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Views & Comments

The Ultrafiltration Process Enhances Antibiotic Removal in the Full-Scale Advanced Treatment of Drinking Water

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1. Introduction

A considerable proportion (30%–90%) of consumed antibiotics are excreted from organisms after intake, and wastewater treatment facilities lack sufficient capacity to remove antibiotics in water [1]. Thus, the issue of antibiotics contamination in drinking water is raising increasing attention. Adverse consequences of antibiotics in drinking water include potential human health risks (e.g., they may be carcinogenic or provoke allergic reactions) and risks to the aquatic ecology due to the promotion of bacterial-resistant genes [2,3]. Advanced treatment processes are essential to ensure the security of drinking water quality. The most commonly used advanced treatment process comprises ozone (O_3)/biological activated carbon (BAC) process. Recently, ultrafiltration (UF) membrane separation technology has been extensively studied and applied to eliminate microorganisms and organic matter, and has the advantages of excellent effluent quality, moderate operating conditions, and no chemical substances [4]. However, the effect of the UF process on antibiotics removal in complex water quality scenarios within full-scale drinking water treatment plants (DWTPs) is still unclear. Moreover, attention must be paid to assessing the human health risk of exposure to trace levels of antibiotics in drinking water. Therefore, it is essential to study the occurrence, fate, and human health risk of antibiotics in water treatment engineering to enable future improvement and optimization.

2. Advanced treatment of drinking water

It is necessary to adopt advanced treatment technologies to address the issue of antibiotics in drinking water, since conventional drinking water treatment is not designed to remove micropollutants. The most commonly used and promising advanced drinking water treatments include advanced oxidation processes (e.g., oxidation by ozone, hydrogen peroxide, and ultraviolet (UV) light), adsorption onto materials (e.g., adsorption onto granular or powder activated carbon and ion exchange resin), and membrane processes (e.g., microfiltration, ultrafiltration, nanofiltration, and reverse osmosis) [5]. These treatment processes may be applied independently or in combination. In the present article, advanced treatment for antibiotics removal was investigated in four full-scale DWTPs in Shanghai, China. To determine the effect of the UF process on antibiotics removal, the DWTPs were divided into two groups: the control group (conventional + O_3/BAC process) and the study group (conventional + O_3/BAC + UF process) (Fig. 1). Sampling points were set at the following stages: influent (Inf.), coagulation–sedimentation (CS) effluent, sand filtration (SF) effluent, ozonation (O_3) effluent, BAC, UF effluent, and finished effluent (Eff.). As the four DWTPs under study use the same reservoir as their water source, the antibiotic levels in the influents of both groups were similar.

3. Elimination of antibiotics in full-scale drinking water treatment

The occurrence and fate of antibiotics in full-scale DWTPs are key issues in drinking water security. The concentrations of trace levels of antibiotics in water were analyzed via an ultra-performance liquid chromatography (UPLC)-triple quadrupole mass spectrometer, after water samples enriched by solid-phase extraction (SPE). We analyzed a total of 30 target antibiotics, 17 of which (seven sulfonamides, four quinolones, three macrolides, two antifungal pharmaceuticals, and one chloramphenicol) were detected in the water samples. Table 1 lists the concentrations and detection frequencies of these antibiotics in the influents and effluents. In the influents, the concentrations of the target antibiotics ranged from below the limit of quantification (LOQ) to 105.1 $ng\cdot L^{-1}$, with mean values of 0.13–15.33 $ng\cdot L^{-1}$, whereas the concentrations in the effluents significantly decreased to a range from < LOQ to 19.5 $ng\cdot L^{-1}$. Sulfonamides were the most abundant category, and sulfamethazine (SMT), sulfamonomethoxine (SMM), sulfaquinoxaline (SQX), and sulfamethoxazole (SMZ) all had a detection frequency of 100% in the influents, with maximum concentrations of 84.6, 5.0, 105.1, and 42.5 $ng\cdot L^{-1}$,

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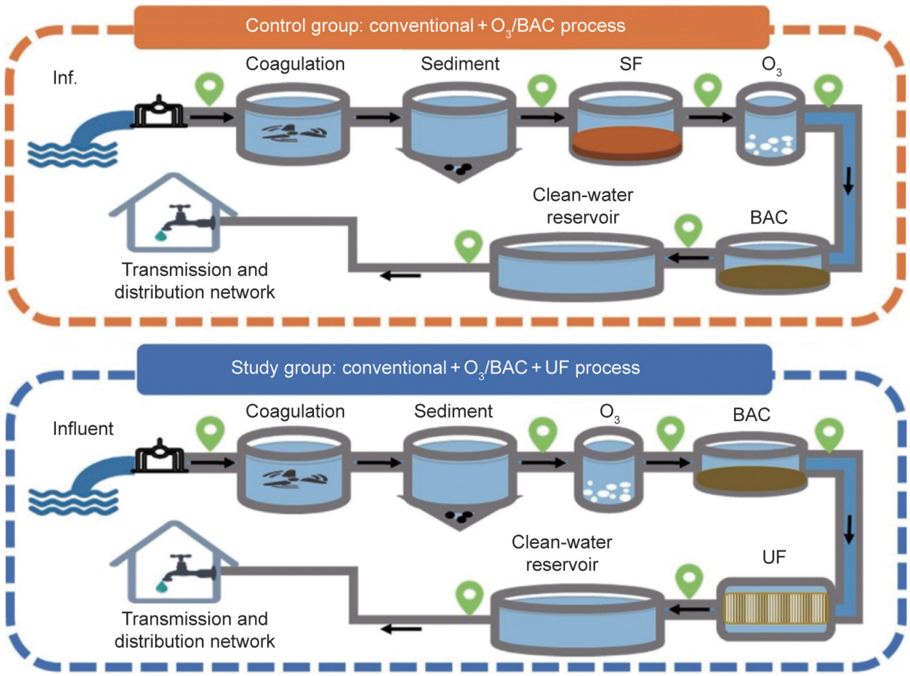

Fig. 1. Schematic diagram of the treatment processes of the investigated DWTPs.

Table 1
Concentrations and detection frequencies of antibiotics in the influents and effluents of the four full-scale DWTPs.

Family	Compound	LOQ ($ng·L^{-1}$)	Influent ($ng·L^{-1}$)				Effluent ($ng·L^{-1}$)			
			Mean	Maximum	Minimum	Freq. (%)	Mean	Maximum	Minimum	Freq. (%)
Sulfonamides	Sulfadiazine (SDZ)	0.007	6.76	57.0	0.3	81.3	0.48	9.3	< LOQ	33.3
	Sulfamethazine (SMT)	0.02	9.05	84.6	0.4	100	0.15	2.3	< LOQ	27.1
	Sulfamonomethoxine (SMM)	0.008	1.53	5.0	0.4	100	0.056	0.7	< LOQ	29.2
	Trimethoprim (TMP)	0.0008	1.95	8.0	< LOQ	91.7	0.30	5.0	< LOQ	29.2
	Sulfaquinoxaline (SQX)	0.01	15.33	105.1	0.9	100	0.23	3.4	< LOQ	39.6
	Sulfadimethoxine (SMX)	0.001	0.97	23.2	< LOQ	45.8	0.029	0.2	< LOQ	20.8
	Sulfamethoxazole (SMZ)	0.05	7.04	42.5	< LOQ	100	1.72	19.5	< LOQ	85.4
Macrolides	Lincomycin (LIN)	0.08	1.75	14.8	0.1	93.8	0.008	0.2	< LOQ	4.2
	Erythromycin (ETM)	0.008	0.13	1.1	< LOQ	33.3	0.029	0.9	< LOQ	10.4
	Roxithromycin (RTM)	0.02	0.43	1.2	0.1	87.5	0.052	0.4	< LOQ	31.3
Quinolones	Lomefloxacin (LOM)	0.04	1.87	19.7	0.2	50.0	0.26	2.0	< LOQ	33.3
	Ofloxacin (OFC)	0.05	3.62	41.7	0.3	79.2	2.01	13.0	0.1	72.9
	Fleroxacin (FLX)	0.03	1.21	8.6	0.1	50.0	0.28	1.6	0.2	41.7
	Difloxacin (INN)	0.03	0.94	4.8	0.1	52.1	0.21	1.1	0.1	33.3
Antifungal agents	Ketoconazole (KTC)	0.09	0.83	11.2	< LOQ	68.8	0.28	4.6	< LOQ	50.0
	Miconazole (MCZ)	0.02	0.55	14.8	< LOQ	45.8	0.14	1.2	< LOQ	33.3
Chloramphenicols	Thiamphenicol (TAP)	0.08	0.54	2.6	0.1	43.8	0.13	0.8	< LOQ	31.3

Freq.: detection frequency of each antibiotic in all water samples (n = 288).

respectively. Another study has also reported a high concentration of sulfonamides in drinking water treatment processes in eastern region of China (SMZ had a maximum concentration of 67.27 $ng·L^{-1}$) [6]. The high levels and abundant species of sulfonamides in drinking water correspond with the large-scale production and consumption of sulfonamides in China, for example, the usage of 313 tonnes of SMZ and 1440 tonnes of SQX was reported in 2013 [7,8]. In addition, quinolones and macrolides were also present at $ng·L^{-1}$ levels, with the highest-level antibiotics detected in each family being ofloxacin (OFC) and lincomycin (LIN), respectively. Concentrations of antifungal agents and chloramphenicols in drinking water were relatively low, with average concentrations lower than 1 $ng·L^{-1}$.

It was noteworthy that the levels of antibiotics in drinking water showed seasonal variation. In general, the antibiotics concentrations were significantly higher in autumn and winter than in spring and summer ($p < 0.05$), as the increased occurrence of colds and respiratory diseases in autumn and winter results in greater use of antibiotics [9]. In contrast to the other antibiotics, the detected concentrations of quinolones were higher in summer, probably because quinolones are frequently used to treat intestinal infections, which often occur in summer [10]. Overall, the average concentration of antibiotics in the finished water of the four DWTPs was reduced by approximately 88% relative to the antibiotic concentration in the influents, indicating the effectiveness of target antibiotics removal by the DWTPs with advanced treatment process.

In particular, we found that the conventional treatment processes (i.e., coagulation–sedimentation and sand filtration) used in the full-scale DWTPs exhibited limited effectiveness for the removal of soluble antibiotics, even though such processes can effectively remove suspended particulate matter. In our study, the removal efficiencies of conventional processes for antibiotics were found to be lower than 40%, with the exception of antifungal agents, which were removed using conventional processes with an efficiency of 46.2%. Furthermore, the usage of the advanced processes of O_3/BAC alone or O_3/BAC in addition to UF improved the antibiotics removal to different extents. Fig. 2 compares the variation in antibiotic levels after each treatment process in the two groups of DWTPs. In the control group, the total removal efficiencies for the five categories of antibiotics ranged from 52.9% to 94.8%. Sulfonamides had the highest concentration in the influents with an average concentration of 41.3 $ng{\cdot}L^{-1}$, and the total removal efficiency for the sulfonamides in the control group was as high as 92.3%, of which the removal efficiency of the O_3/BAC process was as high as 80.1%. These results indicate that oxidation and adsorption effects were the main mechanisms that removed sulfonamides in the drinking water treatment process. The aniline moiety in the sulfonamides undergoes electrophilic attack by O_3; for example, SMZ can be attributed as the fast-reacting antibacterial compound with O_3, with an apparent second order rate constant for the reaction ($k''_{O_3,\ app}$) of about $5 \times 10^5\ (mol{\cdot}L^{-1})^{-1}{\cdot}s^{-1}$ [11]. O_3 oxidation also plays an important role in macrolides removal, with a total removal efficiency of 94.8% and a removal efficiency in ozonation of 77.2%. The average concentration of macrolides in the effluents was as low as 0.1 $ng{\cdot}L^{-1}$. In contrast, it was observed that, O_3 oxidation exhibited a low removal efficiency for quinolones (52.9% for the entire treatment processes vs 8.7% for ozonation process) and antifungal pharmaceuticals (60.2% vs 11.4%). Thus, it can be concluded that the O_3/BAC advanced treatment is more effective for the removal of sulfonamides and macrolides than for quinolones and antifungals.

In the study group, the total removal efficiencies for the five categories of antibiotics were as follows: macrolides (96.8%) > chloramphenicols (96.3%) > sulfonamides (95.5%) > quinolones (84.1%) > antifungal agent (66.7%). Since sulfonamides and macrolides were effectively degraded with remarkable efficiency by the ozonation process (85.5% and 93.8%, respectively), the UF process contributed little to their removal. For quinolones, the average concentration was decreased from 12.6 $ng{\cdot}L^{-1}$ in the influents to 2.0 $ng{\cdot}L^{-1}$ in the effluents. It was notable that the total removal efficiency for quinolones in the study group increased significantly (84.1%) relative to that in the control group (52.9%). The elimination of antifungal pharmaceuticals was also improved in the DWTPs using the UF process. These results indicate that the drinking water treatment systems with both O_3/BAC and UF as advanced processes had a higher removal efficiency than the systems with just O_3/BAC, demonstrating the effectiveness of membrane treatment for antibiotics removal.

4. The effect of the UF process on antibiotics removal and human health risk reduction

The pore size of the UF membrane used in municipal engineering is generally in the range of 0.001–0.200 μm, which can effectively remove pollutants such as particles, microorganisms, and macromolecular organic matter in water. Although the UF process cannot retain micropollutants, micropollutants removal can be enhanced via adsorption by membrane materials and retention by cake layers [12]. Overall, we found that the UF process enhanced the removal of antibiotics. The removal efficiency in the studied DWTPs with UF increased by an average of 21% compared with the removal efficiency in the DWTPs without UF. The effect of the UF process on antibiotics removal in full-scale drinking water treatment varied depending on the antibiotics' characteristics. The sulfonamides and macrolides were susceptible to ozonation and could be further removed through the BAC process via adsorption and biodegradation; therefore, the addition of UF after the O_3/BAC process contributed little to their removal. In contrast, for the antibiotics that were resistant to ozonation (e.g., the quinolones and antifungal agents), the addition of UF process in advanced drinking water treatment effectively enhanced the removal of the antibiotics.

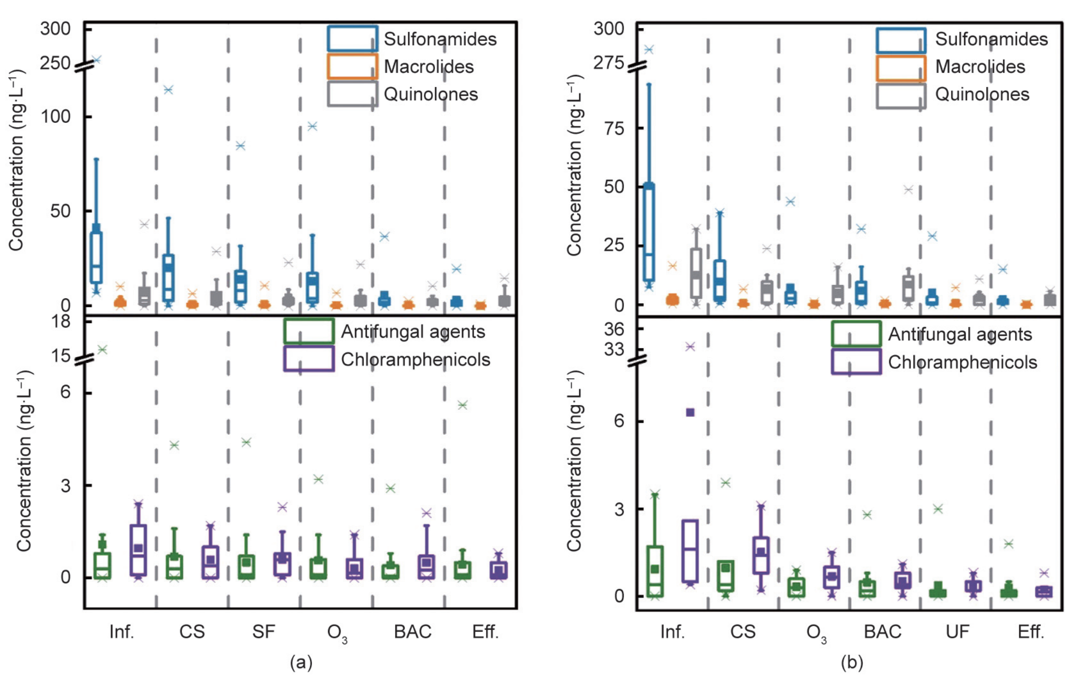

Fig. 2. Variations in antibiotic concentrations after each process in (a) DWTPs in the control group and (b) DWTPs in the study group.

Since the pore size of the UF membrane is larger than the sizes of microcontaminant molecules, the enhancement demonstrated by the UF process was due to the action of the membrane surface, which included physical action (enmeshment) and chemical action (adsorption). It has also been reported that the application of the UF process enhances the removal of various pesticides, and that adsorption onto the UF membrane may be dominant mechanism [13]. It should be noted that the negative removal efficiency for antibiotics may appear in drinking water treatment, as antibiotics adsorbed onto natural organic matter may release into the aqueous phase during O_3 aeration, resulting in increased concentrations in the effluent [14,15].

Health risk of antibiotics through drinking water exposure to humans at different life stages was evaluated through risk quotients (RQs) [16]. RQs $\geq$ 1.0 are defined as posing a potential risk related to exposure through drinking water. The maximum detected concentrations of the antibiotics were used in the assessment of the human health risk in order to provide a conservative "worst-case scenario" approach. The respective RQs for the representative antibiotics for people at different age intervals were estimated.

For all the antibiotics, the RQs were highest for infants aged 0–3 months when exposed through drinking water. The antibiotics with the highest RQs in this age group were SMT (RQ = 0.01), RTM (RQ = 0.005), and OFC (RQ = 0.004); all of the other antibiotics presented RQs $\leq$ 0.002. It should be noted that all the RQs of the antibiotics detected in the four DWTPs were far lower than 1.0 for all life stages, indicating a negligible health risk to the consumer. De Jesus et al. [16] also reported that exposure to trace levels of pharmaceuticals in a water supply system resulted in RQ values were all below 0.01. However, Leung et al. [17] reported that four pharmaceuticals in tap water—namely, dimetridazole, TAP, SMT, and clarithromycin—had an RQ $\geq$ 0.01 for at least one life-stage, and recommended that increased attention should be paid to these pharmaceuticals.

Fig. 3 shows the effect of the UF process on reducing health risk to humans in the age interval of 0–3 months. In the control group, all RQs of antibiotics in the effluents were reduced to less than 0.0003; furthermore, the reduction efficiencies for the antibiotic RQs were greater than 70.0% except for OFC and ETM. In comparison, the DWTPs in the study group exhibited a greater ability to reduce the RQs, with a higher reduction efficiency of 87% on average.

The influence of seasonal variation on the reduction of RQs in drinking water treatment was not found to be significant. Throughout the whole year, the reduction efficiency for the RQs of most of the studied antibiotics was high ($\geq$ 70%). In particular, in autumn and winter, when the antibiotic levels in drinking water were

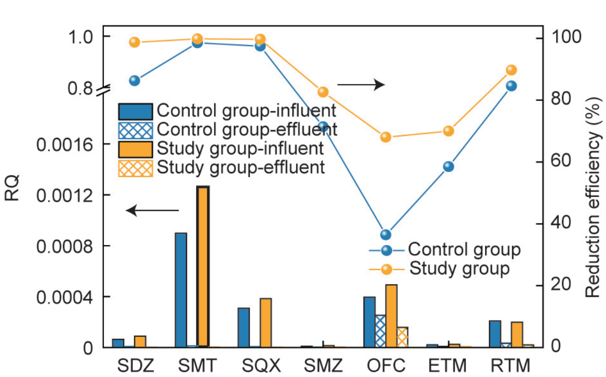

Fig. 3. RQs in influent and effluent and corresponding reduction efficiencies in the control group and study group of the investigated DWTPs (age interval of 0–3 months).

higher, the studied DWTPs still exhibited a reduction efficiency of 70%–98%, indicating that the low temperature did not restrict the reduction of RQs. This is mainly because O_3 solubility increases with a lower water temperature, which promotes the reduction of RQs during advanced oxidation treatment in DWTPs.

5. Conclusions

In combination with O_3/BAC, the UF process is commonly applied in advanced drinking water treatment to remove the biofilms and granular impurities falling from the activated carbon, in order to ensure the microbial safety of the effluent. In this paper, we report the insight that application of the UF process in full-scale advanced drinking water treatment can enhance the elimination of antibiotics and the reduction of the corresponding health risks in drinking water, especially for antibiotics resistant to ozonation (e.g., quinolones and antifungal agents). This study also provides guidance for the health risk management of micropollutants in drinking water. It should be noted that the mixed toxic effects of antibiotics and their metabolites may result in higher risks than the antibiotics on their own [18], which should be considered in future studies.

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