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The performance of quaternized magnetic microspheres on control of disinfection by-products and toxicity in drinking water

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HIGHLIGHTS

- A novel quaternized magnetic resin NDMP was efficient for the reduction of DBPs FP.
- The formation of THMs, HAAs and HANs were decreased with increasing ammonia levels.
- Increasing bromide levels will enhance the formation of THMs, HAAs and HANs.
- NDMP resin could greatly reduce the cytotoxicity of the raw water.
- Bromide and ammonia will enhance the cytotoxicity to cells in raw water.

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ABSTRACT

The aim of this study was to evaluate the performance of quaternized magnetic microspheres (NDMP) on control of disinfection by-products (DBPs) and toxicity in drinking water. High concentrations of dissolved organic carbon (6.7 mg/L) and bromide (185 μg/L) were present in the raw water. The NDMP showed good performance on removing dissolved organic matter, bromide and dissolved organic nitrogen. In the present study, we investigated the formation potential (FP) of DBPs as well as the human hepatoma cells cytotoxicity and genotoxicity before and after resin treatment. The results showed that the FP of trihalomethanes (THMs), haloacetic acids (HAAs) and haloacetonitriles (HANs) were greatly reduced by the NDMP treatment with maximum removal efficiency of 73%, 56% and 81%, respectively. Additionally, the NDMP resin greatly reduced the cytotoxicity and genotoxicity of the raw water during subsequent chlorination. With increasing bromide levels, the FP of THMs, HAAs and HANs were increased by 31%, 36% and 27%, respectively. On the contrary, the FP of THMs, HAAs and HANs were reduced by 85%, 77% and 69% when the ammonia concentration reached to 10.5 mg/L. The addition of bromide increased the toxicity after chlorination due to the formation of more toxic brominated DBPs. NDMP can efficiently control the DBPs formation and toxicity in treated water, which provide us a new kind of advanced drinking water treatment technology in the future.

1. Introduction

Drinking water safety has received great attention around the world because huge numbers of disinfection by-products (DBPs) have emerged. Dissolved organic matter (DOM), which widely presents in natural waters, is the main precursor of DBPs [1], and it can react with chlorine and form trihalomethanes (THMs) and haloacetic acids (HAAs) [2]. The two major groups of the halogenated DBPs are regulated by many countries and organizations due to its potential threat [3,4]. In detail, THMs including chloroform and bromodichloromethane (BDCM) are both regulated at 60 μg/L, while dibromochloromethane (DBCM) and bromoform are required to stay below 100 μg/L according to Drinking Water Standards (GB5749-2006) in China. Meanwhile, the dichloroacetic acid (DCAA)and trichloroacetic acid (TCAA) were also controlled at 50 μg/L and 100 μg/L, respectively. Except for the regulated THMs and HAAs, some nitrogenous DBPs (N-DBPs) such as haloacetonitriles (HANs) have also been reported at high levels during the chlorine disinfection [6]. HANs is one kind of the unregulated semi-volatile N-DBPs, which can exert particular mutagenic or carcinogenic effects on mice [7]. The World Health Organization

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has suggested guideline values of 20 μg/L for dichloroacetonitrile (DCAN) and 70 μg/L for dibromoacetonitrile (DBAN) [8]. The formation of DBPs in water systems has raised growing attention because of their potentially adverse health effects, e.g., cancer and reproductive defects, in the past several decades [9]. In conclusion, the control of DBPs including regulated THMs, HAAs and HANs in drinking water treatment is of great importance to public health.

Magnetic ion exchange technology has been proven as an alternative way for DOM elimination and DBPs control. Recently, the magnetic ion exchange resin (MIEX®) developed by Orica Watercare® has been increasingly used for the removal of DBPs precursors. MIEX® treatment could eliminate both DOM and bromide ion, thereby reducing the formation of DBPs during disinfection [10,11]. Additionally, the MIEX® resin treatment could dramatically reduce the formation potential (FP) of HAAs, THMs and N-DBPs (i.e. halonitromethanes) [12]. However, due to the quaternary amine functional groups of the anion exchange resins, it may serve as precursors for N-DBPs, such as nitrosamines, nitramines, and halonitromethanes [13]. Gan et al. have observed that the N-nitrosodimethylamine (NDMA) was increased significantly after the MIEX® process in the effluent impacted water [14]. Recently, a new quaternized magnetic resin (NDMP) has been developed to treat both drinking water [15] and industrial wastewater in China by Nanjing University [16–18]. However, the ability of the NDMP in reducing the DBPs in raw water containing high levels of DOM and bromide ion remains unknown, and the toxicity evaluation after magnetic anion exchange resin treatment still needs to be studied.

Bromide can be oxidized to hypobromous acid (HOBr) by chlorine [19], whereas HOBr shows higher activity than hypochlorous acid (HOCl) to promote the formation of brominated DBPs with higher health risks than their chlorinated analogs [20]. The effect of ammonia concentration on the formation of DBPs has been extensively studied during the chlorination of drinking or natural waters [21,22]. A previous study has shown that the formation of THMs and HAAs were suppressed with increasing ammonia concentration [21]. It can be explained by quick reaction of ammonia with free chlorine and the formation of monochloramine during chlorination. The reactivity of chloramines was much weaker than that of free chlorine, and the chloramines were more slowly to form DBPs during the reaction with DOM in water. Therefore, the reactions between DOM and chlorine during disinfection of drinking water are complex in the existence of bromide and ammonia.

The Tong-Yu River is an important branch of the Yangtze River, it provides most of cities in the northern part of Jiangsu province in China for source water. The main objective of this research was to investigate the performance of NDMP on the removal of dissolved organic carbon (DOC), UV absorbance at 254 nm (UV_{254}) and dissolved organic nitrogen (DON). The amount and speciation of THMs, HAAs, HANs and the toxicity of concentrated organic fractions before and after NDMP resin treatment in raw water were explored. Moreover, the effects of bromide and ammonia concentrations on the formation of THMs, HAAs and HANs, as well as the toxicity of concentrated organic fractions after chlorination, were also evaluated.

2. Methods and materials

2.1. Sample collection and chemical analyses

Raw water was collected from the Tong-Yu River which located at Jiangsu province in China. The DOC, UV_{254}, DON and pH value were immediately analyzed after transportation to the lab. The specific UV absorbance at 254 nm ($SUVA_{254}$) of each water was calculated as UV_{254} (cm^{-1})/DOC (mg/L) * 100, in units of L/mg m. 1 L of water sample was set aside for ion analysis such as bromide, ammonia, nitrate and sulfate. Another 6 L of raw water was used for ion exchange experiments, XAD fraction, and subsequent THMs, HAAs and HANs analysis after chlorination. All water samples were filtered through 0.45 μm micropore membranes and stored at 4 °C in the dark until use.

DOC and UV_{254} were measured using a TOC analyzer (TOC-V CSH, Shimadzu Corp., Japan) and a spectrophotometer (UV-1800, Shimadzu Corp., Japan), respectively. Total nitrogen (TN) and ammonia nitrogen concentrations were measured according to the Standard Examination Methods for Drinking Water [23]. Sulfate, chlorine, bromide, nitrate and nitrite ions were analyzed by an ion chromatography system (ICS-1100, Dionex, USA) with an AG19 guard column and AS19 analytical column. DON was obtained by subtracting nitrate, nitrite and ammonia nitrogen concentrations from TN.

2.2. Fractionation of DOM by resin adsorption

Amberlite XAD-8 and XAD-4 resins (Rohm and Haas, Philadelphia, PA, USA) were used to fractionate the water samples [24–26]. The resins were cleaned and conditioned as described by Leenheer [27]. The DOM fractionation procedure was shown in Fig. S1 (Supporting Information). The fractionation set-up consisted of two glass columns packed with 12 mL of XAD-8 resin and 12 mL of XAD-4 resin, respectively. The water sample to be fractionated was first acidified to below pH 2 with concentrated HCl. One liter of the sample was then pumped through the top of XAD-8 resin at 4 mL/min. The first 12 mL (i.e. one bed volume) of effluent from the column was discarded. The effluent from XAD-8 column was then pumped through XAD-4 resin. The effluent from the connected two columns was hydrophilic organic fraction (HPI). Hydrophobic acids (HPO) and transphilic acids (TPI) were desorbed from XAD-8 and XAD-4 resin with 0.1 mol/L NaOH, respectively.

2.3. Characterization of NDMP resin

Magnetic anion exchange resins NDMP were provided by Nanjing University. Their physical and chemical indexes were listed in Table 1. Scanning electron microscopy (SEM) was used to determine the surface characterization of the resins (Fig. S2) (Supporting Information). NDMP resins were turned into chloride form and then washed with distilled water before used.

2.4. Treatment of source water

During the NDMP resin procedures, different volumes of resin were added into 1 L of the raw water to obtain various doses ranged from 2 mL/L to 15 mL/L. The mixtures were stirred for 30 min at 150 rpm and then allowed to settle for 20 min based on previous study [15]. After settling, the samples were used for DOC, UV_{254} and DON analyses. The resin procedures were all carried out at room temperature (20 ± 2 °C). The rest of the treated water samples were used in the FP tests of DBPs.

Six concentrations of bromide (0, 50, 100, 150, 200 and 250 μg/L) were added into raw water to evaluate its effects on the FP of DBPs. The spiked solutions were prepared by dissolving a predetermined mass of potassium bromide in the raw water. The effect of ammonia nitrogen on the FP of DBPs was also investigated by adding ammonium chloride (2, 4, 6, 8 and 10 mg N/L) into the raw water. The synthetic water samples were then used for the FP test of DBPs.

2.5. FP tests of DBPs

Chlorination was performed by adding sodium hypochlorite (NaOCl) at 20 mg/L as Cl to the solutions. The samples were stored