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Original Research Paper

Investigation of the Removal Efficiency of Foulants by Anoxic/Aerobic Membrane Bioreactor Treating Pickle Wastewater

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ABSTRACT

Pickle wastewater was treated by anoxic/aerobic membrane bioreactor. Three groups of experiments were designed under the condition of different feed loadings to research on treating pickle wastewater by mixed MBR with PVDF. In the case of normal temperature, the salinity was 2-3%, the bio-film density was 15% in both of the anoxic and aerobic zones; DO was 1mg/L and MLSS was 2000 mg/L in the anoxic zone; DO was 4-5mg/L and MLSS was 6000 mg/L in the aerobic zone. The ratio of the recycling mixture was 200%; the sorption pumps were turned off for 3 minutes in every 10minutes; the pressure gradient was 15KPa. According to the study of removal efficiencies of organic pollutant, it indicates that when the feed loading is 1.2 kgCOD/(m^3.d), the removal efficiency is optimal. And the effluent concentrations of COD, NH_4^+-N and SS satisfy the requirement of the first class discharge standard of comprehensive discharge standard of sewage (GB8978-1996).

INTRODUCTION

Nowadays, many food industrial wastewaters are discharged without effectively treated. Because of their high salinity, complex water quality and the defective treatment, the receiving water environment is imperiled by the pickle wastewater.

In the pickle wastewater, the salinity was as high as 2%~15%. There are plentiful kinds of inorganic ions in it like Cl^-, SO_4^{2-}, Na^+, Ca^{2+}. The organic pollutants were 3~25 g/L, and the level of nitrogen and phosphorus was high. Therefore, treatment of this wastewater was hard to complete.

For now, the emphasis is mainly on organics removal during high salinity wastewater treatment, with only a few studies on dechlorination and phosphorus removal. Campos et al. (2002) found that activated sludge system would lose effect when the salinity was higher than 3% (measured by NaCl). Chen et al. (2003) found the maximum nitrification of activated sludge system as 6.5g/L. Dincer & Kargi (2001) indicated that the minimum sludge age for nitrification in activated sludge system should increase from 12d with no salinity to 25 d with 3% salinity. Yu et al. (2003) studied the nitrifying capacity of wastewater mixed with seawater; they support SSND would be taken place in domestic wastewater mixed with not more than 10.5% seawater (salinity was about 0.38%). Zhou et al. (2005) treated saline wastewater generated by seafood processing industries with an SBR under the salinity ranging from 0.03% to 0.2%, and the effect of denitrification was good. There are many elements affecting the effect of denitrification, but DO and pH are the main factors. Ng et al. (2000) treated artificially mixed wastewater with SMSBR. They found that the effect of nitrification was ideal when the nutrients and DO were suitable for the system. Surmacz et al. (1996) kept the pH at 8.0 in influent and the density of FA in the range of 1~6 mg/L in mixed liquor, and the rate of nitrification was about 0.06 gN/g MLSS.d. Sridang et al. (2008) found MBR sludge could accept real seafood processing wastewater (salinity stress was 1.4-1.6 g/L) and tolerate a wide range of influent COD. Compared with SBR, the removal rate of TN with a low feed loading in the membrane bioreactor was obviously higher.

It reports that, the removal rate of TP in MBR can reach 74–82%, when treating synthetic domestic wastewater after thermo chemical pretreatment. Biological phosphate removal in an MBR is because of the development of PAOs. Biological phosphorus removal process was affected by high salinity. Kargi & Dincer (1998) found that the phosphate removal rate in activated sludge system was decreased from 84% to 22%, as salinity increased from 0 to 6%. The phosphate removal rate in system which was seeded with salt-tolerant bacteria was 31% with the salinity of 5%. Panswad & Anan (1999) found that the biological phosphate removal rate was decreased from 48% to 10%, as salinity was increased from 0 to 3%. Those showed biological phosphorus removal with high salinity, became a difficult issue.

MBR is an efficient biological treatment technology that is a combination of membrane efficient filtration and biological treatment technology. It was difficult to treat the pickle wastewater, because of its large water quantity, and high density of organic matter.

Traditional secondary sedimentation tank was replaced by membrane separation assemblies to get rid of the influence of sludge settlement, and the MBR would gather much of microbial biomass to reduce the restraint to active sludge by high salinity and the influence of the treatment system. Efficient solid-liquid separation in membrane module and biodegradation in bioreactor are combined by the MBR. Even though, there were some reports indicating that the membrane filtration process would be affected by rapid salinity changes with relatively high salt density, with high-level automatic control, the pickle wastewater treatment system could be easier controlled.

The purpose of this investigation was to develop an acclimation strategy to find the effect on dechlorination and phosphorus removal in an anoxic/aerobic membrane bioreactor and measure other targets such like COD, SS at the same time.

MATERIALS AND METHODS

Pickle wastewater: The pickle wastewater was obtained from an anaerobic tank located in Chongqing fuling pickle group wastewater treatment station. The characteristics of the aniline wastewater were as follows: salinity, 2%-3%; COD, 770-1240 mg/L; NH_4^+-N, 103-191 mg/L; TN, 207-409 mg/L; PO_4^{3-}, 21-48 mg/L, SS, 237-525 mg/L.

Anoxic/aerobic membrane bioreactor: The anoxic/aerobic membrane bioreactor used in this experiment was welded together with PVC board, whose size was 1m×0.5m×1.38m, the effective depth was 1.3 m, and the effective volume was 0.65 m^3. Three zones (anoxic zone, aerobic zone, bio-film formation zone) were divided by PVC board. The size of anoxic zone was 0.2m×0.5m×1.38m, the size of aerobic zone was 0.5m×0.5m×1.38m, and the size of bio-film formation zone was 0.3m×0.5m×1.38m. A blender was set in the anoxic zone, perforated pipe sparkers were set in aerobic zone and bio-film formation zone was independent. Semi soft bio-film filler was set in the aerobic zone, the bio-film density was 15%, the hollow fiber membrane module produced by Tianjin Motimomembrane technology Co. LTD., was set in the bio-film formation zone, the area of membrane was 1 m^2, the diameter of micro-void was 0.2 μm, and the material was PVDF membrane. Each membrane module was controlled by independent valve which could control the water volume by open and close. Because of the pressure difference caused by sorption pumps between membranes' inside and outside, the pickle wastewater could be pressed into the inside of membrane, and after the treatment, the wastewater was discharged through the collector pipe. At the bottom of the reactor a micro-void pipe with the diameter of 20 mm was set for aeration, and the pipe got the air from an air pump. The anoxic/aerobic membrane bioreactor is shown in Figs. 1 and 2.

The way by which the reactor operated is continuous injection and intermittent drainage. Firstly, the wastewater was pressed to the anoxic zone by sorption pumps. In the anoxic zone the wastewater is mixed with the reflux liquid which came from the aerobic zone, and got the nitrogen pollutant removed by denitrification. Then the most of the organic

Fig. 1: The profile and photograph of test device.

Fig. 2: The profile and photograph of test device.

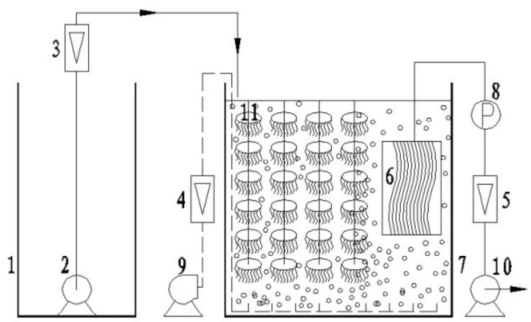

Fig. 3: The flow diagram of the reactor.

pollutants in mixed liquor were removed by microorganisms in the bio-film zone. Because of the high density of activated sludge around the membranes, the organic pollutants could be removed completely. Finally, under the pressure of the sorption pumps, the wastewater was pressed into the inside of membranes becoming treated water. The sorption pump worked intermittently and controlled by PLC. The flow in reactor was counterclockwise circulation which was driven by air. It was realized by aeration intensity control in anoxic zone and aerobic zone. The flow diagram is shown Fig. 3.

Analytical methods: Samples were analyzed by using methods described in MEP China (2002).

pH was measured with the rapid determination method; SS by the filter weight method; DO by the rapid determination method; temperature by the thermometer; COD by the potassium dichromate method; BOD_5 by the standard oxygen difference method; TN by ultraviolet spectrophotometry method; NH_4^+-N by the Nessler's reagent spectrophotometry method; and phosphorus by the resistance of alkali fusion-antimony molybdenum spectrophotometry method. The structure of micro-void was observed by scanning electron microscope.

RESULTS AND DISCUSSION

Reactor startup: The reactor was seeded with the sludge from secondary sedimentation tank located in Fuling wastewater treatment plant. The color of seed sludge was gray, and a large number of ciliates and rotifera were found in the seed sludge with microscope. A part of seed sludge was poured into hydrolysis zone keeping the MLSS at 2g/L. The rest of seed sludge, whose color was dark red after 48h stuffy aeration, was poured into membrane zone without supinate. The MLSS in bio-film zone was kept over 5g/L. The fillers taken from Fuling pickle group wastewater treatment station aerobic zone were placed in bio-film formation zone with the density of membrane at 15%. The HRT was kept on 24h, DO<1 mg/L in anoxic zone, DO>3 mg/L in aerobic and membrane zone, and the reflux ratio of mixed liquor as 200%.

The influent was from Fuling pickle group wastewater treatment station. After 20 days of acclimating activated sludge, the COD removal rate was kept over 80% in this system; it indicates that the reactor startup was completed for removing organic pollutants. During the acclimation, at a high level of reflux ratio, the DO was hard to be kept below 1 mg/L in hydrolytic zone; the rate of denitrification was retarded much. The best reflux ratio, reached from several experiments, is 200%; under this ratio, the DO can be kept below 1 mg/L.

COD: The COD removal rates with different feed loadings are shown in Figs. 4 and 5. When feed loading was 0.7 kgCOD/(m^3.d), average value of COD was 971.21 mg/L in influent and 48.89 mg/L in effluent; the COD removal average rate was 94.91%. The level of COD in effluent was less than 50mg/L at last. Because of most of organic macromolecules were filtered by membrane module, the COD in effluent was at a low level.

When feed loading was 0.9 kgCOD/(m^3.d), average value of COD was 960.16 mg/L in influent and 80.43 mg/L in effluent; the COD removal average rate was 91.67%. Compared with feed loading at 0.7 kgCOD/(m^3.d), the COD removal rate dropped 3.24%, from 94.91% to 91.67%. It indicates that the increase of feed loading does not much affect the COD removal rate; the resisting impact loading ability of this system is stronger.

When feed loading was 1.2 kgCOD/(m^3.d), average value of COD was 1022.26 mg/L in influent and 136.86 mg/L in effluent with the COD removal rate of 86.85%. Compared with feed loading at 0.9 kgCOD/(m^3.d), the COD removal rate dropped 4.82%, from 91.67% to 86.85%. The reason might be that a high level of MLSS made the endogenous respiration of microorganisms stronger and microorganisms produce more soluble metabolin. Strong endogenous respiration made microorganisms lyses, the activity of sludge was reduced by this cell debris and soluble metabolin. The level of COD in effluent was beyond 100 mg/L, the needs of the first class discharge standard of comprehensive discharge standard of sewage (GB8978-1996).

NH_4^+-N: The ammonical nitrogen removal rates with different feed loadings are shown in Figs. 6 and 7. When feed loading was 0.7 kgCOD/(m^3.d), average concentration of NH_4^+-N was 140.86 mg/L in influent and 5.36 mg/L in effluent; the NH_4^+-N removal average rate was 96.41%. At the beginning, the NH_4^+-N removal average rate was only 75.20%, the reason might be that the proliferation rate of nitrobacteria was low; it would take more time to reach a sufficient quantity to get a suitable NH_4^+-N removal rate. At the 13d, the MLSS in system was stable and specific growth rate of sludge was 0; the COD removal average rate was at a high level and the NH_4^+-N removal average rate has increased because of the increase of nitrobacteria. Compared with aerobic membrane bioreactor, the NH_4^+-N removal average rate was better obviously. The reason might be after anoxic zone set, the nitrite and nitrate accumulated in aerobic zone were taken by reflux, helping the nitrification.

When feed loading was 0.9 kgCOD/(m^3.d), average concentration of NH_4^+-N was 131.79 mg/L in influent and 12.48 mg/L in effluent; the NH_4^+-N removal average rate was 90.61%. The average concentration of NH_4^+-N fluctuated in influent, but the average concentration of NH_4^+-N was kept at a low level all the time, the nitrification was almost complete. The reason might be that the nitrobacteria with long generation cycle were enriched by intercepting effect of membranes; because of the high salinity, the settling ability of sludge was poor, and the dispersion degree of sludge was high. This benefited the oxygen transfer between cells, it was a suitable environment for growth. Compared with feed loading at 0.7 kgCOD/(m^3.d), the NH_4^+-N removal rate dropped 5.8%, from 96.41% to 90.61%. It indicates that there are some effects on NH_4^+-N removal, but the cencentration of NH_4^+-N in effluent is within 15 mg/L, the needs of the first class discharge standard of comprehensive discharge standard of sewage (GB8978-1996).

When feed loading was 1.2 kgCOD/(m^3.d), average cencentration of NH_4^+-N was 141.23 mg/L in influent and 22.21 mg/L in effluent; the NH_4^+-N removal average rate was 83.34%. Compared with feed loading at 0.9kgCOD/(m^3.d), the NH_4^+-N removal rate dropped 6.27%, from 90.61% to 83.34%. The reason might be because of the high feed loading and short HRT; the sludge in membrane zone could not get enough nutrients and the soluble metabolin in membrane zone restrained heterotrophs. This results in the nitrobacteria to get enough oxygen, and the NH_4^+-N removal rate dropped. Under this feed loading, the cencentration of NH_4^+-N in effluent was beyond 15 mg/L, the needs of the first class discharge standard of comprehensive discharge standard of sewage (GB8978-1996).

Total Nitrogen (TN): The total nitrogen removal rates with different feed loadings are shown in Figs. 8 and 9. When feed loading was 0.7 kgCOD/(m^3.d), average value of TN was 278.60 mg/L in influent and 97.49 mg/L in effluent; the TN removal average rate was 64.40%. At the beginning, the TN removal averaged rate was only 38.67%, but as the time went by, the removal averaged rate increased and after the 22d it became stable. Compared with the NH_4^+-N removal, the stable time of TN removal was 9d longer, and the reason for this might be that the enrichment time of denitrifying bacteria was longer than nitrobacteria. Compared with aerobic membrane bioreactor, the TN removal averaged rate was better obviously. The reason might be that the denitrification in aerobic membrane bioreactor took place inside Zoogloea. Inside of membrane and the corner of reactor, the denitrifying bacteria were surrounded by the aerobic bacteria, and the denitrifying bacteria could get enough nutrients. In this system, there was suitable anoxic environment and enough carbon source and nitrate nitrogen; it was beneficial to denitrification.

When feed loading was 0.9 kgCOD/(m^3.d), average value of TN was 289.04 mg/L in influent and 116.31 mg/L in effluent; the TN removal averaged rate was 58.46%. The environment of this system was suitable for living of denitrifying bacteria; and as a result the TN removal averaged rate was higher than that in aerobic membrane bioreactor with higher feed loading,

When feed loading was 1.2 kgCOD/(m^3.d), average value of TN was 302.68 mg/L in influent and 139.47 mg/L in effluent; the TN removal averaged rate was 50.48%. Compared with feed loading at 0.9 kgCOD/(m^3.d), the TN removal rate dropped 7.98%, from 58.46% to 50.48%. The reason for this might be that higher feed loading and short HRT lowered the activity of denitrifying bacteria. The time that the microorganisms affected wastewater was not enough; but under this feed loading, the COD removal averaged rate was also dropped, the rising level of organics in reflux was benefit to denitrifying bacteria. At last the TN removal averaged rate was dropped a little.

Soluble phosphates: The phosphate removal rates with different feed loadings are shown in Figs. 10 and 11. When feed loading was 0.7 kgCOD/ (m^3.d), average value of soluble phosphates was 35.63 mg/L in influent and 27.65 mg/L in effluent; the soluble phosphates removal averaged rate was 22.30%. The density of soluble phosphates in effluent was fluctuated with the density of soluble phosphates in influent. The reason might be that after the reactor startup, the sludge growth rate was slow down, the need of soluble phosphates as nutrients for microorganisms was reduced; and during the experiment, the rich-phosphate sludge was not discharged.

When feed loading was 0.9 kgCOD/(m^3.d), average value of soluble phosphates was 32.12 mg/L in influent and 22.73 mg/L in effluent; the soluble phosphates removal averaged rate was 25.54%. The beginning, the rich-phosphate sludge was washed out during chemical cleaning of the membrane, and this was the reason that crest came out (Fig. 11). Three days later, the soluble phosphates removal rate returned to a low level again. Compared with feed loading at 0.7 kgCOD/(m^3.d), the change of soluble phosphates removal rate was

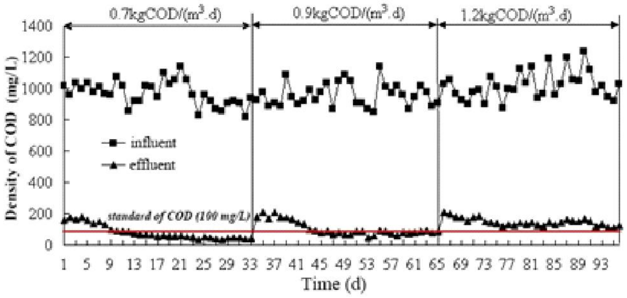

Fig. 4: COD concentration variations in influent and effluent with different feed loadings..

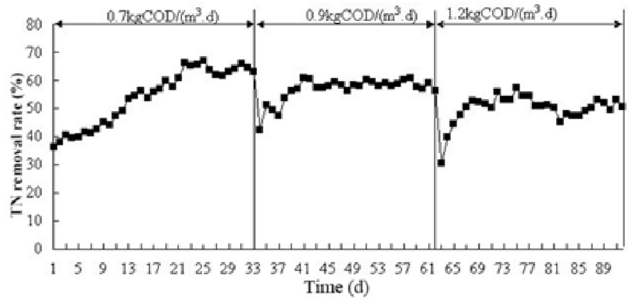

Fig. 5: COD removal rate variations with different feed loadings.

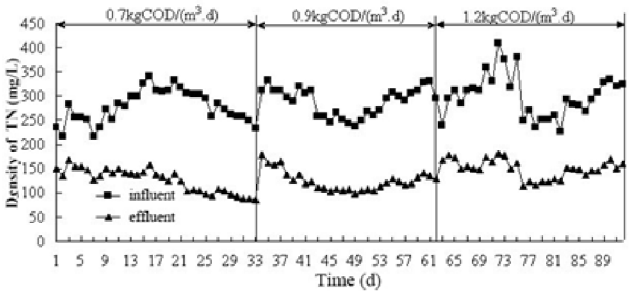

Fig. 6: NH_4^+-N concentration variations in influent and effluent with different feed loadings

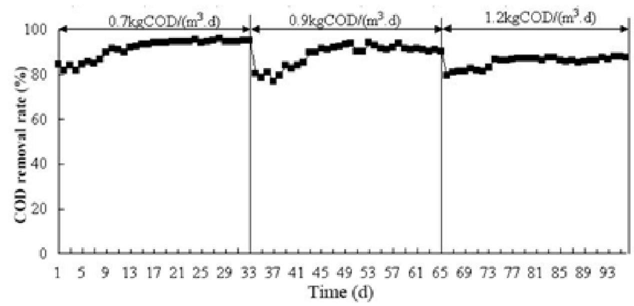

Fig. 7: NH_4^+-N removal rate variations with different feed loadings.

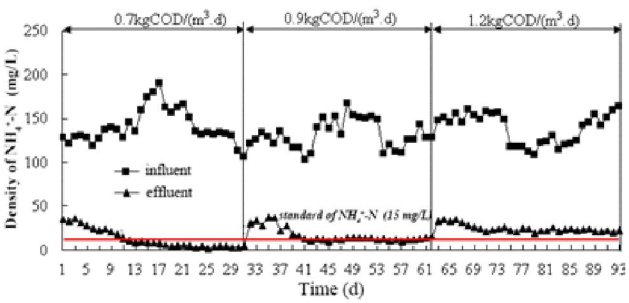

Fig. 8: TN concentration variations in influent and effluent with different feed loadings.

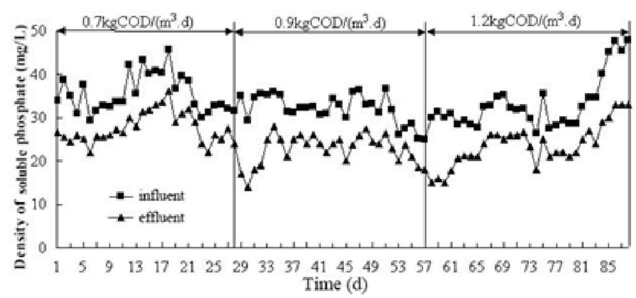

Fig. 9: TN removal rate variations with different feed loadings.

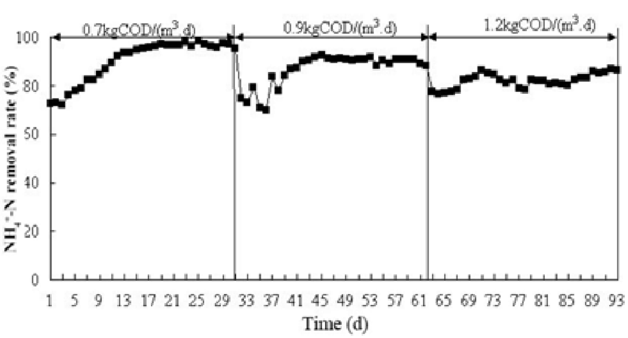

Fig. 10: soluble phosphate concentration variations in influent and effluent with different feed loadings.

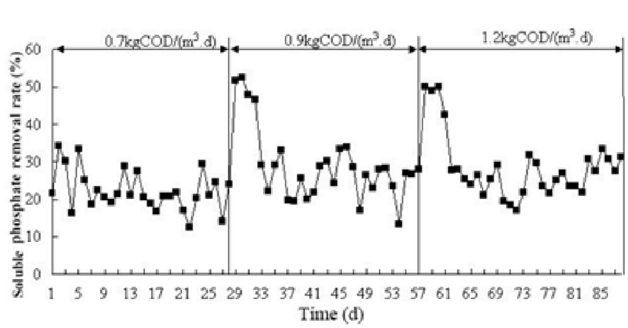

Fig. 11: Soluble phosphate rate variations with different feed loadings.

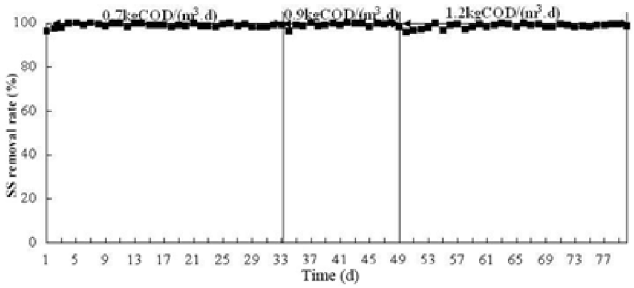

Fig. 12: SS concentration variations in influent and effluent with different feed loadings.

not obvious, which indicates that the influence of higher feed loading to soluble phosphates removal is limited.

When feed loading was 1.2 kgCOD/(m^3.d), average value of soluble phosphates was 33.27 mg/L in influent and 23.73 mg/L in effluent; the soluble phosphates removal averaged rate was 25.73%. **A**t the beginning, the removal rate was same as the feed loading at 1.2kgCOD/(m^3.d), but when system was stable, the rate returned to low level again (Fig. 11).

The results show that biological phosphorus removal is not enough, and a chemical phosphorus removal is necessary to reach the need of the first class discharge standard of comprehensive discharge standard of sewage (GB8978-1996).

Suspended solids (SS): The suspended soilids removal rates with different feed loadings are shown in Fig. 12. When feed loading rate was 0.7 kgCOD/(m^3.d), average value of SS was 395 mg/L in influent and less than 10 mg/L in effluent; the soluble phosphates removal averaged rate was more than 97%. The concentration of SS in influent was high, but the strong filtration of fenestra made the value of SS in effluent at a low level all the time. It seems that under high salinity the sludge particulates will be compact and settling ability will be reduced. Those problems would be solved, because of the filtration through membrane. Compared with aerobic membrane bioreactor, this system's resisting impact loading ability of SS was stronger.

When feed loading was 0.9 kgCOD/(m^3.d), average value of SS was 384 mg/L in influent and less than 10 mg/L in effluent; the soluble phosphates removal averaged rate was more than 98%.

When feed loading was 1.2 kgCOD/(m^3.d), average value of SS was 383.94 mg/L in influent and less than 10 mg/L in effluent with the soluble phosphates removal averaged rate of more than 97%.

CONCLUSIONS

In conclusion, when feed loading was 0.9 kgCOD/(m^3.d), the treatment of pickle wastewater with anoxic/aerobic membrane bioreactor using PVDF membrane was the best option. The COD removal averaged rate was 91.67%; the NH_4^+-N removal averaged rate was 90.61%; the TN removal averaged rate was 58.64%; the SS removal averaged rate was over 97%; but the effect on soluble phosphates removal was not so appropriate, only 25.54% of removal (without discharging the rich-phosphate sludge).

Compared with aerobic membrane bioreactor, the TN removal averaged rate is improved a lot in anoxic/aerobic membrane bioreactor; it raised up to over 80%.

These results indicate that it is feasible to treat pickle wastewater with anoxic/aerobic membrane bioreactor, the concentrations of COD, NH_4^+-N and SS in effluent meet the needs of the first class discharge standard of comprehensive discharge standard of sewage (GB8978-1996).

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