Assessment of wastewater on-line monitoring system in an important industrial park in Tianjin, China

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Abstract. Chemical oxygen demand and ammonia nitrogen were key water pollutants under state control, and key factories were required to conduct online monitoring. In order to evaluate the accuracy of the online instrument, the online equipment comparison monitoring of 20 key factories in 8 industries was conducted for 4 years. The wastewater of factories in the same industry has similar contaminant discharge concentration. The mean value of relative error absolute value was below 20% for medium and high concentration of chemical oxygen demand (above 30 mg/L) and ammonia nitrogen (above 1 mg/L) in water samples. For high chlorine concentration and coloured water samples, the online monitoring error was large, so the method needs to be improved.

1. Introduction

China’s environmental protection law stipulates that key polluters must install online monitoring systems. As the total emission control indicators of The 13th Five-year Plan, chemical oxygen demand (COD) and ammonia-nitrogen (NH₃-N) which reflect the status of industrial emissions and have an important impact on the quality of environmental water need to be monitored. Many large scale factories in many industries in the most important industrial park of Tianjin, Tianjin Economic-Technological Development Area (TEDA), and COD and NH₃-N emissions from them need to be well controlled.

Most of the large scale factories have installed wastewater on-line monitoring system. The on-line instrument must be installed and accepted according to the national standard [1, 2]. However, due to the difference between laboratory standard methods and on-line monitoring methods, the status and accuracy of on-line monitoring instruments need to be evaluated. COD and NH₃-N online monitoring systems of 20 representative factories in 8 industries had been investigated and evaluated by the comparison monitoring of laboratory standard analysis methods and on-line monitoring methods.

2. Method and monitoring plan

2.1. Monitoring plan

Sampling site: Samples were collected at main outlet of wastewater where the on-line monitoring systems have been installed of the representative factories in seven industries, including chemical, food, electronics, electroplating, automotive manufacturing, pharmaceutical and sewage treatment.
plants. Drainage discharges were measured and sample properties were marked. The monitoring indices were COD and NH$_3$-N.

Evaluation method: After the water samples were collected, they were divided into two parts. One part was analyzed with on-line monitoring instrument, and the other was analyzed with laboratory standard methods. The relative errors of on-line monitoring data were calculated by taking the data obtained by laboratory method as the true value, and indicated the quality of the on-line monitoring instruments.

Sampling frequency: The comparison monitoring had been carried out once a season from 2015 to 2018. Three water samples were collected at a time and no less than 10% of parallel samples were monitored.

2.2. Monitoring methods

The laboratory methods selected were the National standard methods [3-5]. The on-line instrument method was similar to the international method [6-7]. The principles of wastewater on-line monitoring systems were similar to the National standard methods, but there were differences in water sample volume, sample pre-treatment method and reaction time (See table 1 for details). As the chloride ion was the main interfering factor of COD, the laboratory method of COD selected dichromate method for samples of Cl$^-$ no more than 1000mg/L and chlorine emendation method for samples of Cl$^-$ between 1000mg/L and 2000mg/L. Chromaticity has an important influence on the analysis of NH$_3$-N, which can be removed by pre-treatment such as distillation in the laboratory method. Duration time of on-line monitoring instruments was less than that of laboratory method, and COD can be reduced by more than half. Since the online instruments were continuous sampling analysis, the cost of a single sample was 3/1 to 1/2 of the laboratory method, taking into account the cost of the online instruments.

### Table 1. Comparison of parameters between on-line instrument and laboratory method.

| Parameters              | COD Principle | COD on-line instrument | COD laboratory method | NH$_3$-N on-line instrument | NH$_3$-N laboratory method |
|-------------------------|---------------|------------------------|-----------------------|-----------------------------|---------------------------|
|                         | Dichromate method | Dichromate method (Cl$^-$ no more than 1000mg/L) | Chlorine emendation method (Cl$^-$ between 1000mg/L and 2000mg/L) | Nessler’s reagent spectrophotometry | Nessler’s reagent spectrophotometry |
| Sample volume           | 2 ml Cl$^-$    | 20 ml Cl$^-$           | 2ml Colour            | 50ml Colour                 |                           |
| Pre-treatment method    | Mercury sulfate masking | Mercury sulfate masking | Dilute                | Distil                      |                           |
| Duration time.          | 1hour          | 2.5 hour               | 20min                 | 30min                       |                           |
| Cost                    | 15RMB          | 50RMB                  | 15RMB                 | 30RMB                       |                           |

3. Results and discussion

3.1. Information of the wastewater of factories in different industries

Drainage conditions, water sample characteristics, and the average of the concentration of wastewater of 20 representative factories in 8 industries (battery manufacturing, electroplating, electronic industry, petrochemical industry, automobile making, bio-pharmaceutical industry, food processing, and sewage treatment plant) have been investigated (Table 2). The discharge amount of waste water is divided into several levels and special water samples (high concentration chloride ion or coloured sample) were marked. Average of the concentration of wastewater and confidence interval were calculated.

Perhaps because of the similar production process, the wastewater of factories in the same industry has similar discharge concentration of COD and NH$_3$-N. The wastewater of sewage treatment plant
was large while COD and NH$_3$-N concentration was low. For colored wastewater in biopharmaceutical industry and food processing, the uncertainty of NH$_3$-N was relatively large. Due to the large proportion of domestic sewage, the pollutant concentration of industries with lower wastewater discharge was relatively stable.

### Table 2. Information of the wastewater of factories in different industries.

| Industry               | Factory code | Wastewater discharge (m$^3$/h) | Wastewater character | Mean of the concentration of wastewater |
|------------------------|--------------|--------------------------------|----------------------|-----------------------------------------|
| Battery manufacturing  | A            | <10                            | -                    | 21±3 (mg/L), 1.68±0.17 (mg/L)          |
| Electroplating         | B            | <10                            | -                    | 84±14 (mg/L), 15.2±2.03 (mg/L)         |
| C                      | <10          | -                              |                      | 28±3 (mg/L), 1.69±1.10 (mg/L)         |
| Electronic industry    | D            | 10–50                          | -                    | 34±6 (mg/L), 0.58±0.06 (mg/L)         |
|                        | E            | 50–100                         | -                    | 26±3 (mg/L), 2.12±0.28 (mg/L)         |
| F                      | <10          | -                              |                      | 59±11 (mg/L), 4.21±1.06 (mg/L)        |
| Petrochemical industry | G            | 50–100                         | -                    | 56±8 (mg/L), 3.03±0.79 (mg/L)         |
|                        | H            | <10                            | -                    | 96±17 (mg/L), 0.82±0.17 (mg/L)        |
|                        | I            | <10                            | -                    | 53±5 (mg/L), 15.2±1.27 (mg/L)         |
| J                      | 50–100       | -                              |                      | 155±27 (mg/L), 1.93±0.54 (mg/L)       |
| Automobile making      | K            | 10–50                          | -                    | 60±6 (mg/L), 9.99±1.07 (mg/L)         |
|                        | L            | 10–50                          | -                    | 93±9 (mg/L), 12.7±0.94 (mg/L)         |
|                        | M            | 10–50                          | -                    | 136±12 (mg/L), 17.8±1.01 (mg/L)       |
| Bio-pharmaceutical     | N            | 50–100                         | 1000mg/L, coloured   | 203±26 (mg/L), 2.90±0.83 (mg/L)       |
| Industry               | O            | 10–50                          | -                    | 32±2 (mg/L), 0.43±0.13 (mg/L)         |
| Food processing        | P            | 10–50                          | coloured             | 189±45 (mg/L), 2.24±0.41 (mg/L)       |
|                        | Q            | 10–50                          | coloured             | 59±9 (mg/L), 1.31±0.42 (mg/L)         |
| Sewage treatment plant | R            | >1000                          | -                    | 24±2 (mg/L), 0.37±0.13 (mg/L)         |
|                        | S            | >1000                          | -                    | 35±5 (mg/L), 0.76±0.21 (mg/L)         |
|                        | T            | 50–100                         | -                    | 30±1 (mg/L), 0.56±0.06 (mg/L)         |

#### 3.2. Accuracy of online monitoring data

The relative errors of on-line monitoring data at different concentrations of COD and NH$_3$-N were showed in Figure 1 and Figure 2. Obviously, the relative errors of higher concentration of wastewater were smaller. The relative errors of lower the concentration of wastewater were more dispersive and more outliers appeared.

The comparison data were divided into four categories according to the concentration of wastewater. The mean value of relative error absolute value (MARE) and standard deviation of relative error (SRE) were calculated respectively to evaluate the accuracy of on-line instruments. As illustrated in Table 3, the on-line instruments were very accurate for wastewater of high concentration (COD above 100 mg/L and NH$_3$-N above 15mg/L). The MARE and SRE of wastewater of medium concentration (COD 30-60 mg/L and 60-100 mg/L, NH$_3$-N 1-5mg/L and 5-15 mg/L) were almost the same and at the acceptable range. The MARE and SRE of wastewater of low concentration (COD below 30 mg/L and NH$_3$-N below 1 mg/L) were large, and it showed that the on-line instrument had a big error to low concentration wastewater.
3.3. Analysis of comparison results of special water samples

Some substances in wastewater can interfere with monitoring. High concentrations of chlorine ions will make the COD data high, and the coloured water had interfered with the monitoring of NH$_3$-N. The comparison results of water samples with special characteristics were shown in Table 4. Mercury sulphate was used to mask Cl$^-$ in the dichromate method, but water samples with high chlorine

Table 3. Accuracy of on-line monitoring at different concentrations.

| COD Concentration (mg/L) | MARE (%) | SRE (%) | NH$_3$-N Concentration (mg/L) | MARE (%) | SRE (%) |
|-------------------------|----------|---------|-------------------------------|----------|---------|
| <30                     | 25.8     | 32.9    | <1                           | 32.9     | 56.2    |
| 30-60                   | 19.0     | 24.6    | 1-5                          | 14.5     | 21.3    |
| 60-100                  | 17.5     | 20.8    | 5-15                          | 13.9     | 18.8    |
| >100                    | 13.2     | 16.9    | >15                           | 4.1      | 4.0     |
concentrations ($m\ [Cl^-] > 1000\text{mg/L}$) were not completely masked. Chlorine emendation method used in the laboratory can solve the problem effectively. So MARE of high chlorine concentrations was much larger than other water samples of the same concentration (positive error). As for ammonia nitrogen monitoring, water colour was removed by distillation and pure water was used as reference (zero value) in laboratory methods, while the on-line monitor adopts raw wastewater as reference colour. When the water was coloured, the use of raw wastewater as a reference can lead to low correction absorbance, which leads to low monitoring results. This was why MARE of coloured wastewater was much larger than other water samples of the same concentration (negative error).

### Table 4. Accuracy of on-line monitoring of special water samples.

| Wastewater character | COD Concentration (mg/L) | MARE (%) | SRE (%) | NH$_3$-N Concentration (mg/L) | MARE (%) | SRE (%) |
|----------------------|--------------------------|-----------|---------|-----------------------------|-----------|---------|
| m[Cl$^-$] > 1000mg/L | >100                     | 36.9      | 26.1    | -                           | -         | -       |
| Coloured             |                          |           |         | 1.5                         | 27.1      | 30.0    |

4. Conclusion

The on-line instrument can provide continuous wastewater monitoring data, which can make up for the problem of low manual monitoring density and small data amount, and is an important part of the monitoring system. The online instrument comparison data of 20 key factories in 8 industries over a period of 4 years shows that the online instrument has a good accuracy in monitoring medium and high concentration of COD and NH$_3$-N in water samples. Considering that online instruments were used to monitor high concentrations of water, especially when the emission standard limit was exceeded, the on-line instrument can meet the daily supervision requirement. Compared with the laboratory method, the anti-interference ability of the on-line instrument is poor. It is suggested to add the pre-treatment module or improve the monitoring method to meet the demand for special wastewater.

References

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