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Original Research

Treatment of Mixed Chemical Wastewater by a Two-Stage A/O Process for Elimination of COD Nitrogen and Toxic Matters

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Abstract

In our work a two-stage A/O system consisting of two independent A/O subsystems was used to remove high concentrations of COD, nitrogen, and toxic matter from mixed wastewater discharged by a comprehensive chemical group. The mixed liquid return was not adopted, and the sludge return ratio was kept at a high value of 100-200% to maintain high usable activated sludge concentration. Adequate $NaHCO_3$ was added to keep the influent alkalinity/KN ratio around 7.14 to 1. The system was running stably during the whole experimental period. Subsystem one obtained high COD and organic nitrogen removal capability without being influenced by the increasing COD loading. 87.6% COD was removed and 75.7% org-N was transformed to NH_4^+-N. Due to the low COD/KN ratio created by subsystem one, the nitrification efficiency of subsystem two reached a high value of 92.1%. Besides, aerobic biological oxidation of oxic tank one showed excellent ability on toxic matter elimination. The acute toxicity of the whole system dropped from 0.165 to 0.042 mg $HgCl_2$/L. It has been proven by this study that, using the two-stage A/O system with sludge return only to treat COD nitrogen and toxic matters, laden mixed wastewater from comprehensive chemical groups may be feasible.

Keywords: high kjeldahl nitrogen, two-stage A/O system, independent nitrification, acute toxicity

Introduction

Large comprehensive chemical groups always consist of different chemical factories such as fluorochemicals, petrochemicals, coal-chemicals, chloro-alkali chemicals, pharmaceuticals, etc. The mixed wastewater discharged from these groups contains highly concentrated COD, nitrogen, and toxic matters like fluoride, phenol, cyanide, persistent organic compounds, etc. [1, 2]. Direct discharge of the sewage can pollute the receiving waterbody seriously and poison the aquicolous and terricolous creatures. Therefore, removal of COD, nitrogen, and toxic matters before discharge is of great importance.

To treat wastewater discharged from a single chemical factory, many physicochemical technologies were used in the former studies, such as: catalytic wet air oxidation [3], supercritical water oxidation [4], and O_3 and O_3/H_2O_2 processes [5], etc. Although these technologies can obtain good COD and nitrogen removal, the main constraints for their application are their strict operating requirements and

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Table 1. Sizes, volumes, and HRTs of units in a two-stage A/O system.

Unit		Size (cm)		Active volume	HRT
		Diameter	Height	(L)	(h)
Subsystem one	anoxic tank	41	95	78.4	7.84
	oxic tank	47	84	136.4	13.64
	settling tank	50	40	96.2	
Subsystem two	anoxic tank	50	75	90.4	9.04
	oxic tank	57	100	220.7	22.07
	settling tank	50	45	113.8	

high running costs. Comparatively, bio-treating processes like anaerobic/anoxic/oxic process (A^2/O) [6, 7], membrane bioreactor (MBR) [8, 9], biofilm reactor [1, 2], and anaerobic baffled reactor (ABR) [10], which are easier to manage and much lower in cost, are more popular in lab-scale experiments and full-scale applications. However, Stronge inhibition of high COD and toxic matters on microorganisms is a knotty problem for mixed chemical wastewater treatment, thus the research on treatment of such wastewater was rarely reported.

Oxygen affinity of heterotrophic COD oxidizers is higher than autotrophic nitrifiers, thus in bio-treating systems under adequate biodegradable COD conditions, nitrification is inhibited by heterotrophic COD oxidation [11]. Mosquera-Corral et al. [12] found fed C/N ratio higher than 0.3 g TOC/g N could drastically decrease NH_4^+-N oxidation to 10% with a SHARON reactor. Rene et al. [13] studied the COD/N ratio effects on the performance of sequencing batch reactor, and claimed that within the first hour of aerobic reaction, over 95% of influent COD was removed with little NH_4^+-N removal. Other studies [14-16] also reported the inhibition of NH_4^+-N nitrification due to high organic matter concentration or high COD/KN ratio.

On the other hand, under low substrate COD/N ratio, nitrifying bacteria were enriched in the granules in a novel granular sludge sequencing batch reactor [17]. Similar phenomena had been observed in biofilm reactors [18, 19].

COD oxidation and nitrification are carried out by two kinds of completely different microorganism, which can inhibit each other under two opposite COD/N ratio conditions. Thus an independent COD oxidation and nitrification system is necessary, especially for high COD, kjeldahl nitrogen concentration, and COD/N ratio wastewater treatment [20].

In this study, we introduced a two-stage A/O process with an independent sludge system, which separates COD oxidizers and nitrifiers in two subsystems. Real mixed wastewater produced by a comprehensive chemical group containing high concentrations of COD, nitrogen, and toxic matters was treated. COD and nitrogen removal efficiency was examined, the acute toxicity of the wastewater from different treating units was bioassayed, and the whole system's feasibility was evaluated.

Materials and Methods

Two-Stage A/O System

The two-stage A/O system consists of two subsystems: subsystem one for COD removal and subsystem two for nitrogen removal. Each subsystem was a whole A/O system with an anoxic tank, an oxic tank, and a settling tank that could finish its removal work independently. The schematic diagram of the two-stage A/O system is presented in Fig. 1, the sizes and active volumes of units of the Two-stage-A/O system are presented in Table 1.

The influent flux was maintained at 10 L/h during the whole experiment period, the HRTs of different units were listed in Table 1. The mixed liquid returns of the two subsystems were not setted and the sludge return ratios were set at 100~200% to maintain a high usable sludge concentration.

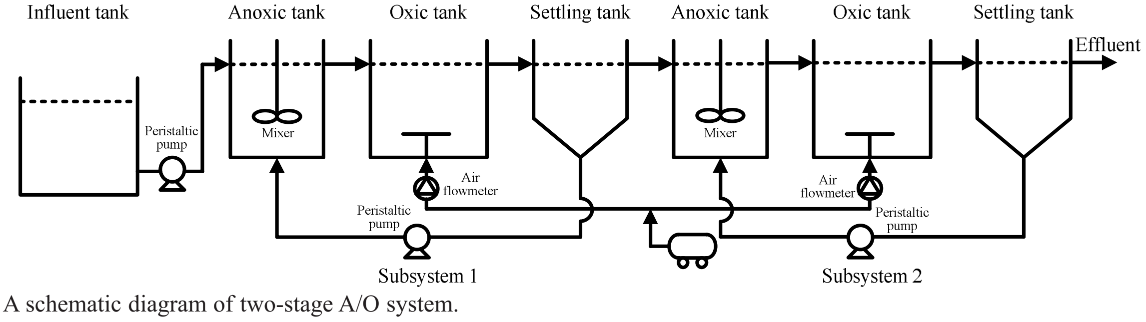

Fig. 1. A schematic diagram of two-stage A/O system.

Table 2. Soluble pollutants acute toxic classification.

Toxic grade	Light-inhibiting rate/%	$HgCl_2$/(mg/L)	Toxicity
I	<30	0.07	Low
II	30-50	0.07-0.09	Middle
III	50-70	0.09-0.12	Heavy
IV	70-100	0.12-0.16	High
V	100	>0.16	Virulent

The temperatures of subsystem one and subsystem two were maintained at 25±2ºC and 30±2ºC, respectively, by putting a controllable glass heater in reactors. Mixing velocity of two anoxic tanks was kept at 60 r/min. The two oxic tanks were aerated continuously with rubber diffusers to keep DO concentrations at 3~5 mg/L.

Chemical Wastewater

The mixed chemical wastewater used in this study was obtained from the equalizing tank of Juhua wastewater treatment plant (WWTP), Juhua Group Corporation, Zhejiang province, China. The organic nitrogen (Org-N) in the wastewater of Juhua WWTP was mainly from PVN production. So in this study, $C_6H_{11}NO$ (raw material of PVN) was added into the wastewater to enhance Org-N loading rate, NH_4Cl was added to enhance NH_4^+-N loading rate, the Org-N/NH_4^+-N ratio was kept at approximately 1:1, and $NaHCO_3$ was added to keep influent alkalinity/KN ratio at about 7.14:1.

Seed Sludge

The seed sludge used in this study was the condensed sludge of Juhua WWTP. The MLSSs of seed sludge inoculated for subsystems one and two were 10,025 mg/L and 10,828 mg/L, respectively. The system had run for 67 days before this study to adapt the mixed chemical wastewater. No excess sludge was discharged from both subsystems during the whole experiment time, the average MLSSs in subsystem one and two were 10,071 mg/L and 11,218 mg/L, respectively.

Analytical Methods

Concentrations of KN, NH_4^+-N, NO_3^--N, COD, alkalinity, MLSS, and MLVSS were measured according to the standard methods (APHA, 1998). pH and temperature were determined by a pH meter (model6010, JENCO, USA), DO was determined by an oxygen meter (hi9143, HANNA, Italy).

Acute Toxicity Bioassay

Marine luminescent bacterium was used to estimate acute toxicity. Eq. 1 was the luminescent reaction, and Table 2 showed the toxic calssification. The bioassays were carried out by adding 2 ml wastewater and 10 μl bacterial suspension to a low-background vitreous tube. After 15 min exposure, the relatively light units of wastewater from different tanks and blank control were recorded by the luminator (Berthold, Germany). The whole process was performed at a constant temperature of 15ºC, the acute toxicity was evaluated according to Table 2.

$$\mathrm{FMNH_2 + RCHO + O_2 \xrightarrow{\text{luminescent bacterium}}}$$
$$\mathrm{FMN + RCOOH + H_2O + light} \tag{1}$$

Results and Discussion

COD Removal

Fig. 2 showed the orginal COD concentration in the influent and the outlets COD concentration from the two subsystems during the whole operation period. The two-stage A/O system showed excellent performance in COD removal. Average influent COD concentration of subsystem one of days 1-9, 10-19, and 20-52 were around 943.5, 1,310.6, and 1,563.3 mg/L, respectively. With different $C_6H_{11}NO$ additions these COD increases didn't make any influence on COD removal efficiency. The average effluent concentrations were 129.3, 166.4, and 190.5 mg/L, respectively. From Fig. 3A it can be seen that average COD removal efficiency was 87.6% and R2 was 0.989, which meant subsystem one had a very efficient and stable COD removal capacity. Subsystem two had a further removal of COD, and average removal efficiency was 50.1% based on subsystem one effluent (Fig. 3B). The COD concentration in the effluent was 90.0±6.9 mg/L, which meets the requirements of the National Discharge Standard of China (GB8978-1996). The average removal efficiency of the whole system was 93.3%.

COD was mostly removed by subsystem one with little nitrification. According to [13], under rich organic matter and sufficient oxygen condition heterotrophic COD oxidizers could consume organic carbon prior to their being a carbon source and energy. After that, autotrophic nitrifiers oxi-

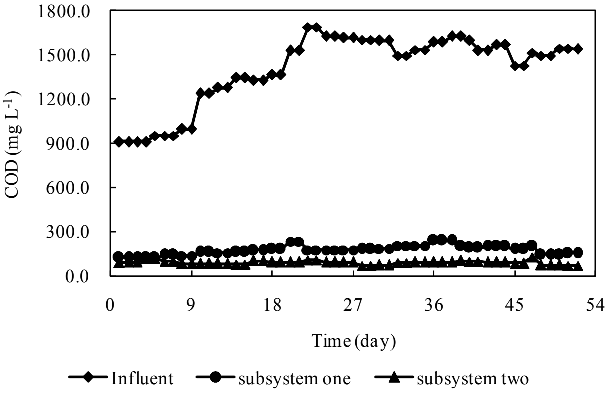

Fig. 2. COD concentration of influent and the two subsystem effluents.

dized ammonium for their energy. Furthermore, the influent was virulent in acute toxicity. We presumed that autotrophic nitrifiers were more sensitive than heterotrophic COD oxidizers, and the inhibition of toxic matters was stronger for nitrifiers than COD oxidizers, which could also well explain the fact that most of the COD was removed but very little ammonium was oxidized.

Nitrogen Removal

Subsystem One

The nitrogenous pollutants in the influent were mainly nitrogenous organic matters and ammonium attributed to the Group's production lines, resulting in average 50% Org-N of the influent KN. Org-N removal occured simultaneously with aerobic or anaerobic degradation of nitrogenous organic pollutant and led to NH_4^+-N release. In subsystem one, accompanied with high efficient COD removal, 75.6% Org-N was removed (Fig. 4E) with an almost doubled NH_4^+-N concentration, the NH_4^+-N/KN value raised from 0.50 to 0.86, while little KN was removed. This might be because KN consisted of NH_4^+-N and Org-N, Org-N removal was actually the internal transformation of KN.

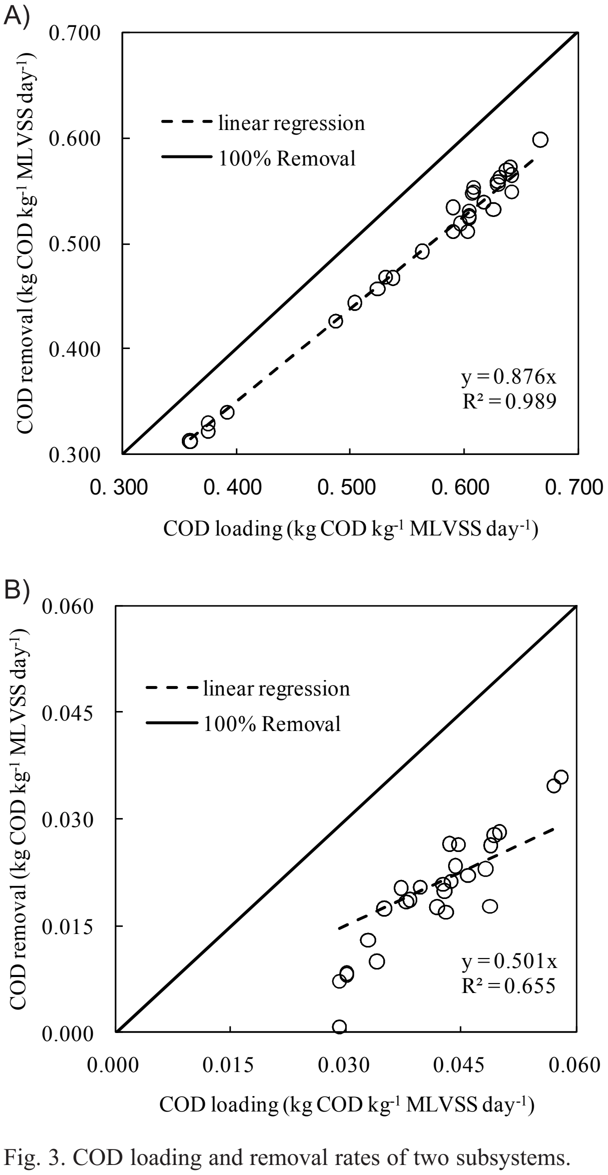

Fig. 3. COD loading and removal rates of two subsystems.

The average KN removal efficiency of subsystem one was only 6.8%, and KN removal loading rate was 0-0.014 kg KN/(kg MLVSS day), which wasn't enhanced with the increasing KN loading rate. This might demonstrate that KN was removed due to a microorganism's assimilation, but not nitrification. Nitrification was seriously inhibited for the high influent COD/KN ratio of subsystem one, which had an average value of 7.84.

Subsystem Two

The fraction of nitrifying microorganisms over heterotrophic microorganisms increases and the nitrifying microorganisms become more and more dominant with decreasing COD/N ratio [17, 21, 22], which means nitrifying microorganisms can be enriched and nitrification can be stimulated at low COD/N ratios. After the efficient removal of COD in subsystem one, influent COD/KN ratio dropped to 1.04. Under this low influent COD/KN ratio condition, subsystem two gained very strong and stable nitrification ability (Fig. 4B, D). An average of 93.3% of the influent NH_4^+-N in subsystem two was nitrified (R^2=0.962), which resulted in 92.1% removal of KN (R^2=0.958). The relatively high influent COD (300-400 mg/L) of subsystem two in days 53-57 caused an increase in the effluent KN, showing that the nitrification could easily be affected by influent COD concentration.

The average Org-N concentration in subsystem two influent was 22.7 mg/L. Meanwhile, subsystem two had a further removal of Org-N at this comparatively low influent Org-N concentration owing to the organic matter used by denitrification in an anoxic tank (Fig. 4F). Average 86.0% Org-N was transformed to NH_4^+-N. This further removal of Org-N was important to keep effluent KN at a low concentration (averagely 13.6 mg/L KN with 9.9 mg/L NH_4^+-N and 3.7 mg/L Org-N).

Acute Toxicity Evaluation

The acute toxicity of the system influent was 0.165 mg $HgCl_2$/L (Fig. 5), so it was virulent (Table 2) and might severely inhibit life activities. After coagulation, the acute toxicity was droped to 0.100 mg $HgCl_2$/L (Fig. 5B), suggesting that a part of toxic matters could be removed by the coagulating process. This may be due to the fact that PAC could agglomerate certain organic toxic matters and eliminate them from raw wastewater. The acute toxicity of anoxic tank one dropped slightly and still remained at a high level (without coagultion) and a heavy level (with coagulation). The acute toxicity of oxic tank one dropped obviously and the toxic level became middle (without coagultion) and low (with coagulation). This indicated that toxic matters in the coal-chemical industry wastewater mainly consisted of organic matters and the majority of toxic matters could be removed by aerobic organic matter oxidation (about 55% without agulation). This result was different from the studies performed by Sponza and Demirden [23]. In their studies, the acute toxicity of the pharmaceutical wastewater was almost completely eliminated by an anaerobic baffled reactor. Subsystem two could further remove toxic matters. The effluent toxicity of subsystem two was low, suggesting that it was innoxious to humans.

Both coagulation and aerobic biological oxidation could eliminate toxic matters efficiently. However, aerobic biological oxidation was more efficient than coagulation (Fig. 5A, B). Coagulation just transferred toxic matters from wastewater to deposits, while aerobic biological oxidation changed toxic matters to nontoxic matters like CO_2, N_2, and H_2O. From Figs. 5A, B, it can be found that the

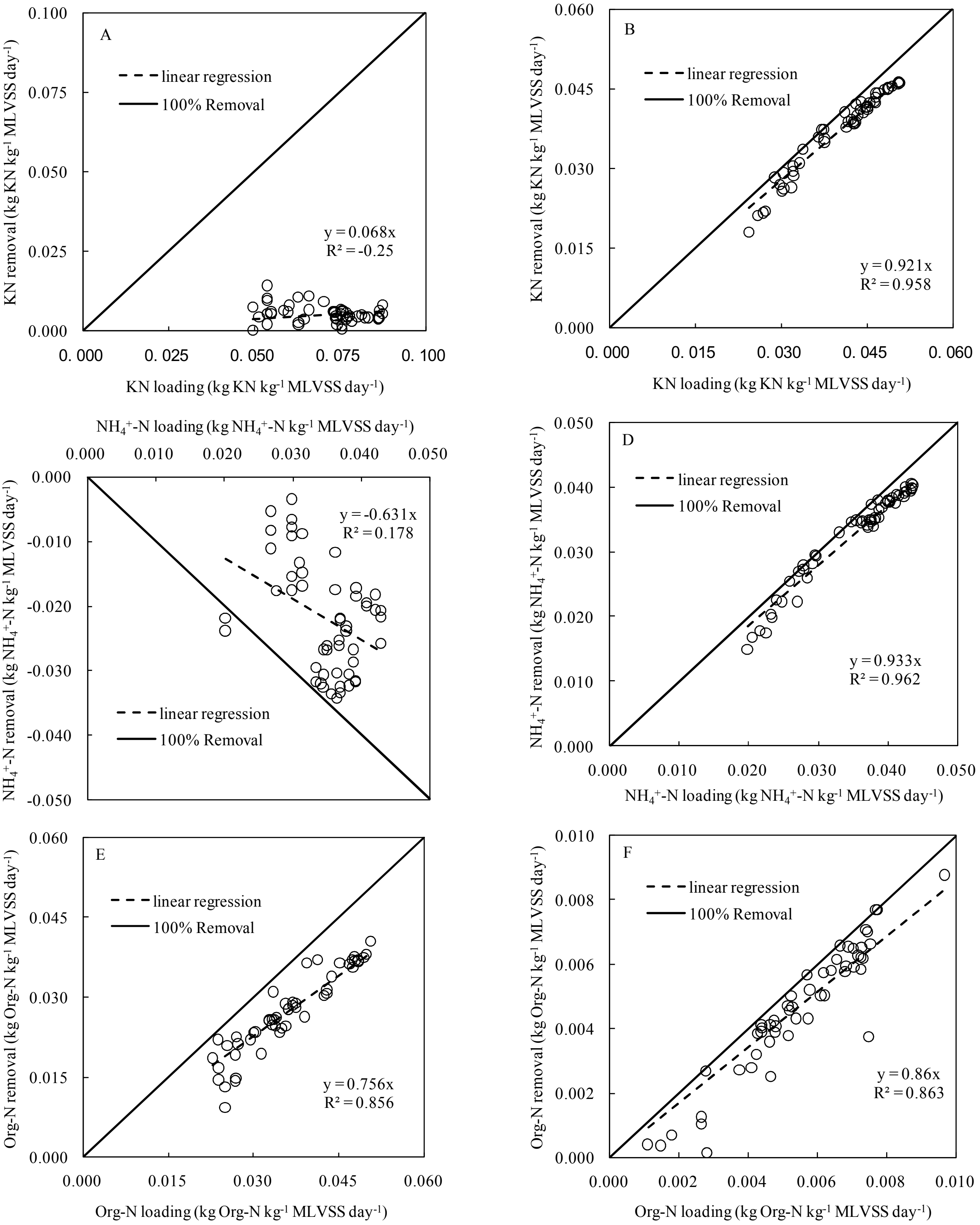

Fig. 4. KN NH_4^+-N Org-N loading and removal rates of two subsystems.

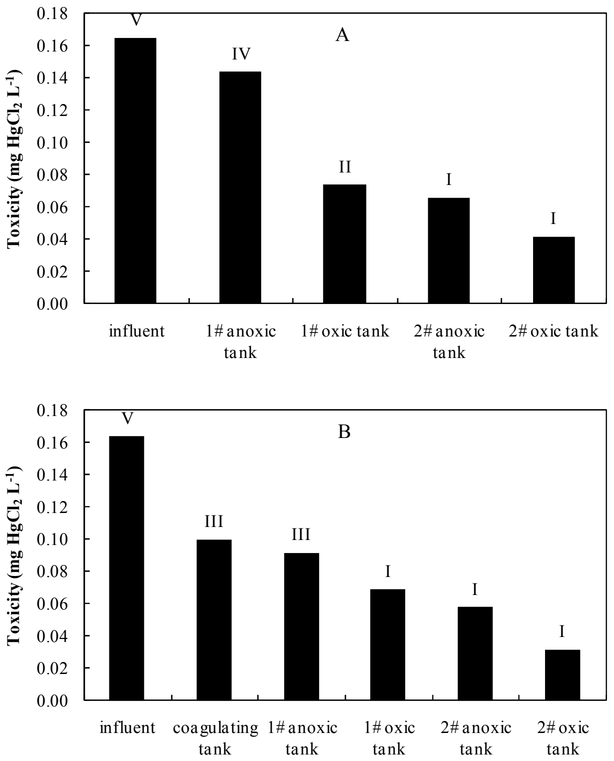

Fig. 5. Wastewater acute toxicity of different units in a two-stage A/O system.

acute toxicity of oxic tank showed almost the same performances without or with coagulation with values of 0.74 and 0.69 mg $HgCl_2$/L, respectively.

On the aspect of eliminating toxic matters from chemical industry wastewater, the two-stage A/O process was sufficient enough. Whether coagulating or not made little impact on the acute toxicity of subsystem two effluent.

Whole System Evaluation

In the present study, the two-stage A/O system, which could remove 87.63% COD, 92.1% KN, and eliminate 75% acute toxicity, performed excellently. Using an A/O system (subsystem one in this study), A/O/O system (Juhua WWTP) and SBR system (our other study) to treat the same wastewater under the same HRT, most of the COD was removed but KN was slightly removed (below 20%). Comparing these four biological systems, the sludge system was the main difference. In a two-stage A/O system, each subsystem had an independent sludge system. Heterotrophic COD oxidizers and autotrophic nitrifiers were strictly separated in two subsystems. Organic carbons were removed and toxic matters were eliminated in subsystem one. These all guaranteed high nitrifying activity in subsystem two. However, in the latter three biological systems, which both used mixed sludge systems, heterotrophic COD oxidizers would plunder oxygen with autotrophic nitrifiers and toxic matters adsorbed by the sludge would release again and inhibit the nitrifying activities.

Conclusions

The two-stage A/O system can remove COD and KN efficiently from mixed chemical wastewater with two completely independent microorganism subsystems performing different functions under their own optimal COD/KN ratio.

Under sufficient dissolved oxygen and high influent COD/KN ratio condition, subsystem one obtained high COD and Org-N removal capability while nitrification was totally inhibited with only 7.6% KN assimilated by microorganism.

Subsystem two had high nitrification capacity because of low influent COD/KN ratio and low nitrification toxicity, 92.1% KN removal efficiency was achieved. Subsystem two also had a further removal of COD and Org-N.

Aerobic biological oxidation of oxic tank one showed excellent toxic matter eliminating ability and the two-stage A/O system can eliminate most of the toxic matters effectively.

It could be demonstrated that establishing independently functional activated sludge systems may be necessary and robust in treating mixed wastewater discharged by comprehensive chemical groups that contains high concentrations of COD, nitrogen, and toxic matter.

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