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Occurrence and fate of ten sulfonamide antibiotics in typical wastewater treatment plants in the City of Jinan of Northeastern China

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ABSTRACT

This study investigated the concentration levels and removal efficiencies of sulfonamide antibiotics in the effluents of different sections of wastewater treatment plants (WWTPs) and explored the removal of sulfonamide antibiotics from the effluent of each section by modified activated carbon. The results showed that the wastewater treatment process has a certain removal effect on the nine sulfonamide antibiotics except on the negative removal of trimethoprim, which had a removal rate of less than 60%. The effect of WWTP pH was found to be obvious, demonstrating a negative correlation with the occurrence of antibiotics. The occurrence of sulfadimethoxine and sulfachloropyridazine was found to be mainly affected by total nitrogen, NH_3–N and NO_3^-–N. After equilibrium adsorption by MAC-1 (activated carbon modified by $FeCl_3$) and MAC-2 (activated carbon modified by hexadecyltrimethylammonium bromide) for 24 h, the removal efficiencies of sulfonamide antibiotics in the effluent of each section ranged from 87.37% to 100%. Our results suggest that the removal rates of ten sulfonamide antibiotics in WWTPs are not clear.

Keywords: Sulfonamide antibiotics; Wastewater treatment plant; Adsorption experiment; Modified activated carbon

1. Introduction

The potential threats of antibiotics to the environment and human health have intensified significantly in recent years. Both the consumption and production of antibiotics in China are the highest in the world due to the country's rapid economic development and large population, resulting in high detection frequencies and concentrations of antibiotics in aquatic environments [1,2]. More importantly, such trends can impact the development and spread of microbial resistance. Wastewater treatment plants (WWTPs), hospitals, livestock and poultry farms and aquaculture systems are have played a major role in enhancing the intrinsic resistance of microbes in the environment, and this has especially been the case for WWTPs for urban water bodies [3–6].

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Sulfonamide antibiotics (SAs) found in the environment are suspected to be translocated into the food web and to initiate the formation of resistant microorganisms [7]. As the most concerning group or class of drugs, antibiotics have a high detection rate in WWTPs, which are the main sources of antibiotics in the environment and which constitute the last barrier preventing antibiotics from entering the environment [8]. In recent years, the fate of antibiotics in WWTPs, including their occurrence, removal and transformation, has become a major focus of related research [9]. The ultimate fate of antibiotics in water environments depends on whether they can be effectively removed by WWTPs. Traditional WWTPs were mainly used to reduce levels of conventional pollutants. Many studies have shown that WWTPs cannot fully remove all antibiotics in wastewater [10–12]. Although some studies have reported on the migration and transformation behaviors of antibiotics in WWTPs and on removal mechanisms, a consensus has not been reached, and further discussion is required.

WWTPs are the main facilities that remove various pollutants from domestic and industrial sewage. The objective of this study was to investigate the occurrence and fate of 10 SAs in various areas of WWTPs and to preliminarily comprehend pollution levels of SAs found in WWTPs in the city of Jinan in Northeastern China. In addition, removal effects and practical applications of modified activated carbon on SAs in municipal wastewater were explored through adsorption experiments.

2. Materials and methods

2.1. Standards and reagents

Ten SAs were investigated in this study (Table 1). Analytical standards were purchased from Dr. Ehrenstorfer GmbH (Germany). Internal standards (ciprofloxacin (CIP)-D_8, sulfamethoxazole (SMZ)-D_4, trimethoprim (TMP)-$^{13}C_3$, and demeclocycline (DMC)) were obtained from Sigma-Aldrich (St. Louis, MO, USA) except for sulfamethazine-$^{13}C_6$ (SMX-13C_6), which was obtained from Cambridge Isotope Laboratories (Andover, MA, USA). All other chemicals and solvents used were purchased from Fisher Chemicals (Fair Lawn, NJ, USA).

2.2. Sample collection

This study was performed in a WWTP in the city of Jinan. Influent and effluent water from each section of the WWTP was collected to study the occurrence and fate of SAs in March 2017. The WWTP was built as a large-scale operation sewage treatment facility where the main process is anaerobic-anoxic-oxic (A^2/O). The facility adopts advanced treatment processes involving primary sedimentation, biochemical and secondary sedimentation tanks. The water quality of plant effluent complies with first-class type A standards of the Discharge Standards for Municipal Wastewater Treatment Plants (GB18918-2002). Water quality parameters for each process unit of the WWTP are presented in Table 2. A stainless steel water sample collector was used to collect water samples. Brown glass bottles were used to collect water samples to avoid photolysis. Then, 5 mL methanol was added, and the samples were transported to a laboratory for preservation in a refrigerator at 0°C–4°C. Sample pretreatment was completed within 15 h. Three parallel samples were collected from each processing unit. To ensure the accuracy of our experimental data, all glassware was soaked in 10% (V/V) nitric acid solution for 24 h and then rinsed with 50% methanol-water (V/V) 2–3 times. 4 L of surface water samples from the top 0.5 m of the water surface were collected in sterile containers, immediately stored in a cooler, and treated at the laboratory within 12 h.

2.3. Sample preparation and analysis

Samples were pretreated by Liu et al. [13]. We filtered 1 L of the samples through a 0.45 μm glass fiber filter adjusted with 0.1 M HCl to pH = 3. Then, 0.5 g Na_2 ethylenediaminetetraacetic acid was added to the samples, and 20 μL of internal standards (1.0 mg L^{-1}) containing CIP-D_8, SMZ-D_4, TMP-$^{13}C_3$, DMC was added. Waters Oasis HLB cartridges (500 mg, 6 mL) were used to enrich the treated solutions, which were sequentially rinsed with 6 mL of methanol and 6 mL of ultrapure water, and then water samples were introduced into the cartridges at a flow rate of 3–5 mL min^{-1}. The cartridges were rinsed with 6 mL of 5% methanol aqueous solution and 6 mL of ultrapure water and dried for 2 h under a vacuum. Antibiotics remaining on the Oasis HLB cartridges were eluted with 6 mL of methanol and 6 mL of 5% NH_3–H_2O methanol solution, and the eluent was concentrated to near dryness under a gentle stream of nitrogen in a 40°C water bath. Methanol/water solution (9:1, V:V) was used to fix the volume to 1 mL. The lower layer of liquid was removed and filtered through a 0.22 μm membrane to remove particles; the final extract was then transferred to a 2 mL amber glass vial for further analysis.

The target antibiotics were analyzed via ultraperformance liquid chromatography-tandem mass spectrometry (ACQUITY UPLC-XEVO-TQMS) (USA, Waters) with a UPLC BEH-C_{18} column (50 mm × 2.1 mm × 1.7 μm) as described by Liu et al. [14]. The column was held at 40°C during sample analysis. It consisted of eluent A (0.3% formic acid and 0.1% ammonium formate in ultrapure water) and eluent B (acetonitrile:methanol = 1:1). The flow rate was set to 0.8 mL min^{-1}, and the injection volume was set to 10 μL.

2.4. Quality assurance and control

The internal standard method was used. The calibration curves (0.5–100 μg L^{-1} concentrations) for analyte detection exhibit good levels of linearity (R^2 > 0.999). The recoveries of SAs in WWTPs were tested and ranged from 74.41% to 100.06% with relative standard deviations (RSD) of 1.12% to 6.99% for the seven samples; specific values are provided in Table 3. The limit of quantification (LOQ) and limit of detection (LOD) calculated with signal/noise ratios of 10 and 3 were measured as 0.05–0.20 ng L^{-1} and 0.06–0.13 ng L^{-1}, respectively.

2.5. Adsorption experimental design

Two kinds of modified activated carbon (MAC-1 and MAC-2) were used for the advanced processing of effluent

Table 1
Detailed information of 10 SAs

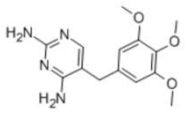
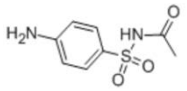
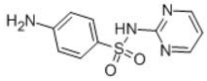
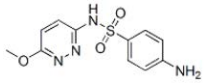
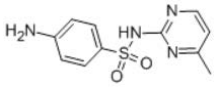
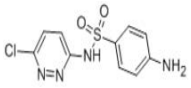
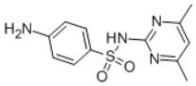
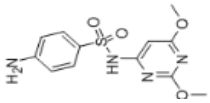
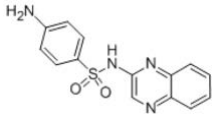
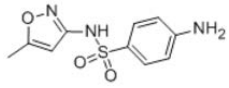
Antibiotics	Structural formula	CAS	Purity	Molecular formula	Molecular weight	Melting points (°C)
Trimethoprim (TMP)		738-70-5	≥99%	$C_{14}H_{18}N_4O_3$	290.32	199–203
Sulfacetamide (SCM)		144-80-9	≥98%	$C_8H_{10}N_2O_3S$	214.24	182–184
Sulfadiazine (SDZ)		68-35-9	≥98%	$C_{10}H_{10}N_4O_2S$	250.28	253
Sulfamethoxypyridazine (SMP)		80-35-3	≥99%	$C_{11}H_{12}N_4O_3S$	280.3	182–183
Sulfamerazine (SMR)		127-79-7	≥99%	$C_{11}H_{12}N_4O_2S$	264.30	234–238
Sulfachloropyridazine (SCP)		80-32-0	≥99%	$C_{10}H_9ClN_4O_2S$	284.72	186–187
Sulfamethazine (SMX)		57-68-1	≥99%	$C_{12}H_{14}N_4O_2S$	278.33	176
Sulfadimethoxine (SDM)		122-11-2	≥98%	$C_{12}H_{14}N_4O_4S$	310.33	200
Sulfaquinoxaline (SQX)		59-40-5	≥98%	$C_{14}H_{12}N_4O_2S$	300.34	247–248
Sulfamethoxazole (SMZ)		723-46-6	≥99%	$C_{10}H_{11}N_3O_3S$	253.28	166

Table 2
Water quality parameter at each process unit of the wastewater treatment plant

Samples	pH	Chemical oxygen demand (mg L^{-1})	TN (mg L^{-1})	NH_4^+–N (mg L^{-1})	NO_3^-N (mg L^{-1})	Total phosphorus (mg L^{-1})
Influent	7.5	350	45	35	5	5
Primary sedimentation tank effluent (PSTE)	7.2	304.39	34.67	30.21	4.27	4.31
Biochemical tank effluent (BTE)	7.6	101.86	2.83	1.69	0.45	0.49
Secondary sedimentation tank effluent (SETE)	7.3	76.91	1.90	1.00	0.67	0.11
Final effluent (FE)	7.6	12.12	0.15	0.11	0.02	0.09

from each section of the WWTP. The specific experimental conditions were as follows: measure 1 L of sewage sample at room temperature, place it in a 1.5 L beaker, weigh 100 mg of MAC-1 or MAC-2 into the beaker, and wrap the beaker with aluminum foil to prevent photolysis. Place the beaker on a magnetic stirrer, stir the solution for 24 h at a constant temperature of 200 rpm, centrifugate for 15 min at 5,000 rpm, extract the supernatant, filter it to a 0.22 μm

Table 3
Ten SAs recoveries of solid-phase extraction, RSD, LOD and LOQ (water)

Antibiotics	Recoveries (%)	RSD (%)	LOD (ng L^{-1})	LOQ (ng L^{-1})
TMP	88.72	6.99	0.06	0.11
SCM	96.21	4.82	0.11	0.18
SDZ	90.11	2.91	0.13	0.20
SMP	74.41	3.66	0.05	0.08
SMR	86.93	3.84	0.06	0.10
SCP	87.92	2.09	0.03	0.05
SMX	96.17	4.12	0.09	0.12
SDM	82.64	2.39	0.10	0.16
SQX	94.84	1.93	0.04	0.05
SMZ	100.06	1.12	0.07	0.10

polytetrafluoroethylene microporous filter membrane, detect the residual concentration of SAs in the solution according to the analysis method given in section 2.3, and calculate the adsorption capacity and removal rate. Eight treatments were tested in the adsorption experiment, and each uses three parallel treatments (Fig. 1).

3. Results and discussion

3.1. SA content in each WWTP section

The contents (C) and detection frequencies (DF) of 10 SAs from each WWTP section, containing influent, primary sedimentation tank effluent, biochemical tank effluent, secondary sedimentation tank effluent and final effluent (FE), are presented in Table 4; 10 SAs were detected in five samples at concentrations of 0.05–356.91 ng L^{-1} while the main contaminants were SMZ, SMX and SDM. Similar results are given in the reported literature. Cui et al. [15] found that SMZ, SDM and sulfadiazine (SDZ) present high detection frequencies in influent (88%–100%) and effluent (88%–94%).

DF of TMP, SMX and SMZ was observed in 100% of the influent, and the DF of SDZ, sulfamerazine (SMR) and SDM exceeded 80% while those of sulfacetamide (SCM), sulfamethoxypyridazine (SMP), sulfachloropyridazine (SCP) and

Fig. 1. Adsorption experiment method.

Table 4
Concentrations of detected SAs at each section of wastewater treatment plant (ng L^{-1})

Antibiotics	Influent		PSTE		BTE		SETE		FE	
	C	DF	C	DF	C	DF	C	DF	C	DF
TMP	23.94	100%	20.61	95%	32.49	90%	17.26	80%	35.78	90%
SCM	3.01	50%	2.16	30%	2.61	25%	2.45	25%	1.74	25%
SDZ	3.53	80%	2.69	50%	2.22	50%	1.75	30%	1.56	30%
SMP	0.09	10%	0.08	20%	0.07	20%	0.05	10%	0.06	10%
SMR	38.43	80%	32.24	80%	39.53	75%	20.62	70%	16.74	60%
SCP	0.37	25%	0.36	20%	0.29	20%	0.25	20%	0.16	20%
SMX	105.99	100%	86.95	100%	90.36	90%	84.38	80%	93.11	85%
SDM	100.53	95%	94.23	95%	66.52	90%	62.1	80%	54.89	80%
SQX	0.39	50%	0.34	25%	0.38	30%	0.28	25%	0.24	20%
SMZ	356.91	100%	269.25	100%	321.93	95%	247.69	95%	257.08	95%

sulfaquinoxaline (SQX) were less than 50%. Concentrations of SMZ in the influent were the highest at 356.91 ng L^{-1} followed by SMX > SDM > SMR > TMP while other SAs were found at low concentration. The average concentration of SMZ in the FE was high at 257.08 ng L^{-1}, which might be related to large applications of SMZ.

Many WWTPs in China and other countries have shown high concentrations of SMZ. Gao et al. [16] investigated concentrations of sulfonamides found in eight major urban sewage plants in Beijing. The concentration of SMZ in the influent was 1.2 (±0.45) μg L^{-1}, and concentrations of SMX in the influent were second only to those of SMZ at 105.99 ng L^{-1}. After sedimentation in primary sedimentation tanks, some SMX settled from the sewage. After biochemical tank treatment, concentrations of SMX were elevated, which may be the case because conjugated metabolites of antibiotics polymerize or biotransform to increase the target substance content [17,18]. The detection rate and concentration of SDM in the influent were 95% and 100.53 ng L^{-1}, respectively. After treatment, the final concentration of SDM in the effluent was 54.89 ng L^{-1}. The detection rate of SMR in the influent was 80%, its concentration reached 38.43 ng L^{-1}, and its final concentration in the effluent reached 16.74 ng L^{-1}.

TMP, the synergist of sulfonamides, is often used with SMZ and SDZ with a proportion of 1:5. TMP has a relatively high detection rate and concentration and was detected in effluent from each section of the WWTP at a detection rate of 100% while the concentration in the influent was 23.94 ng L^{-1}. It is worth noting that the concentrations TMP in the effluent from the biochemical tank were higher than those in the effluent from the primary sedimentation tank, and the FE concentration was 1.5 times higher than that of the influent (35.78 ng L^{-1}). TMP may have been adsorbed into suspended solids or sludge that may have been released into the water body medium, creating high concentrations in the effluent.

In addition, the SDZ detection rate was 80%, the detection rate of the other four SAs was lower than 50%, and the detection concentrations of the five antibiotics were also low at below 5 ng L^{-1}, which might be related to the small amounts used.

The detection rate of SMX and SMZ was measured as 100%; those of TMP, SDM and SMR exceeded 80%; and those of the other five antibiotics were less than 50%. The highest SMZ concentration was 247.69 ng L^{-1} followed by those of SDM, SMX, SMR and TMP, which ranged from 20 to 100 ng L^{-1}. Concentrations of the other five SAs were less than 3 ng L^{-1}. In effluent from the biochemical and secondary sedimentation tanks, 10 kinds of SAs were detected. Some were effectively removed from the biochemical tank, and concentrations of SDZ, SMP, SCP and SDM decreased. With the exception of the high concentrations of SDM observed (66.52 ng L^{-1}), all levels were lower than 3 ng L^{-1}, which might be related to the biodegradation of microorganisms throughout the process, indicating that the four kinds of SAs show high levels of biodegradability. Concentrations of the other six SAs increased and negative removal occurred. After secondary sedimentation tank treatment, although concentrations decreased again, such trends were more gradual. Concentrations of SMZ reached 321.93 ng L^{-1} in the effluent of the biochemical tank, 247.69 ng L^{-1} in the effluent of the secondary sedimentation tank, 90.36 ng L^{-1} in the effluent of the biochemical tank and 84.38 ng L^{-1} in the effluent of the secondary sedimentation tank, showing that the removal efficiency of sulfonamide antibiotics in a WWTP is relatively low. In the FE, detection rates of TMP, SMR, SMX, SDM and SMZ exceeded 60%, and detection rates of the other five antibiotics were lower than 30%. The detection concentration of SMZ was the highest at 257.08 ng L^{-1} followed by those of SMX, SDM and TMP, which were higher than 30 ng L^{-1}. The concentration of SMR was 16.74 ng L^{-1}, and concentrations of the other five target antibiotics were less than 2.00 ng L^{-1}.

The cumulative concentration distribution of SAs in the effluent from each section is shown in Fig. 2. It is evident that the antibiotic content of different sections of the sewage plant exhibits certain differences. Concentrations of 10 sulfonamides in the influent were the highest at roughly 633.19 ng L^{-1}. SMZ was the main contributing factor, accounting for more than 56.37%. SMZ is one of the most commonly used SAs and is often added to feed as a treatment and prevention drug for livestock and poultry and aquatic products. It is used large amounts, is relatively stable and is

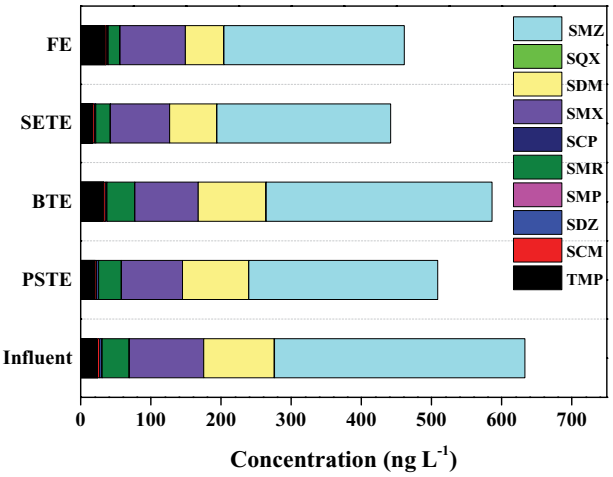


Fig. 2. The accumulative concentration of detected SAs at each section of the wastewater treatment plant.

highly detectable in water environments. It is one of the 14 sulfonamides that must be detected preferentially according to the US Food and Drug Administration (FDA). SMZ was also detected in the influent of the studied sewage plant. SMX and SDM were the second most common with contribution rates of 16.74% and 15.88%, respectively. SDM and SMX, as commonly used veterinary drugs, are widely employed for the treatment of the respiratory, urinary, and digestive tracts and to treat local infections in livestock. They can also be used as feed additives to improve the disease resistance and production performance of livestock and poultry, for which their use is increasing. The accumulated concentration of SAs in the effluent from the primary sedimentation tank was measured as 508.91 ng L^{-1}. After sedimentation, some antibiotics adsorbed onto large particles and settled, causing the accumulated concentration of sulfonamides to decrease. The concentrations of certain antibiotics in the effluent from the biochemical tank decreased, potentially due to the degradation of microorganisms. In addition, the concentrations of other sulfonamides increased to varying degrees. The cumulative concentration of each SA was 556.40 ng L^{-1}, which is higher than that found in the effluent of the primary sedimentation tank, which might be resistant to sulfonamides. The adsorption and desorption of elements on the surfaces of activated sludge are related. After sedimentation in the secondary sedimentation tank, the cumulative concentration of sulfanilamide antibiotics decreased to 436.83 ng L^{-1}. Throughout this process, with the exception of sludge separation, sludge concentrations were present. Concentrations of activated sludge mixture were high with high levels of flocculation and the potential to absorb sulfanilamide antibiotics. UV disinfection is the last process applied at the studied WWTP. Some studies have shown that UV can effectively degrade antibiotics [18]. We found that concentrations of SCM, SDZ, SMR, SCP, SDM and SQX in the FE had decreased significantly, indicating that UV light had decomposed some antibiotics. However, concentrations of TMP, SMP, SMX and SMZ increased, and the cumulative concentration of sulfonamides in the FE was 461.36 ng L^{-1}, which is higher than that found in the secondary sedimentation tank. According to Garcia et al. [19], ultraviolet irradiation can change the structures with which the binding bodies of substances form free bodies. Due to changes in interactions between substances in the matrix, more target substances are released to increase the detection concentration.

3.2. Degradation law of SAs in a WWTP

Fig. 3 shows the removal of SAs through different processes at the studied WWTP. The SA removal rate in each section of the WWTP fluctuates greatly as shown in Fig. 3a. In the primary sedimentation tank, some antibiotics are adsorbed onto the surfaces of larger particles. With the sedimentation of particles, SAs can be removed. In this stage, the removal efficiency of SAs is generally low, except for SCM, SDZ and SMZ, which present values of 28.24%, 23.80% and 24.56%, respectively. The removal efficiencies of the other seven SAs are less than 20%, which is related to the solid-liquid distribution coefficient of antibiotics [20]. Antibiotics in the primary sedimentation tank enter the biochemical tank with sewage and part of the sludge is returned from the secondary sedimentation tank. The adsorption of activated sludge and microbial transformation can play a role in the removal of SAs. The removal efficiency of SMP is the highest, reaching up to 28.57%. SDZ and SCP are also partially removed in the biochemical pool at removal rates of 4.93% and 12.00%, respectively. This may occur due to the biodegradation of organisms. Although SAs can be removed as a carbon source of microorganisms, high concentrations of antibiotics can inhibit the biological metabolism of microorganisms, causing microbial action to remove fewer SAs [21]. Moreover, some antibiotics can be adsorbed onto activated sludge for removal. However, TMP, SCM, SMR, SMX, SDM, SQX, and SMZ exhibited negative removal at this stage, potentially due to the conversion of some SAs metabolites into original antibiotics under anaerobic conditions, resulting in an increase in effluent concentrations. Some studies have shown that N(4)-acetyl-SMZ, the human metabolite of SMZ, can be transformed into SMZ through biological treatment [22]. After the solid–liquid separation in the secondary sedimentation tank, some of the removed compounds are adsorbed onto the activated sludge and then precipitated into the sludge concentration tank. At this stage, the removal efficiencies of SMR and TMP are the best with removal rates of 47.84% and 46.88%, respectively. The removal efficiencies of SCM, SMX and SDM are less than 10%.

The total removal rates of SAs in the studied WWTP are shown in Fig. 3b. The negative removal of TMP may be attributed to the release of TMP adsorbed onto sludge in the water body during the treatment, creating high concentrations of TMP in the effluent while concentrations of other SAs in the FE decrease to varying degrees. While the studied WWTP was found to have a certain removal effect on the nine sulfonamides, these removal rates are below 60% (SCM (42.19%), SDZ (55.81%), SMP (33.33%), SMR (56.44%), SCP (56.76%), SMX (12.15%), SDM (45.40%), SQX (38.46%), and SMZ (27.97%)). It is apparent that the wastewater treatment process cannot currently fully remove antibiotics from wastewater. The observed differences in removal efficiencies of SAs at the studied WWTP show that removal

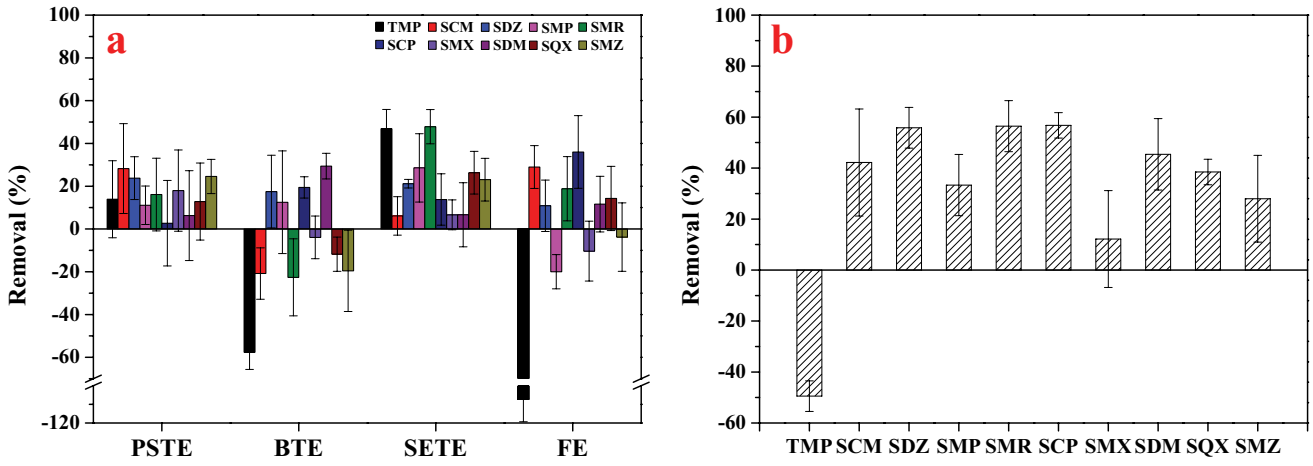


Fig. 3. (a) Removal of the 10 SAs during each section and (b) total removal of the 10 SAs in the wastewater treatment plant.

efficiency depends not only on the properties of various drugs but also on treatment processes and the operation conditions of various processes (e.g., sludge retention time, hydraulic retention time, temperature, pH, the total number of microorganisms, etc.). Therefore, to improve the removal efficiency of SAs in WWTPs, more advanced treatments are required.

3.3. Correlation analysis of main water quality indexes and SAs in WWTPs

To explore the impact of conventional water quality indicators on the occurrence of antibiotics in the studied WWTP, pH, chemical oxygen demand, total nitrogen (TN), total phosphorus, NH_3–N, and NO_3^-–N were measured, and Canoco 4.5 software was used for a direct gradient analysis. Two models have been developed for the direct gradient analysis of the relationship between pollutants and chemical parameters of a water body redundancy analysis (RDA) and canonical correspondence analysis (CCA) [23]. According to CCA, the first axis size value of lengths of a grade is 0.145, which is less than 3. Therefore, the RDA model is used for our analysis. See Fig. 4 for the results. In the RDA sequence diagram, arrows pointed in the same direction denote a positive correlation while arrows pointed opposite directions denote a negative correlation; the lower the cosine value of the angle between data arrows, the stronger the correlation. Factors with weak correlations are automatically eliminated.

Fig. 4 shows that pH has a significant effect on the occurrence of antibiotics in a WWTP, is negatively related to SDM, SCP, SCM, SDZ, SQX, SMR, SMP, SMZ and SMX, and has the greatest impacts on SQX, SMR and SMP. pH not only affects existing forms of antibiotics (mainly related to the acid separation constant pKa of antibiotics) but also produces activated sludge and microorganisms in WWTP TN, NH_3–N, and NO_3^-–N, which mainly affect SDM and SCP. TN, NH_3–N, and NO_3^-–N removal in a WWTP mainly involves nitrification, denitrification, ammoniation and other important reaction processes. SDM and SCP removal may be greatly affected by these processes. Many kinds of pollutants are found in sewage, which are very complex systems,

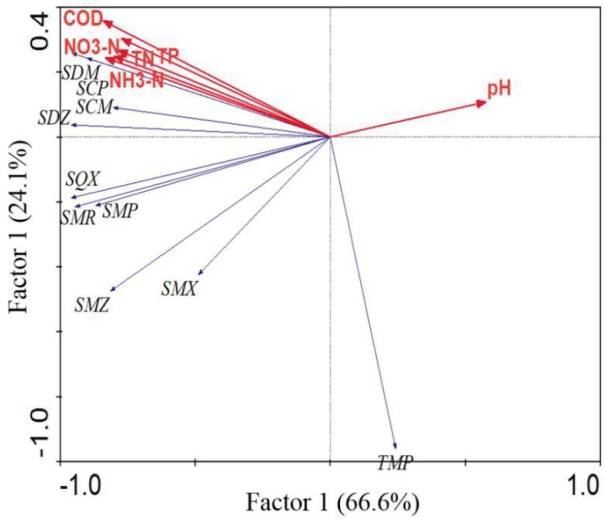


Fig. 4. The RDA-sort graph of antibiotics and main water factors.

and the occurrence of pollutants is affected by several factors. The occurrence relationship between conventional pollutants and antibiotics and the relationships between these and water treatment technologies require further study.

3.4. Study on the adsorption of SAs by modified activated carbon

The test results show the removal rates of the 10 SAs to be less than 60%, which indicates that the removal efficiency of SAs in a WWTP is not high. We found that SAs in sewage cannot be fully removed from WWTPs. Therefore, in this experiment, two kinds of modified activated carbon were selected as adsorbents to treat SAs in the effluent of each process unit. The dose of modified activated carbon was set to 100 mg, the solution volume was set to 1 L, and the equilibrium adsorption period was set to 24 h. Concentrations of the 10 SAs in influent and effluent water from each section after treatment with modified activated carbon are shown in Fig. 5.

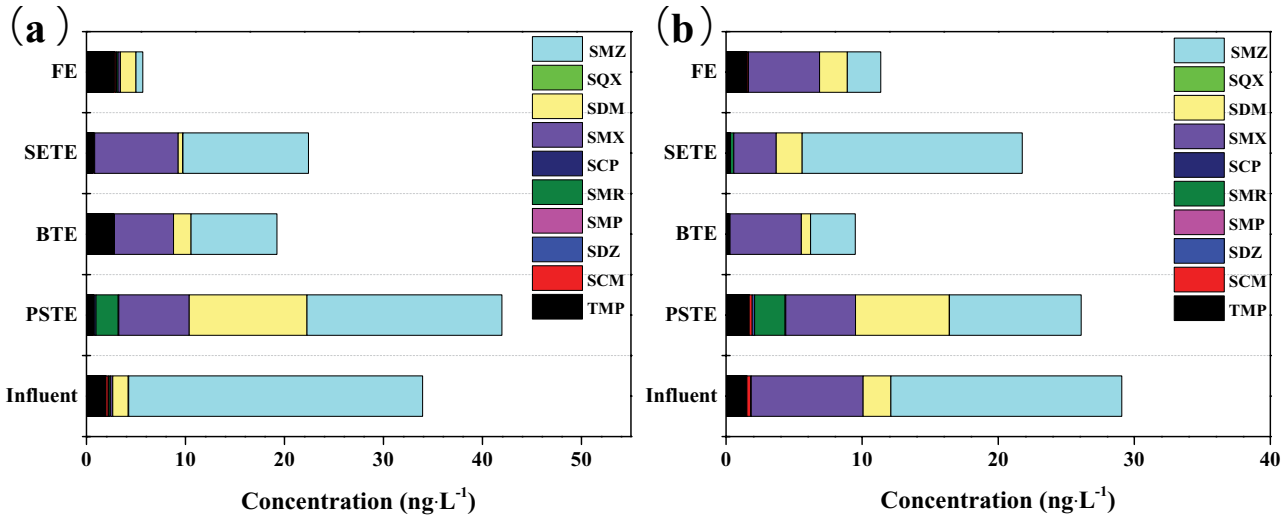


Fig. 5. The concentration of 10 SAs at each process unit of wastewater treatment plant with adsorption of MAC (a) MAC-1 and (b) MAC-2.

Concentration levels of the 10 SAs in the effluent of each treatment unit after being adsorbed by MAC-1 are shown in Fig. 5a. After influent treatment, the concentration of residual SAs ranged from n.d.-29.68 ng L^{-1} and the cumulative concentration was 33.95 ng L^{-1}; in the effluent of the primary sedimentation tank, concentrations of residual sulfonamide antibiotics ranged from n.d.-19.32 ng L^{-1} and the cumulative concentration was 41.58 ng L^{-1}; in the effluent from the biochemical tank, concentrations of residual sulfonamide antibiotics ranged from n.d.-29.68 ng L^{-1}. Concentrations of biotin ranged from n.d. to 8.79 ng L^{-1}, and the cumulative concentration was 19.34 ng L^{-1}. In effluent of the secondary sedimentation tank, concentrations of residual sulfonamides ranged from n.d. to 12.67 ng L^{-1}, and the cumulative concentration was 22.42 ng L^{-1}. In the total effluent, concentrations of residual sulfonamides ranged from n.d. to 2.84 ng L^{-1}, and the cumulative concentration was 5.69 ng L^{-1}. In Fig. 5b, the concentrations of the 10 SAs after the effluent of each treatment unit was adsorbed by MAC-2. After influent treatment, concentrations of residual SAs ranged from n.d.-16.97 ng L^{-1} and the cumulative concentration was 29.08 ng L^{-1}. In effluent of the primary sedimentation tank, concentrations of residual SAs ranged from n.d.-9.68 ng L^{-1} and the cumulative concentration was 26.09 ng L^{-1}. In effluent of the biochemical tank, concentrations of residual sulfonamide antibiotics range from n.d.-16.97 ng L^{-1}. In effluent of the secondary sedimentation tank, concentrations of residual sulfonamides ranged from n.d. to 5.24 ng L^{-1}, and the cumulative concentration was 9.51 ng L^{-1}. In effluent of the secondary sedimentation tank, concentrations of residual sulfonamides ranged from n.d. to 26.18 ng L^{-1}, and the cumulative concentration was

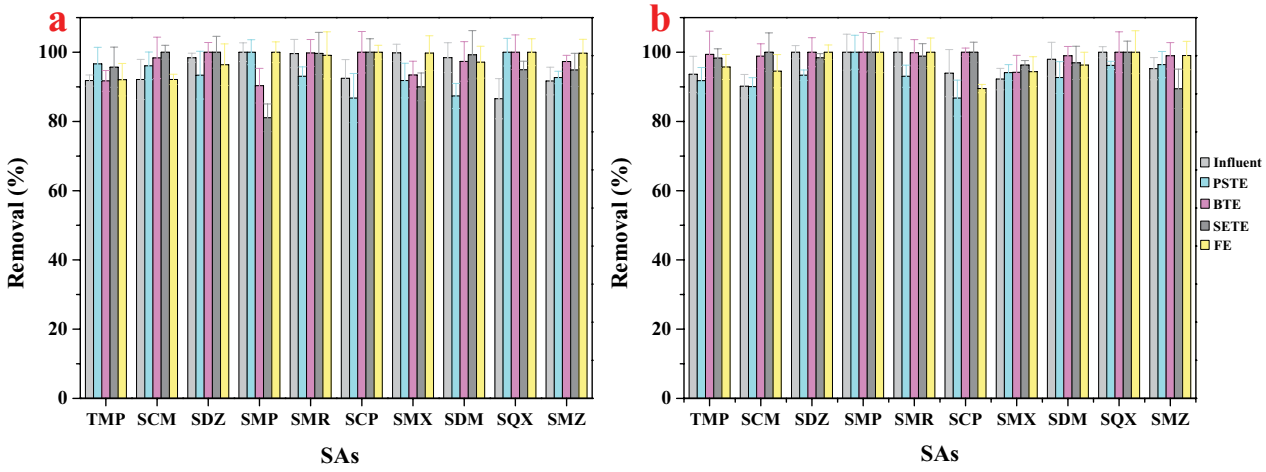


Fig. 6. Removal of 10 SAs onto modified activated carbon during each treatment unit in wastewater treatment plant (a) MAC-1 and (b) MAC-2.

31.76 ng L^{-1}. In the FE, concentrations of residual sulfonamides ranged from n.d. to 5.22 ng L^{-1}, and the cumulative concentration was 11.36 ng L^{-1}.

MAC-1 and MAC-2 are respectively used for the adsorption and removal of sulfonamides in influent and effluent water of each section. Fig. 6 shows that the SAs removal efficiencies of the two forms of modified activated carbon from the effluent of each treatment unit ranged from 87.37% to 100%, demonstrating good practical applications and potential applications to actual sewage systems.

4. Conclusions

This study investigated concentration levels and removal efficiencies of SAs found in the effluent from different sections of WWTPs and explored the removal of SAs in the effluent of each section by modified activated carbon. Our main conclusions are as follows:

- Ten SAs were detected in influent and effluent water from each section. Average concentrations of sulfonamides in influent water, effluent water from the primary sedimentation tank, effluent water from the biochemical tank, effluent water from the secondary sedimentation tank and FE water were 0.09–356.91 ng L^{-1}, 0.08–269.25 ng L^{-1}, 0.07–321.93 ng L^{-1}, 0.05–247.69 ng L^{-1}, 0.06–257.08 ng L^{-1}, respectively.
- Except for the negative removal of TMP, the wastewater treatment process has removal effects on the other nine SAs with removal rates of less than 60%. These removal rates are as follows: SCM (42.19%), SDZ (55.81%), SMP (33.33%), SMR (56.44%), SCP (56.76%), SMX (12.15%), SDM (45.40%), SQX (38.46%), and SMZ (27.97%).
- Effect of pH on the occurrence of antibiotics in a WWTP is obvious and shows a negative correlation. TN, NH_3–N and NO_3^-–N mainly affect SDM and SCP.
- After equilibrium adsorption for 24 h, the removal rate of SAs in the effluent of each section ranged from 87.37% to 100%.

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