Water Reuse

A modified spectrophotometric method for selective determination of trace urea: application in the production process of ultrapure water

Shilong Jiang[a,b], Jianglei Xiong[b], Song Cheng[a], Jiashun Cao[a,]* and Runbo Yuan[b]

[a] College of Environment, Hohai University, Nanjing 210098, China
[b] Environmental Engineering Research Institute, China Electronics System Engineering No. 2 Construction Co., Ltd, No. 88, Juqu RD, Wuxi 214000, China
*Corresponding author. E-mail: caojiashun@126.com

ABSTRACT

Conventional spectrophotometric methods were unable to accurately detect urea concentrations below 100 μg/L. A modified spectrophotometric method was developed to determine the trace urea in the ultrapure water (UPW) production process of the semiconductor manufacturing industry. This method was optimized based on the dosage of chemical agents, length of the optical path, and mode of the water bath. Metal ions were added to promote the stability of the chromogenic system. A calibration graph was observed with ideal linearity in the range of 0.8–100 μg/L. The detection and quantification limits of urea were 0.24 and 0.80 μg/L, respectively. The distribution of urea in raw water for the UPW production process was observed and the urea in tap water was 10–20 μg/L. The urea of municipal reclaimed water was 24–40 μg/L, which was twice that of industrial reclaimed water at 10–18 μg/L. The total removal rate of urea by the UPW production process was 50–70%. Reverse osmosis membranes played a critical role in the removal of urea (over 30%). The urea in the final UPW produced from tap water was approximately 4.1 μg/L, which creates a potential risk of excessive total organic carbon.

Key words: reclaimed water, spectrophotometry, total organic carbon, ultrapure water, urea

HIGHLIGHTS

- A spectrophotometric method for the determination of trace urea during ultrapure production process was first established.
- Stability of the absorbance in the color reaction was increased by doping metal ions.
- The urea concentration of municipal reclaimed water was twice that of industrial reclaimed water.
- The urea removal efficiencies in each unit of the ultrapure water production process were explored.

Graphical Abstract
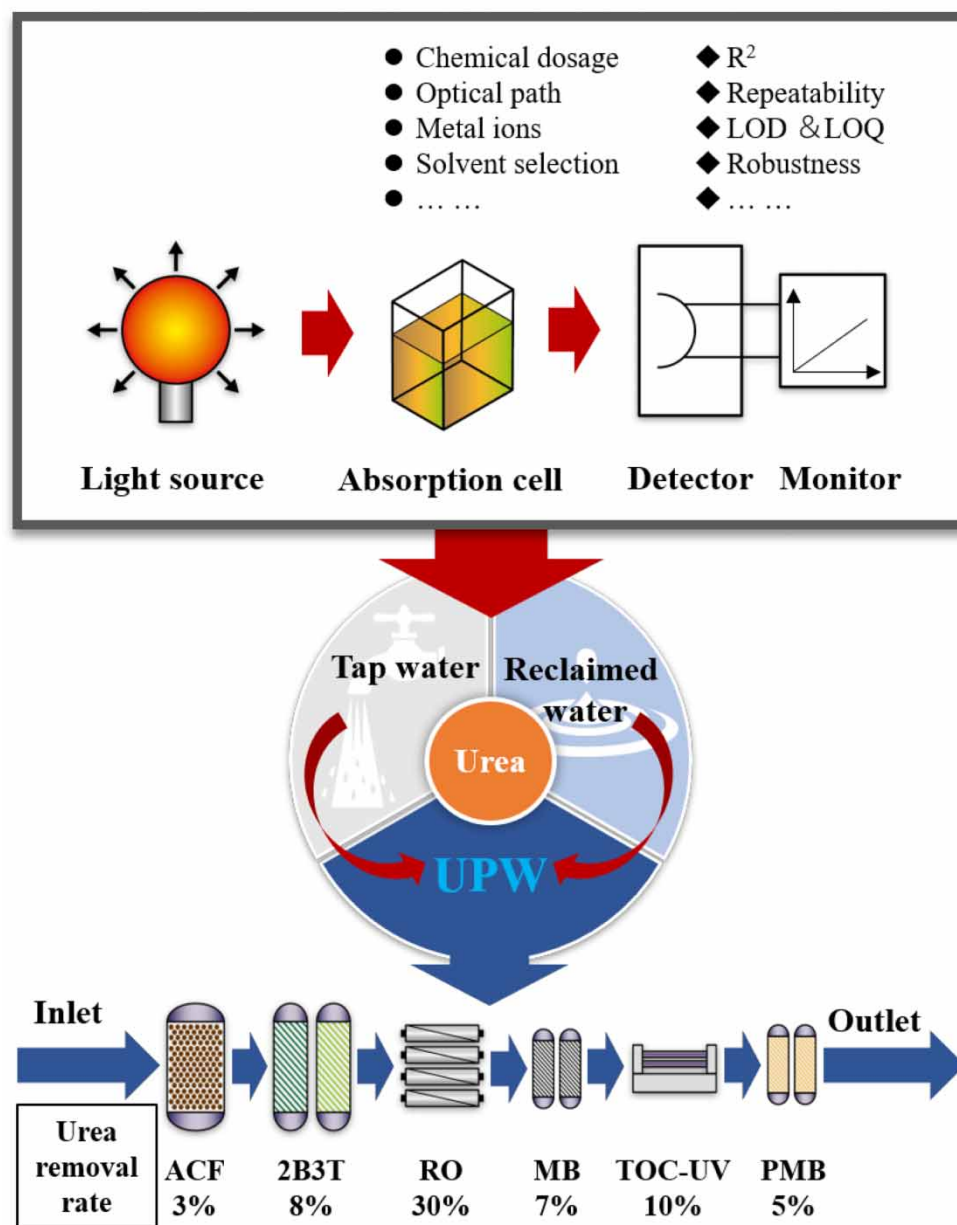
ABBREVIATIONS

2B3T	mixed bed resins and absorbing tower
ACF	activated carbon filter
AR	analytical reagent
CV	coefficient of variation
DAM	diacetylmonoxime
LOD	limit of detection
LOQ	limit of quantitation
MB	mixed bed resin

MDG   membrane degassing
MMF   multimedia filter
POU   point of use
RO   reverse osmosis
TOC   total organic carbon
UF   ultrafiltration
UPW   ultrapure water
UV   ultraviolet

1. INTRODUCTION

In recent years, the semiconductor manufacturing industry has developed rapidly. Ultrapure water (UPW) is an important auxiliary material that is used in chip production. Its consumption is tremendous, and 32 kg of water is used to produce a chip weighing 2 g. Therefore, the use of reclaimed water instead of tap water to produce UPW has received widespread attention. There have been many reports on the use of reclaimed water for landscape reuse, groundwater recharge, etc. (Zhu & Dou 2018), but few for UPW production because of the stringent requirements for the quality of UPW. There are strict regulations on the concentration of total organic carbon (TOC), metal ions, anions, and other substances in the UPW.

However, this industry has stringent requirements for the quality of UPW; there are strict regulations on the concentration of TOC, metal ions, anions, and other substances in the UPW. For example, in some microelectronic industries (line width of chip 14–28 nm), the concentration of TOC in the UPW is required to be less than 0.5 µg/L, which puts forward stricter requirements for the quality of raw water in the UPW production process (Melnik & Krysenko 2019). Therefore, it is important to guarantee the quality of UPW from different water sources.

Recent studies (Choi et al. 2016; Lee et al. 2016) have found that neutral, low-molecular-weight organics in reclaimed water have a potential risk of excessive TOC in the final UPW. Among these low molecular weight organics, urea has recently become a research focus. The molecular weight of urea is 60, and the removal rate of urea by the reverse osmosis (RO) membrane is only approximately 50% (Choi & Chung 2019). In addition, it has been reported that urea cannot be effectively removed by ion-exchange method because of its non-ionic structure (MacKeown et al. 2021). The conventional UPW production process (Figure 1), with membrane filtration, ion-exchange adsorption, and ultraviolet (UV) mineralization as the primary units to remove TOC, had unsatisfactory effects on urea removal (Zhang et al. 2021; Wang et al. 2022).

Owing to the decomposition of nitrogen-containing organics such as proteins in the wastewater, the urea concentration in reclaimed water is commonly higher than that in tap water (Choi & Chung 2019). This is one fundamental reason for the excessive TOC in the UPW treated by the conventional UPW production process with reclaimed water. It is necessary to determine the distribution of urea in raw water and the removal regularity during the UPW production process.

Currently, there are few suitable methods for determining trace urea in UPW. Urea determination methods can be divided into direct and indirect methods. Direct colorimetric determination methods use chemical reagents that react with urea to generate colored products. Diacetylmonoxime (DAM)-antipyrine spectrophotometry (GB/T18204.2-2014) (NIEHS 2014) is a classic direct method. The effective determination range of urea by this method is 60–600 µg/L. It
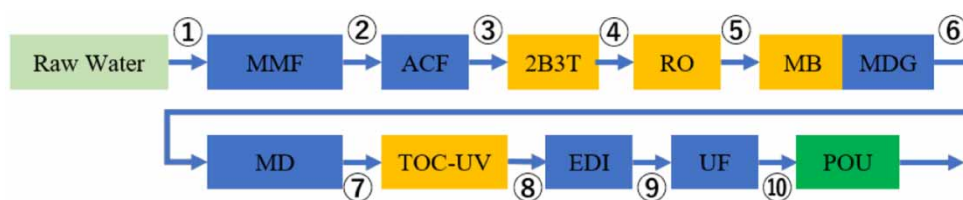

Figure 1 | Conventional UPW production process (MMF, multimedia filter; ACF, activated carbon filter; 2B3T, anion and cation bed and degassing tower; RO, reverse osmosis; MB, mixed bed; MDG, membrane degassing; TOC-UV, TOC ultraviolet disinfector; EDI, electrode ionization; UF, ultrafiltration; POU, point of use).

cannot accurately determine urea concentration below 60 µg/L because the measured absorbance is close to the detection limit (Long *et al.* 2019). This method can hardly achieve the urea determination requirement of the UPW production process in the semiconductor manufacturing industry. In addition, direct methods include the fluorescence method and high-performance liquid chromatography, which have limitations such as complicated operations and erratic reproducibility depending on the state of the instruments. Indirect methods convert urea into nitrate, ammonia, or nitrogen molecules through a series of chemical reactions and indirectly determine the urea concentration through conventional analytical techniques (Revilla *et al.* 2005; Han *et al.* 2019). The indirect methods usually require a shorter reaction time and are more convenient to operate, but they are easily affected by pH, temperature, and salt concentration during the reaction, resulting in significant detection errors (Gonzalez-Rodriguez *et al.* 2002; Alizadeh *et al.* 2017; Zhang *et al.* 2019). Therefore, the demand for accurate and stable determination of trace urea is evident in the production process of UPW. To the best of our knowledge, the determination of trace urea using a spectrophotometric method has scarcely been carried out.

In this study, a modified spectrophotometric method was first developed for the determination of trace urea in UPW. The calibration graph of the method was linear in the range of 0.8–100 µg/L, and the analytical parameters for assessment, such as accuracy and reproducibility, were evaluated. The concentration trend of urea in tap water, municipal reclaimed water, and industrial reclaimed water was explored using the method proposed in this study. The degradation of urea and TOC during the UPW production process was revealed. Thereby, feasible measures were put forward to guarantee the quality of UPW.

2. METHODS AND MATERIALS

2.1. Chemicals and instruments

The chemicals used in this study were urea (purity 99.5%, Aladdin, USA), DAM (analytical grade (AR), Sinopharm, China), acetic acid (AR, Sinopharm, China), antipyrine (CP, Sinopharm, China), sulfuric acid (AR, Sinopharm, China), phosphoric acid (AR, Sinopharm, China), and ferric chloride (AR, Sinopharm, China). Distilled water was purchased from Watson (China). A standard urea solution (100 µg/mL, AOKE, China) was diluted to different concentrations and used to evaluate the method of determination.

A water bath (HH-8, Guohua, China) was used to heat the chromogenic solution. The urea concentration in the solution was analyzed using a dual-beam UV spectrophotometer (TU-1900, Puxi, China). The amount of TOC in the water was measured using a TOC analyzer (Sievers 500, General Electric, USA).

2.2. Production of the calibration curve

DAM solution: DAM was weighed, dissolved in acetic acid, diluted to 100 mL with 10% acetic acid, and stored in a brown bottle at 25 °C. Acid solution: Antipyrine and ferric chloride were weighed and dissolved in 80 mL of sulfuric acid (1 + 1). Moreover, 20 mL of mixed acid (sulfuric acid and phosphoric acid) was added and stored in a brown bottle. Standard urea solution (0.1 g): 0.1 g of urea powder was weighed and diluted with distilled water in a 1 L volumetric flask. 100 µg/L (0.1 µg/mL) urea solution: 1 mL of standard urea solution was taken and diluted with distilled water into a 1 L volumetric flask. 1,000 µg/L (1 µg/mL) urea solution: 1 mL of standard urea solution was diluted with distilled water in a 100 mL volumetric flask.

Individually, 0, 1.5, 2, 2.5, and 5 mL of 100 µg/L urea solution and 1, 1.5, 2, and 2.5 mL of 1,000 µg/L urea solution were added to nine 50 mL brown colorimetric tubes. Standard concentrations of 0, 6, 8, 10, 20, 40, 60, 80, and 100 µg/L urea solution were prepared. 2 mL of DAM solution and 2 mL of acid solution were added and diluted to 25 mL with distilled water. Brown colorimetric tubes were heated in a boiling water bath for 50 min and cooled in running tap water for 2 min. Pure water was used as a control, and the absorbance of each tube was immediately measured at 460 nm using a 5 cm cuvette.

The absorbance was contrasted with the urea concentration to make a calibration graph.

2.3. Sample production

The water samples were reclaimed water and tap water used as raw water for the UPW production process in the semiconductor manufacturing industry, as well as the water body in the UPW production process. The urea concentration in the water samples ranged from 0.8 to 100 µg/L.

The DAM and acid solutions were added to a brown 50 mL colorimetric tube and diluted to 25 mL with the water sample. The tube was heated in a boiling water bath for 50 min, and then cooled in running tap water for 2 min. The distilled water was used as a control, and the absorbance of each tube was immediately measured at 460 nm using a 5 cm cuvette.

The corresponding urea concentration was obtained according to the calibration graph.

2.4. Machine conditions

A dual-beam UV-visible spectrophotometer was used to analyze the urea concentration. The wavelength range was 190–900 nm. When the emitted light passed through the measured substance solution, the absorbance of light of the substance varied with the wavelength of the light. In this study, through parameter optimization, it was determined that the product of this method had maximum absorbance at a wavelength of 460 nm. The absorbance of the sample solution at a certain concentration was measured at the maximum absorption wavelength and compared with that of the prepared standard sample to determine the concentration of the sample solution.

2.5. Reaction principles and calculation

Urea and diacetyl were condensed to form orange-red diazine derivatives by heating under acidic conditions. DAM is generally used as diacetyl is unstable at room temperature. Diacetyl was formed from DAM under strongly acidic conditions. Condensation of diacetyl and urea generated orange-red diazine derivatives. Both antipyrine and metal ions added in the system promote the stability of the product. The orange-red color of the product was reflected in the absorbance detected by the spectrophotometer, which corresponded to different concentrations of urea. In addition, the reaction product was unstable under light. Therefore, the reactions and measurements were performed in brown test tubes.

3. RESULTS AND DISCUSSION

3.1. Method optimization

3.1.1. Variables optimization

The variables affecting the urea concentration determination method were studied under various conditions. The optimal values are listed in Table 1. Under the optimal conditions, the absorbance of the reaction system exhibited the highest sensitivity.

3.1.2. Metal ions

When DAM reacts to form diacetyl, hydroxylamine is produced, which inhibits the reaction between urea and diacetyl. Previous studies have reported that metal ions can eliminate the interference of hydroxylamine in the reaction, thereby increasing the stability of the system (Francis et al. 2002). However, the comparison between the effects of different metal ions and the appropriate dosing concentrations still requires further exploration.

In this study, based on the above preferred conditions, Fe^{3+}/Mn^{2+} solutions of different concentrations were added for the determination of 50 μg/L urea. After the mixed solution was digested in a water bath for 50 min, colorimetry was carried out

Table 1 | Optimization of variables

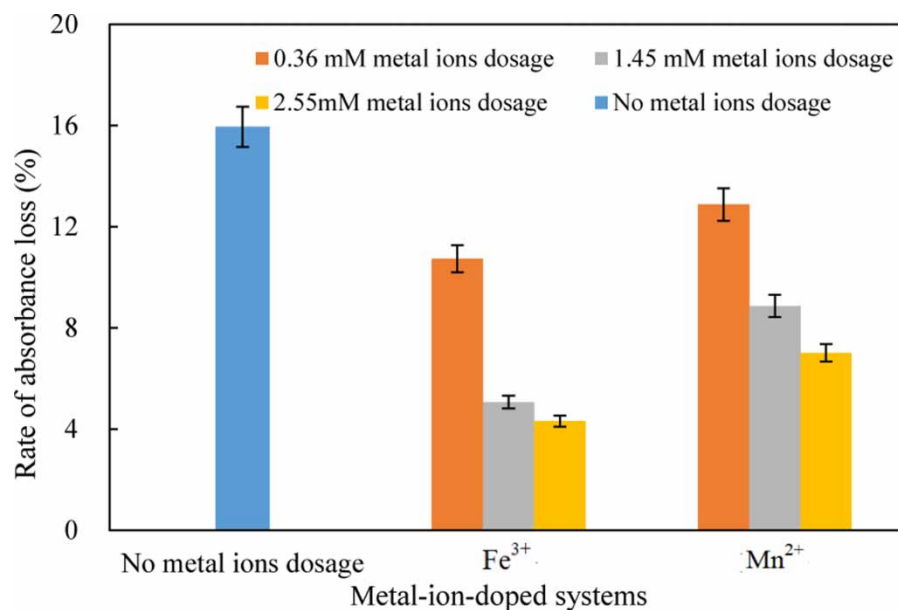| Variable	Tested range	Optimum value
Chemical		
DAM	2–8%	5%
Antipyrine	0.2–0.8%	0.5%
Wavelength	350–550 nm	460 nm
Optical path	1, 3, and 5 cm	5 cm
Water bath temperature	80–100 °C	100 °C
Water bath calefaction time	40–60 min	50 min

Figure 2 | Influence of metal ions on the stability of the reaction at 24 h.

at 460 nm using a spectrophotometer with distilled water as the background. Figure 2 shows the rate of loss of absorbance in different metal-ion-doped systems.

It was found that doping with Fe^{3+} and Mn^{2+} increased the stability of the reaction system, and the obtained results were consistent with the conclusions of Beale *et al.* (Beale & Croft 1961). The rate of absorbance loss with Fe^{3+} (1.45 mM) was much lower than that with Fe^{3+} (0.36 mM) or Mn^{2+} (0.36, 1.45, and 2.55 mM), and close to that of the reaction system with Fe^{3+} (2.55 mM). This study recommended doping with Fe^{3+} (1.45 mM) to enhance the absorbance stability of the reaction system.

The reaction path of this optimized method and the shielding effect of metal ions are shown in Figure 3. DAM was hydrolyzed to generate diacetyl under acidic conditions. The byproduct was hydroxylamine. The chromogenic reaction of diacetyl and urea generated the postulated products A or B (Francis *et al.* 2002). These two postulated products yielded absorbance at 460 nm for the quantitative determination of urea. Hydroxylamine has been reported to have a destabilizing effect on colored products (Beale & Croft 1961). Therefore, metal ions (Fe^{3+}/Mn^{2+}) were added to the original antipyrine. Under acidic conditions, both antipyrine and metal ions exhibit strong oxidizing properties that destroy hydroxylamine and generate N_2O. The addition of metal ions promoted the stability of chromogenic substances, which made the determination more accurate.

3.1.3. Solvent selection

In spectrophotometry, lower blank values can reduce the degree of data dispersion and improve the reproducibility and accuracy of results (de Oliveira e Silva *et al.* 2018). In the method for the determination of trace urea, it is critical to control the blank values of the standard samples to lower concentrations as possible. This results stringent requirement for the concentration of urea in the solvent used to prepare the standard samples.

Distilled water and deionized water were separately used as solvents to prepare standard urea solutions and establish calibration graphs in this study. The correlation coefficients of distilled water ($r^2 = 0.9991$) and deionized water ($r^2 = 0.9988$) were similar. To clarify the relatively lower urea concentration of the solvents, distilled water and deionized water were alternated as blank samples for each other, and the same pretreatment and determination were performed. The average absorbance of deionized water was +0.007 when distilled water was used as blank samples, indicating a lower concentration of urea in distilled water. This was probably because the urea was hydrolyzed and changed the original form during the heating process for the production of distilled water (Fan *et al.* 2020). Therefore, this study recommends using distilled water as the solvent to prepare a urea solution and determine the urea concentration.
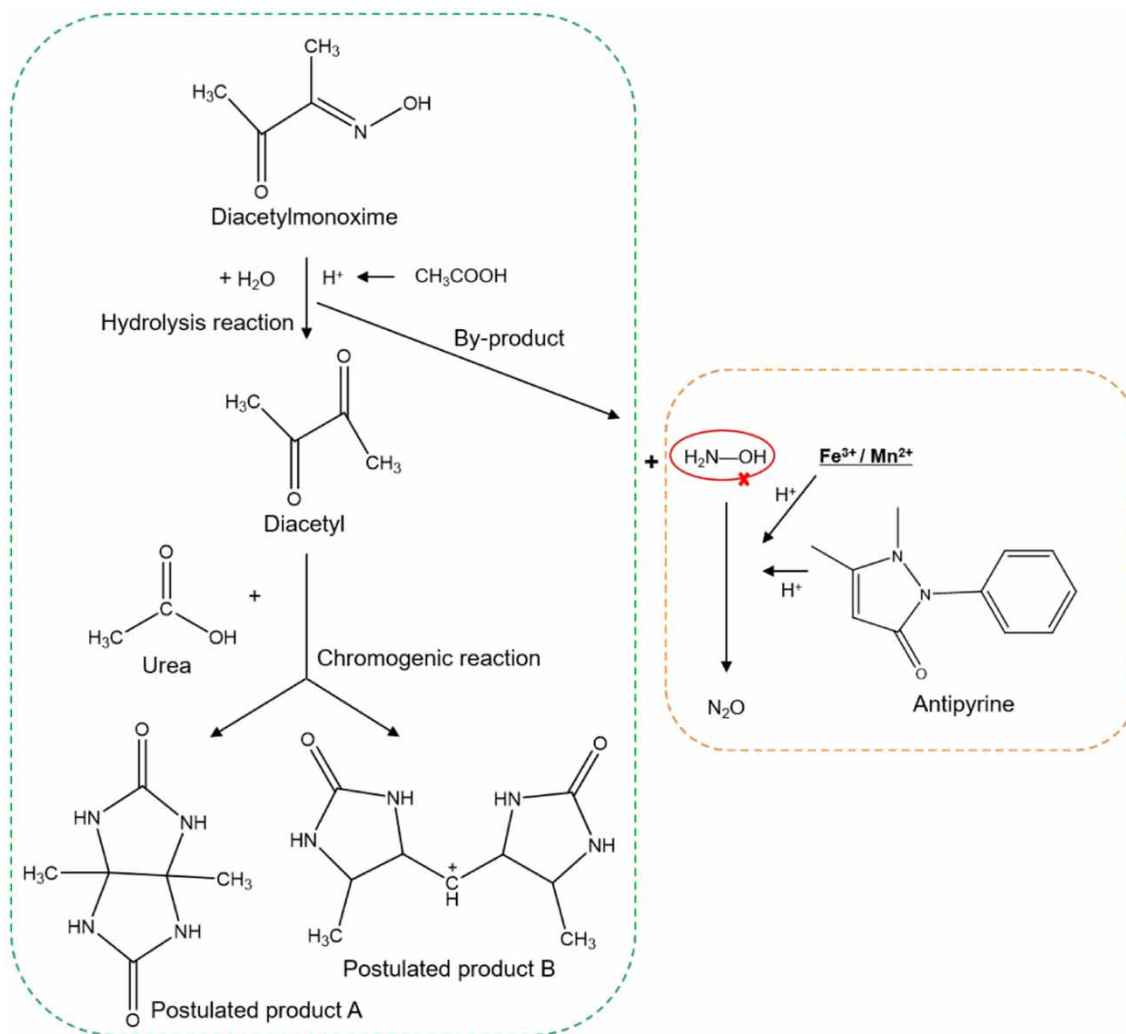
Figure 3 | Reaction path of the optimized method.

3.2. Method characterization

3.2.1. Calibration curve

A linear calibration graph was established in the range of 0.8–100 µg/L. Each point in the calibration graph represents the average of three determinations. The calibration graph is shown in Figure 4, where the slope is 3.8816, the intercept is 0.0056, and the correlation coefficient (r^2) is 0.9993, indicating ideal linearity.

The coefficient of variation (CV) for the standard urea solutions was 1.79% at a concentration of 2 µg/L urea and 0.24% at 100 µg/L urea, indicating ideal precision.

3.2.2. Evaluation of the method

Standard urea solutions of different concentrations were used for evaluation. The evaluation included repeatability, recovery rate, limit of detection (LOD), limit of quantitation (LOQ), and robustness.

• Repeatability

Standard urea solutions of 10, 40, and 80 µg/L were prepared, and six repeatability and recovery experiments were performed. According to the experimental results, the CVs of the urea solutions with low, medium, and high concentrations
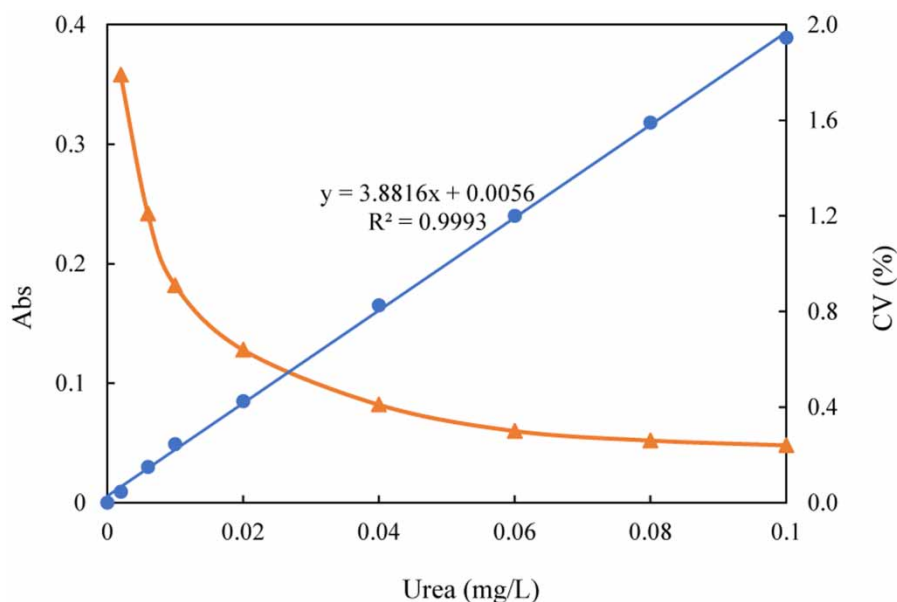
Figure 4 | Calibration curve of the trace urea detection method.

were 0.8, 0.5, and 0.3% (CV <1%), and the recovery rates were 102, 105, and 95% (95% ≤ P ≤105%), respectively. Table 2 presents the results.

- Limit of detection (LOD) and limit of quantification (LOQ)

The lowest concentrations that could be detected and quantitatively measured were defined as LOD and LOQ. In this study, the value of LOD (0.27 μg/L) and LOQ (0.80 μg/L) were calculated using the equations given below referred to the ICH Q2(R2) guideline (Bhavna *et al.* 2022).

$$LOD = \frac{3.3\sigma}{S}$$

$$LOQ = \frac{10\sigma}{S}$$

The standard deviation of y-intercepts of the regression lines was used as σ and the slope of the calibration curve was used as S. The specific calibration curve was evaluated using samples containing analytes in the range of the LOD and LOQ.

- Robustness study

This study also conducted a bias analysis using the Youden–Steiner method (Gonzalez-Rodriguez *et al.* 2002). The important variables in the system (i.e., water bath temperature, water bath time, and chemical dosage) were tested with ±10% of the optimal value, and the results showed that the errors were all less than 5%, proving that the method had ideal stability.

Table 2 | Coefficient of variation and recovery rate of water samples with different concentrations

Number	Value (μg/L)	Coefficient of variation	Recovery rate
1	9.9, 10.1, 10.0, 9.9, 9.9, 10.0	0.8%	102%
2	40.2, 40.1, 39.7, 40.3, 40.2, 40.1	0.5%	105%
3	79.8, 80.1, 80.3, 79.8, 80.1, 79.6	0.3%	95%

Table 3 | Comparison of evaluation parameters

	r^2	CV	Recovery rate	LOD (µg/L)	LOQ (µg/L)	Loss rate of absorbance (24 h)
Improved method	0.9993	≤1%	95% ≤ P ≤ 105%	0.27	0.81	5%
GB/T18204.2-2014	0.9995	≤2%	90% ≤ P ≤ 110%	20	60	13%

CV, Coefficient of variation; LOD, limit of detection; LOQ, limit of quantitation.

In addition, DAM-antipyrine spectrophotometry (GB/T18204.2-2014) was used as a reference, and r^2, CV, recovery rate, LOD, LOQ, and loss rate of absorbance (24 h) are compared in Table 3. The linearity and repeatability of the two methods were found to be similar. The LOD and LOQ of the improved method were lower, indicating that the improved method is more suitable for trace urea in reclaimed water and UPW. In addition, the improved method had a lower loss rate of absorbance (24 h) owing to the addition of metal ions.

3.3. Urea distribution in raw water for the UPW production process

The raw water for the UPW production process is mainly tap water, as well as municipal and industrial reclaimed water. In this study, in order to provide suggestions and references for the final effluent TOC control of UPW production system, the concentration distribution regularity of urea in tap water and reclaimed water in various regions of China was investigated using the modified method. Tap water and RO effluent from the water recycling plant in five regions were selected, and the average results of multiple determinations are shown in Figure 5.

These five regions include the cities with developed electronics industry in northern part (A and B), central part (C), eastern part (D), and southern part (E) in China. Among them, the samples of reclaimed water in regions A, B, and C were obtained from the municipal water recycling plant, and the others were obtained from industrial water recycling plants.

Through the water quality analysis of tap water in the northern region (A and B), central region (C), eastern region (D), and southern region (E) in China, it was found that the TOC concentrations were similar in these different areas. This distribution showed a slight difference, with a higher TOC concentration in the north than in the south. This is because most tap water is taken from natural water bodies, such as rivers and lakes. After treatment processes, such as chemical coagulation, activated carbon filtration, and chlorination disinfection, the organic matter in the effluent was decomposed to a similarly low level. Southern China experiences a large amount of precipitation, dense distribution of lakes and rivers, and less pollution of natural water bodies, which caused a slight difference in TOC values as observed in this study.

The urea concentrations in tap water from different regions of China were determined. The urea concentrations were between 10 and 20 µg/L, which was close to the distribution of TOC. Tap water remains the primary source of water for UPW production. When tap water was used as the raw water, the removal rate of urea by the UPW production process was 50–70%. As the TOC contributed by urea was only 1/5th of its mass, the traditional production process can effectively guarantee TOC ≤ 1 µg/L (Lee *et al.* 2016). However, with the increasing precision of the line width in chip production (such as 28 nm/14 nm/7 nm), some semiconductor facilities have stricter requirements for the TOC value of UPW (such as TOC ≤ 0.5 µg/L) (Melnik & Krysenko 2019). This may bring a new challenge to water quality guarantee measures when continuing to use traditional UPW production processes.

Another source of raw water for UPW production is the reclaimed water. The results showed that the TOC of municipal and industrial wastewater was different owing to the various water qualities and membrane pore sizes in membrane filtration. The determination of urea showed that the urea concentration in municipal reclaimed water was higher than that in tap water, which is in line with the conclusions of previous reports (Choi & Chung 2019). In addition, we found that the urea content of municipal reclaimed water (24–40 µg/L) was approximately twice that of industrial reclaimed water (10–18 µg/L). This is probably due to the continuous degradation of nitrogen-containing organics, such as proteins and humus, during the treatment process of municipal wastewater. The organics in industrial wastewater were primarily organic solvents such as isopropanol and acetone added during production, whereas little protein or other nitrogen-containing organics could exist during the regeneration process. Therefore, the urea concentration in the reclaimed industrial water was significantly lower than that in the municipal reclaimed water.
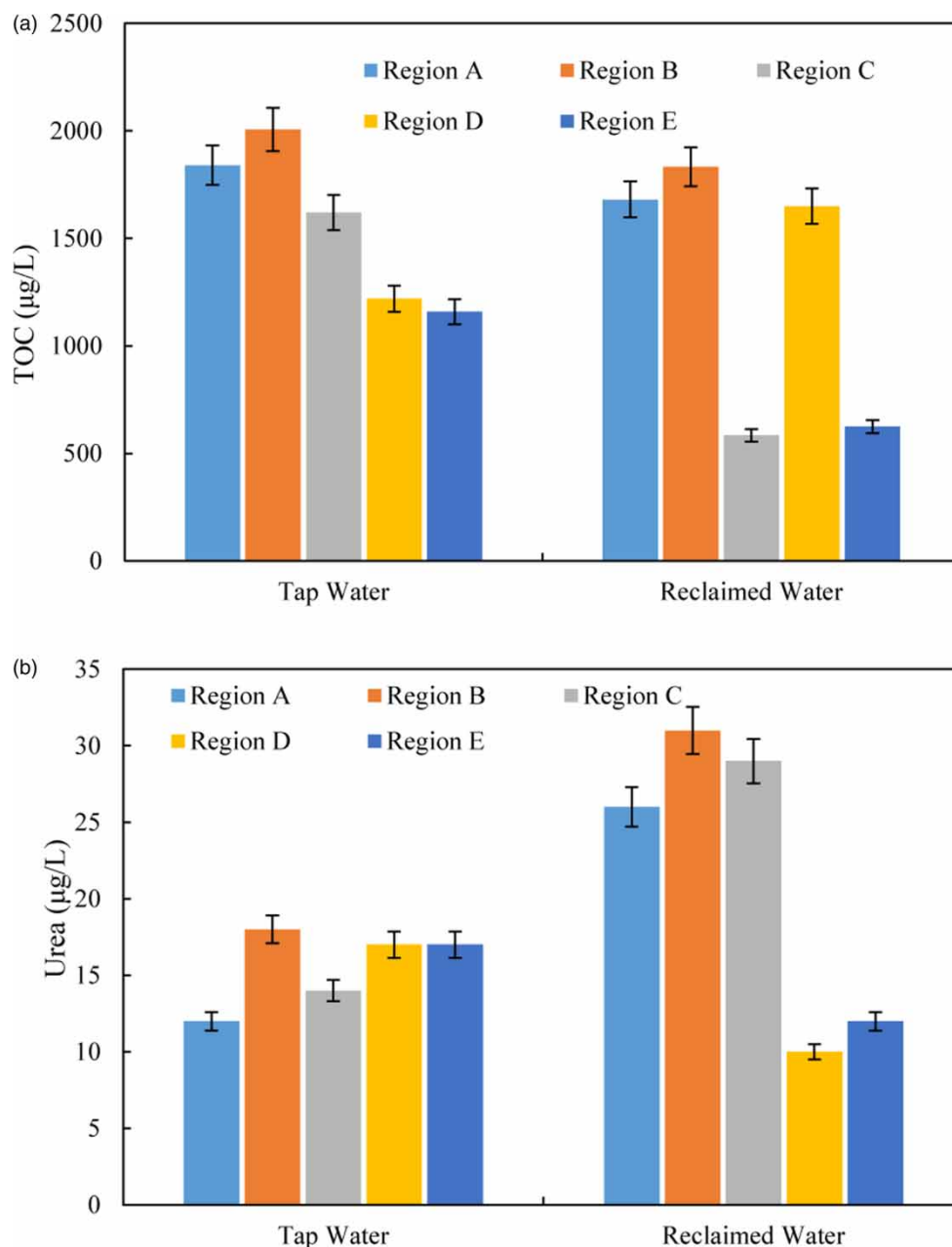
Figure 5 | The distribution of total organic carbon (TOC) (a) and urea (b) in tap water and reclaimed water (Region A – Daxing District, Beijing; Region B – Dongli District, Tianjing; Region C – Xinwu District, Wuxi; Region D – Hongshan District, Wuhan; Region E – Pingshan District, Shenzhen).

Owing to the shortage of water resources and large demand for UPW, the use of recycled water to produce UPW in the semiconductor manufacturing industry has become a trend (Yang *et al.* 2022). In semiconductor manufacturing industries, the quantity of industrial reclaimed water can hardly guarantee the UPW production. Therefore, it is critical to evaluate the feasibility of using municipal reclaimed water as raw water for higher concentrations of urea. Advanced removal methods for urea should be developed in the future studies to effectively deal with different raw waters and guarantee water quality standards.

3.4. Urea degradation in the UPW production process

Compared with traditional spectrophotometric methods, the modified method provided a lower detection limit and more stable absorbance for trace urea. Therefore, the degradation of urea and TOC during the conventional UPW production
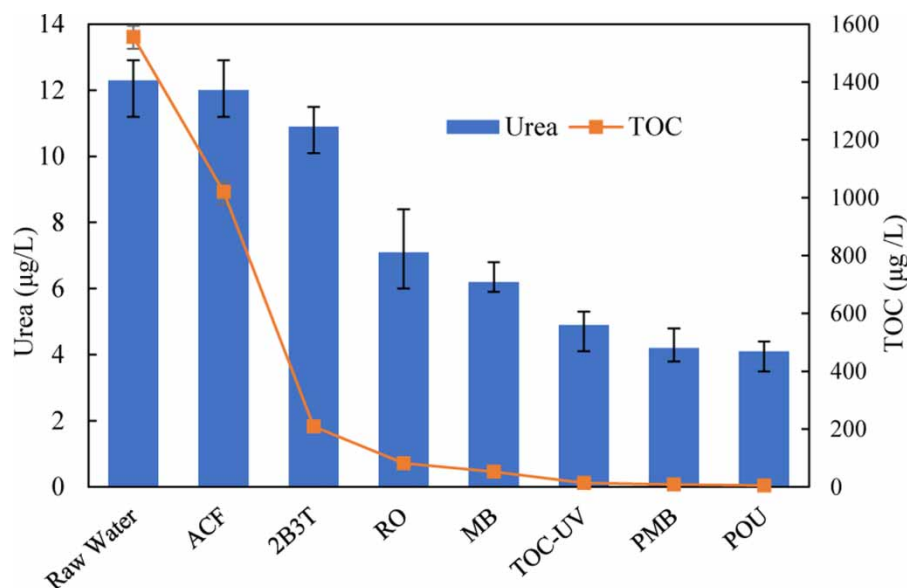
Figure 6 | Degradation trend of urea in the whole process of the ultrapure production process. TOC, total organic carbon.

process (Figure 1) was further explored. The selected process includes all units in the traditional UPW production process in the electronics industry. The UPW yield produced by this process was 2 m³/h, and raw water was obtained from tap water. The urea concentration in the effluent of each unit was determined several times, and the average values were recorded. The TOC concentrations in the effluent of each unit were simultaneously determined as comparative data. The results are shown in Figure 6.

In this pilot-scale system, both urea and TOC concentrations gradually degraded. The total removal rates of urea and TOC were 66.5 and 99.7%, respectively. Most organic matter was removed from the system. Urea was partially removed because of its trace concentration and properties such as neutrality and low molecular weight. The urea concentration in the final effluent was approximately 4.1 μg/L, which is equivalent to a TOC of 0.82 μg/L. This means that urea contributed to approximately 32% of the TOC in the final effluent.

To further explore the removal characteristics of urea in the UPW system, six typical TOC removal units from eight UPW production processes in five cities (Section 3.3) were selected. The average removal rates of urea and TOC are shown in Figure 7.

Each unit of the UPW production process had a urea removal effect. The RO unit was the main unit for removing organics, but the average removal rate of urea was only approximately 30%, which is related to the unique properties of urea. It is difficult to remove urea through the steric hindrance effect and charge repulsion of the RO membrane (Yoon & Lueptow 2005). The urea removal rate by the 2B3T unit was only 8.9%. Because urea is a non-ionic compound, it cannot be effectively treated in an ion-exchange manner (MacKeown et al. 2021). In addition, TOC-UV is also an essential organic removal unit in the process because it releases strong UV light to oxidize organic matter (Zhang et al. 2022). However, the removal rate of urea by direct irradiation with UV-185 nm was only 10.6%, which is similar to the data reported by Choi et al. (Choi & Chung 2019). The total urea removal rate of the UPW production process is approximately 50–70%.

The existence of urea may lead to excessive TOC in the UPW in the following situations: (1) the TOC detecting instruments for the UPW were from the Sievers series of General Electric Company that could detect urea through our previous experience of semiconductor projects; (2) with the improvement of the manufacturing accuracy, the standards for UPW quality have been raised. Therefore, it is necessary to explore an effective removal unit embedded at the end of the wastewater reuse process to reduce urea in the UPW production process.

Rydzewski et al. (Rydzewski & Carr 2003) used NaBrO produced by the oxidation reaction of NaBr and O₃ to oxidize urea. The oxidation unit was placed after the primary RO unit during the UPW production process, which had a positive effect on
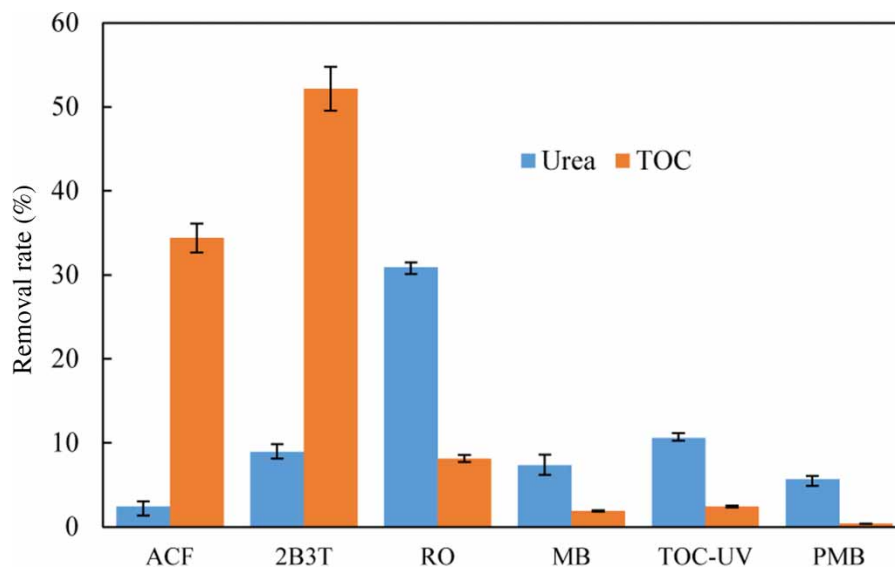
Figure 7 | Removal rate of urea and TOC in typical removal units of the UPW production process.

urea removal. Joko *et al.* (Joko & Miwa 2000) used NaClO as an oxidant and added it to a raw water tank as an effective method to remove urea. In the reactions above, the concentration of NaOCl/NaOBr is two to three orders of magnitude higher than that of urea. Although these methods could degrade part of the urea, significant amounts of inorganic ions were added, which brought more pressure to the subsequent desalination units. Choi *et al.* (Choi & Chung 2019) reported that UV-185 nm light could activate persulfate (20 μmol/L), and the removal rate of trace urea was 58–71%. This provides the possibility of improving the removal efficiency by adding solid-phase catalysts in future research.

The above studies were based on a situation in which the urea concentration in the influent was greater than 35 μg/L. Therefore, with a modified method that can detect trace urea accurately and stably, it is possible to develop and evaluate a process for removing trace urea in an actual water environment.

4. CONCLUSION

In this study, a modified spectrophotometric method was proposed for the selective determination of trace urea in the semi-conductor manufacturing industry. A calibration graph was constructed with a detection range of 0.8–100 μg/L. This calibration graph was suitable for trace urea in the UPW production process. The calibration graph for this method showed ideal linearity ($r^2 = 0.9991$), high repeatability (RSD ≤5%), recovery rate (90% ≤ recovery rate ≤110%), and stability (error ≤5%). Compared with other conventional urea determination methods, the quantification limit of this method was lower, and the detection results were more accurate and stable in the range of 0.8–100 μg/L. Metal ions increased the stability of the chromogenic system, and analysis of the reaction path provided a theoretical basis.

Using a modified spectrophotometric method, the study found that urea distribution in different regions of China was not significantly different. However, the urea concentration in municipal reclaimed water was higher than that in tap water and twice that in industrial reclaimed water. In addition, the removal rate of urea in the UPW production process was 50–70%, and the removal rate of the RO unit was approximately 30%. The final UPW contained 4.1 μg/L of urea, which was a pro-minent reason for the excessive TOC. Compared with the previous urea removal methods, it is necessary to explore advanced heterogeneous oxidation with lower ion addition and higher removal efficiency, which can ensure the quality of UPW in the semiconductor manufacturing industry.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

Alizadeh, T., Ganjali, M. R. & Rafiei, F. 2017 Trace level and highly selective determination of urea in various real samples based upon voltammetric analysis of diacetylmonoxime-urea reaction product on the carbon nanotube/carbon paste electrode. *Analytica Chimica Acta* **974**, 54–62.

Beale, R. N. & Croft, D. 1961 A sensitive method for the colorimetric determination of urea. *Journal of Clinical Pathology* **14**, 418–424.

Bhavna, K., Ojha, A. & Bhargava, S. 2022 Chapter 3. International Council for Harmonisation (ICH) guidelines. *Regulatory Affairs in the Pharmaceutical Industry*. Academic Press, Amsterdam.

Choi, J. & Chung, J. 2019 Evaluation of urea removal by persulfate with UV irradiation in an ultrapure water production system. *Water Research* **158**, 411–416.

Choi, J., Kim, J. O. & Chung, J. 2016 Removal of isopropyl alcohol and methanol in ultrapure water production system using a 185 nm ultraviolet and ion exchange system. *Chemosphere* **156**, 341–346.

de Oliveira e Silva, A. F., de Castro, W. V. & de Andrade, F. P. 2018 Development of spectrophotometric method for iron determination in fortified wheat and maize flours. *Food Chemistry* **242**, 205–210.

Fan, X., Kang, S. & Li, J. 2020 Plasma-enhanced hydrolysis of urea and SCR of NOx over V_2O_5-MoO_3/TiO_2: decrease of reaction temperature and increase of NOx conversion. *Fuel* **277**, 118155.

Francis, P. S., Lewis, S. W. & Lim, K. F. 2002 Analytical methodology for the determination of urea: current practice and future trends. *TrAC – Trends in Analytical Chemistry* **21**, 389–400.

Gonzalez-Rodriguez, J., Perez-Juan, P. & de Castro, M. D. L. 2002 Method for monitoring urea and ammonia in wine and must by flow injection-pervaporation. *Analytica Chimica Acta* **471**, 105–111.

Han, L. Q., Huang, X. T., Zhang, L., Zhang, Q. X., Wang, J. B., Lin, H. B., Yan, J., Zhuang, J. H. & Huang, X. Z. 2019 Candidate reference measurement procedure for determination of urea in serum by liquid chromatography-tandem mass spectrometry. *Journal of Pharmaceutical and Biomedical Analysis* **162**, 124–129.

Joko, I. & Miwa, S. 2000 Treatment method for water containing nitrogen compounds. US Patents (US6132627A). Ltd. KWI.

Lee, H., Jin, Y. & Hong, S. 2016 Recent transitions in ultrapure water (UPW) technology: rising role of reverse osmosis (RO). *Desalination* **399**, 185–197.

Long, L. C., Bu, Y. A., Chen, B. Y. & Sadiq, R. 2019 Removal of urea from swimming pool water by UV/VUV: the roles of additives, mechanisms, influencing factors, and reaction products. *Water Research* **161**, 89–97.

MacKeown, H., Gyamfi, J. A., Delaporte, M., Schoutteten, K., Verdickt, L., Ouddane, B. & Criquet, J. 2021 Removal of disinfection by-product precursors by ion exchange resins. *Journal of Environmental Chemical Engineering* **9**, 9.

Melnik, L. A. & Krysenko, D. A. 2019 Ultrapure water: properties, production, and use. *Journal of Water Chemistry and Technology* **41**, 143–150.

NIEHS 2014 *Examination Methods for Public Places – Part 2: Chemical Pollutants. GB/T 18204.2-2014*. National Institute of Environmental Health, China.

Revilla, M., Alexander, J. & Glibert, P. M. 2005 Urea analysis in coastal waters: comparison of enzymatic and direct methods. *Limnology and Oceanography-Methods* **3**, 290–299.

Rydzewski, J. H. & Carr, G. 2003 Advanced organics oxidation – removing urea from high-purity water. *Ultrapure Water* **20**, 20–26.

Wang, Q., Luo, L., Huang, N., Wang, W., Rong, Y., Wang, Z., Yuan, Y., Xu, A., Xiong, J., Wu, Q. & Hu, H. 2022 Evolution of low molecular weight organic compounds during ultrapure water production process: a pilot-scale study. *Science of The Total Environment* **830**, 154713.

Yang, Y. Y., Zhang, X. B., Ngo, H. H., Guo, W. S., Li, Z. N., Wang, X., Zhang, J. Q. & Long, T. W. 2022 A new spent coffee grounds based biochar – persulfate catalytic system for enhancement of urea removal in reclaimed water for ultrapure water production. *Chemosphere* **288**, 8.

Yoon, Y. & Lueptow, R. M. 2005 Removal of organic contaminants by RO and NF membranes. *Journal of Membrane Science* **261**, 76–86.

Zhang, F., Wang, M. K., Zhang, L. L. & Su, X. G. 2019 Ratiometric fluorescence system for pH sensing and urea detection based on MoS_2 quantum dots and 2, 3-diaminophenazine. *Analytica Chimica Acta* **1077**, 200–207.

Zhang, X. B., Yang, Y. Y., Ngo, H. H., Guo, W. S., Wen, H. T., Wang, X. A., Zhang, J. Q. & Long, T. W. 2021 A critical review on challenges and trend of ultrapure water production process. *Science of The Total Environment* **785**, 13.

Zhang, Y. L., Wang, W. L., Lee, M. Y., Yang, Z. W., Wu, Q. Y., Huang, N. & Hu, H. Y. 2022 Promotive effects of vacuum-UV/UV (185/254 nm) light on elimination of recalcitrant trace organic contaminants by UV-AOPs during wastewater treatment and reclamation: a review. *Science of The Total Environment* **818**, 151776.

Zhu, Z. F. & Dou, J. 2018 Current status of reclaimed water in China: an overview. *Journal of Water Reuse and Desalination* **8**, 293–307.