon and energy content of starch through conventional anaerobic digestion may be applicable if a hydrolysis step is preceded. This hydrolysis step should produce biodegradable compounds and not necessarily the final monomer of glucose. The conventional chemical (strong acids) and enzymatic hydrolysis cannot be applied due to technical and economical reasons. In this paper a new approach in the hydrolysis of starch waste is proposed by use of Fenton's reagents.

2. Materials and methods

2.1 Raw Materials

The raw material used in all experiments was pure starch of analytical grade and was purchased from E. Merck AG (Darmstadt, Germany). The suspensions of starch in several concentrations were prepared by mixing the proper amounts of distilled water and pure starch.

2.2 Apparatus

2.2.1. Hydrolysis apparatus

It was clear from bibliographic data as well as from preliminary experiments that starch hydrolysis is not possible without heat transfer to the starch suspension. For uniform heat transfer, mechanical stirring was also applied. So, the apparatus used for the starch hydrolysis is presented in Figure 2.

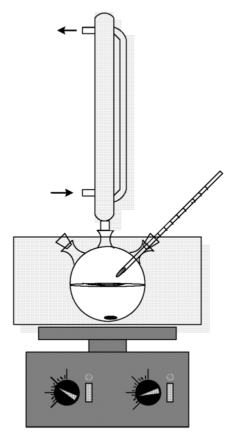

Figure 2: Laboratory apparatus of starch hydrolysis

2.2.2. Apparatus for the anaerobic treatment of starch

For the second stage of the anaerobic treatment of starch suspensions, an anaerobic digestion pilot plant was set up in the laboratory. For its operation, sludge as inoculum from the UASB reactor of a potato processing industry in Greece was used.

2.3 Experimental procedure

The starch suspension according to the predetermined concentration was prepared and set to the magnetic stirrer for stirring and heating. When the temperature of the suspension reached 61°C, the Fenton's reagents were added and the solution was left to react. The concentration of soluble organic carbon (TOC) was chosen as the means to control the efficiency of the starch hydrolysis, taking into consideration that assuming that 1g of starch corresponds to 0,375g TOC. An experiment where the hydrolysis of starch was performed with the addition of sulfuric acid was also carried out.

Then a certain amount of the hydrolysed solution was added to the anaerobic digestion apparatus and the amount as well as the time course of the methane production was recorded. An extra experiment where acetic acid was added to the anaerobic digestion pilot plant was performed.

3. Results

3.1 Hydrolysis with sulfuric acid

140mL/L sulfuric acid were added to each starch suspension (50, 60, 70, 80g/L starch) and the solutions were left to react for 2 hours at 65°C. After the completion of the experiments, the COD concentrations of the solutions were measured. The efficiencies of the hydrolysis with sulfuric acid were 95, 90, 87 and 85% respectively. Each experiment was repeated three times and the results mentioned above are the mean values deriving from the three experiments.

3.2 Hydrolysis with Fenton reagents

After several preliminary experiments, the following experimental plan was designed. In Table 1 the starch hydrolysis efficiencies using fenton reagents are presented.

Table 1.Starch hydrolysis results

A/A	$FeO_4S.7H_2O$ (g/L)	H_2O_2 (ml/L)	Time (h)	TOC_{in} (ppm)	TOC_{out} (ppm)	Efficiency %
1	5	5	1	20000	19800	99
2	2	2	0,5	20000	13600	68
3	2	2	1	20000	17600	88
4	1	1	0,5	20000	15600	78
5	1	1	1	20000	17000	85
6	0.5	0.5	-	20000	-	0

It was proved that the reagents concentrations ($FeSO_4 \cdot 7H_2O$, H_2O_2) = (1, 1) are adequate for the progress of starch hydrolysis, in contrast to concentrations (0.5, 0.5) where the solution was gelatinised and no hydrolysis was observed.

3.3 Anaerobic digestion of hydrolysed starch

In the beginning, acetic acid was added as substrate in the anaerobic digestion pilot plant. The choice of this substrate was made since acetic acid is the "key" substrate for the last stage of anaerobic digestion, methanogenesis. This way, it was possible to estimate the activity of the anaerobic biological sludge. From this experiment it was proved that 95% of carbon content of acetic acid was regained in the biogas. The respective efficiencies of the hydrolysed samples reached 78%. The samples hydrolysed with sulfuric acid led to anaerobic system failure, since the efficiencies were lower than 10%.

Conclusively, it is obvious that the hydrolysis of starch with Fenton's reagents could be used as a pretreatment step for the utilization of carbon and energy content of starch in biological processes.

4. Conclusions

From the experimental data, it was proven that the hydrolysis of the starchy stream in a potato processing industry could be achieved by the application of Fenton oxidation. The flow diagram of the modified treatment process is presented in Figure 3.

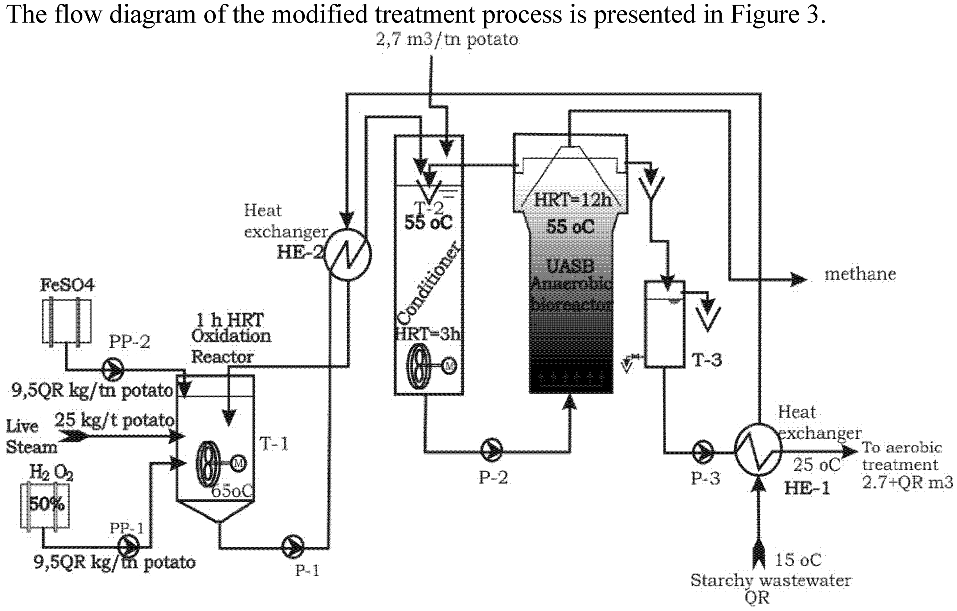

Figure 3: Modified flow diagram of wastewater treatment plant in a potato processing industry.

In order to reveal the main advantages of hydrolysis step incorporation in the wastewater treatment plant, the mass balances of nitrogen and carbon were conducted in the three possible solutions. The mass balances were calculated in the anaerobic digestion unit, where the energy profit derives and the C/N ratio of the effluent could be estimated. In Figure 4 the results of mass balances are presented.

It is obvious that the conventional solution faces the ploblem of low C/N ratio in the effluent of anaerobic digester. Thus the nitrification/denitrification processes are inhibited. The by-pass of untreated wastewater in the second solution manages to control the C/N ratio in the desired levels, but the biogas production is reduced by 14%. By the proposed solution, the C/N ratio can be easily regulated with a simultaneous increase in the biogas production. The energy profit is increased up to 66%.

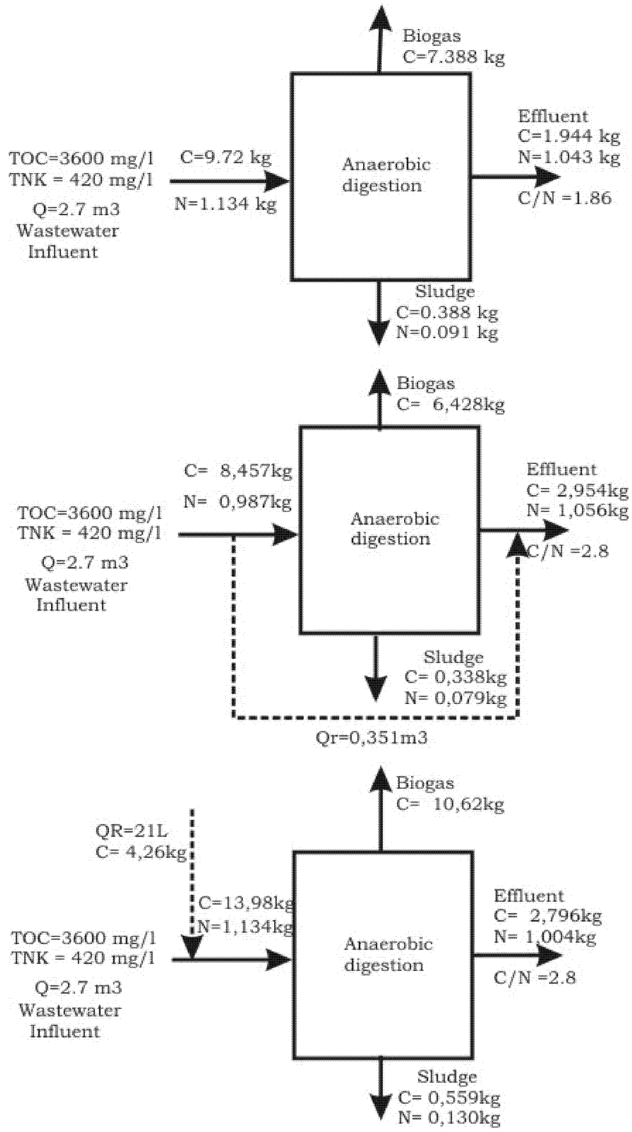

Figure 4: Mass Balances of the alternative treatment schemes of wastewater in a potato processing industry

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