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Classification of Contaminant of Acrylic Fibrous Wastewater

Yang Shuangchun, Guo Shaohui and Yan Guangxu

***Abstract*—The token of size distribution of pollutants and the particle effects on the pollution controlling attract much attentions recently. After investigation to the main technology in FUSHUN factory and the running state of wastewater plant , two key sources of wastewater were as the key objects. The COD of polymer wastewater is complicated, involving colloid (1-5nm) (accounting for 58.59% COD), particles < 0.1μm portions (accounting for 21.41% COD), and substances of no more than 200 molecular weight (accounting for 20% COD). The ammonia-nitrogen mainly is the small molecular (accounting for 88.30%), which can be removed by UF and RO membrane. SO_3^{2-} is same as the ammonia-nitrogen, and SO_3^{2-} of the polymer tower effluent is 122.57 mg/L. As to the solvent recovery effluents, the PSD based COD of the more than 0.1μm portion, colloid, nanometer grade and soluble COD fractions account for 1/4 . The ammonia-nitrogen of effluents for the solvent recovery tower is irregular. The total cyanide contribution of particle size beyond 0.1μm accounted for 91%. Acrylonitrile, as small molecule ,could be absorbed by colloid particles(1-2 nm) and then cut off by NF grade. And DMF could be absorbed by colloid, and the remaining could be separated by RO.**

***Index Terms*— acrylic fibrous wastewater, particle size distributions, water quality analysis, wastewater treatment.**

I. Introduction

By the end of 2006, China was the biggest production and consumption country of acrylic fibers in the world, and the productive capacity of acrylic fiber reached to 8.25 million tons per year, which ranked among the first in the world. And the apparent demand of acrylic fiber will increase at high speeds of 3%-5% every year in prediction [1][2]. The dry-spun acrylic fiber, which is the patent production of American Du Pont Company, has excellent textile performances and is more welcome in the international trade. However, because of the discharge of unmanageable acrylic fibrous wastewater, some foreign acrylic fiber enterprises such as American Du Pont Company, Mitsubishi Chemical Corporation and Germanic Bayer Company have already decreased or stop production[3]. So far, the anaerobic-aerobic-biological active carbon technology is main craft to treat dry-spun acrylic fibrous wastewater, but the result could not attain the national discharge standards of industrial wastewater of China(GB8978-88) [4][5]. Most of research is blind and concentrate on the quick-easy combination of physical-chemistry and bio-chemistry method, which hasn't solved practical problems till now[6-11]. The purpose of this study was to measure particle size distributions(PSD) [12-14] in acrylic fibrous wastewater and to quantify wastewater characteristics within different particle size fractions. Then information in wastewater will guide our choice of treatment technology.

II. Materials And Methods

A. Experiment system

According to size of membrane pore and the difference of substance separated, the membrane separation technology could be classified into micro filtration, ultra filtration, Nan filtration and Reverse osmosis. At present the criterion for the membrane separation technology differ in the relative literature, mostly the micro filtration and ultra filtration were employed[15-18]. And investigation on acrylic fibrous wastewater by NF technology was reported recently[19], thus the five gradient membrane separation equipment involved NF was developed by Environmental Centre of Chemical of Technology Institute of University of Petroleum. The analysis system involved Ⅰ grade(PF) - clarifying and removing the visible particles, Ⅱ grade(MF) - isolating the filter and the solution of small particles and colloid, Ⅲ grade(UF) - the polysulfide ultra filtration membrane of MWCO values of 50, 10 and 6 kDa, Ⅳ and Ⅴ grade(NF and RO) - excluding the low molecular and monovalent ion. No interference due to interaction between the filters and the wastewater was expected since the filter materials were chemically compatible with a wide range of solvents and they were recommended to have no adsorptive capacity for soluble organics by manufacturers.

B. Analysis methods

After every grade separation, all samples were analyzed in triplicates to reduce experimental error, and the fraction was quantified as chemical oxygen demand(COD), biochemical oxygen demand(BOD), Ammonia-nitrogen, SO_3^{-2}, *et al.* COD was measured based on the closed reflux method (GB 11914-89), ammonia-nitrogen measurement was conducted following the hydrochloride titration method (GB 7478-87); the total cyanide concentration measurement followed the isonicotinic acid-pyrazolone or silver nitrate titration method

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(GB 7486-87) according to the various concentration; SO_3^{-2} concentration was measured following the potassium iodide chemical titration method Du Pont Company test method.

III. Investigation

A. Investigation of acrylic fibrous factory

In China so far five dry-spun acrylic fibrous manufactures, involved Qilu Petro-chemical acrylic fibrous factory, Jinyong factory in Ningbo, Qinhuangdao factory, Anqing factory and Fushun factory. Our investigation was carried on in Fushun. The representative first dry-spun acrylic fibrous factory in China was investigated in this study, Fushun fiber factory. For the demand of production, both Sohio Process set and dry-spun acrylic fiber set are built in Fushun factory. Thus wastewater source was relative with these two important technologies. As to the Sohio process, Propylene and Ammonia were oxidized to produce acrylonitrile, meanwhile much wastewater generated but easy to degrade.

Another source of dry-spun acrylic fibrous wastewater was effluents from the dry-spun acrylic polymer process. The polymer was dried and curled in drier machine, polymer could be broken down or blasted at high temperature, thus the drying vehicles needed to wash frequently. The polymer process wastewater, involving polymer recovery towers(monomer recovery tower) effluents and solvent recovery tower effluents, were more than other source wastewater and was our analysis object in this study.

B. Investigation of wastewater treatment

There are sixteen real-time sampling spots, and the partial statistical data in year 2007 were shown in attachment Table 1. It can be seen that COD of the monomer recovery tower effluent and acrylonitrile(AN) set effluent exceeded others, moreover SO_3^{2-} of the monomer recovery tower effluent was very high and DMF(Dimethylformamide) in the solvent recovery tower was 344.59 mg/L.The running state of wastewater plant was investigated, as can be seen as the Fig. 1.

By investigation much foam overflowed from anoxic pond, biological fluid tank and nitrification tank. Sometimes the color of biological fluid tank was dark red. The removal of COD was only 49.78%, and ammonia nitrogen increased to 330.35 mg/L which probably caused by transformation of some nitrogen compounds. The given DO data showed aerobic tank and anoxic pond were ineffective, while the total cyanide increased. The two recovery towers effluents were more and the amount of other effluent was little less, such as acid cleaning wastewater, spinning overflow and washing water.

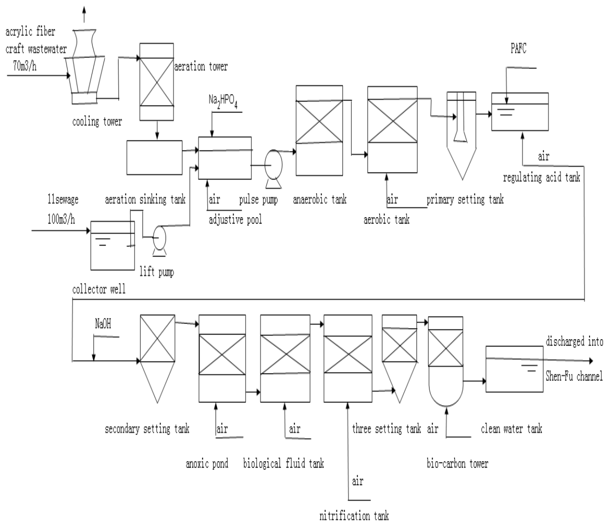

Figure 1. The flow of acrylic fibrous wastewater treating plant

The designed treatment capacity is 6000 m^3/d and the influent involved two sections, the mixture stream (of the monomer recovery and the solvent recovery towers), and washing water produced from acrylonitrile technology .The sample of adjustment pool, anaerobic tank, aerobic tank, secondary clarifier, less aerobic tank, biological fluent pool, nitrification tank and third clarifier were traditional analyzed as Tab. 1.

TABLE I. The variety of analysis data of main treatment unit

treatment unit	Ammonia / mg/L	COD / mg/L	DO / mg/L	pH	Total Cyanide / mg/L	SS / g/L
Adjustment	120.23	892	0.5	7.36	0.115	0.37
Anaerobic	215.58	1851	0.7	7.31	0.113	1.03
Aerobic	244.05	612	0.7	8.31	0.165	0.57
Secondary clarifier	245.99	635	0.7	8.13	0.103	0.44
Anoxic pond	253.93	511	6.8	8.11	0.896	0.27
Biological fluid tank	274.32	517	6.6	8.31	1.002	0.48
Nitrification	184.28	487	7.7	6.26	0.846	1.07
The third clarifier	330.35	448	6.2	6.35	0.855	0.26

IV. Results And Discussion For Monomer Recovery Tower Effluents

The monomer polymerization equipment, designed by Chemtex Company, was introduced from American Du Pont Company. As one of rectifying tower, the monomer recovery tower was composed of fifteen sieve plates. The polymer slurry of polymerization entered the monomer tower through the first washing set and the second washing set, and the distillated water joined the wastewater treatment plant. Meanwhile much cooling water, desalted water and washing water were used for.

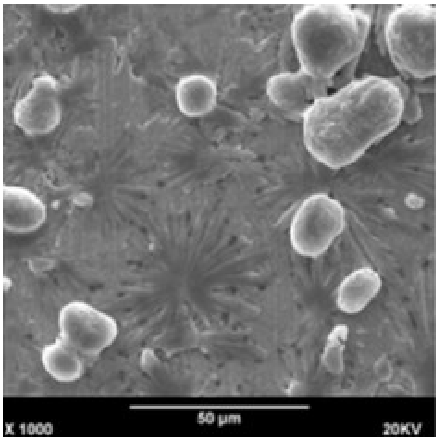

Figure 2. The scan electron microscope of monomer recovery tower effluents

The particle substances in the effluent of monomer recovery tower were much, appearing milk white and after a time the thick grain floor deposited. At room temperature water sample was volatilized to dryness in a germfree environment, and we could observed particle morphology and size feature with SEM (as shown as Fig. 2). The results showed that there was not only micron grade and colloid spherical particles but also some ramiform polar substances. COD measurements for raw sample were no quiescent settling, not filtered, and the total COD content was the sum of the settlable, suspended, supra colloidal, colloidal and soluble portions. COD, ammonia-nitrogen and SO_3^{2-} based on particles size distribution (PSD) obtained from polymer monomer recovery tower sewage were plotted in Fig. 3-Fig. 5.

A. COD distribution of polymer wastewater

COD PSD-based characterization was as shown as in Fig. 3. It can be seen that COD continuously decrease with the increasing filtrating grade and the descant extent were respectively 11.29%, 10.12%, 6.35%, 52.24% and 20%. Then 21.41% of COD was attributed to large grain (> 0.1μm). As to the large grain, some of large grain settled in aeration sedimentation tank, most of granular matters flowed into wastewater treatment plant. Water quality was deteriorated by large grain because granular matters could as the adsorption core for low molecule toxic pollutant. Most COD of polymer wastewater were colloid (1-5nm, 58.59% COD) and no more than 200 Molecular Weight substance (20% COD). Also the colloid matter is hard to biodegraded, because it is difficult to reach the active position of microorganism.

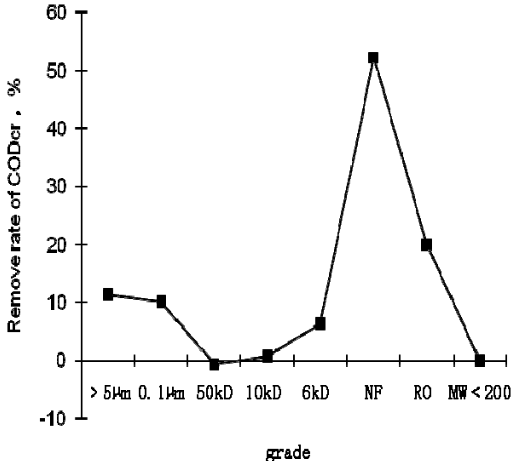

Figure 3. PSD-based COD of the monomer recovery tower effluents

B. ammonia-nitrogen distribution of polymer wastewater

It can be seen that the continuous decrease of ammonia-nitrogen with the increasing filtrating grade, and the descant extent were respectively 3.32%, 1.75%, 3.09%, 55.05% and 33.25%. The ammonia-nitrogen based PSD was mostly in small molecular range (88.30%), which can be removed by UF and RO. 3.54% ammonia-nitrogen is no more than 200 Molecular Weight. And merely 5.07% (as shown as Fig. 4) of the ammonia-nitrogen can be attributed to the granular matters (> 0.1 μm).

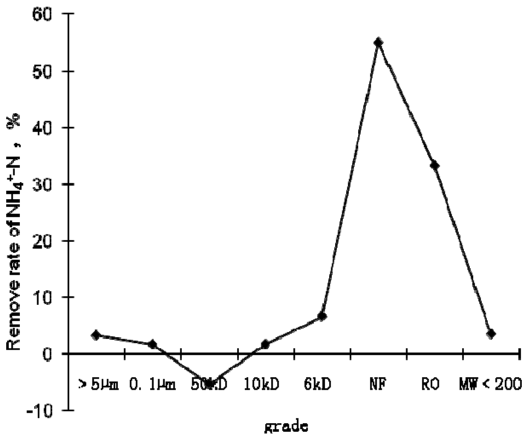

Figure 4. PSD-based NH^{4+}-N of the monomer recovery tower effluents

C. SO_3^{2-} distribution of polymer wastewater

The trend of SO_3^{2-} was not same as ammonia-nitrogen, and SO_3^{2-} of raw polymer wastewater was 122.57mg/L. The descant extent were respectively - 6.98%, - 10.88%, 16.83%, 45.61% and 55.03%. SO_3^{2-} increased with sequential Ⅰ and Ⅱ grade(as shown as Fig. 5). Probably the dynamic equilibrium of monomer polymerization reaction was destroyed because of the removal of linear macromolecules. Then the balance reaction would positive transfer, thus more excessive solicitation potassium per sulfate and sodium hydrogen sulfites were needed, which could result to the increase of SO_3^{2-}.

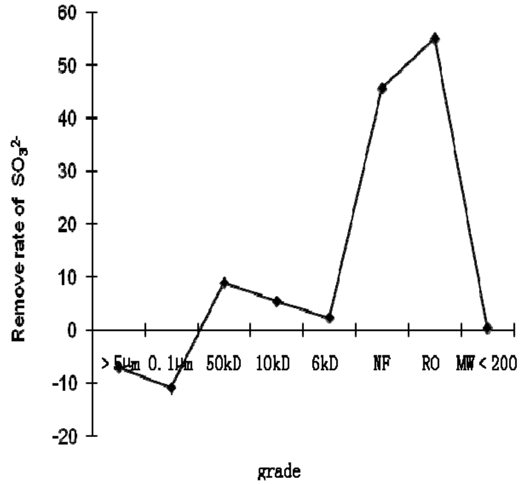

Figure 5. PSD-based SO_3^{2-} of the monomer recovery tower effluents

The descent SO_3^{2-} contribution by UF 50 kDa was 9.04%, but COD and ammonia-nitrogen increased, which presumably resulted from the membrane material of PP(poly- acrylonitrile) decomposed by the solicitation. Then SO_3^{2-} based PSD decreased a little by UF 10 kDa and UF 6 kDa.

By NF and RO grade, the decrease amount of SO_3^{2-} accounted for 45.61% and 55.03% (as shown as Fig. 5). So substrates with SO_3^{2-} was small molecular and inorganic.

V. Results And Discussion For Solvent Recovery Tower Effluents

The solvent recovery tower, the rectifying tower, mainly reclaim DMF solvent. The dilute feed concentration was about 20% and feed comprised of useless washing water for silk, the wastewater from traction process, effluents from tar tower and effluents from deionizer set. After heating with steamer, vaporizing DMF and water vapor mixed into the solvent recovery tower. Then the sewage from overhead, mostly flow into wastewater treating plant. As can be seen as the Fig. 6 of SEM, no micron grade and few colloid particles appeared. SS(suspended solid) content was little, and 91.7 % of substance in solution was organic compounds by the Solid Burned Method. Thus Ⅱ-Ⅴ four grades were selected, and UF 6 kDa was as the mere Ⅲ grade.

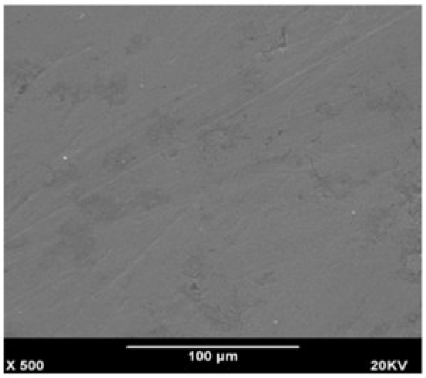

Figure 6. The scan electron microscope of solvent recovery tower effluents

No quiescent settling was applied prior to the experiments, thus the total COD value (272.5mg/L), reflected the sum of supra colloidal, colloidal and soluble COD fractions. The ammonia-nitrogen, the total cyanide of raw effluents of the solvent recovery tower were merely 1.0365 mg/L and 0.255 mg/L, whereas 54.4 mg/L and 5.2 mg/L of DMF and AN were comparatively high. After four sequential membrane separation, COD, DMF and AN were decreased to 82 mg/L, 11 mg/L, 3.2 mg/L, and the ammonia-nitrogen and the total cyanide were little.

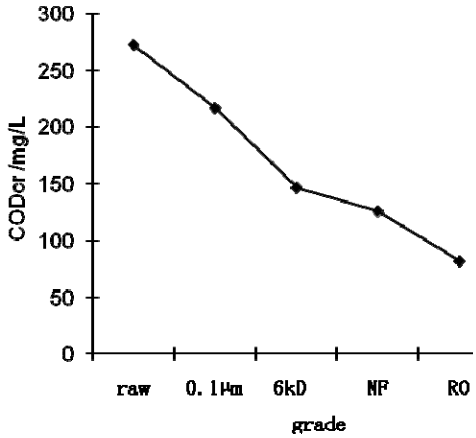

Figure 7. PSD-based CODcr of the solvent recovery tower effluents

The suspended solid was little, and the substances of the effluents for the solvent recovery tower were mostly organic by Solid Burning Experiment. PSD-based COD mainly distributed Ⅱ, UF 6 kDa, and RO grade (as shown as Fig. 7). The portion of particle size of less than 0.1μm accounted for 29.13% COD, as much as 90.98% of total cyanide (as shown as Fig.11), which was presumed to be macromolecule organic compounds containing special cyanogens group, and it was reported that the cyanogens group is inexistent in the physiology. DMF and AN content increased slightly for the DMF molecule and AN molecule adsorbed by particles meanwhile filtrating, which resulted to the slight increase of ammonia-nitrogen.

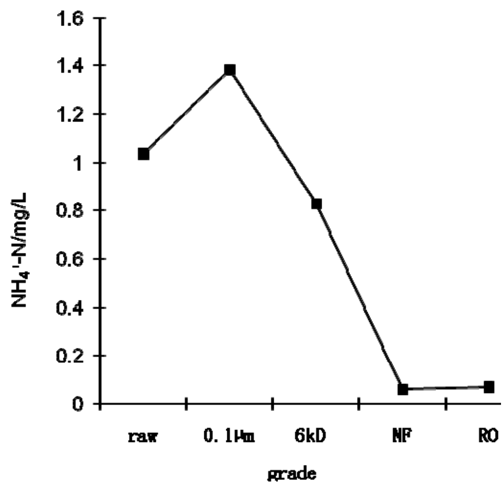

Figure 8. PSD-based NH^{4+}-N of the solvent recovery tower effluents

The particles separated by UF 6 kDa account for 36.75% COD, and DMF decreased 38.71%(as shown as Fig. 9). And changes of ammonia-nitrogen, the total cyanide and AN were small in this grade.

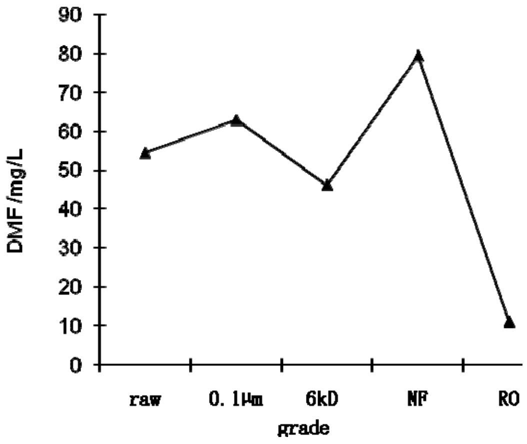

Figure 9. PSD-based DMF of the solvent recovery tower effluents

By NF filtration, 11.02% decline of COD and 95% decreasing of AN, it is suggested that the size of acrylonitrile molecule is over the pore range of NF membrane filter. Ammonia-nitrogen decreased largely and the total cyanide was declined slightly. But DMF increased intensively because under the high pressure dimethylformamide molecule was easily penetrate and then concentration.

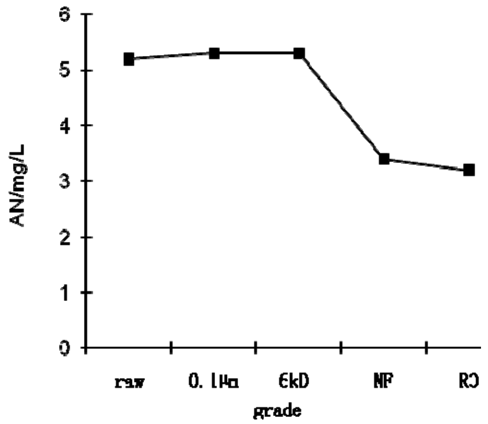

Figure 10. PSD-based AN of the solvent recovery tower effluents

By RO filtration, COD decreased 23.10% and AN, ammonia-nitrogen and the total cyanide decreased slightly. At the same time DMF decreased dramatically, which is resulted from the cut-off of all dimethylformamide molecule.

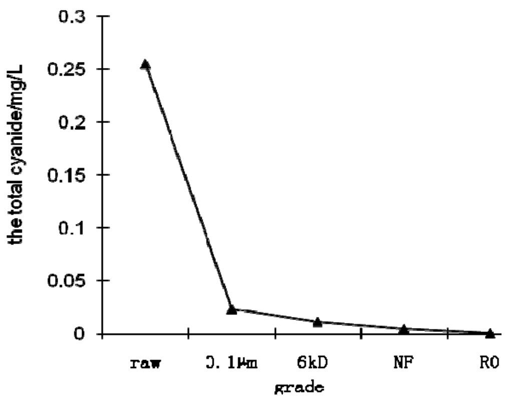

Figure 11. PSD-based total cyanide of the solvent recovery tower effluents

VI. Conclusion

The pollutants in the wastewater have great effects on the effective treatment process, thus the information of particle size distribution enable to estimate the treatment effects and feasibility of process, but also reveal the potential combination of technology. In the light of the results presented in the preceding sections, the concluding remarks of this study may be outlined as follows:

1) The present wastewater treatment plant of dry-spun acrylic fibrous factory was ineffective and costly. The investigated result showed that the removal of COD was only 49.78%, ammonia nitrogen of effluents increased to 330.35 mg/L, and the total cyanide increased. And DO data indicated that aerobic tank and anoxic pond were ineffective.
2) The extension of particle size for effluents of the solvent recovery tower was narrow, and PSD-based COD of more than 0.1μm portion, colloid, nanometer grade and soluble COD fractions accounted for 1/4. COD for monomer recovery tower effluents was relatively complicated, involving colloid (1-5 nm) (58.59 % COD) , no more than 200 molecular weight substance (20 % COD), and more than 0.1μm portions (21.41% COD).
3) PSD-based character, the fingerprint of water quality, are as follow. It is reported that anaerobic process of the biological treatment was restrained by SO_3^{2-}, and SO_3^{2-} of the monomer recovery tower was 122.57mg/L. And SO_3^{2-} could be cut off 45.61% and 55.03% by UF and RO. As for the solvent recovery tower effluents, Ammonia-nitrogen was irregular, but ammonia-nitrogen of the monomer recovery tower could decreased by NF and RO filtration.
4) So the significant particle size distribution method offers us a new insight for the analysis of complex wastewater. Then similar studies are recommended for different wastewaters, particularly for the assessment and the study of particle size distribution of industrial wastewater.

Appendix

Attach 1. The partial statistical data of Fushun factory in 2007

Kinds of sewage	pH	COD_{cr} / mg/L	SO_3^{2-} /mg/L	DMF /mg/L	SS / mg/L
Sewage from the monomer recovery unit	6.94	1529.7	739.46	25.88	121.37
Sewage from the solvent recovery unit	7.40	585.24	76.28	344.59	98.64
Back spinning sewage	7.58	180.47	-	44.5	-
Acrylonitrile unit wastewater	7.22	2378.26	-	-	22.4
Sewage from factory Shun-neng	8.85	370.35	-	-	-
NO.11 line mixed sewage	7.80	705.21	150.00	136.88	114.00

Influent of sewage treatment plant	7.43	1078.44	153.59	84.75	208.96

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REFERENCES

[1] Bo-zhang Qian, Jian-fang Zhu. The analysis of the market about acrylonitrile production at home and abroad [J]. Jiangsu Chemical Industry, 2007, 35(1), pp. 56-59.

[2] Xi-hong Chen. Current situation and Development analysis of Arylic fiber in recent years in China [J]. Hebei Textile, 2006, (3): pp. 1-4.

[3] Song Qian. Acrylonitrile production analysis at home and abroad [J].Economic analysis of China petroleum and chemical industry, 2006, (21): pp. 22-25.

[4] Zhi-bing Xu, Xue-jun Kong, chuan-gang Wang. The study on the treatment of acrylic fiber wastewater [J]. Journal of Anqing Teachers College (Natural Science Edition), 2006, 12(1), pp.89-91.

[5] Jing Lou, Ni-sha Jin. Study progress on wastewater treatment technology of Dry-spun acrylic fiber [J]. the Chinese Institute of Environmental Management Journal, 2005, 15(1): pp. 45-47.

[6] Dong Guo, Hong Cao. Treatment acrylic fibrous wastewater with Coagulation- Overpotential three- dimensional electrolysis-microaerobic- aerobic technology [J]. Technology of Water Treatment, 2009, 29(7): pp. 35-37.

[7] Jinyuan Jiang, Yong Li, Guowei Wang, Yuexi Zhou. Acrylic fibrous wastewater treatment with Fenton [J]. Environmental scientific research, 2010, 23 (7): pp. 897-901.

[8] Yong Li, Jinyuan Jiang, Yuexi Zhou, Guowei Wang. Acrylic fibrous wastewater treatment with integration Fenton reactor [J].Hebei teacher-training college journal(natural edition), 2010, 34 (3): pp. 335-338.

[9] M.Sarla, M Pandit, JC Kapoor, et al. Photo-oxidation of cyanide in aqueous solution by the UV/H2O2 process[J]. Chemical Technology & Biotechnology, 2004, 80 (1): pp.13-19.

[10] Yinsi Tang, Yuansheng Li. Removal of Ammonia-nitrogen for acrylic fibrous wastewater[J]..Environmental Chemistry, 2009, 29 (2): pp. 154-156.

[11] Chongtian Yang, Zhiyong Tian, Yonghui Song, Rongtao Cui, Hong Yang, Guanglei Qiu. Acrylic fibrous wastewater treatment with MBR[J].Environmental Science Research, 2010, 23 (7): pp.912-917.

[12] A.D.Levine, G.Tchobanoglous, T.Asano. Size distributions of particulate contaminants in wastewater and impact on treatability[J]. Water Research, 1991, 25 (8): pp. 911-922.

[13] Bing-zhi Dong, Wei-ying Li, Chen Yan, Wei Jin, Dawen Cao, Jinchu Fan. Evaluation with the change of organics MW distribution for effect of organics removal by different treatment method [J]. Technology of Water Treatment, 2003, 29(3): pp. 155-158.

[14] D. Ebru, Serdar Dogˇ ruel, O¨ zlem Karahan, D. Orhon. Size distribution of wastewater COD fractions as an index for biodegradability[J]. Water Research, 2006, 40(2): pp.273-282.

[15] O. Karahan. Dogruel, E. Dulekgurgen, D. Orhon. COD fractionation of tannery wastewaters-particle size distribution, biodegradability and modeling[J]. Water Research, 2007, 42 (4-5): pp.1083-1092.

[16] Dong Yun Ha, Soon Haing Cho, Young Kwon Kim, Leung SW. A new approach to characterize biodegradation of organics by molecular Mass distribution in landfill leachate[J]. Water Environment Research, 2008, 80 (8): pp.748-757.

[17] P. J. Roeleveld, M. C. M.van Loosdrecht. Experience with guidelines for wastewater characterization in the Netherlands[J]. Water Science and Technology, 2002, 45 (6): pp.77-87.

[18] Heukelekian, H., Balmat, J.L. Chemical composition of particulate fractions of domestic sewage [J]. Sewage and Ind Wastes, 1959, 31: pp. 413-423.

[19] Yong-feng Zhang, Wang Yu, Zhen-liang Xu, Fengkai Lin, Zheng Xu, Mei Jiang. Study on the treatment of polyacrylotrile wastewater with nanofiltration [J]. Industrial water treatment, 2004, 24(10): pp. 13-16.

BIOGRAPHY

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1. A study on the treatment of emulsified-oil containing wastewater with calcium sulfate whisker. Industrial Water Treatment, 2005
2. The research of acrylonitrile production wastewater treatment. Synthetic Fiber in China, 2008
3. Progress in wastewater treatment of dry-spun PAN fiber. Synthetic Fiber in China, 2010

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