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Biodegradability evaluation of pollutants in acrylonitrile wastewaters based on particle size distribution

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ABSTRACT

Acrylonitrile wastewaters (ANWs) treatment is a big trouble for chemical fiber industry in China, and there was not yet an effective biological treatment technology for ANWs due to the lack of detailed analysis on the biodegradability of pollutants. In this work, two typical point-source ANWs, acrylonitrile synthesis wastewater (ANSW), and acrylonitrile polymerization wastewater (ANPW) were fractionated by gradient membrane separation method based on the pollutants particle size distribution (PSD). Moreover, biochemical oxygen demand/chemical oxygen demand (COD) ratios, oxygen uptake respirometric tests, dehydrogenase activity tests, and simulated aeration tests were integrated to evaluate the biodegradability of PSD-based pollutants in ANWs. The results showed that most COD were from dissolved fractions in both of ANSW and ANPW. For ANSW, the soluble fractions had greater biodegradation potential than particulate and colloidal fractions. Colloidal fractions are easier to be biodegraded than particulate and soluble fractions in ANPW. The simulated aerobic tests showed that, only 54.72 and 21.62% of COD was removed from ANSW and ANPW, respectively. It indicated that activated sludge treatment process was inadequate to ANWs. The correlations between PSD-based pollutants and their biodegradability of ANWs can be used to guide the development of ANWs treatment technologies.

Keywords: Acrylonitrile wastewaters; Organic pollutants; Gradient membrane separation; Particle size distribution; Biodegradability

1. Introduction

Acrylonitrile wastewaters (ANWs) were mainly generated from the acrylonitrile synthesis and polymerization processes, in which more than 30 kinds of raw materials, additives, AN, polyacrylonitrile (PAN), and related by-products existed [1]. ANWs are characterized by the complex composition of pollutants, especially high-concentration recalcitrant and toxic pollutants including copolymers, organic nitriles, ammonia nitrogen, cyanide, sulfonate, sulfite, and sulfate [2,3]. The main point sources of ANWs with the

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largest flow and highest pollutant load are acrylonitrile synthesis wastewater (ANSW) and acrylonitrile polymerization wastewater (ANPW), which were mixed with all the other point sources from AN and PAN production processing and discharged into wastewater treatment plant. The anaerobic/aerobic/biological activated carbon treatment process for ANWs has been adopted by most acrylic fiber production enterprises in China [1]. However, such treatment process could not meet the national wastewater discharge standard of China (GB 8978–1996), in which the maximum allowable discharge concentrations of NH_4^+-N is 15 mg L^{-1}, and the maximum value of chemical oxygen demand (COD) and BOD_5 are 100 and 30 mg L^{-1}, respectively.

Great efforts have been paid to improve ANWs' treatment processes such as bioaugmentation units by introducing high-efficiency degradation strains [4], pre-ameliorating biodegradability by advanced oxidation (Fenton's reagent, ozone), or electrochemical oxidation (iron-carbon internal electrolysis). In addition, two-phase anaerobic, anoxic, biological aerated filter, and ozone-activated carbon oxidation have also been used to optimize ANWs treatment process to improve NH_4^+-N and COD removal [5,6]. Although the treatment performances were improved by these efforts in some way, the longer process increased the treatment cost and occupied larger area. Therefore, it is important to identify the distribution and properties of pollutants in ANWs before developing a proper method to treat such wastewater effectively. Generally, the pollutants in wastewater can be classified into particulate fraction (>0.45 μm), colloidal fraction (0.45 μm–2 nm), and soluble fraction (<2 nm) in terms of particle size [7,8]. Pollutants with different particle size ranges showed different behavior in biological treatment process [9]. The significance of particle size distribution (PSD) has been recognized and the relationship between PSD and biodegradability can make more sense in developing and optimizing the ANWs treatment technology [10,11].

Recently, advanced separation technologies, such as microfiltration (MF) and ultrafiltration (UF), were successfully used to physically segregate pollutants in wastewater into narrow particle size ranges [7,8,12]. Gradient membrane separation (GMS) makes it possible to evaluate the biodegradability of pollutants in ANWs based on PSD. The biodegradability of wastewater is affected by multiple factors: internal factors including particle sizes, chemical properties, and physical forms of pollutants; external factors including microbial activity, temperature, and other environmental parameters. Different biodegradability evaluation methods are proposed. Among these methods, BOD_5/COD ratios were widely used with the advantages of simple and direct, but the evaluation results were not so accurate for wastewater containing complicated organic pollutants [13]. Oxygen uptake respirometric (OUR) tests were adopted recently to evaluate the biodegradability of organic wastewater, by taking CO_2 production or O_2 consumption during microbial respiratory as evaluation parameters [14]. Besides, dehydrogenase and adenosine triphosphate had been used to evaluate the biodegradability by measuring the biomass and enzyme activity during pollutants biodegradation [15,16]. However, apparent differences in biodegradability results by these methods exist in terms of different reaction mechanisms and testing conditions. In order to obtain accurate evaluating results of wastewater, it is feasible to integrate multiple biodegradability evaluation methods.

In this work, ANWs were separated into three sub-fractions by the GMS with sequential MF and UF containing particulate pollutants (>0.45 μm), colloidal pollutants (0.45 μm–2 nm), and soluble pollutants (<2 nm). The biodegradability of such PSD-based pollutants was measured by BOD_5/COD ratios, triphenyltetrazolium chloride (TTC)-dehydrogenase activity (DHA) tests, OUR tests, and simulated aeration tests. Meanwhile, the correlations between PSD and biodegradability in ANWs were investigated.

2. Materials and methods

2.1. ANWs samples

Two types of point-source ANWs samples, ANSW and ANPW, were both taken from the Fushun Acrylic Chemical Plant (FACP) of China National Petroleum Corporation. Approximately, 15 $m^3 h^{-1}$ of ANSW and 45 $m^3 h^{-1}$ of ANPW were generated in the plant, which were discharged into a wastewater treatment plant mixed with other point-source ANWs from FACP. The wastewater was treated by an anaerobic–aerobic contact oxidation–biological activated carbon-treatment process, and the average NH_4^+-N and COD of the effluent are 180 and 350 mg L^{-1}, respectively.

2.2. GMS method

The GMS flow diagram is shown in Fig. 1. The raw ANWs were filtrated by sequential MF membrane with average pore size of 0.45 μm and UF membrane with average pore size of 2 nm. The filtrate from MF membrane is used as the influent of UF. The filtrate from 0.45 μm MF membrane (0.45 μm filtrate) is mainly considered to be containing colloidal fractions and soluble fractions, because the 0.45 μm membrane

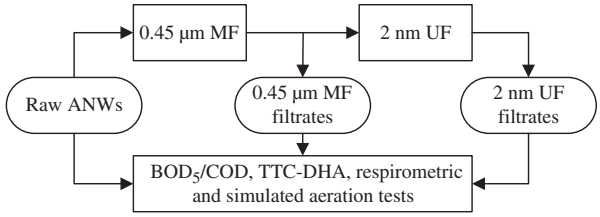

Fig. 1. Flow diagram of GMS for ANWs.

traps the particulates with particle size larger than 0.45 μm. Similarly, the filtrate from 2 nm UF membranes (2 nm filtrate) only contains soluble pollutants. Therefore, the biodegradability of particulate fractions, colloidal fractions, and soluble fractions can be deduced indirectly through comparing the differences of biodegradability among the raw ANWs, 0.45 μm filtrate, and 2 nm filtrate [7].

MF and UF membranes in this work were provided by Millipore Corporation, USA. Sedimentation layer and concentration polarization of membranes were effectively avoided by controlling operating pressure and stirring rate. To eliminate the membrane fouling and restore the membrane flux, MF and UF membranes were washed by sequential HCl (0.1 mol L^{-1}), NaOH (0.1 mol L^{-1}), and deionized water before and after use. Each membrane was limited to less than five times use.

2.3. Biodegradability evaluation

2.3.1. COD and BOD_5/COD

The ratio of BOD_5/COD is the most convenient indicator to quantitatively evaluate the biodegradability of organic pollutants [13]. Generally, wastewater with BOD_5/COD greater than 0.3 is considered to be potentially biodegradable, on the contrary, is recalcitrant to be biodegraded. Especially, once the BOD_5/COD ratios are less than 0.2, traditional biological treatment processes are regarded to be fundamentally unsuitable to this type of wastewater [17]. The COD and BOD_5 of the raw ANWs and filtrates were determined according to the standard methods (APHA, 2005) [18], and the corresponding values of BOD_5/COD were calculated.

2.3.2. TTC-DHA tests

TTC-DHA test results are closely related to the PSD and composition of pollutants in activated sludge wastewater system [16]. As an artificial electron and hydrogen acceptor, the colorless TTC can be converted to red-colored triphenyl formazan (TF) under microbial dehydrogenases action, and the microbial DHA can be acquired by measuring TF concentration. The activated sludge for TTC-DHA tests was sampled from an aerobic contact oxidation reactor (OCOR) of the wastewater treatment plant of FACP. Before use, the sludge was pretreated by centrifugation to remove supernatant liquid, physiological saline washing, and diluting to initial volume. Mixed liquor volatile suspended solid (MLVSS) of the activated sludge was controlled at 2,000 mg L^{-1}.

During TTC-DHA tests, prepared activated sludge of 2 mL was added into a stoppered tube, quickly followed with 1.5 mL Tris–HCl buffer (pH 7.6), 0.5 mL Na_2SO_3 solution (0.36%, c), 0.5 mL TTC solution (0.4%, m/v), and 0.5 mL raw ANWs or filtrates. Then, the stoppered tube was immediately placed into an oscillator at 37 ± 1℃ in the dark; after 30 min of enzyme reaction, 1 mL formaldehyde was added to terminate the reaction. Then, the produced TF was extracted into a 5 mL toluene; after 10 min oscillation and 5 min centrifugation, the optical density (OD) of supernatant liquid was measured by a spectrophotometer (a-1860, China) at 485 nm. If the OD value is greater than 0.8, supernatant liquid sample should be measured after appropriate dilution. In addition, the blank test was conducted, in which 0.5 mL TTC solution and 0.5 mL raw ANWs or filtrates were replaced by 1 mL deionized water.

The TF content was calculated by a predetermined standard curve as Eq. (1):

$$A - A_0 = 0.006\ C_{TF} + 0.01279 \quad (1)$$

where A is the OD value of TF produced by raw ANWs or filtrates, A_0 is the OD value of TF produced by blank tests, and C_{TF} is the concentration of produced TF.

The DHA was calculated from Eq. (2):

$$DHA = C_{TF} \times r \times n \quad (2)$$

where r is the dilution ratio of OD measurement, n is the corrected chromogenic reaction time, and DHA is expressed as μg TF mL^{-1} h^{-1}.

2.3.3. OUR tests

The microbial respirometric characteristics reflect the aerobic degradation behaviors of organic pollutants in the wastewater. The biodegradability of wastewater can be evaluated with contrast to OUR

curve and endogenous OUR (EOUR) curve of microbes. Generally, the wastewater is biodegradable if the OUR curve is above the EOUR curve, while non-biodegradable if the OUR curve is below the EOUR curve [19]. The OUR tests were conducted with acclimated activated sludge (AAS) sampled from the OCOR of FACP, and the AAS was pre-aerated for 24 h to consume adsorbed organic pollutants before tests.

The batch OUR experiments were performed in an aerobic bioreactor as shown in Fig. 2. During OUR tests, the AAS and 0.8 L diluted raw ANWs or filtrates were mixed into the reactors with initial MLVSS concentration of 2,000 mg L^{-1} and food/micro-organism ratio of 0.2. Besides, 10 mg nitrification inhibitor (allylthiourea, ATU) was added to eliminate endogenous nitrification of AAS. The mixture of AAS and wastewater was aerated to obtain initial dissolved oxygen (DO) of 5.0 mg L^{-1}; then, aerobic reactors were sealed, and DO concentrations were measured every three min until a stable value observed. Meanwhile, the blank tests were also conducted by replacing raw ANWs or filtrates by equal volume of deionized water.

2.3.4. Simulated aeration tests

The biodegradability of raw ANWs or filtrates was evaluated intuitively by simulated aeration tests. 2 L aeration tank with the same AAS as respirometric tests was used to simulate the biological treatment process. During the simulated aeration tests, 1 L raw ANWs or filtrates were added into the aeration tanks with MLVSS concentration of 2,000–3,000 mg L^{-1} and DO concentration of 2–3 mg L^{-1}. COD values of the mixture were measured every 0.5 or 1 h. Besides, the blank tests were also carried out by replacing raw ANWs or filtrates by equal volume of deionized water.

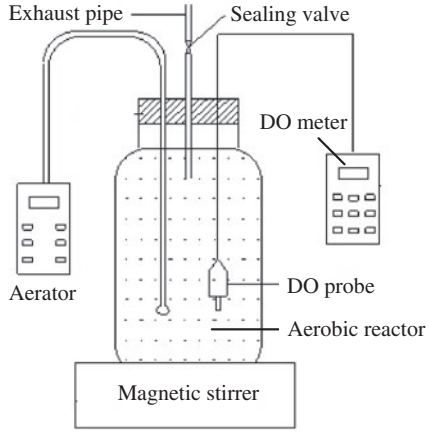

Fig. 2. Flow diagram of the batch respirometric tests for ANWs.

3. Results and discussion

3.1. PSD-based COD and BOD_5/COD

Table 1 exhibits the COD, BOD_5, and BOD_5/COD values of the raw ANWs and filtrates. The raw ANSW and ANPW contains high-concentration organic pollutants with average COD values of 3,370 and 1,710 mg L^{-1}. Traditional biological process cannot effectively treat the two types of wastewaters with the average BOD_5/COD of 0.22 and 0.16, which may be the reason that the effluent from all of the acrylic fiber plants in China could not meet the standard of GB 8978–1996.

Pollutants with large particle sizes in ANWs were gradually intercepted, and COD values of the filtrates were decreased gradually by GMS process. For ANSW, only 340 mg L^{-1} COD was removed after MF with 0.45 μm membrane, and 1,340 mg L^{-1} COD was removed after UF with 0.2 nm membrane. For ANPW, the removal concentrations of COD by 0.45 μm membrane and 0.2 nm membrane are 340 and 320 mg L^{-1}, respectively. According to the results, the soluble fractions contributed 79.82% COD of ANSW and 61.4% COD of ANPW indicated that the main organic pollutants in ANSW and ANPW were soluble fractions. Compared to the variation tendency of BOD_5/COD ratio during GMS, it was found that the refractory pollutants in ANSW are distributed in particulate and colloidal fractions, but those in ANPW are mainly distributed in particulate and soluble fractions.

3.2. PSD-based TTC-DHA

Fig. 3 shows the TTC-DHA levels of ASS to ANWs and filtrates. The DHA of 0.45 μm filtrate and 2 nm filtrate increased to 20.00 and 20.89 μg TF mL^{-1} h^{-1} when compared with that of 18.33 μg TF mL^{-1} h^{-1} of raw ANSW. The DHA differences showed that the soluble pollutants exhibited the better biodegradability than particulate and colloidal fractions in ANSW. The DHA of raw ANPW was 7.01 μg TF mL^{-1} h^{-1}, 9.01 μg TF mL^{-1} h^{-1} of 0.45 μm filtrate, and 7.8 μg TF mL^{-1} h^{-1} of 2 nm filtrate. Totally, the TF concentration of ANPW was lower than that of ANSW. The reason could be the lower pollution load of ANPW. COD of ANPW was almost half of ANSW. Besides , the DHA value of 0.45 μm filtrate was significantly higher than the others by cutting off particulate fractions. The DHA value of 2 nm filtrate was as low as raw ANPW

Table 1
COD, BOD_5, and BOD_5/COD values of raw ANWs and filtrates

Samples	COD (mg L^{-1})	BOD_5 (mg L^{-1})	BOD_5/COD
Raw ANSW	3,370 ± 71	740 ± 20	0.22
0.45 μm filtrates	3,030 ± 70	750 ± 5	0.25
2 nm filtrates	2,690 ± 110	740 ± 8	0.27
>0.45 μm ANSW	340	–	0
2 nm–0.45 μm ANSW	1,340	10	0.01
<2 nm ANSW	2,690	740	0.28
Raw ANPW	1,710 ± 11	274 ± 8	0.16
0.45 μm filtrates	1,370 ± 20	288 ± 12	0.21
2 nm filtrates	1,050 ± 10	158 ± 8	0.15
>0.45 μm ANPW	340	–	0
2 nm–0.45 μm ANPW	320	130	0.41
<2 nm ANPW	1,050	158	0.15

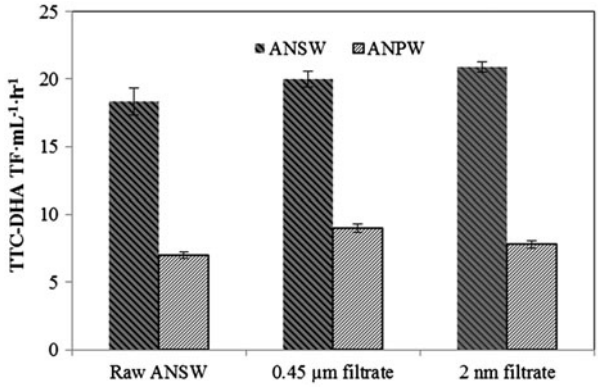

Fig. 3. TTC-DHA variations of ASS to raw ANWs and filtrates.

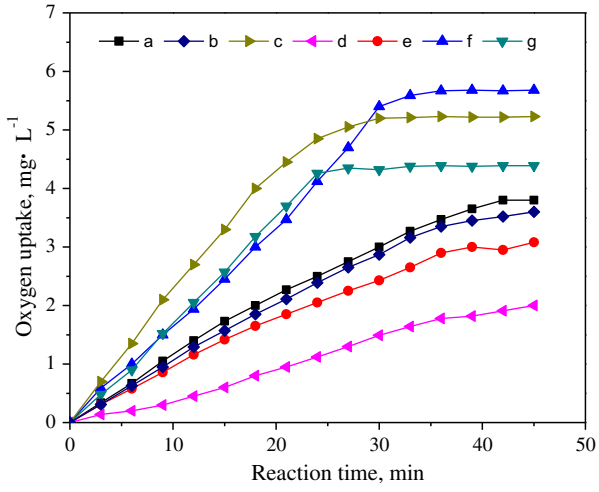

Fig. 4. The OUR curves of raw ANWs based on various dilution ratios: (a) blank; (b) raw ANSW; (c) 5 times diluted ANSW; (d) raw ANPW; (e) 5 times diluted ANPW; (f) 10 times diluted ANPW; (g) 15 times diluted ANPW.

because of containing only soluble fractions. It demonstrated that the particulate and soluble fractions had stronger biological inhibitory effect than colloidal fractions in ANPW. The TTC-DHA tests results of ANWs and filtrates are generally inconsistent with that of BOD_5/COD ratios in spite of tiny differences in details.

3.3. PSD-based OUR

The ANWs samples should be diluted before the OUR tests to avoid the biological inhibitory effect caused by high-concentration refractory organic pollutants. The appropriate dilution ratios of ANWs and filtrates were determined by prior OUR tests. Fig. 4 shows the OUR curves of raw ANWs based on various dilution ratios. It is indicated that ANSW and filtrates should be diluted five times, while ANPW and filtrates need to be diluted 10 times.

Fig. 5 shows the OUR curves of raw ANWs and filtrates with optimal dilution ratios. The OUR curve of 2 nm filtrate was above that of raw ARW and 0.45 μm filtrate. It revealed that the soluble fractions had greater biodegradation potential than particulate and colloidal fractions in ANSW. The OUR curves of raw ANPW and 2 nm filtrate were approximate coincidence, both below that of 0.45 μm filtrate. The results showed that the colloidal fractions are easier to be biodegraded than particulate and soluble fractions in ANPW. The result of biodegradability among the three fractions in ANWs by the OUR tests is almost in agreement with that of BOD_5/COD ratios and TTC-DHA tests.

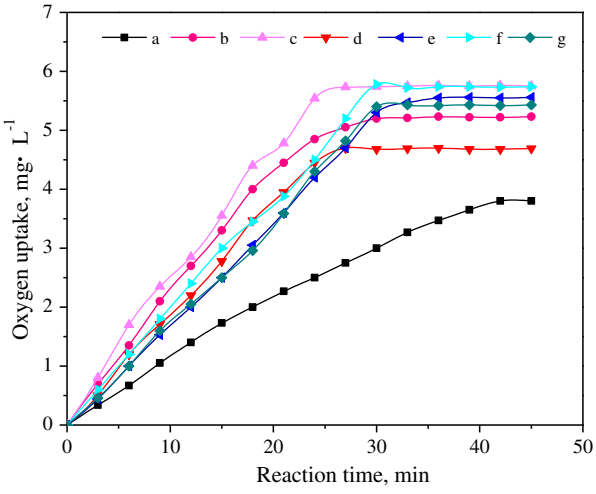

Fig. 5. OUR curves of raw ANWs and filtrates with appropriate dilution ratio: (a) blank; (b) raw ANSW; (c) 0.45 μm filtrate of ANSW; (d) 2 nm filtrate of ANSW; (e) raw ANPW; (f) 0.45 μm filtrate of ANPW; (g) 2 nm filtrate of ANPW.

3.4. PSD-based simulated aeration tests

The biodegradability of the ANWs and filtrates was further investigated by simulated aeration tests to obtain comprehensive evaluation results. Fig. 6 exhibits the variations of COD concentration during aeration process. The COD concentration of ANWs and filtrates declined significantly in the early 2 h aeration, and slowed down to a stable level after 7 h aeration.

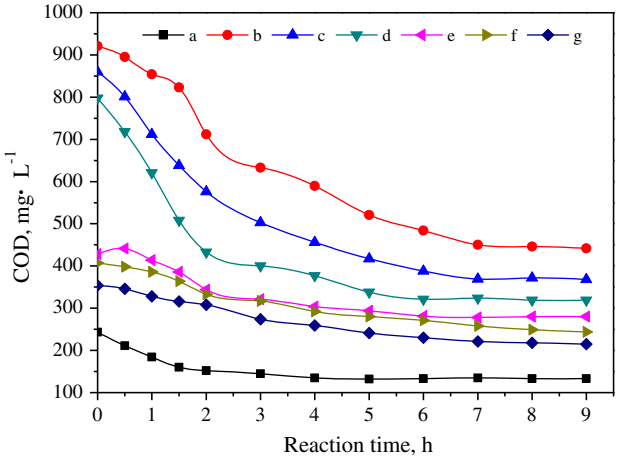

Fig. 6. COD variations of ANWs and filtrates during simulated aeration tests: (a) blank; (b) 5 times diluted raw ANSW; (c) 5 times diluted 0.45 μm filtrate of ANSW; (d) 5 times diluted 2 nm filtrate of ANSW; (e) 10 times diluted raw ANPW; (f) 10 times diluted 0.45 μm filtrate of ANPW; (g) 10 times diluted 2 nm filtrate of ANPW.

The COD removal rate of 2 nm filtrate of ANSW is obviously faster than that of raw ANSW and 0.45 μm filtrates during aeration, however, the COD removal rate of 2 nm filtrate of ANPW is slower than that of raw ANPW and 0.45 μm filtrate during aeration, especially in the first 2 h.

The COD values of the blank tests are mainly from organic pollutants adsorbed by AAS and microbial endogenous respiration products. The absolute removal values of COD for ANWs and filtrates can be calculated by subtracting the blank COD values. Correspondingly, the final COD removal rates of raw ANSW, 0.45 μm filtrate, and 2 nm filtrate are 54.72, 62.24, and 66.85%, respectively. Moreover, the final COD removal rates of raw ANPW, 0.45 μm filtrate, and 2 nm filtrate are 21.62, 33.54, and 27.93%, respectively. The results indicated that the soluble fractions had better biodegradability than colloidal and particulate fractions for ANSW, while the soluble fractions had poorer biodegradability than colloidal and particulate fractions for ANPW. Besides, after 9 h biodegradation, the COD value was still higher than 200 mg L^{-1} in each sample and could not be discharged directly. Even for dissolved fractions in 2 nm filtrate, organics could not be sufficiently utilized by bacteria. It is demonstrated that the traditional activated sludge treatment process is not appropriate for ANWs. Chemical treatment method should be combined to degrade those biorefractory compounds to reduce negative effects on water environments. Further research will be studied to investigate the appropriate treatment process for ANWs.

4. Conclusion

GMS method was adopted successfully in this work to fractionate pollutants in ANWs based on the PSD. The biodegradability of raw ANWs, 0.45 μm filtrates, and 2 nm filtrates were evaluated synthetically by BOD_5/COD ratios, TTC-DHA tests, OUR tests, and simulated aeration tests. The integrated biodegradability evaluation results showed that for ANSW, the soluble fractions had the best biodegradability, while the same fractions in ANPW showed the worst biodegradability among all the PSD organic pollutants. The physico-chemical treatment technologies such as coagulation/flotation and adsorption/filtration could eliminate the particulate pollutants in ANWs effectively; thus, the key organic pollutants of restricting ANWs biological treatment mainly exist in the soluble fractions. With regard to soluble fractions in ANWs, the appropriate pretreatment aimed at water quality improvement is imperative before biological treatment

in order to meet the increasingly strict national wastewater discharge standards.

Acknowledgments

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