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Combined Biologic (Anaerobic-Aerobic) and Chemical Treatment of Starch Industry Wastewater

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Abstract

A combined biologic and chemical treatment of high-strength (total chemical oxygen demand [COD_{tot}] up to 20 g/L), strong nitrogenous (total N up to 1 g/L), and phosphoric (total P up to 0.4 g/L) starch industry wastewater was investigated at laboratory-scale level. As a principal step for COD elimination, upflow anaerobic sludge bed reactor performance was investigated at 30°C. Under hydraulic retention times (HRTs) of about 1 d, when the organic loading rates were higher than 15 g of COD/(L·d), the COD_{tot} removal varied between 77 and 93%, giving effluents with a COD/N ratio of 4–5:1, approaching the requirements of subsequent denitrification. The activated sludge reactor operating in aerobic-anoxic regime (HRT of about 4 d, duration of aerobic and anoxic phases of 30 min each) was able to remove up to 90% of total nitrogen and up to 64% of COD_{tot} from the anaerobic effluents under 17–20°C. The coagulation experiments with Fe(III) showed that 1.4 mg of resting hardly biodegradable COD and 0.5 mg of phosphate (as P) could be removed from the aerobic effluents by each milligram of iron added.

Index Entries: Activated sludge reactor; coagulation; nutrient removal; starch wastewater; upflow anaerobic sludge bed reactor.

Introduction

The current Russian food industry is demonstrating impressive growth and is one of the biggest starch consumers. The volume of the starch market was 110,000 t in 1999 and continues to grow *(1)*. Although the starch industry compared to the other branches of food industry is potentially

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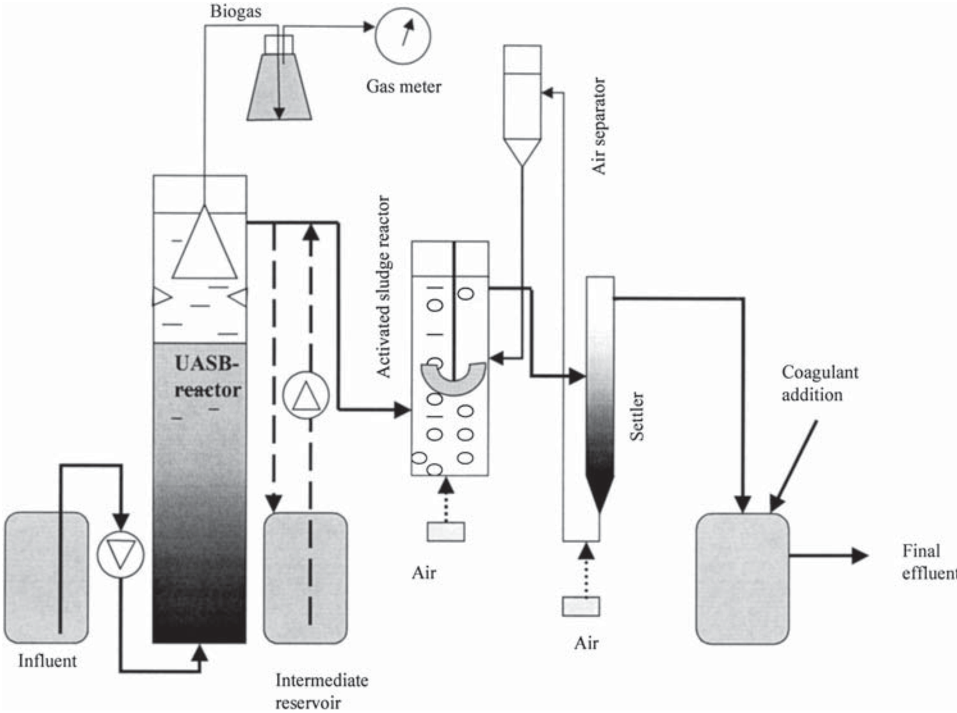

Fig. 1. Flow sheet of laboratory installation for treatment of starch industry wastewater.

able to operate with a closed water cycle, up to 40% of its wastewater in Russia is discharged on wastewater treatment plants of neighboring towns or directly on so-called filtration fields. Such a practice not only increases expenses (i.e., payments to the wastewater treatment plants for treatment and increased concentrations of chemical oxygen demand (COD) and nutrients, penalties to the ecologic authorities) but also severely damages the environments and leads to nonrational usage of arable land. The internal starch production in Russia accounts for 45,000 t with 1.5 million cubic meters of wastewater to be treated *(1)*. The wastewater content is highly variable, but the most typical concentrations of main pollutants in this wastewater are the following: 10 g/L of total COD (COD_{tot}), 2.5 g/L of suspended solids (SS), 0.6 g/L of total nitrogen, 0.15 g/L of total phosphorus *(1)*. A possible solution for utilization/treatment of starch industry liquid refuses would include separation into a solid and a liquid fraction. The solid fraction, mainly consisting of gluten, can be reused in a main technological process while the liquid fraction should be treated before discharge.

The objective of this study was to develop a technology for treatment of starch industry wastewater targeting the aforementioned main pollutants. As a first step, the upflow anaerobic sludge bed (UASB) reactor was investigated for the elimination of the major part of COD and SS. This is a

Table 1
Range of Variation of Some Characteristics of Wastewater from Starch-Producing Factory Ibred (Ryazan' province)

Parameter	Variation
pH	4.19–7.03
COD_{tot} (g/L)	2.98–26.22
COD_{SS} (g/L)	0.35–9.83
COD_{col} (g/L)	0.12–0.95
COD_{sol} (g/L)	2.47–15.44
SS (g/L)	0.23–5.48
Ash content of SS (%)	18.8–33.7
Total protein (g/L)	1.02–5.21
Soluble protein (g/L)	0.42–2.58
Total nitrogen (g N/L)	0.204–1.042
N_{NH_3} (g N/L)	0.049–0.115
Total phosphorus (g P/L)	0.050–0.385
Soluble sugars (g/L)	0.18–6.69

usual treatment step for starch-containing wastewater having a high strength *(2–8)*. In a second step, the conventional activated sludge process operating in an aerobic-anoxic regime was used for removal of remaining biochemical oxygen demand and nitrogen. Finally, iron coagulation was applied for effluent clarification and phosphate precipitation. The flow sheet of the integrated laboratory installation used in this study is shown in Fig. 1.

Materials and Methods

Wastewater

Wastewater was directly taken from gluten decanters of factory Ibred (Ryazan' province) producing starch from maize. The range of variation of some characteristics of this wastewater is given in Table 1.

UASB Reactor

A laboratory UASB reactor (rectangular cross-section: 38 cm^2; height: 85 cm; total working volume: 2.68 L) made from transparent plastic and equipped with six sampling ports along the reactor height was used. An operating temperature of 30 ± 1°C was maintained by placing the reactor into a thermostat TS-80 (Mashzavod, Odessa, USSR). The reactor was seeded with 1 L of sludge (55 g of SS/L; ash content: 30%; specific aceticlastic activity: 0.55 g of COD/[g of VSS·d] at 30°C) originating from a submesophilic UASB reactor treating pig manure wastewater *(9)*. Anaerobic batch biodegradability and activity assays were conducted as described by Lettinga and Hulshoff Pol *(7)*.

Activated Sludge Reactor

The continuous-flow stirred tank type of reactor (Fig. 1) was made from transparent plastics and equipped with a mechanical stirrer. It had a working volume of 0.8 L and functioned at ambient laboratory temperatures (17–20°C) in alternating aerobic/anoxic regime for treatment of the anaerobic effluents. During the aerobic phase, the feeding was stopped, while air at a flow rate of 1 L/min was pumped through the reactor. Aeration was switched off during the anoxic phase, while the continuous feeding was restored. The effluent passed through the external settler. The sludge return was organized via air lift with an additional air separator (Fig. 1). A programmable multichannel timer controlled all pumps used. Additionally, in the reactor, an electronic sensor (Datchik, Russia) was inserted for online monitoring of soluble oxygen. The electric signal from this sensor was transferred to a programmable data logger system. Data were recorded every 30 s and were averaged (when necessary) over 3-min intervals. A personal computer programmed to function as a terminal emulator was used to communicate with the data logger. Secondary sludge from Kur'yanovskaya wastewater treatment plant (Moscow) was used as a seed sludge (initial concentration: 1.5 g of mixed liquor suspended solids [MLSS]/L). Excess sludge was periodically withdrawn from the settler. Nitrification and oxygen uptake rates (OUR) were determined as described by Klapwijk and Rensink *(10)*.

Coagulation Assays

The assays were performed with 200 mL of aerobic effluent in a laboratory glass under continuous stirring and pH control. Addition of coagulant ($FeCl_3 \cdot 6H_2O$) was carried out at 200 rpm. Then the intensity of stirring was reduced to 40 rpm to complete a flocculation process during which pH was maintained at 7.2–7.5 by the addition of NaOH.

Analyses

COD was analyzed spectrophotometrically using Hach tubes. Raw samples of influents or effluents were used to determine COD_{tot}, 4.4-µm-folded-paper-filtered (Schleicher & Schuell $595_{1/2}$, Germany) samples to determine filtrated COD (COD_{filt}), and 0.45-µm-membrane-filtered (Schleicher & Schuell ME 25, Germany) samples to determine soluble COD (COD_{sol}). The suspended solids COD (COD_{SS}) and colloidal COD (COD_{col}) were calculated by the differences between COD_{tot} and COD_{filt}, and between COD_{filt} and COD_{sol}, respectively. All other analyses were performed three to five times per week or as described previously *(8,9)*. All gas measurements were recalculated to standard conditions (1 atm, 0°C). Statistical analysis of data was performed using Microsoft Excel.

Results and Discussion

Performance of UASB Reactor

Since the preliminary batch tests showed a quite high (~95%) anaerobic biodegradability of starch industry wastewater and the seed sludge was

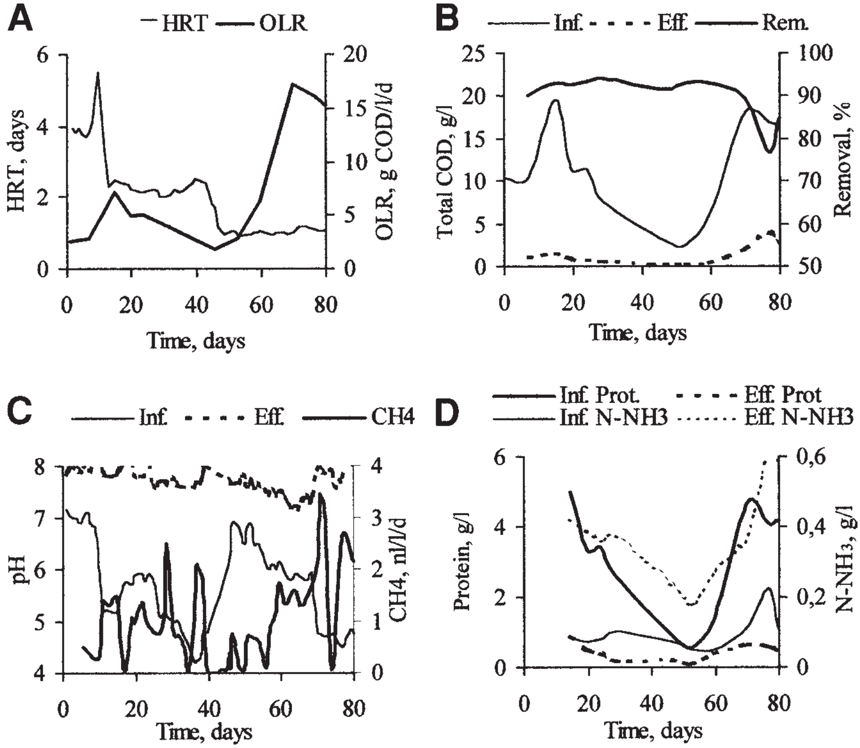

Fig. 2. Performance of UASB reactor. **(A)** HRT and OLR; **(B)** Influent and effluent total COD concentrations and removal efficiency; **(C)** Influent and effluent pH and specific methane production; **(D)** Influent and effluent protein and ammonia concentrations.

sufficiently active (specific aceticlastic activity of 0.55 g of COD/[g of volatile SS·d]), the UASB reactor reached 90% of COD_{tot} removal in a week (Fig. 2B). Then the hydraulic retention time (HRT) was reduced to ~2 d; however, the organic loading rate (OLR) decreased (d 15–46, Fig. 2A) owing to reduced strength of incoming wastewater (d 15–46, Fig. 2B). As a result, the COD_{tot} removal was quite high (>90%) in this period (Fig. 2B). After a subsequent decrease in HRT to ~1 d, the OLR reached values >15 g of COD/(L·d) (d 47 onward, Fig. 2A), while the COD_{tot} removal varied between 77 and 93% (d 47 onward, Fig. 2B). In spite of acidic effluents fed to the UASB reactor, the effluent pH was fairly stable, slightly oscillating around 7.9 throughout the entire study (Fig. 2C). This was owing to consumption of volatile fatty acids (data not shown) and production of ammonia as a result of protein degradation (Fig. 2D). The methane production rate was subject to significant fluctuations (Fig. 2C). This was related to entrapment and subsequent slow hydrolysis of SS from incoming wastewater. In spite of the fact that the entrapped yellow aggregates were sometimes seen inside the sludge bed, no difficulties in the UASB reactor performance (e.g., sludge lifting as reported in refs. *7* and *8*) were observed. The effluent COD/N ratio varied between 4 and 5, i.e., lower than practically established values (usually around 6) to fulfill the requirements for subsequent denitrification *(11)*. To avoid a deficiency of COD for nitrogen removal under planned implementation of the proposed technology, the COD removal efficiency of the UASB reactor can be decreased by decreasing HRT or working temperature *(9)*.

Performance of Activated Sludge Reactor

An activated sludge reactor was started up in a nitrifying mode using the anaerobic effluents containing low concentrations of biodegradable COD (run N1, Table 2). When the nitrification efficiency reached values around 80%, the reactor was switched on alternating (aerobic-anoxic) operation using anaerobic effluents having higher COD (run DN1). During this run, when aerobic and anoxic phases lasted 40 and 20 min, respectively, the average HRT was 1.24 d while the average OLR was 2.28 g of COD/(L·d) (Table 2). The average COD_{tot} removal accounted for 83% with the COD_{tot} effluent concentrations oscillating at about 0.39 g of COD/L (run DN1, Table 2). However, because of the high ammonia loading rate (ALR) applied (443 mg of N/[L·d], on average), the average efficiency of nitrification was low (49%) (run DN1, Table 2). Together with a relatively low denitrification efficiency observed (60%, on average), this resulted in an average total nitrogen removal of 26% (run DN1, Table 7).

To improve nitrogen removal, the HRT was increased to 2.33 d (on average) while duration of aerobic and anoxic phases was set as 30 min each during run DN2 (Table 2). Such an operational regime immediately led to almost complete denitrification (98%, on average); however, the average nitrification efficiency remained at a relatively low level (54%) (run DN2, Table 2). This can be related to the inhibiting pH values for nitrification observed in the reactor; they oscillated around 9.0 (run DN2, Table 2) owing to generation of alkalinity by denitrification and stripping of CO_2. In spite of these unfavorable conditions for nitrification, the average total nitrogen removal increased to 53% while the average COD_{tot} removal slightly dropped (to 72%) during run DN2 compared with run DN1 (Table 2).

For balancing nitrification-denitrification processes, the HRT during run DN3 was further increased to 4.18 d (on average) while keeping the same ratio between aerobic and anoxic phases as in run DN2 (Table 2). This resulted in a significant improvement in nitrification efficiency (87%, on average) with almost no losses in denitrification efficiency (92%, on average), giving an average total nitrogen removal of 81% (run DN3, Table 2). The effluent COD_{tot} concentrations oscillated at about 1 g/L, resulting in a further drop in COD_{tot} removal to an average value of 64% (run DN3, Table 2). It is likely that this remaining COD, which comprises about 5% of the initial strength of starch industry wastewater, is hardly biodegradable in either anaerobic or aerobic conditions.

The observed efficiencies of nitrification, denitrification, and total nitrogen removal are plotted in Fig. 3 vs the imposed ALR. For the investigated activated sludge system (1.5–2.5 g of MLSS/L), a total nitrogen

Table 2
Operational Parameters and Efficiency of Activated Sludge Reactor Treating Anaerobic Effluents[a]

Parameter	N1	DN1	DN2	DN3
Aerobic phase (min)	60	40	30	30
Anoxic phase (min)	0	20	30	30
HRT (d)	0.85–1.33 (0.93)	0.97–1.49 (1.24)	2.19–2.57 (2.33)	3.98–5.17 (4.18)
OLR (g COD/[L·d])	0.20–0.28 (0.23)	1.67–3.24 (2.28)	0.89–0.93 (0.91)	0.55–0.63 (0.59)
Influent COD_{tot} (g/L)	0.20–0.27 (0.25)	1.76–2.53 (2.23)	2.00–2.04 (2.02)	2.51–2.83 (2.65)
Effluent COD_{tot} (g/L)	0.07–0.10 (0.08)	0.24–0.52 (0.39)	0.44–0.67 (0.56)	0.94–1.00 (0.97)
COD_{tot} removal (%)	63–70 (66)	79–87 (83)	67–78 (72)	63–65 (64)
Influent pH	7.60–8.34 (8.08)	7.70–8.33 (7.94)	7.80–8.10 (7.98)	7.88–8.10 (7.92)
Effluent pH	5.95–7.65 (6.74)	8.16–9.08 (8.57)	8.80–9.13 (9.04)	7.23–8.78 (7.91)
ALR (mg $N\text{-}NH_3$/[L·d])	186–262 (216)	390–541 (443)	254–257 (256)	33–114 (85)
Influent $N\text{-}NH_3$ (mg/L)	181–256 (228)	378–613 (530)	562–571 (567)	131–475 (338)
Effluent $N\text{-}NH_3$ (mg/L)	43–52 (49)	119–379 (266)	205–306 (260)	18–81 (39)
Nitrification efficiency (%)	76–80 (78)	32–68 (49)	46–62 (54)	80–96 (87)
Effluent $N\text{-}NO_3$ (mg/L)	135–196 (166)	9–253 (136)	2–8 (5)	8–32 (18)
Denitrification efficiency (%)[b]	—	22–95 (60)	98–99 (98)	89–98 (92)
Total N removal (%)[c]	2–3 (2)	15–34 (26)	45–61 (53)	72–95 (81)
Influent $P\text{-}PO_4$ (mg/L)	27–47 (35)	84–160 (130)	146–148 (147)	157–182 (170)
Effluent $P\text{-}PO_4$ (mg/L)	22–28 (24)	60–136 (97)	128–135 (131)	135–161 (150)

[a]Average values for the period are given in parentheses.
[b]Calculated as follows: $\{1 - [N\text{-}NO_3]_{ef}/([N\text{-}NH_3]_{in} - [N\text{-}NH_3]_{ef})\} \times 100$.
[c]Calculated as: $\{1 - ([N\text{-}NO_3]_{ef} + [N\text{-}NH_3]_{ef})/[N\text{-}NH_3]_{in}\} \times 100$.

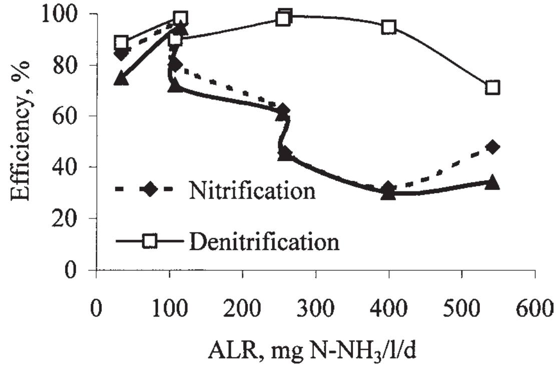

Fig. 3. Efficiencies of nitrification, denitrification, and total nitrogen removal vs imposed ALR.

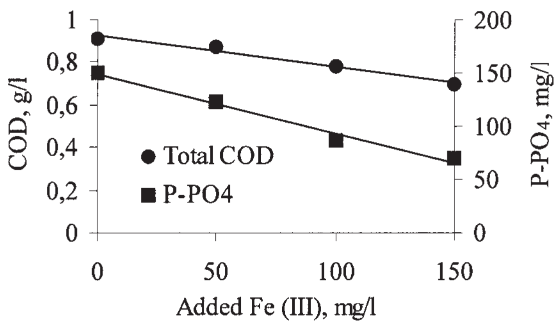

Fig. 4. COD and phosphate concentrations in aerobic effluents after coagulation with different concentrations of iron (III).

removal >90% could be obtained only under relatively low ALR (about 100 mg of N-NH_4/[L·d]). Under such conditions, the effluent total nitrogen concentrations were about 50 mg of N/L (run DN3, Table 2), i.e., in the range for direct discharge into municipal wastewater treatment plants without additional charges for excessive nitrogen concentrations.

The concentrations of phosphates slightly dropped during all nitrification-denitrification runs (Table 2), probably owing to partial precipitation on the activated sludge, taking into account that the pH values in the reactor were about or higher than 8.0 (i.e., favorable for hydroxyapatite and struvite precipitation) *(9)*.

Performance of Coagulation Step

Since the concentrations of COD_{tot} and phosphate remained relatively high in the aerobic effluents (Table 2), efficiency of their coagulation with iron (III) was investigated (Fig. 4). The remaining COD and phosphate concentrations were adversely proportional to the iron concentration used. From the data in Fig. 4, one can calculate that 1.4 mg of COD and 0.5 mg of phosphate (as P) were removed by each milligram of iron added, respec-

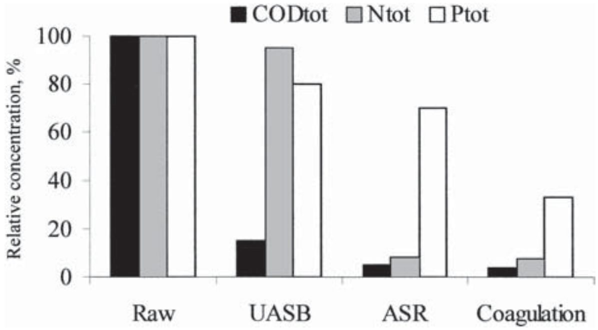

Fig. 5. Relative decrease in total COD, N, and P concentrations after each treatment step.

tively. In addition, about 1.2 mg of NaOH/mg of iron should be added for pH correction to the optimal for the coagulation range (7.2–7.5).

Conclusion

Figure 5 summarizes the average data showing decreases in COD_{tot}, nitrogen, and phosphorous concentrations for the raw starch industry wastewater after each treatment step in laboratory-scale investigations. About 85% of COD_{tot} could be removed in a UASB reactor; however, it is essential to avoid too deep exhaustion of biodegradable COD in order to fulfill subsequent denitrification requirements. Up to 90% of total nitrogen could be removed from the anaerobic effluents using an activated sludge reactor operating in an aerobic-anoxic regime. Since the generated effluents still contained significant concentrations of hardly biodegradable COD (about 1 g/L) and phosphates (about 150 mg of P/L), a coagulation step with iron (III) could be applied for effluent clarification and P removal. Generally, the application of the three step treatment that we investigated could produce effluents approaching the limits established for discharge into a sewage treatment system, which is often an option for the starch-producing industry in Russia. If more stringent limits for effluent quality should be fulfilled, some posttreatment steps such as constructed wetlands can be recommended.

Acknowledgment

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