Nitrogen and Phosphorus Pollutants in Cosmetics Wastewater and Its Treatment Process of a Certain Brand

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Abstract. Cosmetics wastewater is one of the sources of nitrogen and phosphorus pollutants that cause eutrophication of water bodies. This paper is to test the cosmetics wastewater in the production process with American Hach method, and the pH and other indicators would be detected during a whole production cycle. The results show that the pH value in wastewater is 8.6~8.7 (average 8.67), SS 880~1090 mg.L⁻¹ (average 968.57), TN 65.2~100.4 mg.m⁻³ (average 80.50), TP 6.6~11.4 mg.m⁻³ (average 9.84), NH₃-N 44.2~77.0 mg.m⁻³ (average 55.61), COD 4650~5900 mg.m⁻³ (average 5490). After pollutant treatment, the nitrogen and phosphorus pollutants in wastewater can reach the standard discharge.

1. Introduction
With the continuous improvement of people's living standards, the demand for cosmetics is growing. According to reports [1-2], the national cosmetics retail sales amounted to 204.9 billion with more than 20,000 kinds of products, and the import amounted to 74,000 tons, export 437,000 tons.

Along with the increasing demand, the amount of wastewater caused by the production of cosmetics is also growing. There are various and complex cosmetics pollutants, including heavy metals, such as lead, mercury, arsenic, and inorganic compounds, such as soluble ammonium salts, nitrates, phosphates, as well as organic compound, such as fat, grease, surfactants, hydrocarbons [3-7].

Due to the heavy concentration and much nitrogen and phosphorus, random emission must cause serious pollution to the regional ecological environment and exacerbate the degree of eutrophication of water. Therefore, how to properly handle the nitrogen and phosphorus pollutants in cosmetics wastewater has become a hot topic in water pollution control.

2. Testing Materials and Methods

2.1. Origin of Wastewater
Wastewater stems from a large cosmetics manufacturing enterprises in Suzhou, producing cosmetics, skin care products and hair care products.

2.2. Indicators
The indicators of cosmetics wastewater include six indicators, those are pH, SS, TN, TP, NH₃-N and COD.

2.3. Instruments and equipment
American HACH DR2800 spectrophotometer, HACH DRB200 digester, and HACH DRHQ11D pH meter.
2.4. Reagents

2.4.1 Reagent Bottles. HACH COD reagent bottle, HACH NH$_3$-N reagent bottle, HACH TN reagent bottle, TN Reagent(C) reagent bottle, and HACH TP reagent bottle.

2.4.2 Reagent Packs. Ammonia Salicylate, Ammonia Cyanurate, TN Persulfate Reagent, TN Reagent(A), TN Reagent(B), Potassium Persulfate, and Phosver 3 powder packs.

2.4.3 Other reagents. NaOH standard solution and deionized water.

2.5. Detection Methods
With American Hach test methods of pH, SS, TN, TP, NH$_3$-N, and COD, the continuous detection is done during a production cycle, which is equivalent to test seven times.

3. Test Results and Analysis

3.1. Pollutant content
As can be seen from Table 1, the pH of cosmetics wastewater is 8.6-8.7, with an average of 8.67; SS 880-1090 mg.L$^{-1}$, with an average of 968.57 mg.L$^{-1}$; TN 65.2-100.4 mg.m$^{-3}$, with an average of 80.50 mg.m$^{-3}$; TP 6.6-11.4 mg.m$^{-3}$, with an average of 9.84 mg.m$^{-3}$; NH$_3$-N 44.2-77.0 mg.m$^{-3}$, with an average of 55.61 mg.m$^{-3}$; COD 4650-5900 mg.m$^{-3}$, with an average of 5490 mg.m$^{-3}$.

| Time        | pH (Dimensionless) | SS (mg.L$^{-1}$) | TN (mg.m$^{-3}$) | TP (mg.m$^{-3}$) | NH$_3$-N (mg.m$^{-3}$) | COD (mg.m$^{-3}$) |
|-------------|-------------------|------------------|------------------|-----------------|------------------------|------------------|
| Sunday      | 8.7               | 880              | 86.3             | 6.6             | 62.5                   | 4650             |
| Monday      | 8.7               | 950              | 76.7             | 9.9             | 44.2                   | 5460             |
| Tuesday     | 8.7               | 1030             | 100.4            | 11.2            | 53.4                   | 5900             |
| Wednesday   | 8.7               | 980              | 82.6             | 10.9            | 55.4                   | 5770             |
| Thursday    | 8.7               | 930              | 65.2             | 9.5             | 55.4                   | 5390             |
| Friday      | 8.6               | 1090             | 68.9             | 11.4            | 65.9                   | 5950             |
| Saturday    | 8.6               | 920              | 83.4             | 9.4             | 77.0                   | 5310             |
| average     | 8.67              | 968.57           | 80.50            | 9.84            | 55.61                  | 5490.0           |
| amplitude   | 8.6-8.7           | 880-1090         | 65.2-100.4       | 6.6-11.4        | 44.2-77.0              | 4650-5900        |

3.2. The stability of pollutant content
The results show that the pH value is the most stable, while the contents of SS and COD are relatively stable, with change range about ±10%. The content of TN, TP and NH$_3$-N are relatively large, about 30% (Table 1).

3.3. Relation of pollutants
Figure 1 shows that SS, TP and COD trends are basically the same, suggesting that TP, COD and SS are more closely related; the changes of TN, NH$_3$-N are different from SS, TP, COD, suggesting that TN, NH$_3$-N and SS are less related.

Although Figure 1 shows that the trend of change between TN and NH$_3$-N is inconsistent, it can be seen from Table 2 that the nitrogen-containing pollutant is mainly NH$_3$-N, accounting for 69.1% of the TN content, up to 95.6%.
Figure 1. The relation of pollutants content changes.
(Unit: SS is 100mg.L⁻¹; TN is 10mg.m⁻³; TP is mg.m⁻³; NH₃-N is 10mg.m⁻³; COD is 1000mg.m⁻³.)

Table 2. NH₃-N / TN ratio of a brand of cosmetics wastewater.

| Time       | Sunday | Monday | Tuesday | Wednesday | Thursday | Friday | Saturday | Average |
|------------|--------|--------|---------|-----------|----------|--------|----------|---------|
| NH₃-N/TN(%)| 72.4   | 57.6   | 53.2    | 67.1      | 85.0     | 95.6   | 92.3     | 69.1    |

4. Treatments

4.1. Process

4.2. Explanation of process

4.2.1 Adjusting tank. Cosmetics wastewater quality is often unstable, with a strong randomness. Through the adjustment of the pool, the fluctuations of wastewater can be reduced, so that the cosmetics wastewater can be stable, to provide a stable and optimized operating conditions for the subsequent water treatment system. pH ranges from 5.7-7.8, not more than 8.2.

4.2.2 Coagulating tank. Add polyaluminium chloride coagulant to reach coagulation through which more than 80% of fat and oil can condense into alum, convenient for the following treatment. However, this automate management needs more medication and costs highly. Meanwhile, in the coagulation process, there are often some problems to be dealt with, as shown in Table 3.

4.2.3 Air floating pool. Apply pressurized dissolved air flotation through which cosmetics wastewater can remove grease, to ensure the normal operation of biochemical system. In operation, the filter of sewage pump is easy to be plugged, and regular cleaning should be done.
4.2.4 Biochemical tank. Apply the flowing activated sludge treatment. According to the season, determine the aeration time, sludge in sedimentation tank and sludge discharge. In summer, the aeration should be 4 hours with 1 hour stop, and mud age should be controlled in 20 days, MLSS in 2000 mg. L^-1; in spring and autumn, aeration should be 2 hours with 1 hour stop, and mud age should be controlled in 25 days, MLSS in 2500 mg.L^-1; in winter aeration should be 1 hour with 1 hour stop, with mud age should be controlled in 30 days, MLSS in 3000 mg.L^-1. This method helps to produce easily settlable sludge, to achieve a large number of nitrogen and phosphorus removal, but the energy consumption and noise is high.

4.2.5 Sedimentation tank. Apply vertical flowing sedimentation tank, convenient to remove sludge, and no mechanical scrapping equipment is needed so that only small room is occupied. However, the problems are high cost, small single pool volume, deep pool, and difficult construction.

4.2.6 Sludge dewatering. By controlling the fluent flow at 6 m^3.h^-1, the sludge solidification rate is about 20%, to achieve good separation of mud and water.

| Problems | Reasons | Counter measures |
|----------|---------|-----------------|
| Flocs at the sedimentation tank, despite normal floc at the end of the reaction tank. | Overload of Sedimentation tank. | Increase the number of sedimentation tank, and reduce the surface hydraulic load. |
| The flocculation of the reaction tank is small and the sedimentation tank is turbid. | Water alkalinity is low | Increase alkalinity |
| At the end of the reaction tank, the floc is loose and the sedimentation tank is turbid. | Excess flocculation dosing. | Reduce the amount of flocculation dosage. |

4.3. Processing effects
The results show that TN, TP, NH_3-N and COD produced in the process of cosmetics production could meet the requirements of "Standard for the discharge of water pollutants in the pharmaceutical industry" (GB21906-2008) (Table 4).

| Program | pH (Dimensionless) | SS (mg.L^-1) | TN (mg.m^3) | TP (mg.m^3) | NH_3-N (mg.m^3) | COD (mg.m^3) |
|---------|-------------------|--------------|-------------|-------------|----------------|--------------|
| Water quality Emission Standards | 7.2 6~9 | 31 ≤50 | 8.4 ≤20 | 0.02 ≤0.5 | 6.5 ≤8 | 69.3 ≤100 |

5. Conclusions
5.1. Pollutants Content and Existential Form
Cosmetics wastewater is weakly alkaline with pH between 8.6-8.7, and it should be reconciled firstly. The average content of suspended solids is 968.57 mg.L\(^{-1}\), the main components of which is ethanol or glycerol and fatty acids to form lipid compounds, and mainly fatty alcohols. COD content is very high, about 4650-5900 mg. m\(^{-3}\).

The content of nitrogen and phosphorus pollutants is highest. TN has an average content of 80.50 mg.m\(^{-3}\) and TP content 9.84 mg.m\(^{-3}\). Among them, NH\(_3\)-N content reaches 55.61 mg.m\(^{-3}\) on average, mainly dissolved ammonium salt, accounting for 69.1% of TN content, which is the main form of nitrogen in cosmetics wastewater. Phosphorus-containing contaminants are mainly present in the form of 2-phosphate-glycerol and phosphocreatine, and some are present as soluble phosphate.

5.2. Effect of Pollutant Treatment
Although the TN, TP, NH\(_3\)-N and COD produced in the process of cosmetics production can meet the emission standards, it is necessary to upgrade the processing technology if it needs to meet the national special emission requirements. Due to the high cost of upgrading the bid, it is suggested to combine the environmental transformation of the cosmetics factory to increase the ecological management of the wetland, and to reduce the processing cost while meeting the special emission standards.

5.3. Reuse of Pollutants
Cosmetics wastewater not only contains high oil, but also has more nitrogen and phosphorus compounds. These pollutants are often valuable industrial and agricultural raw materials or products, semi-products, and they can be reused by extracting fatty alcohols or producing organic fertilizer necessary for flowers and seedlings, so as to achieve reuse of wastewater and reduce pollution and damage to the ecological environment.

Acknowledgments
This research was financially supported by “Qinglan Project” of Universities in Jiangsu province (Grant NO. 2016-15), Jiangsu province “333 High-level Personnel Training Project”(Grant NO. BRA2016489), and Jiangsu province “Six Talent Peaks Project” (Grant NO. 2016-NY-093).

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