Mercury speciation transformation in sewage of the sewage treatment process

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Abstract: In order to reveal the occurrence characteristics and speciation transformation of mercury in the sewage treatment plant, the sewage of each process unit in Mai dao sewage treatment plant was taken as the research object, the total mercury (THg), particulate mercury (PHg) and dissolved mercury (DHg) in the samples was determined for 7 consecutive days. The results showed that the THg in influent water was 474.6±148.4 ng/L, and had a large daily variance, and that in effluent was 27.8±8.2 ng/L. THg in wastewater was closely related to the degree of organic pollution. PHg accounted for a larger proportion in raw sewage (PHg/THg was 73.5%), and the proportion of DHg increased after treatment. The total removal efficiency of THg was 94.1%, and PHg contributed a lot. The removal of mercury mainly occurred in the secondary biological treatment process.

1. Introduction
Mercury (Hg) is a highly toxic heavy metal element, which has different chemical speciation in water[1], such as particulate mercury (PHg), dissolved mercury (DHg), methylmercury (MeHg). Different speciation of mercury have different effects on the environment and bioavailability because of their different physical and chemical properties. The composition of wastewater is complex, Mercury speciation changes with different processes, and redistributes in each phase, some mercury will re-enter the environment. Wastewater treatment plant is one of the important anthropogenic sources of mercury in the environment. In 2015, the mercury released from sewage treatment plants to water, soil and atmospheric environment was 23t, 120t and 15t respectively[2]. The results show that the total mercury concentration in the raw sewage of urban sewage fluctuates greatly with time and place[3-5]. Only a small part of the mercury entering the sewage treatment plant is discharged with the effluent; most of it is absorbed by the activated sludge and discharged with the remaining sludge. Many studies have been conducted on the migration and removal efficiency of THg and MeHg in activated sludge process and oxidation ditch[5, 6], however, the research on mercury in biofilter process is still scarce. In this study, THg, PHg and DHg in the sewage of each section of biofilter process were measured, which attempts to explore the mercury speciation transformation in this process.
2. Materials and methods

2.1. sewage treatment plant and its treatment process
Maidao sewage treatment plant is located in the eastern coastal area of Qingdao city. It mainly receives sewage from the area to the east of Nanhai road and the west of Wushan mountain, with a service area of 35 km². The nitrification denitrification Biofilter Process (Fig. 1) is adopted with a treatment capacity of 140000 m³/d, and the source of sewage is domestic sewage.

2.2. sample collection and preservation
From September 16 to September 23, 2020, 9:00, the water samples were collected continuously for 7 days. Six sampling points (①~⑥) were set up in different sections (Fig. 1), Meanwhile, the temperature (T), pH and dissolved oxygen (DO) were measured on site by YSI pro1020 portable water quality analyzer.

Figure 1. Process flow and sampling point layout of sewage treatment plant

2.3. sample analysis
THg and DHg were determined with reference to USEPA 1631 method[7]. The unfiltered and filtered water samples were oxidized with 0.1 mL BrCl for 24 h, and then added with 0.1 mL 300 g/L NH₂OH·HCl to remove excess halogen, and then added with 0.5 mL 200g/L SnCl₂ solution for reduction. The samples were analyzed by atomic fluorescence spectrometry (brooksrand lab, merx-T) The results were THg and DHg. The concentration of PHg was the difference between THg and DHg. The determination of chemical oxygen demand (COD), total nitrogen (TN), total phosphorus (TP) and suspended particulate matter (SS) in sewage was determined according to the monitoring and analysis method for water and wastewater[8].

3. Results and discussion

3.1 sewage THg
THg in the influent was 474.6±148.4 ng/L, ranging from 235.7 to 699.9 ng/L, with a coefficient of variation of 31%, which was similar to the research results at home and abroad. THg concentration of sewage treatment plant has a great difference with the change of time and space[3-5]. THg in the influent was lower than that of two sewage treatment plants in Henan Province[5, 9]. The average THg concentration of the effluent of the grit chamber was 618.5±224.8 ng/L, and the concentration was higher than that of the inflow water. It is mainly affected by the sludge dehydration and return flow. THg in the effluent of the sedimentation tank was 233.9±101.9 ng/L, and the removal efficiency of THg after the primary treatment was 49.3%. THg in the influent was removed with the settlement of some particles. The effluent of denitrification filter is the secondary biological treatment effluent, with an average value
of 35.0±9.1 ng/L. Compared with the effluent removal rate of sedimentation tank, other studies also believe that activated sludge has a good removal effect on THg\cite{3, 5, 6}. Through the nitrification and denitrification of biofilter, the organic matter in sewage was decomposed by microorganisms and mercury combined with organic substances was released. It can be absorbed by biofilm or into the microorganism, and mercury can be transformed from water to solid phase and removed from water. Therefore, THg has a higher removal rate in the secondary treatment.

THg in the effluent was 27.8±8.2 ng/L, and the total removal rate was 94.1%. The treatment efficiency was higher than that of Chongqing Tangjiaqiao sewage treatment plant using traditional activated sludge process (76.4%), slightly lower than that of Jiaozuo No.1 sewage treatment plant using oxidation ditch process (98.2%)\cite{9}. There was a significant positive correlation between THg and COD (r = 0.916, P < 0.01), TN (r = 0.786, P < 0.01) and TP (r = 0.808, P < 0.01), which indicated that THg in wastewater had a great relationship with the degree of water pollution.

![Figure 2. concentration of THg in sewage](image)

3.2. DHg and PHg

The concentrations of DHg and PHg in the influent were 120.0±36.3 ng/L, 354.7±136.9 ng/L, respectively. PHg/THg was 73.5%, particulate mercury was the main speciation in the influent, which mainly existed in various organic residues. As shown in Figure 3, similar to THg, the concentrations of DHg and PHg in the effluent of grit chamber increased, which was mainly affected by the return flow input of sludge dewatering. PHg in the effluent of the sedimentation tank was 123.6±56.1 ng/L. The precipitation occurs through the inclined plate to remove the mercury attached to the suspended solids. The removal efficiency of PHg in the primary treatment was 65%. There was a significant positive correlation between THg, PHg and SS (r = 0.701, P < 0.01; r = 0.706, P < 0.01) in primary treatment. THg in sewage was greatly affected by particles. Mercury enters the aquatic environment and is easy to be adsorbed on suspended particles, resulting in the increase of particulate mercury\cite{10}. At the same time, THg was mainly removed with the removal of PHg. The removal efficiencies of DHg and PHG in the secondary treatment process were 76.0% and 93.2% respectively. The organic matter bound mercury was converted into DHg with the decomposition of organic matter. The DHg was further adsorbed by the biofilm to form sludge for removal. DHg was the main speciation in sewage. After secondary treatment, there was a significant negative correlation between PHg and pH (r = -0.554, P < 0.01), the decrease of pH would lead to the enhancement of mercury adsorption capacity of particles\cite{11}.
DHg and PHg in sewage and their proportion in THg

DHg and PHg in the effluent were 21.3±7.2 ng/L and 6.5±1.2 ng/L, respectively, and the total removal efficiencies were 82.3% and 98.2%, respectively. The removal efficiency of PHg was higher, which was similar to other research results at home and abroad[4, 12]. In the treatment process, PHg/THg decreased from 73.5% to 24%, and decreased significantly in the effluent of sedimentation tank and nitrification biofilter.

4. Conclusion
The daily variation of THg concentration in influent was 474.6±148.4 ng/L, and that in effluent was 27.8±8.2 ng/L. The total removal rate was 94.1%. The removal of THg mainly occurred in the secondary biological treatment process. THg in wastewater was closely related to the degree of organic pollution.

The PHg/THg was 73.5% in the influent. PHg was significantly positively correlated with SS in the primary treatment process, and decreased with the removal of particulate matter. PHg was negatively correlated with pH in secondary treatment, and the decrease of pH led to the increase of PHg concentration. The DHg/THg in the wastewater treatment process showed an upward trend, and DHg became the main speciation of mercury in the secondary treatment process.

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