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Application of permanganate/bisulfite process for treatment of sulfamerazine contaminated water

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ABSTRACT

The permanganate/bisulfite (PM/BS) process is highly efficient in the oxidation of refractory contaminants due to the generation of a large number of reactive manganese species and radicals. However, a lot of concerns need to be addressed for the application of the PM/BS process in real sulfamerazine (SMZ) contaminated water treatment. The factors affecting the degradation efficiency of SMZ by PM/BS and the influences of PM/BS pre-oxidation on the formation and toxicity of trihalomethanes (THMs) during the subsequent chlorination of simulated SMZ-contaminated waters were investigated in this study. The PM/BS process exhibited fast oxidation of SMZ at acidic/neutral pH and low SMZ concentration (5 μm) with more than 80% of SMZ removal within 15 s. The permanganate was efficiently activated by bisulfite and exhibited high efficiency in SMZ degradation when permanganate/bisulfite dosage was 50 μm:250 μm. The co-existing protein bovine serum albumin caused less than 10% inhibition of SMZ degradation in the PM/BS process at pH 6 and 7. However, humic acids and alginate inhibited the removal of SMZ by 18%–57%. PM/BS pre-oxidation of SMZ-contaminated waters achieved a 28%–64% reduction of THM formation in the subsequent chlorination, greatly decreasing the toxicity risk in chlorination.

Keywords: Reactive manganese species (RMnS); Sulfonamides; pH; Co-existing dissolved organic matters (DOM); Disinfection byproducts (DBPs)

1. Introduction

Due to irrational use and disposal, an increasing quantity of antibiotics have been released into the environment [1–3], with more and more antibiotics observed in various water bodies, which drew wide attention [4,5]. Sulfonamides (sulfa drugs) are important synthetic antibiotics widely used in medical treatment, livestock and poultry farming, and aquaculture. Generally, sulfonamides show a much higher concentration in water environments than other antibiotics, like the most frequently detected macrolides [6]. Sulfonamides were detected to have a concentration varying from 82.5 ng L^{-1} to 1.28×10^6 ng L^{-1} in surface waters, aquafarm water, ditch water, wetland water, and groundwater [6,7], posing prominent threats to the environment.

Since antibiotics are micromolecular refractory compounds with bactericidal effects, existing technologies like coagulation, filtration, and biodegradation are inefficient in their removal. The presence of low-level antibiotics may inhibit activity of functional microorganisms, damage human tissues and organs, cause metabolic disorders, and

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in severe cases, induce the generation of antibiotic-resistant bacteria [8–10]. Besides, sulfonamide antibiotics contain activated aromatic groups, reduced nitrogen, and sulfur functional groups, which have strong reactivity with chlorine (amine) and hence can produce large amounts of toxic disinfection byproducts (DBPs) in the disinfection process [11]. In our previous study, it was discovered that the disinfection byproduct formation potential (DBPFP) of sulfamerazine (SMZ) was 10 times that of ciprofloxacin [12]. Many efforts have been made to remove sulfonamides and control the generation of DBPs in water treatment [13,14]. Various advanced oxidation processes (AOPs) including ultraviolet/chlorine, ultraviolet/ozone, ultraviolet/peroxide, and ultraviolet/persulfate (UV/PS) [14–18], were reported to be efficient in the degradation of sulfonamides, but their effect on the generation of DBPs in the subsequent chlorination process varied. Due to the incomplete mineralization of antibiotics [19], UV/PS pretreatment increased the formation of trichloromethane (TCM) during the subsequent chlorine disinfection of chloramphenicol contaminated waters [20].

Recent studies have found that refractory contaminants could be fast degraded in the permanganate/bisulfite (PM/BS) process, where bisulfite would activate permanganate to generate large quantities of reactive manganese species (RMnS), as well as $SO_4^{\bullet-}$ and $^{\bullet}OH$ radicals [21]. RMnS were demonstrated to be highly selective and reactive to ciprofloxacin with coexisting dissolved organic matter (DOM) [22,23]. The influences of PM/BS pretreatment on the generation and toxicity of DBPs in the following chlorine disinfection process varied with the concentration of ciprofloxacin, the dosage of PM/BS [12], and the coexisting DOM [22]. PM/BS pretreatment at a PM/BS dosage of 500/2500 (μm/μm), was found efficient in reducing the generation of DBPs in the post-chlorination of the pure ciprofloxacin water sample with a concentration of 50 μm [12]. In several simulated low-level ciprofloxacin contaminated natural water samples (5 μm), PM/BS oxidation (50/250 (μm/μm)) was found to have reduced the toxicity caused by DBPs during the following chlorine disinfection process. However, in the ciprofloxacin-contaminated natural water samples containing bromide, PM/BS treatment greatly increased the toxicity of DBPs formed in the chlorination process [22]. To our knowledge, there are few reports on the removal of sulfonamides by the PM/BS system [12]. In a previous study, a high concentration of SMZ (50 μm) in pure water was efficiently removed by PM/BS (2500 μm/500 μm) due to the synergy of RMnS oxidation and colloid MnO_2 adsorption [12], where a large amount of colloid MnO_2 was generated due to the high dosage of PM and BS [24]. However, large quantities of DOM, for example, humic acids (HA) derived from the degradation of natural organic matters, and biomacromolecules including proteins and polysaccharides derived from the metabolism and growth/death of microorganisms, are present in real water or wastewater. It is yet to be found whether PM/BS selectively oxidizes sulfonamides with the coexistence of DOM, and the factors that influence the efficiency of sulfonamide degradation in the PM/BS system have not been systematically investigated. Besides, the influences of PM/BS treatment on DBP generation and toxicity during the subsequent chlorination of SMZ-contaminated surface water or reclaimed water also needs to be evaluated.

Therefore, this study aims to systematically evaluate the influences of SMZ concentration, PM dosage, PM and BS molar ratio, initial pH, coexisting contaminants, such as HA, alginate, and bovine serum albumin (BSA), on the efficiency of SMZ removal by PM/BS. In addition, the influences of PM/BS pretreatment on the production and toxicity of trihalomethanes (THMs) in the subsequent chlorination of SMZ-contaminated water with or without coexisting bromide were studied. The results are expected to prove the feasibility of employing PM/BS treatment to control the risk of water contamination by sulfonamide antibiotics.

2. Materials and methods

2.1. Reagents

Sulfamerazine (SMZ, >99%), HA, BSA, and sodium alginate from Aladdin were used in this study. Table S1 presents the detailed physicochemical properties of SMZ. EPA 551.1 DBP standards were purchased from Sigma-Aldrich. The inorganic reagents are GR grade. Methyl tert-butyl ether used for the extraction of DBPs was chromatographically pure. All solutions were prepared with Milli-Q water.

2.2. PM/BS oxidation and chlorination experiments

PM/BS oxidation was performed in conical flasks at 25°C ± 1°C. $KMnO_4$ solution and a mixed solution of contaminants and bisulfite conditioned to expected pH were freshly prepared before the oxidation reaction [22,24,25]. According to the expected PM/BS molar ration, a certain amount of $KMnO_4$ was rapidly spiked into contaminants and bisulfite mixed solution while mixing vigorously and lasted 15 s [24]. Hydroxylamine hydrochloride of 20-fold excess was used to quench the samples [26], which were then subject to high-performance liquid chromatography (HPLC) and total organic carbon (TOC) analysis.

To estimate the influence of PM/BS pre-oxidation on the DBP formation and toxicity during chlorine disinfection of SMZ contaminated waters, a standard 24 h formation potential (FP) test was run [22,27]. The sample after PM/BS oxidation without quenching [25,28] was immediately filtered through a 0.45 μm membrane and adjusted to pH 7.0, then used for chlorination and FP test. Detailed experiment procedures are shown in Supplementary Information. As bromide is widespread in natural water and wastewater [29,30], 0.5 mg L^{-1} of Br^- was added to samples to evaluate influences of PM/BS pre-oxidation on DBP formation and toxicity during chlorination of waters contaminated with SMZ and bromide. To ensure complete chlorination, the dosage of chlorine was 15 mg L^{-1} (Cl_2:TOC = 3). After 24 h chlorination, samples quenched with sodium thiosulphate were subject to DBP analysis. THMs including TCM, bromodichloromethane (BDCM), dibromochloromethane (DBCM), and tribromethane (TBM) were determined according to the method modified from EPA 551.1.

2.3. Analytical methods

DBPs and SMZ were analyzed by liquid-liquid extraction coupled with gas chromatography with electron capture detection (GC-ECD) and HPLC, respectively, which are present in the Supplementary Information. A Free & Total Chlorine measuring meter and TOC-V$_{CPH}$ analyzer were used for the analysis of residual chlorine and TOC, respectively. A Zeta-sizer 3000HSa (Malvern Instruments, UK) was applied to the analysis of hydrodynamic size distribution and zeta potential.

3. Results and discussion

3.1. Performance of PM/BS in degradation of SMZ

The degradation of SMZ with various initial concentrations (5, 10, 25, and 50 μm) by the PM/BS process at pH$_{ini}$ 7 was evaluated (Fig. 1A). In general, the fraction of SMZ removed by the PM/BS decreased as the initial concentration of SMZ ([SMZ]$_0$) increased. However, when [PM]/[BS] dosage was 50 μm:250 μm, the SMZ removal fraction was not decreased and the amount of removed SMZ greatly increased from 6.02 μm to 14.45 μm with increasing the [SMZ]$_0$ from 25 μm to 50 μm, indicating the improved degradation of SMZ at higher concentration. It might be rationalized that a higher concentration of SMZ enabled a faster reaction between SMZ and short-lifetime RMnS and radicals, which increased the apparent oxidation efficiency of reactive oxidation species and in turn increased the absolute amount of removed SMZ. About 84% of the SMZ with an initial concentration of 5 μm was removed within 15 s by the PM/BS process, where [PM]/[BS] dosage was 50 μm:250 μm. It indicates that the PM/BS process was efficient in the treatment of nature or reclaimed waters slightly contaminated by SMZ. However, the TOC removal in all samples was less than 10% (data not shown) within this study, contradictory with a previous finding that PM/BS oxidation achieved 30% elimination of TOC where the [SMZ]$_0$ was 50 μm and the [PM]/[BS] dosage was 500 μm:2500 μm [12]. In the PM/BS oxidation process, RMnS efficiently attack the –NH$_2$ on the benzene ring and –CH$_3$ on the pyrimidine ring, meanwhile $SO_4^{\bullet-}$ and $^{\bullet}OH$ cause the cleavage of N–S bond and hydroxylation of the pyrimidine ring, which contributes to the oxidation of SMZ [12]. The low TOC removal in this study might be due to the extremely short life of RMnS and radicals, and the low reactivity of RMnS with SMZ oxidation intermediates. In addition to the oxidation removal by RMnS and radicals, the generation of colloidal MnO$_2$ might cause the adsorption removal of SMZ when the dosage of PM and BS is high, which rationalized the high TOC removal in the previous report [12].

The effects of PM dosage and [PM]/[BS] ratio on the degradation of SMZ in the PM/BS process were also evaluated. The removal of SMZ was quantified to be 12%–84%, strongly depending on the [PM]/[BS] dosage as well as the initial concentration of SMZ (Fig. 1B–E).

During the treatment of SMZ at 50 μm and 5 μm, the PM/BS process achieved the most SMZ degradation when the [PM]/[BS] dosage was 50:250 (μm/μm), with the removal efficiency of 30% and 80%, respectively. The degradation of SMZ at 25 μm and 10 μm in the PM/BS process was enhanced at the [PM]/[BS] dosage of 100:500 (μm/μm). It was found that increasing PM dosage to higher than 100 μm had great inhibition on SMZ removal, consistent with a previous study on the degradation of methyl phenyl sulfoxide (PMSO) by PM/BS process [31].

In the PM/BS process, both RMnS, including Mn(VI), Mn(V) [31], and Mn(III) [24,32], and radical species, including $SO_4^{\bullet-}$ and $^{\bullet}OH$ [21], contribute to the oxidation of contaminants. The reactions involved in the activation of permanganate by (bi)sulfite are proposed in several literatures [21,24,31] and simplified as Eqs. (1)–(7).

$$Mn^{(n+1)+} + HSO_3^- / SO_3^{2-} \rightarrow Mn^{(n)+} + SO_3^{\bullet-} + OH^- \quad (n = 1,2,5,6) \tag{1}$$

$$Mn(V) + H_2O \rightarrow Mn(IV) + Mn(VII) + H^+ \tag{2}$$

$$Mn(III) + H_2O \rightarrow Mn(II) + Mn(IV) + H^+ \tag{3}$$

$$SO_3^{\bullet-} + O_2 \rightarrow SO_5^{\bullet-} \tag{4}$$

$$SO_3^{\bullet-} + RMnS \rightarrow SO_4^{2-} (\text{without } O_2) \tag{5}$$

$$SO_5^{\bullet-} + HSO_3^- / SO_3^{2-} \rightarrow SO_4^{\bullet-} \tag{6}$$

$$SO_4^{\bullet-} + H_2O / OH^- \rightarrow {}^{\bullet}OH + HSO_4^- / SO_4^{2-} \tag{7}$$

It indicates that the generation and disappearance of reactive oxidants is a complex chain propagation process, strongly depending on the dissolved oxygen (DO) level, PM/BS dosage, as well as pH in the PM/BS system. As shown in Eq. (1), the [PM]/[BS] dosage and ratio determine the generation of RMnS. An optimized [PM]/[BS] ratio could ensure a maximum activation rather than quenching of PM by BS to achieve high production of RMnS. Inversely, an inappropriate [PM]/[BS] ratio or excessively high dosage would result in the undesired production of MnO$_2$ with lower oxidative activity. Moreover, the accumulation of colloidal MnO$_2$ would restrict the mass transfer of solutes in the PM/BS system, which further reduces the degradation of contaminants. The inhibitory effect of excessively high PM and BS dosage on the oxidation of SMZ in the PM/BS process might also be rationalized by the elimination of O$_2$ by the high concentration of BS. As shown in Eqs. (4) and (5), in the absence of O$_2$, $SO_3^{\bullet-}$ would react with RMnS as a competitor of SMZ [31,33].

With the increase of PM dosage to 200 μm, the dosage of BS was increased over than 1000 μm according to the molar ratio of the PM/BS process. The extremely high concentration of BS resulted in rapid consumption of DO, which resulted in the accumulation of $SO_3^{\bullet-}$ and inhibited the generation of $SO_4^{\bullet-}$ and $^{\bullet}OH$ radicals. Moreover, the extremely high dosage of PM and BS resulted in the overproduction of MnO$_2$ with lower oxidative reactivity rather than RMnS. Overall, when the PM dosage is over 200 μm (BS dosage was higher than 1,000 μm correspondingly), PM was not activated by BS, which inhibited the SMZ removal.

Despite the various initial SMZ concentrations, the efficiency of SMZ degradation in the PM/BS oxidation process

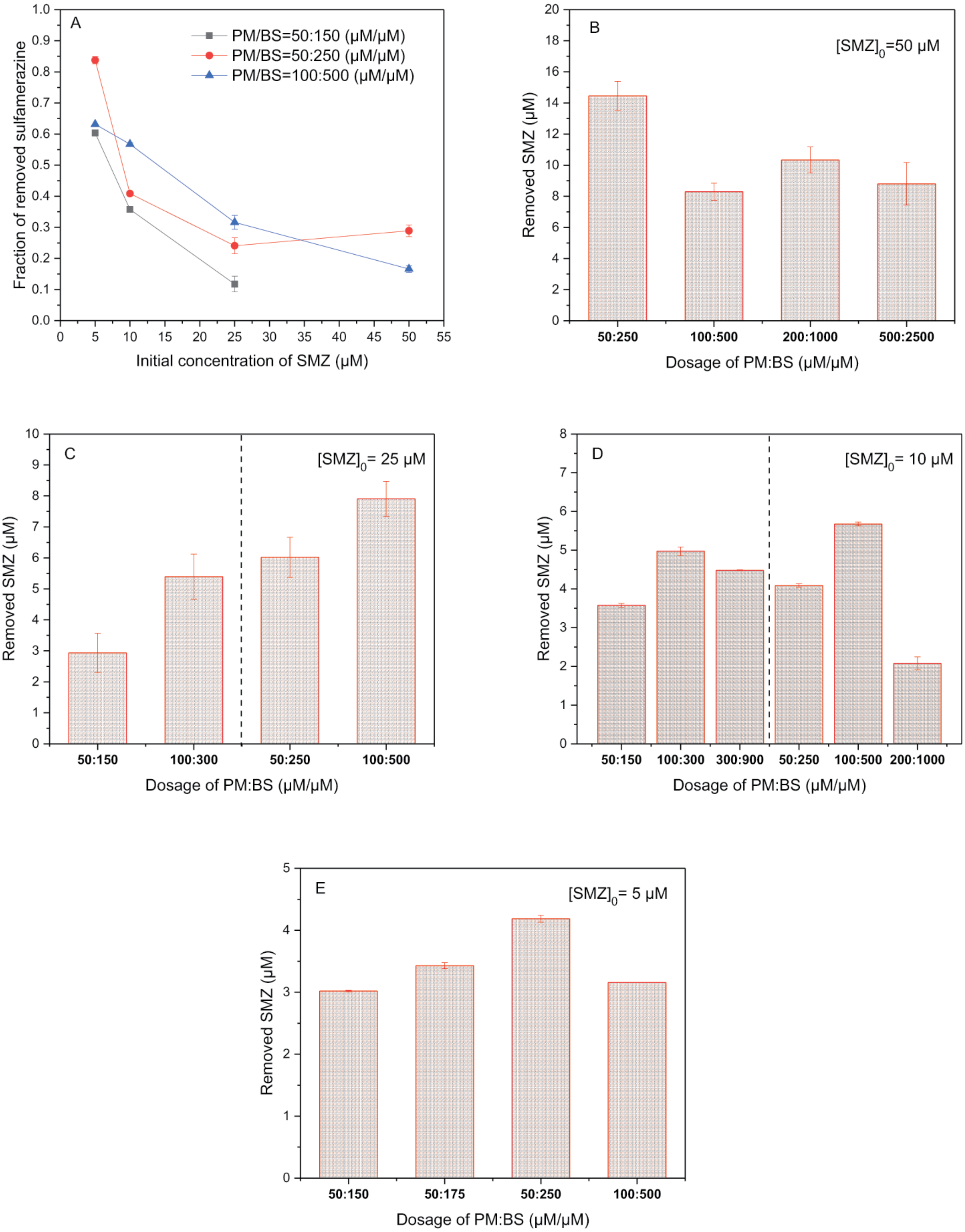

Fig. 1. The influences of initial concentration of SMZ (A) and $KMnO_4/HSO_3^-$ dosage ($[SMZ]_0$ = 50 μm (B), 25 μm (C), 10 μm (D), and 5 μm (E)) on the removal of SMZ in PM/BS oxidation process. Reaction conditions: pH_{ini} = 7 ± 0.1; temperature = 25°C ± 1°C.

reached the highest when the [PM]/[BS] dosage was 50:250 (μm/μm). It further demonstrated that the activation of PM by BS was most active when the [PM]/[BS] ratio was 1:5 and [PM] dosage was 50 μm.

3.2. Effects of initial pH on the removal of SMZ in PM/BS process

The removal of SMZ (5 μm) by PM/BS was investigated at pH_{ini} 6–9 with a fixed [PM]/[BS] ratio of 1:5 ([PM] = 50 μm). As shown in Fig. 2, the difference between the proportions of SMZ removed in PM/BS system at pH of 6 and 7 was not significant, which was around 80%. A further increase of initial solution pH resulted in a significant decrease in SMZ removal. As the pH_{ini} increased to 8, the percentage of SMZ degradation decreased to 30%. With increasing the pH_{ini} to 9, the percentage of SMZ degradation sharply decreased to ~6%. It was consistent with previous reports that alkaline solutions reduced the efficiency of the PM/BS system in the degradation of organic contaminants [12,22,24,31].

As shown in Eqs. (1)–(3) and (7), acidic conditions promote the generation of RMnS, whereas alkaline conditions result in the disappearance of RMnS but the production of $SO_4^{\bullet-}$ and $^{\bullet}OH$ radicals. A mechanistic changeover from RMnS to radicals with the increase of initial pH has been demonstrated during phenol degradation in PM/BS process [21]. Of note, the carboxylic groups formed during the oxidation of SMZ could decrease the pH of the PM/BS oxidation system, which would promote the generation of RMnS and relieve their disproportionation. This might be one of the explanations for that the PM/BS process exhibited the same efficiency in SMZ degradation at pH of 6 and 7. Nevertheless, the pH decrease caused by the formation of carboxylic groups derived from the oxidation of SMZ was not enough to buffer the strong alkaline solutions at initial pH > 8. A mechanistic changeover from RMnS to radicals occurred as the initial solution pH increased to >8 in the PM/BS process [21]. Compared with $SO_4^{\bullet-}$ and $^{\bullet}OH$ radicals, RMnS are more selective to electron-rich compounds [21,31]. What's more important, the concentration of RMnS generated at acidic conditions is much higher than that of $SO_4^{\bullet-}$ and $^{\bullet}OH$ radicals generated at alkaline solutions. Consequently, the efficiency of the PM/BS system in SMZ degradation was decreased when increased pH over 8.

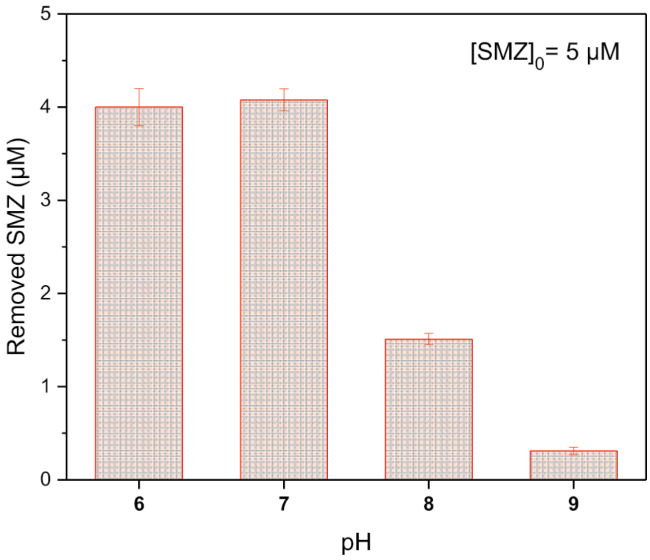

Fig. 2. Effect of initial solution pH on SMZ degradation in the PM/BS system. Reaction conditions: $[SMZ]_0$ = 5 μm; [PM]/[BS] = 50:250 (μm/μm); temperature = 25°C ± 1°C.

3.3. Effects of coexisting DOM on the degradation of SMZ by the PM/BS process

In a real water matrix, SMZ antibiotics are inevitably coexisting with DOM at mg level including humic substances, proteins, and polysaccharides. This study evaluated the effects of coexisting DOM including HA, alginate, and BSA on the degradation of SMZ by the PM/BS process.

As shown in Fig. 3, at pH_{ini} 7, permanganate alone (50 μm, 30 min) oxidized less than 5% of the SMZ in the DOM and SMZ mixed solutions, where the TOC of DOM was 3 mg/L, and the concentration of SMZ was 5 μm. However, the PM/BS system ([PM] = 50 μm, [PM]/[BS] = 1:5) achieved a 33%–80% removal of SMZ within 15 s. It indicates that PM was efficiently activated by BS despite the coexistence of background DOM.

The presence of BSA caused less than 10% inhibition on the degradation of SMZ, whereas HA and alginate significantly decreased the removal of SMZ by 18%–57% in the PM/BS process at pH 6 and 7 (Fig. 4). These findings are quite different from previous reports that coexisting DOM caused less than a 10% reduction in ciprofloxacin degradation in the PM/BS process [22,23]. In addition, a higher concentration of background DOM generally resulted in more inhibition of SMZ degradation in the PM/BS process (Fig. 4B).

The inhibition effects of background DOM on the removal of SMZ in the PM/BS oxidation process were mainly attributed to (1) the consumption of reactive oxidation species as a competitor of SMZ, and (2) the inactivation of SMZ by occupying its reactive sites or groups through the interaction between DOM and SMZ molecules. Because

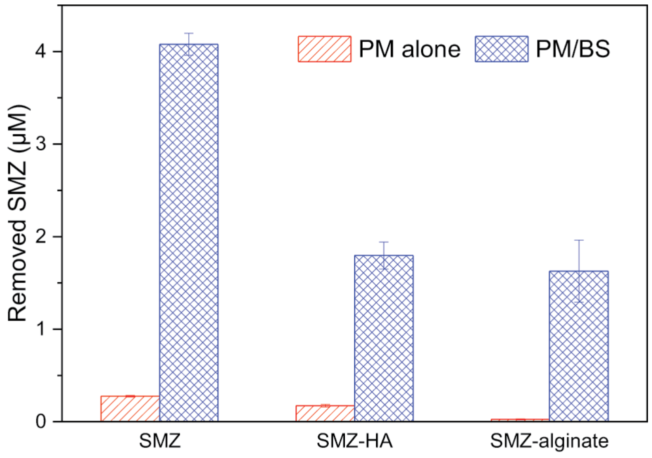

Fig. 3. Removal of SMZ coexistence with background organic matters by PM and the PM/BS process. Reaction conditions: $[SMZ]_0$ = 5 μm; TOC of background DOM = 3 mg L^{-1}; [PM] = 50 μm; [PM]/[BS] = 1:5; pH = 7 ± 0.1; temperature = 25°C ± 1°C.

HA, alginate, or BSA at the concentration of 3 mg L^{-1} (the same as the current study) caused less than 10% reduction in ciprofloxacin degradation in the PM/BS process [22,23], the competitive consumption of active oxidation species by background DOM might be the minor reason for the decrease in SMZ removal. The great changes in the hydraulic size and Zeta potential of HA, alginate, and BSA after mixing with SMZ indicated the interactions between background DOM and SMZ (Fig. 5). Based on the molecule structures (Fig. S1), HA and alginate have a large number of carboxyl and hydroxyl functional groups, which are prone to interact with $–NH_2$ groups in SMZ molecules to generate hydrogen bonds. It was confirmed by the increase of molecular size (Fig. 5A) and the decrease of negative charges in DOM molecules (Fig. 5B). Note that, in the PM/BS process, the $–NH_2$ on benzene ring and $–CH_3$ on pyrimidine ring are the most active sites susceptible to RMnS, which are transformed to $–NO/–NO_2$ and –COH/–COOH undergoing varying levels of oxidation [12]. Since the oxidation reaction was very fast (lasting less than 15 s) in the PM/BS process, it might be a lack of time for the RMnS to destroy the hydrogen bonds and oxidize $–NH_2$ group. It indicates that the inactivation of redox reactive groups $–NH_2$ on SMZ molecules due to the formation of hydrogen bond interaction was the primary reason for the inhibition of HA and alginate on SMZ degradation in the PM/BS process. Different from HA and alginate, BSA has a hydrophobic inner core consist of aromatic benzene rings [34], which would interact with the benzene and pyrimidine rings in SMZ molecules through the hydrophobic interaction rather than occupy the $–NH_2$ groups. Consequently, the coexistence of BSA exhibited little effects on the redox reactivity of SMZ, which

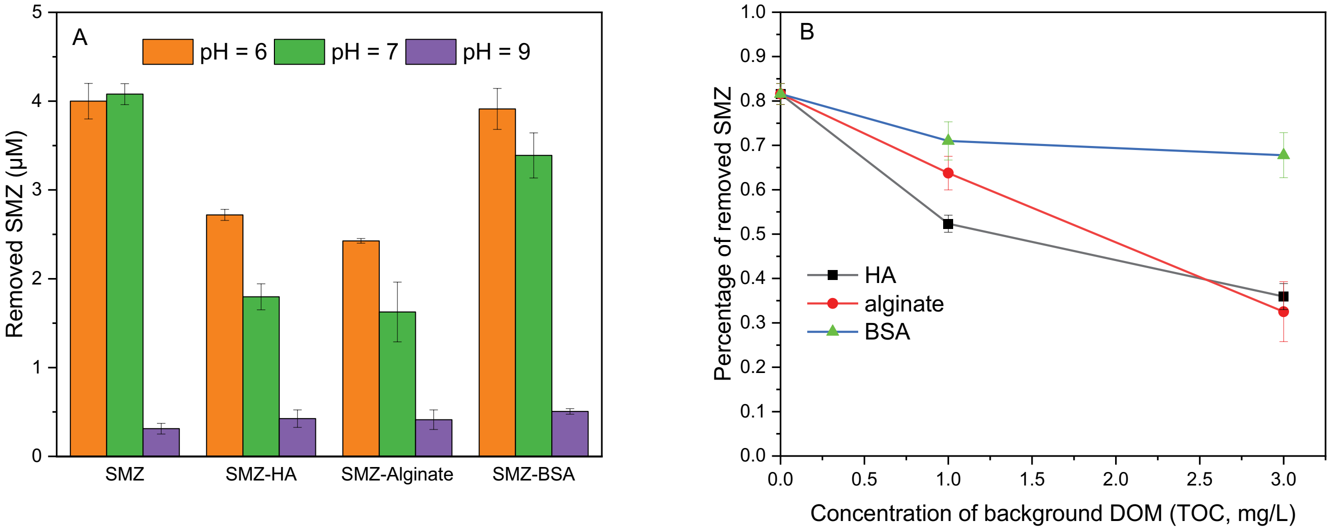

Fig. 4. Degradation rate of SMZ in mixed solutions of SMZ and background DOM by the PM/BS system (A) at different pH conditions and (B) with different amounts of background DOM. Reaction conditions: temperature = 25 °C ± 1°C, [PM] = 50 μm; [PM]/[BS] = 1:5; $[SMZ]_0$ = 5 μm; (A) TOC of background DOM = 3 mg L^{-1} and (B) pH = 7 ± 0.1.

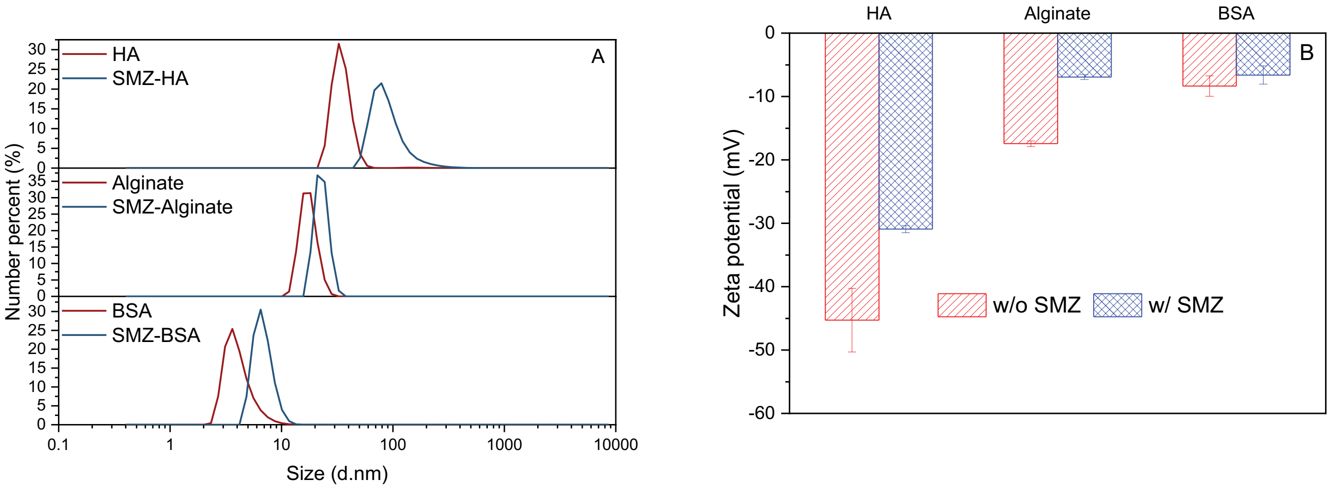

Fig. 5. The number-based hydration particle size distributions (A) and zeta potential (B) of DOM and SMZ mixed solution. Reaction conditions: $[SMZ]_0$ = 5 μm; TOC (organic matter) = 3 mg L^{-1}; pH = 7 ± 0.1; temperature = 25°C ± 1°C.

rationalized the limited inhibition of BSA on the SMZ degradation in the PM/BS process.

It was found that at pH_{ini} 6, the proportion of removed SMZ in the PM/BS process dropped from ~80% in Milli-Q water to 54%, 49%, and 78% in the HA, alginate, and BSA solution, respectively. With the initial solution pH increasing to 7, the presence of background DOM caused 7%–20% more inhibition in the degradation of SMZ than at pH_{ini} 6 (Fig. 4A). The strong buffering capacity of background DOM solution at a neutral condition inhibited the decrease of pH in the PM/BS system, which enhanced the decomposition as well as reduced the generation of RMnS, and consequently decreased the degradation of SMZ. However, at pH_{ini} 9, the presence of background DOM had a neglectable impact on the removal of SMZ in the PM/BS process. The degradation efficiency of SMZ was less than 10% in all samples. The cleavage of the N–S bond and hydroxylation of the pyrimidine ring caused by $SO_4^{\bullet-}$ and $^{\bullet}OH$ were the dominant oxidation processes that occurred in the PM/BS system at pH_{ini} 9 [35].

3.4. Effects of PM/BS pre-oxidation on the formation of THMs in the subsequent chlorination

PM/BS pre-oxidation achieved a 28%–65% decrease of total THM yield during the chlorination of various SMZ-contaminated water both containing and without bromide (Fig. 6). However, in our previous study, PM/BS pre-oxidation was found to increase the specific THM formation potential of ciprofloxacin and ciprofloxacin-contaminated waters, especially in the presence of bromide [22]. It indicates that the efficiency of PM/BS pre-oxidation in controlling DBPs was greatly dependant on the molecule properties of precursors.

In terms of controlling DBP formation, the PM/BS process was most efficient in the SMZ Milli-Q water solution, where the total THM yield was decreased by about 65% after PM/BS pre-oxidation. The coexistence of DOM showed varying degrees of limitation on controlling DBP formation by PM/BS pre-oxidation. In the absence of bromide, after PM/BS oxidation, yields of total THMs during the post-chlorination of SMZ-HA, SMZ-alginate, and SMZ-BSA solutions were reduced by 28%, 37%, and 40%, respectively. In the presence of bromide, PM/BS oxidation achieved 41%, 52%, and 51% decrease of total THM formation in the subsequent chlorination of SMZ-HA, SMZ-alginate, and SMZ-BSA solutions, respectively. It implies that the PM/BS process might be more efficient in controlling DBP formation in secondary effluents that are majored by alginate and proteins.

The presence of bromide reduced the formation of TCM, whereas facilitated the formation of bromine-containing species including BDCM, DBCM, and TBM (Fig. 6B) that has higher combined toxicity values (CTV, cytotoxicity plus genotoxicity) (Table S2). In the presence of bromide, PM/BS pre-oxidation greatly decreased the formation of TCM and BDCM for all samples. However, the yield of DBCM and TBM in the chlorinated SMZ-alginate solution was increased after PM/BS pre-oxidation. Since the cytotoxicity and genotoxicity of individual THM species varied, it's difficult to evaluate the toxicity effects of samples only based on the concentration of THMs. Therefore, the integrated toxic risk value (ITRV) calculated by multiplying the CTV of individual THM by its concentration according to previous reports [25,36] was applied to evaluate the effects of PM/BS pre-oxidation on the toxicity of THMs formed in chlorinated SMZ-contaminated waters.

As shown in Fig. 7, PM/BS pre-oxidation efficiently decreased the ITRV of THMs in SMZ-contaminated waters. Despite that PM/BS pre-oxidation increased the formation of DBCM and TBM with higher toxicity in the SMZ-alginate solution containing bromide, the ITRV of total THMs formed during chlorination was decreased by 56%, which was attributed to the great reduction in TCM yield. Note that, after PM/BS pre-oxidation, the decrease of THM ITRV in SMZ-contaminated waters containing bromide was greater than that without bromide. It was contrary to a previous study that PM/BS pre-oxidation greatly increased the ITRV of THMs formed during chlorination of ciprofloxacin-contaminated waters in the presence of bromide.

4. Conclusions

PM/BS system exhibited fast and efficient oxidation of low concentration SMZ at acidic/neutral pH and selectively

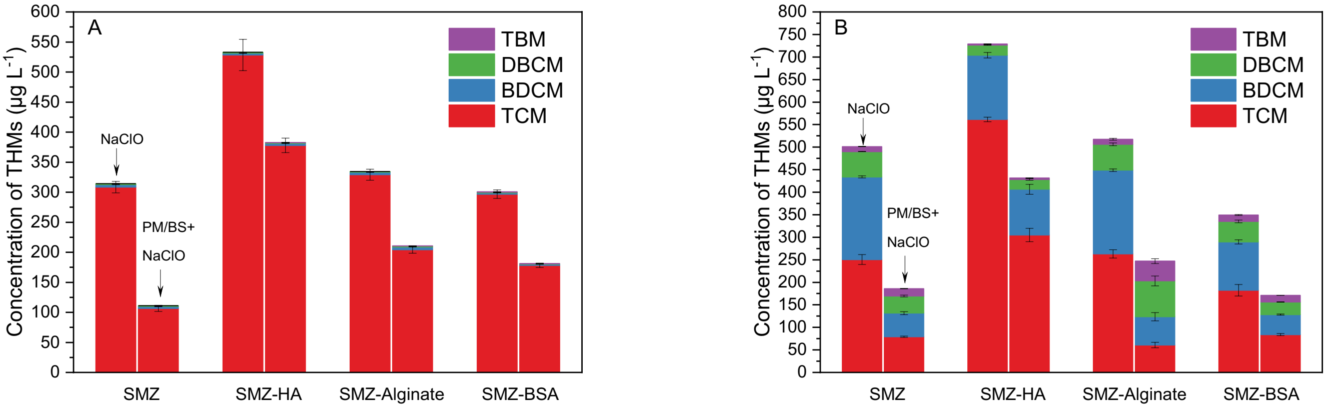

Fig. 6. Effects of PM/BS pre-oxidation on the subsequent THM formation in SMZ contaminating waters without (A) or with (B) bromide (0.5 mg L^{-1}). Reaction conditions: $[SMZ]_0$ = 5 μm; TOC (organic matter) = 3 mg L^{-1}; pH = 7 ± 0.1; temperature = 25°C ± 1°C; [chlorine dose] = 15 mg L^{-1} (as Cl_2); chlorination time = 24 h.

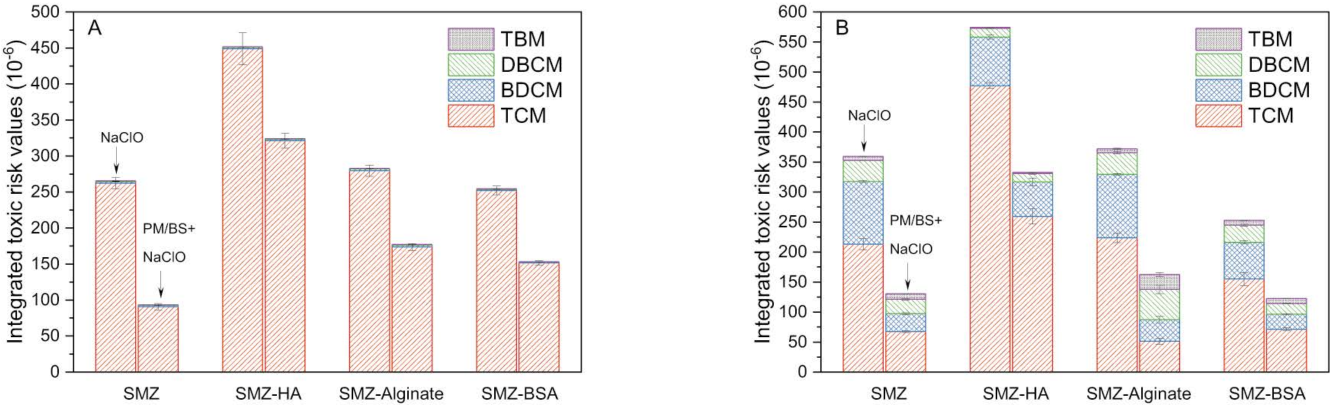

Fig. 7. Effects of PM/BS pre-oxidation on the ITRV of THMs formed during chlorination of SMZ contaminating waters without (A) or with (B) bromide (0.5 mg L^{-1}). Reaction conditions: [SMZ]$_0$ = 5 μm; TOC (organic matter) = 3 mg L^{-1}; pH = 7 ± 0.1; temperature = 25°C ± 1°C; [chlorine dose] = 15 mg L^{-1} (as Cl_2); chlorination time = 24 h.

removed SMZ in mixed aqueous solutions with the coexistence of DOM. PM/BS pre-oxidation greatly decreased the formation of THMs in the subsequent chlorination, reducing the toxicity of chlorinated SMZ-contaminated waters.

The permanganate dosage and permanganate/bisulfite molar ratio had great influences on the degradation of SMZ in the PM/BS process. The permanganate was efficiently activated by bisulfite and exhibited high efficiency in SMZ degradation when permanganate/bisulfite dosage was 50 μm:250 μm. A lower solution pH would facilitate the generation of RMnS and therefore enhance the degradation of SMZ. Interactions between SMZ and coexisting DOM occurred indicated by the increase of DOM hydraulic size and the decrease of the zeta potential after mixing with SMZ. The co-existing protein BSA had limited inhibition on SMZ degradation in the PM/BS process at pH 6 and 7, whereas humic acids and alginate showed great inhibition, which was mostly attributed to the inactivation of redox sites in SMZ molecules caused by interactions between DOM and SMZ.

In our previous study, PM/BS has also been demonstrated to be highly efficient in ciprofloxacin removal despite the co-existing HA, BSA, and alginate. Since the residual manganese species can be easily removed in the following coagulation and membrane filtration processes, the PM/BS process has the potential to be employed as a pre-oxidation technology in the advanced treatment of secondary effluents that are majored by proteins rather than HA.

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Supplementary information

S1. Procedures of the chlorine disinfection experiment

Chlorine disinfection was conducted in Schott brown glass bottles. Before chlorine disinfection, samples were conditioned to the test plan temperature (20°C ± 1°C) and pH (7.0 ± 0.1). Phosphate buffer was added to samples before filling the bottles to ensure that the chlorination was run at a fixed pH of 7.0 ± 0.1. To ensure the complete chlorination of precursors, the dosage of chlorine was 15 mg L^{-1}, achieving a ratio of Cl_2 and total organic carbon of >3:1. The preliminary chlorination experiments showed that the free chlorine residual of all tested samples after 24 h was higher than 1 mg L^{-1}. After 24 h chlorination, 30 mL of solution was taken out for residual chlorine analysis according to the DPD powder pillow photometric method. Meanwhile, sodium thiosulfate was immediately spiked into the remaining sample to quench the residual chlorine. The quenched samples were taken out for disinfection byproducts analysis.

S2. Analysis of trihalomethanes by liquid–liquid extraction coupled with GC-ECD

A water sample of 9 mL was extracted with 3 mL methyl tert-butyl ether containing 1.2 g of anhydrous sodium sulfate. The sample was shaken vigorously for 2 min to complete the extraction. After 5 min settling, 1 mL supernatant was drawn out for analysis.

Trihalomethane (THMs) were analyzed by gas chromatography (GC-2014, Shimadzu, Japan) equipped with Rtx-1 capillary column (30.0 m × 0.25 mm × 0.25 μm). A volume of 2 μL sample was injected into GC in a splitless mode. The GC temperature program was held at 35°C for 22 min, and then ramped to 145°C at 10°C min^{-1} and hold for 2 min. The limits of quantitation (LOQ) for THMs were 0.20 μg L^{-1}. The % relative standard deviation (RSD) values for trichloromethane, bromodichloromethane, dibromochloromethane and tribromethane were 7.5%, 3.1%, 5.6% and 7.5%, respectively.

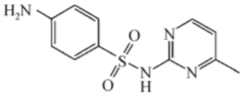
S3. Quantification of sulfamerazine by high-performance liquid chromatography

The high-performance liquid chromatography system equipped with a Waters 2489 UV detector, Waters 1515 pump and Waters 2707 Autosampler was used. Instrument control, data acquisition and data processing were achieved with Waters Breeze Software. Separations were performed at 25°C with HYPERSIL BDS C18 (250 mm × 4.6 mm). The injection volume was 10 μL. The mobile phase was acetonitrile: phosphoric acid solution (v/v) = 20:80 (Phosphoric acid is prepared from 0.68 mL in 1 L of water). The flow rate

Table S2
Combined toxicity values of THMs (Chu et al. [S1]; Plewa and Wagner [S2]; Zhu et al. [S3])

Disinfection byproducts	Combined toxicity values (M^{-1})
Trichloromethane	101.473
Bromodichloromethane	93.366
Dibromochloromethane	131.2164
Tribromethane	144.0561

Table S1
Properties of sulfamerazine

Antibiotics	Chemical formula	Chemical structure	Molecular weight (g mol^{-1})
Sulfamerazine	$C_{11}H_{12}N_4O_2S$		264.30

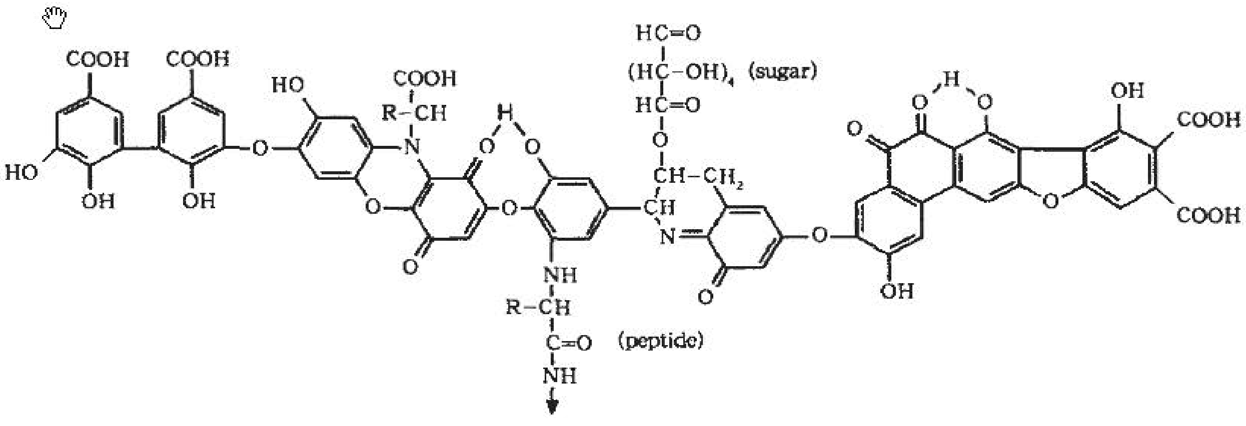


Fig. S1. Humic acid model suggested by F.J. Stevenson.

was 1.0 mL min^{-1}. the detection wavelength was 274 nm. The retention time was 4.9 min. The LOQ was 0.10 μM. The % RSD value was 5.1%.

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