Treatment of tapioca starch wastewater by a novel combination of physical and biological processes

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ABSTRACT

A pilot plant combining dissolved air flotation, anaerobic degradation in an expanded granular sludge bed (EGSB) reactor and aerobic post-treatment in a vertical flow constructed wetland has been used to treat tapioca starch wastewater for more than 2.25 years. It is demonstrated that organic matter (chemical oxygen demand by >98%), nitrogen (Kjeldahl-N by >90%) and cyanide (total cyanide by >99%) can be removed very efficiently under stable operating conditions. The removal efficiency for phosphorus is lower (total-P by 50%). The treatment concept, which includes several sustainable aspects, e.g. production of energy to be used on-site, low operation demands and minimal use of chemicals, could be interesting for small- and middle-sized tapioca processing plants.

Key words | anaerobic treatment, constructed wetland, dissolved air flotation, tapioca wastewater

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INTRODUCTION

A joint Vietnamese–German group of research institutions and companies is working on concepts to reduce water pollution in the Saigon Dong Nai river basin in southern Vietnam. The objective of the project is the development of techniques and management tools to sustainably improve the quality of surface waters in subtropical and tropical zones. In a sub-project, the treatment of tapioca starch wastewater has been investigated on a pilot scale.

The production of tapioca starch is an important economic sector in several countries in Southeast Asia. About 15 m^3 of wastewater highly loaded with organic compounds is produced per tonne of starch during the industrial extraction process. Cyanide as a toxic species is also found, because cyanoglucosides from tapioca roots are released during the production process that rapidly decay to cyanide after enzymatic hydrolysis (FAO 2001).

Some large tapioca starch production plants in other Asian countries treat their wastewater anaerobically using different reactor principles, e.g. up-flow anaerobic sludge blanket (UASB) reactors, up-flow anaerobic filters or anaerobic ponds, most often operated without any pre-treatment (Annachhatre & Amatya 2000; Bal & Dhagat 2001; Rajesh Banu *et al.* 2006; Rajbhandari & Annachhatre 2007; Colin *et al.* 2007). It has been demonstrated that cyanide can be removed both in anaerobic reactor systems (Gijzen *et al.* 2000; Siller & Winter 2004) and under aerobic conditions (Kaewkannetra *et al.* 2009). In a laboratory-scale investigation the potential of natural filters including sand, gravel, soil, coconut fibre and bamboo plait has been assessed (Hidayat *et al.* 2011). The results indicate that wetland systems might also be suited to treat tapioca starch wastewater. Recently the ideas of water reduction and energy conservation in the production process have been studied (Chavalparit & Ongwandee 2009).

In Vietnam, a concept was suggested more than 10 years ago that includes primary sedimentation, anaerobic treatment in an UASB reactor and aerobic post-treatment comprising an attached growth reactor and oxidation ponds (Hien *et al.* 1999). However, due to high investment costs caused by interest rates of more than 20% and slow enforcement of wastewater regulations, the treatment so far has been to let the wastewater flow through a series of anaerobic ponds before being discharged into a river. In the period 2008–2012 a few large factories built anaerobic treatment units, usually UASB reactors, combined with aerobic ponds as part of clean development mechanism (CDM) projects. Funding was provided by Japanese or European partners via emission credits according to the UN Framework

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Convention on Climate Change (UNFCCC 2011). As a low-cost solution, some middle-sized plants have recently started to cover the first anaerobic pond with a synthetic canvas in order to collect and utilize the biogas produced (Hoang 2012). In addition, some small companies have constructed anaerobic filters combined with aerobic post-treatment tanks (Phuoc & Phuong 2012). Since there is no biogas collection, a major benefit of anaerobic processes is not utilized.

The main objective of this study was to find out whether a combination of technical and nature-based treatment processes suited for small- and middle-sized companies can meet the discharge requirements corresponding to 50 mg/L biochemical oxygen demand (BOD_5), 30 mg/L total nitrogen (total-N), 6 mg/L total phosphorus (total-P) and 0.1 mg/L total cyanide according to Vietnam Standard TCVN 5945 class B (MONRE 2005), and whether it can be operated reliably.

MATERIALS AND METHODS

In small companies the starch is separated by sedimentation, while in larger plants centrifugal screen extractors are more common. The latter separation process provides wastewater with a higher fraction of dissolved organic substances and a lower portion of particulate matter. In this study the pilot plant was located at a company that applies centrifugation. In Table 1 the composition of the wastewater investigated is compared with data published by Mai (2006).

Table 1 | Composition of tapioca starch wastewater

Parameter	This study (mean values 2010–2012)	Data from Mai (2006)
Conductivity	1,673 μS/cm	–
pH	4.5[a]	4.0–4.2
TSS	1,700 mg/L	1,500–2,600 mg/L
COD (non-filtered)	11,800 mg/L	14,000–18,000 mg/L
BOD_5	6,900 mg/L	9,000–11,000 mg/L
Total phosphorus	71 mg/L	–
Kjeldahl nitrogen	280 mg/L	–
COD (filtered)	8,840 mg/L	–
Total cyanide	22 mg/L	5.8–96 mg/L

[a]After 3.5 h of microbial acidification. TSS: total suspended solids; COD: chemical oxygen demand; BOD_5: 5-day biochemical oxygen demand.

Accordingly, the wastewater undergoes acidification caused by anaerobic micro-organisms in the pre-treatment units. Although there is a certain amount of nutrients, organic matter is the main component. A comparison of non-filtered and filtered samples reveals that total suspended solids (TSS) make up for about 25% of the chemical oxygen demand (COD). Therefore, TSS removal prior to biological treatment was considered an important element of the process scheme.

The treatment concept developed includes physical pre-treatment, anaerobic degradation of organic substances, and aerobic post-treatment. The process scheme is shown in Figure 1. As far as we know the specific combination of technical and nature-based processes is a novel approach for this type of wastewater. A detailed description of the concept is given elsewhere (Pick *et al.* 2011).

The pilot plant was designed to treat continuously up to 12 m^3/d of wastewater. Before flowing into the plant, the water passes through three buffer tanks with a total hydraulic retention time of 3.5 h. In this stage pH decreases to 4.5 due to rapid microbial acidification. As a result, colloidal organic matter flocculates without adding any chemicals and the removal efficiency in the flotation stage is much better than with fresh wastewater. After this effect had been observed during the first months of operation, pH was no longer adjusted in the neutralization unit.

Dissolved air flotation (DAF) was applied in order to remove the major portion of TSS. An Aquatector® Microfloat® unit (Enviplan Company, Germany) was operated at a hydraulic surface load of 2.5–3.0 m/h. Since dosing of polymeric flocculants prior to flotation improved TSS removal only slightly, flocculants were not added during regular operation.

The central treatment stage was an anaerobic process (expanded granular sludge bed (EGSB) reactor, type ANAFIT-AC, Hager + Elsässer Company, Germany) which converts organic matter into biogas. The performance of the reactor largely depends on stable process conditions and a low suspended solids loading. This was achieved by an optimization of the upstream DAF process. The EGSB reactor was operated at a temperature of 35 °C and a hydraulic load of 4–5 m/h. It was seeded with sludge from a brewery wastewater treatment plant. pH was adjusted to 6.8 by adding sodium hydroxide. There was no need for heating because raw wastewater temperatures were already at the required level.

For post-treatment, a vertical flow constructed wetland (VFCW) was designed. The hydraulic surface load of the unit was about 30 L/($m^2 \cdot d$) and the average organic surface load corresponded to 72 g COD/($m^2 \cdot d$). The effluent was collected in a small basin which was the sampling point, and discharged via a fluid tipper to a lagoon operated by the tapioca starch company.

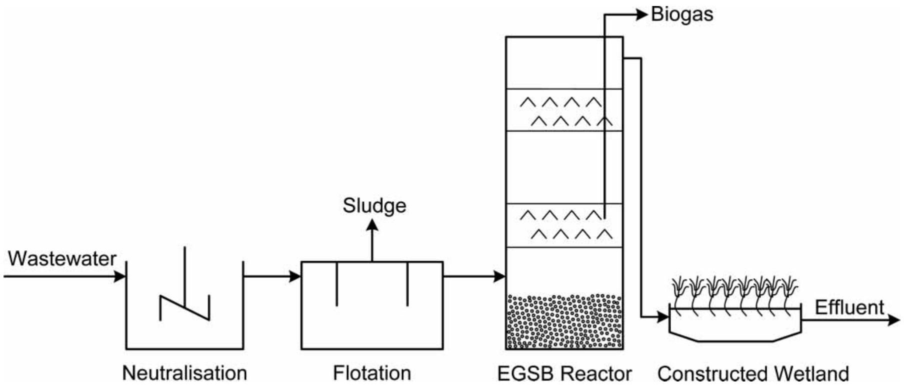

Figure 1 | Scheme of the treatment concept.

The parameters COD, ammonium (NH_4-N), nitrate (NO_3-N), phosphate (PO_4-P) and volatile organic acids were measured onsite with Merck Spectroquant test kits and TSS were determined according to DIN 38409 H2 (1987). In addition, COD, BOD_5, Kjeldahl nitrogen (KN), total-P and total cyanide were measured by the Institute for Environment and Resources according to US *Standard Methods* (APHA 2005). Biogas production was recorded by a bellows-type gas flow meter, and its methane content was measured by a Draeger X-am 7000 instrument.

RESULTS AND DISCUSSION

The technical components of the plant were put into operation in December 2009 while construction of the wetland was finished in autumn 2010.

The data presented in Figure 2 show influent and effluent COD concentrations during 2.25 years of operation. From mid April to June/July the company is not producing starch because no raw material is available. This causes an interruption of the pilot-plant operation for 8–12 weeks. The fluctuation of the influent concentration is due to varying conditions in the starch production process.

It can be concluded from Figure 2 that the anaerobic biomass had to be adapted before an almost constant COD removal by flotation and anaerobic degradation was reached. After wetland operation started on day 350 the treatment train has provided low and stable effluent concentrations.

Mean COD concentrations are shown in Figure 3 for the last five operating phases when all of the treatment units were in use. Accordingly, TSS removal by flotation contributes to COD removal by 20–25%. In the anaerobic reactor,

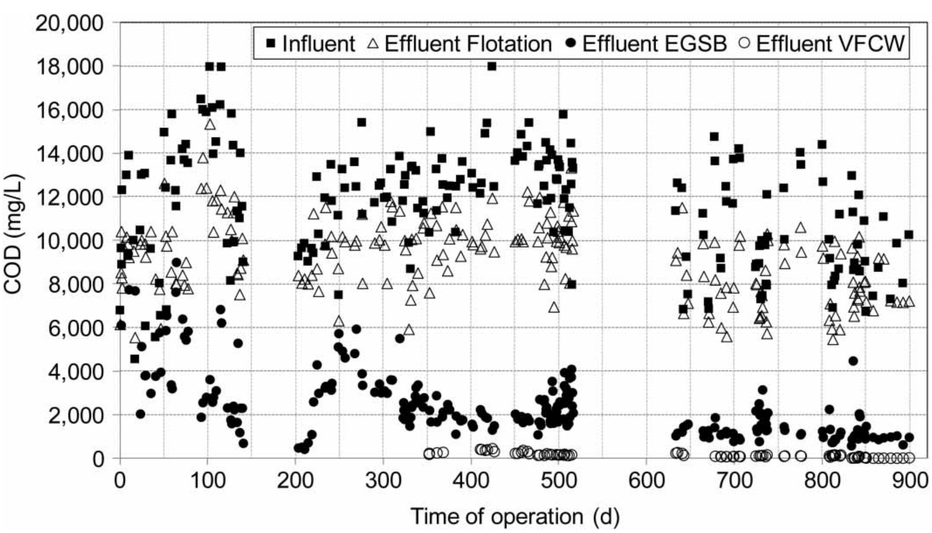

Figure 2 | Influent and effluent COD concentrations during 2.25 years of operation.

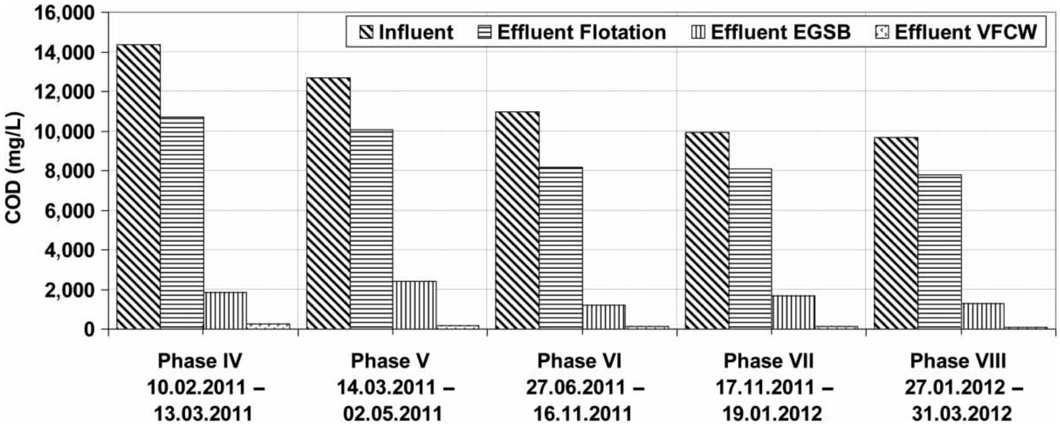

Figure 3 | Mean COD concentrations during the last five operating phases.

COD elimination is on the order of 60%. Further removal takes place in the wetland, which has been operated mainly under aerobic conditions. The mean COD effluent concentration in all phases based on 62 samples was 137 ± 73 mg/L, corresponding to an overall COD removal efficiency of more than 98%. It can be assumed that the remaining organics are predominantly non-biodegradable, because BOD_5 values were well below the Vietnamese standard of 50 mg/L in all of the effluent samples measured.

The organic load of the EGSB reactor is shown in Figure 4 as a function of time. It was quite low in the beginning because of the adaption period of the anaerobic sludge. The design load of 15 kg COD/($m^3 \cdot d$) is indicated in the figure as a 100% line. After more than 1 year of operation this value was clearly exceeded, and during a short-term stress test, a maximum value of 44 kg COD/($m^3 \cdot d$) has been obtained. Some lower values observed occasionally are caused by the fact that the flow rate was not always constant because of uneven wastewater flow during the starch production campaign.

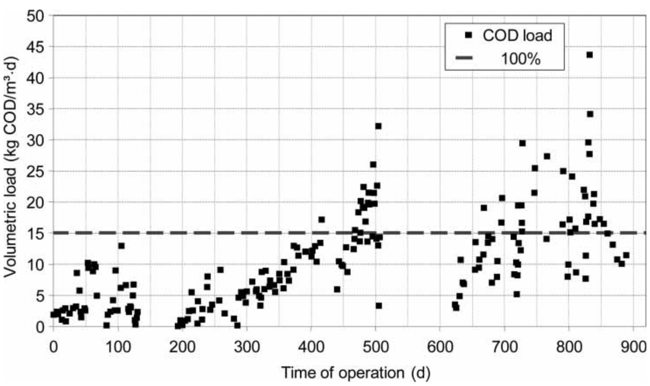

Figure 4 | Organic load of the EGSB reactor.

The biogas produced in the EGSB reactor has been measured with respect to quantity and composition. On an average more than 70% of methane was found. The specific methane yield calculated after correction to normal conditions (V_N) was 0.31 m^3 CH_4 per kg COD (eliminated). This value is close to the stoichiometric methane production of $V_N = 0.35$ m^3 per kg COD (eliminated) showing that the data are conclusive (Austermann-Haun 2008).

During the first phases of plant operation, only KN and ammonia were determined as nitrogen components. It was found that TSS removal by flotation contributes to KN elimination by 10–40%. KN removal in the anaerobic reactor was observed to be quite small, whereas it was significant in the wetland. The latter can be attributed to further degradation of organic matter as well as nitrification.

This conclusion is supported by the concentrations of nitrogen components including nitrate given in Table 2 for the last two operating phases. Accordingly, both organic nitrogen (Org.-N) and NH_4-N concentrations are very low in the VFCW effluent. It is interesting to note that the

Table 2 | Mean concentrations of different nitrogen components

	Operating phase VII			Operating phase VIII		
Sample	**Org.-N (mg/L)**	**NH_4-N (mg/L)**	**NO_3-N (mg/L)**	**Org.-N (mg/L)**	**NH_4-N (mg/L)**	**NO_3-N (mg/L)**
Influent	292	11.3	18.8	228	12.2	15.5
Effluent flotation	230	12.2	18.0	167	12.0	18.0
Effluent EGSB	157	92	0.8	87	80	0.9
Effluent VFCW	5.5	5.3	0.6	17	1.9	115

Table 3 | Mean concentrations of total-P

Sample	Phase IV (mg/L)	Phase V (mg/L)	Phase VI (mg/L)	Phase VII (mg/L)	Phase VIII (mg/L)
Influent	104	106	32	59	66
Effluent flotation	88	97	24	49	54
Effluent EGSB	73	66	25	54	52
Effluent VFCW	8	7	19	35	32

corresponding effluent concentrations of nitrate have always been below 1 mg/L when the water level in the wetland was high, as shown here for phase VII. However, in phase VIII where the water level was low, 115 mg/L of nitrate was found. This indicates that efficient denitrification takes place when the wetland is operated at high water level. Thus, an overall KN removal efficiency of >90% as well as very low total-N concentrations can be obtained.

In Table 3, mean total-P concentrations are shown for the last five operating phases. Total-P removal in the flotation and anaerobic stages is about 10–40%. A significant P elimination in the wetland is observed during the first two phases where the effluent P concentration is below 10 mg/L. Since P removal efficiencies decrease in later phases, adsorption onto soil particles with a limited capacity is supposed to be the main removal mechanism.

Therefore, the overall total-P removal efficiency at steady state is assumed to be on the order of 50%. There were two possibilities to improve the process: either a precipitation unit is put behind the EGSB reactor or granular material with a high binding capacity for phosphorus is put into the wetland. In addition, a scheduled trimming of wetland plants for promoting more plant growth might also help to improve the removal of nitrogen and phosphorus.

Mean concentrations of total cyanide are presented in Table 4 for operating phases IV and V, respectively. In the later phases influent concentrations have varied quite a lot, probably because different types and grades of tapioca roots were processed. According to the data about 10–20% of total cyanide can be removed by flotation. The main portion of cyanide is then eliminated in the anaerobic reactor, resulting in effluent concentrations of about 6 mg/L in phases IV and V. It seems that the wetland also contributes to cyanide removal. During the last 9 months of operation stable effluent concentrations below 0.1 mg/L were obtained.

Table 4 | Mean concentrations of total cyanide

Sample	Operating phase IV (mg/L)	Operating phase V (mg/L)	Operating phases VI–VIII (mg/L)
Influent	27	29	2–30
Effluent flotation	21	26	
Effluent EGSB	6.2	5.8	
Effluent VFCW	0.7	1.5	<0.1

COD removal of more than 80% by solids removal and anaerobic degradation was also found by Annachhatre & Amatya (2000) with 95%, Rajesh Banu *et al*. (2006) with 83–91%, Hien *et al*. (1999) with 90% and Colin *et al*. (2007) with 87%. The respective organic loads were 16, 23, 40 and 12 kg COD/($m^3 \cdot d$). However, all of the studies cited are based on laboratory-scale investigations under well-defined conditions. Only in one study were nutrients included, giving removal efficiencies of 38% for total-N and 20% for total-P (Rajesh Banu *et al*. 2006). The biogas yields reported were lower than those determined in this work.

According to Siller & Winter (2004) anaerobic microorganisms can remove cyanide from tapioca starch wastewater when adapted to the influent conditions. Similar findings are reported by Mai (2006). This confirms the observation that cyanide was removed efficiently in the EGSB reactor.

With respect to the Vietnamese standard, the requirements for effluent BOD_5, total-N and cyanide concentrations can be met, although removal of total-P was insufficient. Mai (2006) suggested an activated sludge system and stabilization ponds for extensive post-treatment. However, equipping the treatment concept presented with an efficient phosphorus sink as discussed above should also allow for complying with the standard.

SUSTAINABILITY CRITERIA

There are many definitions of sustainability and sustainable development, depending on the area people are working in. This study focusses on technological and process-related aspects, that is minimization of material and energy input, utilization of products and residues, and reliability of operation. In particular the following issues contribute to the sustainability of the concept presented:

1. Removal of TSS by flotation and reuse in agriculture, e.g. for feeding cattle. In other process schemes TSS is an additional load to the anaerobic reactor where it is only in part degraded and can cause sludge accumulation and instable process conditions.
2. Reduction of the organic load of the anaerobic reactor. The EGSB can therefore be designed smaller and operated more reliably.
3. Production of biogas that can be used on-site. The starch drying units need an appreciable amount of heat. When no biogas is available, 35–40 L of fuel oil per tonne of starch is needed. About 65% of this amount can be replaced by the biogas produced. It would also be possible to burn the biogas in a combined heat and power unit in order to produce both heat and electricity.
4. Utilization of the advantage of wetlands. Wetlands exhibit high process stability and low operation demands. Their disadvantage is the land requirement. However, for small- and middle-sized plants in rural areas it is usually possible to realize this stage.
5. Minimization of material input. Apart from adding sodium hydroxide in the EGSB reactor no chemicals are needed for the processes.

Furthermore the project includes workshops to disseminate the project outcome to plant owners, consultants and authorities in Vietnam. The companies providing the DAF system and the EGSB have ensured that these units can be operated by workers from the starch companies after appropriate training. Thus a non-technical sustainability of the concept will also be achievable.

CONCLUSIONS

The novel treatment concept combining physical pre-treatment by DAF, anaerobic degradation and aerobic post-treatment, has demonstrated its robustness and its ability to remove organic matter (COD by >98%), nutrients (KN by >90%, total-P by 50%), and total cyanide (by >99%) from tapioca starch wastewater.

The requirements of the Vietnamese standard on effluent BOD_5, total-N and cyanide concentrations can be met. Removal of total-P has been insufficient since the treatment train lacks an efficient phosphorus sink.

Several sustainable aspects are related to the treatment concept, first of all technological in nature. It is expected that the benefits will make the process scheme interesting for technical-scale applications in small- and middle-sized plants.

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