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COMBINED BIOLOGICAL NITRIFICATION AND DENITRIFICATION OF HIGH-SALINITY WASTEWATER

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ABSTRACT

The focusing on the discharge of nitrogen compounds to aquifers has put pressure on power plants to look into removal of nitrogen compounds from the gas scrubbing liquors ($DESO_x$ and $DENO_x$). The scrubber liquor has a high salinity, a high chloride content and a temperature of about 40°. Initial laboratory tests to evaluate the possibility of performing biological nitrification and denitrification showed promise and a pilot-scale test unit was established at one of the Danish coal-fired combined heat and power plant (AVEDØRE 1).

The pilot plant was operated under varying conditions with regard to temperature and chloride concentration. Maximum nitrification and denitrification rates were measured. At 30°C and 20 g Cl^-/l, maximum nitrification and denitrification rates of 2 and 3 mg N/g VSS•h respectively were measured. In the effluent, concentrations of inorganic nitrogen were below 8 mg N/l.

Twice during the test period, inhibition of the biomass activity was caused by high concentrations of heavy metals. The high content of heavy metals was due to malfunction of pH control in the heavy metal removal plant. The nitrification process was more sensitive to heavy metals than the denitrification process, and during the two toxic events the nitrification rate decreased to zero.

The influence of rapid changes in the chloride and nitrite contents on nitrification was also examined. The results from the performed tests can be applied on other wastewaters with similar characteristics as these scrubber liquors i.e. with salinity. As an example fertilizer and pharmaceutical industries can be mentioned.

KEYWORDS

Activated sludge; acute nitrification inhibition; biological denitrification; biological nitrification; FGD wastewater; high salinity; SALWAS.

INTRODUCTION

The environmental problems caused by the emission of sulphur dioxide to the atmosphere have increased the establishment of flue gas desulphurisation (FGD) facilities. The wet lime-gypsum desulphurisation process produces a wastewater, i.e. the bleed-off of scrubber liquid from the absorber. The wastewater is characterised by a high chloride and nitrate content, e.g. 30 g Cl^-/l and 150 mg N/l, respectively, and if $DENO_x$ is implemented also, a varying content of ammonium, e.g. 25 mg N/l.

Furthermore, the wastewater contains a broad range of heavy metals deriving from the fuel source and the alkaline component used in connection with the gas scrubbing.

The heavy metals are removed by chemical precipitation, and for removal of the nitrogen compounds, biological methods using either activated sludge systems or compact fluidised bed systems are alternative options.

The oxidation of ammonia to nitrite and then nitrite to nitrate, the nitrification process, takes place under aerobic conditions (autotrophic bacteria); and reduction of nitrate to nitrogen gas, the denitrification process, takes place under anoxic conditions (heterotrophic bacteria). Lab-scale experiments (Kristensen *et al.*, 1991) examined the denitrification of wastewater from FGD plants. The effect on the biological denitrification of chloride concentration and temperature up to 30 g Cl^-/l and 50°C respectively was examined. Treatment of FGD wastewater in a pilot plant of fixed film type with separate nitrification and denitrification processes, reported in Bettenworth *et al.* 1995, showed satisfactory nitrification and denitrification removal rates at a chloride concentration of 15 g Cl^-/l. In Hagen and Eiken (1995) the activated sludge denitrification process was examined in connection with treating FGD wastewater with chloride concentrations between 5-7 g Cl^-/l.

The aim of the presented work was to examine the feasibility of the combined biological nitrification and denitrification processes in activated sludge using a one-sludge system for removing nitrogen components in flue gas scrubbing liquors. The combined process was examined during the adaption to high temperature and high salinity. Furthermore, the performance during more stable conditions with regard to temperature and saline conditions was observed and finally the effect of shut-downs was studied. Both artificial and FGD wastewater were used. The process parameters, temperature and chloride concentration, varied between 25-30°C and 0-20 g Cl^-/l, respectively.

It was also the aim to provide information on the inhibition of the nitrification process due to rapid changes in the chloride and nitrite concentrations. Knowledge of the inhibition of nitrification is important for the development in operational strategies for full-scale plants.

MATERIALS AND METHODS

A pilot plant was installed at the Avedøre Combined Heat and Power Station in Denmark. The configuration of the pilot plant is illustrated in Figure 1.

The wastewater used in the pilot plant was collected in the effluent sump after the heavy metal precipitation plant (sulphide and hydroxide). It was possible to control the flow and to undertake change of the wastewater properties by dosing the desired chemicals to the influent tank. The two 1 m^3 process tanks could be operated both as nitrification or denitrification tanks. Excess sludge could be taken from the process tanks to a sludge storage tank. A small post aeration tank was placed after the process tanks to remove any surplus organic matter. In the secondary settling tank the sludge was separated from the effluent and the return sludge was pumped back to be mixed with the influent before entering the process tanks.

The pilot plant could be fed with either modified FGD wastewater or artificial wastewater. As the ammonium concentration in the FGD wastewater from Avedøre was too low for the experimental work with the nitrification process, the wastewater properties were modified by adding ammonium chloride. The typical nitrogen content in the modified wastewater was: 120 mg NH_4-N/l and 90 mg NO_3-N/l. The ammonium load on the aerobic biomass was controlled at approx. 1 mg N/g VSS•h. Sodium phosphate and acetic acid were added to obtain COD/N and COD/P ratios of 7 and 100, respectively.

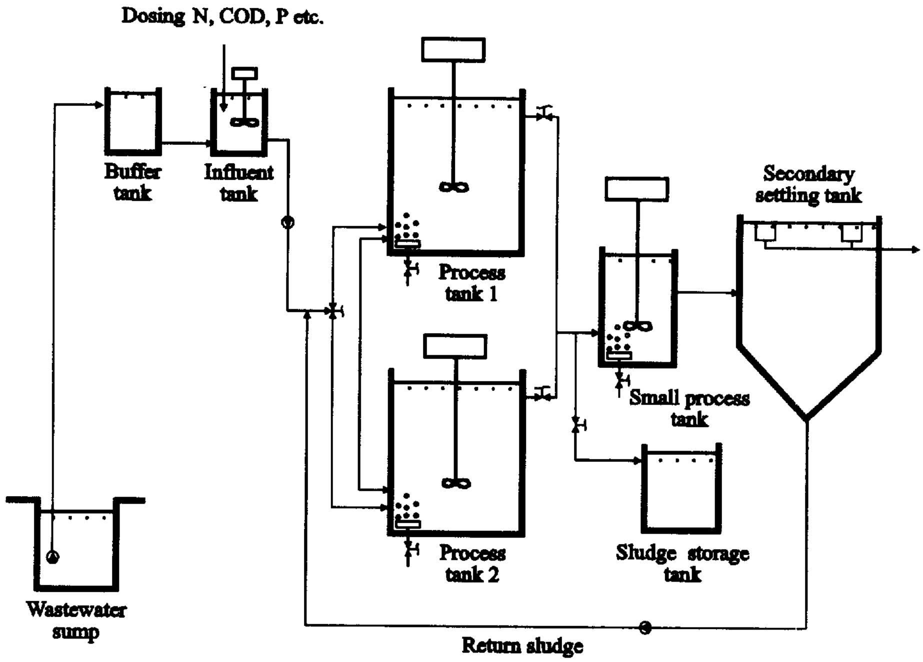

Figure 1. Illustration of the pilot plant configuration.

Artificial wastewater was used during the adaption of the seed sludge (activated sludge from a municipal plant) up to 10 g Cl^-/l. As described later, artificial wastewater was also used during periods with operational problems (pH control) at the heavy metals precipitation plant.

The pilot plant was operated in two different modes, i.e. a recirculation mode and an alternating mode (Biodenitro^{TM}). During the adaption of the seed activated sludge and during approx. the first two months after the adaption period had been concluded, the recirculation mode was applied. The recirculation was performed according to a fixed flow pattern through the pilot plant with nitrification in the first process tank and denitrification in the second process tank. The recirculation was provided by the return sludge flow from the clarifier. During this mode, acetic acid was dosed directly into the denitrification tank.

Later on, the alternating mode was introduced and it was maintained during the rest of the test period. When the plant was operated in alternating mode, the process tanks alternated between nitrification and denitrification according to a chosen cycle, however, denitrification always being the first process step and nitrification the second in the flow direction.

During the experiment, several different process conditions were tested. The first step was adaption of municipal activated sludge to the high-saline process conditions. At the end of the adaption period, bacterial strains extracted from marine sediments were added to the pilot plant to enhance the adaption to the high saline environment.

After the adaption of the activated sludge, the influent was changed from artificial to modified wastewater. The pilot plant was operated under varying conditions with regard to temperature and chloride concentration. The following approximate temperatures and chloride concentrations were used: (25°C and 10 g Cl^-/l), (30°C and 10 g Cl^-/l), (30°C and 15 g Cl^-/l) and (30°C and 20 g Cl^-/l). The pH varied between 7 and 8.3 and was not controlled as the level was satisfactory with regard to the biological processes.

At an operating temperature of 25-30°C, a sludge age of approx. 3 days would be required in a municipal wastewater treatment plant (WWTP) to ensure nitrification (Henze *et al.*, 1990). In experiments examining the adaption of biomass to operational conditions, it typically takes 2-3 sludge ages to adapt the biomass to the operational condition. In the experiment each operational condition was kept for more than one month, and the biomass was expected to be adapted even with some inhibition of the biological processes from the saline environment.

The maximum nitrification and denitrification rates were measured directly in the two process tanks by cancelling all internal flows and dosing systems adding desired chemicals directly into the process tanks and then following the decrease in concentrations.

Inhibition of nitrification

During operation of the activated sludge pilot plant, sludge samples were taken from the plant in order to investigate, in batch laboratory experiments, the impact on the nitrification of sudden changes in the chloride and nitrite concentration. Sudden changes in the chloride concentration can be the result of the change of coal used in the power station or a change of scrubber operation. Sudden changes in the nitrite concentration have been seen during laboratory-scale experiments due to an inhibition of the last step of the nitrification process where the nitrite is oxidised to nitrate, hence nitrite is the end product instead of nitrate. The impact of the anaerobic storage of the biomass on the activity of the nitrifiers was also investigated.

The impact of sudden variations in the chloride and nitrite concentrations was investigated at chloride levels of approx. 10, 16 and 20 g Cl^-/l. The experimental system consisted of five 2 litres plexiglass batch reactors placed in a thermostat controlled water bath. In all experiments the temperature was kept at 30°C. The effect of the anaerobic storage of biomass was investigated at chloride levels of 15 and 20 g Cl^-/l and at a storage temperature of 20-23°C.

With regard to acute chloride inhibition the chloride concentration was varied in the range of approximately ±25% and ±50% compared to the actual chloride concentration of the activated sludge. This means that for activated sludge adapted to 20 g Cl^-/l the chloride concentration range was 10-30 g Cl^-/l. Acute nitrite inhibition was tested with concentrations in the range of approx. 15-200 mg N/l. Finally, anaerobic storage of the activated sludge was tested for one, two and four days.

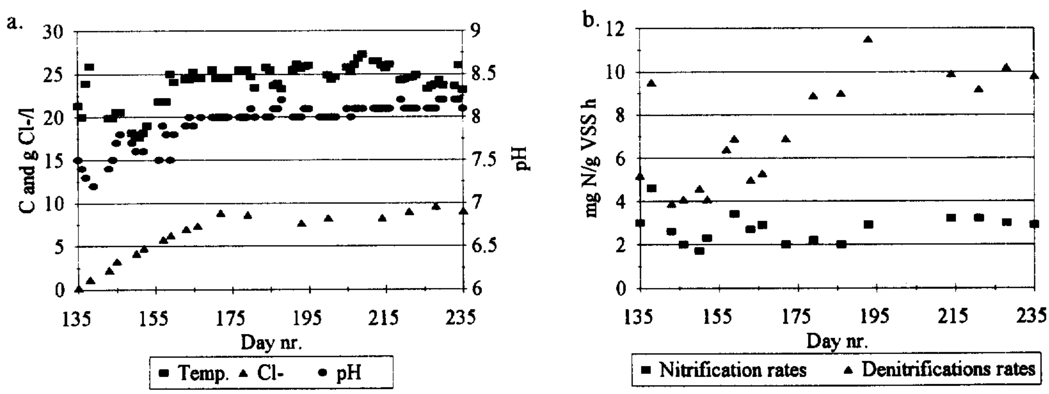

Figure 2. (a) Temperature, chloride concentration and pH during the adaption period of the municipal activated sludge to high salinity. (b) Maximum nitrification and denitrification rates during the adaption period of the municipal activated sludge to high salinity.

RESULTS AND DISCUSSION

Figure 2a shows the process parameters of temperature, chloride concentration and pH during the adaption period of the municipal activated sludge. In Figure 2a it is seen that the chloride concentration increased slowly to approx. 10 g Cl^{-}/l in the course of forty days and the temperature was controlled at 25°C. The pH varied between 7.2 and 8.2. Stable process conditions were kept for sixty days, and the measured maximum nitrification and denitrification rates stabilised at approx. 3 and 10 mg N/g VSS•h, respectively, as shown in Figure 2b.

Figure 3 shows the process parameters temperature, chloride concentration and pH during the periods with varying operational conditions described under Materials and Methods. Maximum nitrification and denitrification rates were measured and the results are shown in Figure 4.

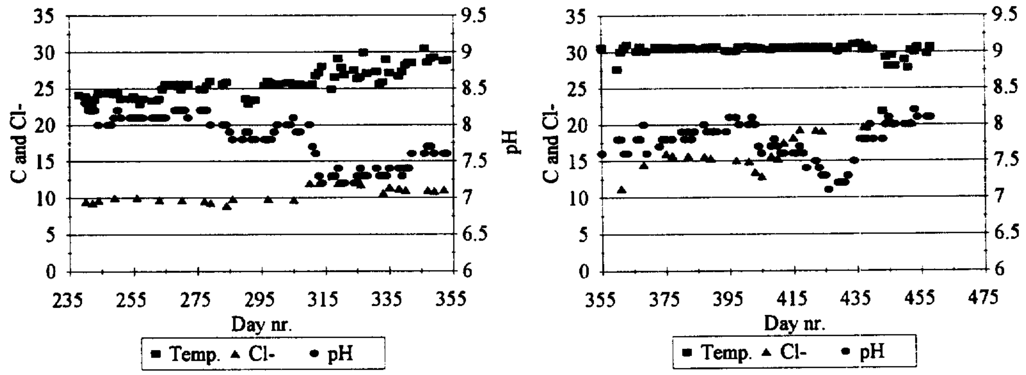

Figure 3. Temperature, chloride concentration and pH.

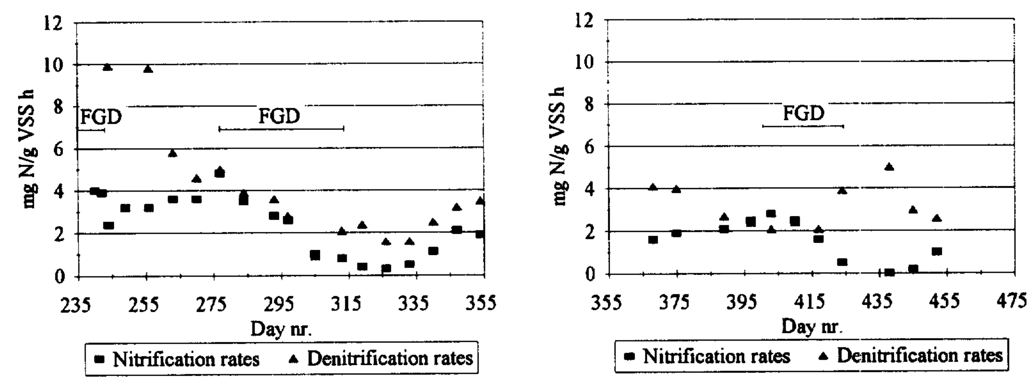

Figure 4. Maximum nitrification and denitrification rates.

Figure 4 shows the periods where modified FGD wastewater was used as influent. During this period, toxic effects on the biomass activity from high concentrations of heavy metals occurred twice due to insufficient removal in the chemical precipitation. Therefore, the pilot plant influent had to be switched to artificial wastewater for approximately half the time to prevent inhibition due to the heavy metals. The nitrification process showed a higher sensitivity to the high concentration of heavy metals than the denitrification process. The nitrification activity decreased to zero during the two toxic events and then increased slowly to the former maximum rates in the course of three weeks. As to the denitrification rates, only a minor reduction was observed in one of the toxic events.

The problem observed with heavy metals stresses the importance of ensuring a reliable control of the chemical precipitation plant to prevent toxic effects on the biological WWTP for the nutrient removal. To prevent plant failure during toxic events a safety system for the biological WWTP must be established, i.e. to ensure immediate restart of the plant with stored adapted sludge. Storage facilities for adapted sludge must therefore be included in the WWTP. During periods without problems caused by heavy metals, only small changes in the rates were found at the different operating conditions. At 30°C and 20 g Cl^{-}/l, maximum nitrification and denitrification rates of approx. 2 and 3 mg N/g VSS•h, respectively, can be expected.

At a load of approx. 1 mg N/g VSS•h the maximum obtainable nitrification rate at the end of the adaption period was about three times this load, which is a typical difference. The difference between the maximum denitrification rate and the load at the end of the adaption period was then ten times as high, which is a high but normal difference. The maximum nitrification rate decreased from three to two times the load when modified FGD wastewater was used as influent. Regarding the maximum denitrification rate a decrease from ten to three times the load was seen. The large decrease in the maximum denitrification rate must be the result of inhibition caused by unknown components in the FGD wastewater. In another experiment under the SALWAS project (see acknowledgement) the denitrification process alone was examined in the same pilot plant and with the same FGD wastewater. The load was approximately 7 mg N/g VSS•h and a maximum denitrification rate of approx. 40 mg N/g VSS•h was found for the same process conditions with regard to temperature and chloride concentration. This means that it is the load combined on the nitrification and the denitrification processes that is decisive for the maximum rates that can be obtained as the percentage of active biomass out of the total biomass depends directly on the total load. Measurement of the volatile suspended solids (VSS) concentration gives the total biomass but not the active biomass. The expected total nitrogen load on the biological processes is therefore important when choosing the design rates of the nitrification and denitrification processes for full-scale plants.

The change of activated sludge properties was followed by measurement of the suspended solid (SS), VSS and of the sludge volume after 30 minutes (SV_{30}). Figure 5 shows the variations in the SS and the VSS concentrations and the percentage of VSS in SS.

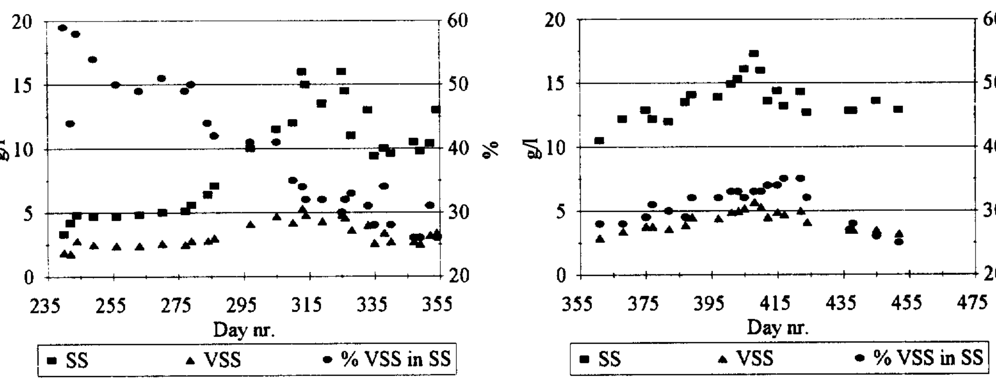

Figure 5. SS and VSS concentrations and percentage of VVS in SS.

The adapted municipal activated sludge loaded with artificial wastewater showed a typical SS/VSS ratio of 60% VSS in the SS. For each period with FGD wastewater influent, the VSS/SS ratio decreased due to the precipitation of gypsum onto the activated sludge. The fluctuations seen in the SS and VSS concentrations were caused by extraction of excess sludge from the process tanks. If modified FGD wastewater is continuously introduced, 25% VSS in the SS can be expected.

Figure 6 shows the SV_{30} and the calculated sludge volume index (SVI) = SV_{30}/SS.

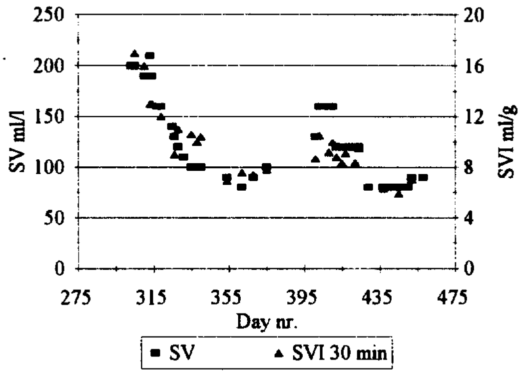

Figure 6. Measured SV_{30} and calculated SVI.

By comparing Figures 5 and 6 the observed SV_{30} and SVI variations can be correlated to the percentage of VSS in the SS. As expected, the settleability of the activated sludge decreased as the percentage of biomass in the sludge increased. The measured SVI was very low compared with SVI for municipal activated sludge, which is typically 150 ml/g, owing to the precipitation of gypsum that serves as carrier media for the biomass and therefore increases the sludge density.

In the effluent, the concentrations of chemical oxygen demand (COD), SS, nitrate-N (NO_3-N), nitrite-N (NO_2-N), ammonium-N (NH_4-N) and total Kjeldahl-N (TKN) were measured. For COD concentrations of approx. 150 mg COD/l were measured. Owing to constant aeration in the small process tank the effluent COD is expected to consist mostly of inert COD and partly of COD from the SS in the effluent. Despite good settleability of the activated sludge the effluent concentrations were approx. 40 mg SS/l. This indicates a poor flocculation of the biomass, and a coagulation chemical is needed to decrease the SS concentration in the effluent. As to the TKN concentration, high levels at approx. 15-20 mg TKN/l were measured as a result of high COD concentrations in the effluent. A concentration of inorganic nitrogen below 8 mg N/l was found.

Inhibition of nitrification

As regards acute chloride inhibition no significant indication could be found in the experimental series with 10 g Cl^-/l. The increased activity found, when lowering the chloride concentration by 50% was approx. 40% for the 16 and 20 g Cl^-/l. The decrease in activity resulting from the 50% chloride increases was approx. 20% and 30% for the 16 and 20 g Cl^-/l references, respectively. As to the chloride level the experiments did not prove that the sensitivity of the nitrifiers increased at high chloride concentrations.

The results of the acute nitrite inhibition tests generally showed an inhibition in the range of approx. 10-15% at the low and high chloride levels, when the nitrite nitrogen concentration was increased up to 15-20 mg N/l. At all chloride levels an increase of the nitrite concentration up to approx. 100 mg N/l resulted in an inhibition of approx. 40% of the reference nitrifying activity. The phenomenon of inhibition by nitrite is pH dependent, so that inhibition increases as the pH drops. As the pH was not controlled in the experiments, it cannot be excluded that some of the effects were due to the varying pH, however as the pH in all events was above 7.4 the effect would have been very limited.

The investigation of the acute inhibition of the nitrifiers from chloride or nitrite concentrations demonstrated that acute inhibition can be expected if the process conditions are not controlled properly. Nevertheless, the experiments also demonstrated that with suitable operational strategies the inhibition of the nitrifiers from rapid changes in the chloride and nitrite concentrations can be managed.

Anaerobic storage of activated sludge during up to four days only slightly affected the nitrification activity, as approx. 80% of the initial activity was left after four days. The experiments showed that it is possible to store excess sludge anaerobically up to four days to serve as backup sludge for restarting the plant.

CONCLUSION

With an adequate adaption period and slowly increased temperature and chloride concentration, municipal activated sludge can be adapted to the high-temperature and high-salinity wastewater.

When using combined nitrification and denitrification an overgrowth of the autotrophic nitrificants by the heterotrophic denitrificants was not observed. The activated sludge process is therefore able to perform the combined nitrification and denitrification of the high-salinity wastewater in a one-sludge system.

The activated sludge could be adapted to operational conditions of up to 30°C and 20 g Cl^-/l with maximum nitrification and denitrification rates of approx. 2 and 3 mg N/g VSS•h, respectively.

The nitrification process was very sensitive to elevated concentrations of heavy metals as heavy metals accumulated in the sludge and caused a toxic effect on the nitrifiers.

Inhibition of the nitrifiers in the case of a rapid increase of chloride or nitrite concentration was found, but with suitable operational strategies inhibition can be limited.

Only around 20% of the nitrifying activity was lost after four days of anaerobic storage of activated sludge at 20-23°C.

In the effluent, concentrations of inorganic nitrogen below 8 mg/l can be obtained.

The settleability of the activated sludge was good due to a precipitation of gypsum onto the activated sludge but the flocculating properties were still poor which calls for coagulation chemicals to ensure the effluent quality.

ACKNOWLEDGEMENT

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