



# Effects of sodium, magnesium, and calcium salts on the coagulation performance of cucurbit [8]uril for humic acid removal from synthetic seawater



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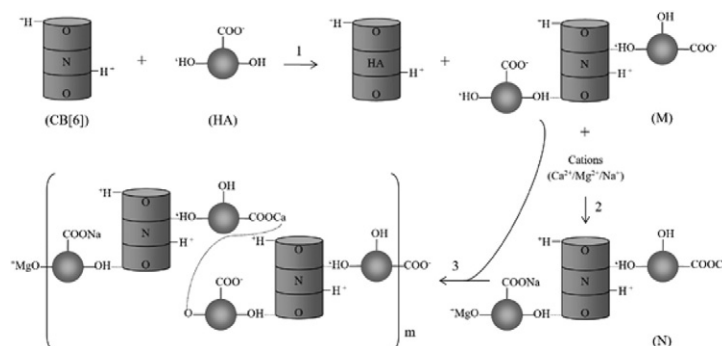
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## HIGHLIGHTS

- The coagulation of HA by cucurbit [8]uril (CB [8]) is primarily a physical process.
- The type of anion has a significant effect on the solubility of cucurbit [8]uril.
- HA coagulation efficiency from the synthetic seawater was 83–90% at pH 7.5–8.5.
- The formation of CB [8]-HA hydrogen bonds contribute to the destabilization of HA.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 4 December 2015

Received in revised form 24 February 2016

Accepted 28 February 2016

Available online 4 March 2016

### Keywords:

Coagulation  
Cucurbit [8]uril  
Humic acid  
Seawater

## ABSTRACT

This study evaluates the coagulation performance of cucurbit [8]uril (CB [8]) for HA removal and the effects of salts on this process. Experimental results showed that HA removal efficiency improved as the increase of CB [8] dosage. When the CB [8] dosage was 0.2 mmol/L, less than 50% of the HA was removed from the synthetic freshwater at pH above 7.5. The presence of salts improved both the solubility and coagulation capacity of CB [8], which varied depending on the type of anion and cation, respectively. For the synthetic seawater with 1.0 mmol/L of  $\text{Ca}^{2+}$ , 8.0 mmol/L of  $\text{Mg}^{2+}$ , and 0.4 mol/L of  $\text{Na}^+$  co-existing, the HA removal efficiency increased considerably from less than 50% to 83–90% at pH 7.5–8.5. Relative to the amount of HA removed by adsorption, an additional 20–40% of the HA was removed by CB [8] coagulation under the same water quality condition. Further in-depth analysis showed that HA coagulation by CB [8] is primarily a physical process. In addition to charge neutralization and electrical double-layer compression, the formation of hydrogen bonds between CB [8] and HA also contributed to HA destabilization and led to a complete loss in stability before all the negative charges on the HA were neutralized.

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## 1. Introduction

With the ever growing demand for fresh water, the use of reverse osmosis (RO) for seawater desalination has increased rapidly in many countries worldwide [1]. As in fresh water, humic acid (HA) is a major organic component in seawater [2,3]. Its concentration is typically 2–5 mg/L, but it can be higher when HA washes into the seawater from

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ivers [4]. The presence of HA promotes membrane fouling, leading to a decline in the water flux. HA also readily reacts with disinfectants to form toxic disinfection by-products [5,6]. A high residual HA concentration in treated water leads to an increase in its color and odor and to bacteria re-growth [7]. A combination of coagulation and ultrafiltration is commonly used to pretreat seawater before RO desalination and is highly effective at removing HA [8,5]. However, the HA is primarily removed from the seawater during the ultra-filtration process [9]. Only 10–50% of the HA removal is attributed to coagulation [10], which could affect the operation of a hybrid coagulation-membrane system, particularly when the seawater has a high HA content.

Voutchkov [11] reported that membrane bio-fouling does not occur if the total organic carbon (TOC) concentration in seawater is reduced to 0.5 mg/L or less. However, when the seawater TOC concentration is higher than 2.0 mg/L, bio-fouling is likely to occur. An excess of coagulants is typically used to enhance HA removal by coagulation [8,12]. However, the removal capacity of low molecular weight HA is typically low. After coagulation, the residual HA concentration is suggested to be 1.0–2.0 mg/L for subsequent seawater desalination [13]. Although ozonation can mineralize part of the HA, the small organic compounds that form during the oxidation process can also cause membrane fouling [1]. According to Wang et al. [9], the effects of the filtration efficiency and fouling of a hybrid coagulation-ultrafiltration process on HA removal strongly depend on the type of coagulant employed. Moreover, the use of traditional coagulants, such as  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ , and polyaluminum chloride (PACl) does not lead to a reduction in membrane fouling [9]. Therefore, new coagulants that can overcome the aforementioned shortcomings of traditional coagulants must be developed. This paper evaluates the coagulation performance and HA removal capacity of a novel functional material cucurbit[n]uril (CB[n]).

Similar to most organic coagulants, CB[n]s are macrocyclic molecules made of  $n$  glycoluril monomers linked by methylene bridges. They can form stable clathrate compounds with pollutants via Van der Waals forces [14,15], hydrophobic interactions [16], electrostatic forces [17], and hydrogen bonding interactions [18]. Moreover, CB[n] has a stable structure and low toxicity to aquatic organisms [19]. Accordingly, its application in water and wastewater treatment has received much attention in recent years. In 2001, CB[n] was first used to treat printing and dyeing wastewater by an adsorption process and was found to exhibit high adsorption efficiencies [18]. Lim et al. [14] reported that CB [6] could capture metal cations with high selectivity under acidity conditions. Recently, Yang et al. [20] found that magnetic CB[n] could adsorb HA in natural waters. The adsorption process was well modeled by the Freundlich isotherm equation and by pseudo-second-order kinetics.

However, a high CB[n] dosage was required for successful HA removal by adsorption; specifically, a CB[n] concentration of 1000 mg/L was needed to remove 80% of the HA from fresh water [21]. Unlike other pollutants, HA is composed of a mixture of many molecules, some of which consist of aromatic nuclei linked together by phenolic and carboxylic substituents [10]. Accordingly, it exhibits typical colloidal characteristics. Because of its strong adsorption capacity, CB[n] could be used as a competitive coagulant to improve HA removal in seawater pretreatment processes. However, studies of the coagulation performance of CB[n] have rarely appeared in the literature. Nonetheless, the interactions between CB[n] and HA might also be different under saline conditions than under freshwater conditions. Therefore, the primary objectives of this study are to investigate (i) the coagulation performance and mechanisms of CB [8], and (ii) the effects of salts on both the solubility and HA removal efficiency of CB [8].

## 2. Experimental materials and methods

### 2.1. Synthetic test water

The HA used in this study was purchased from the Shanghai Chemical Co., China. The stock solution was prepared as follows: 5.0 g of HA

were dissolved in 100 mL of a 0.1 mol/L NaOH solution. After 12 h settlement, the solution was filtered through a 0.45  $\mu\text{m}$  glass fiber membrane filter and stored at 4 °C. Synthetic water was prepared by adding 10.3 mL of the HA stock solution (485 mg/L) to 989.7 mL tap water to obtain HA concentration of 5.0 mg/L. The tap water is supplied by a local plant fed by the Heihe Reservoir in Xi'an, China. PACl coagulation, sand filtration, and  $\text{Cl}_2$  disinfection processes are used in the plant. To avoid the destruction of residual  $\text{Cl}_2$  on the structure of HA, the tap water was pretreated with granular activated carbon filtration. Water temperature was maintained at 15 °C. Except for the experiment investigating the effects of pH on HA removal, the pH of the synthetic water was controlled at 7.5 (Table 1). The background concentrations of alkalinity,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  in the synthetic test water were determined to be 1.2, 0.006, 0.4, and 0.5 mmol/L, respectively, without extra alkali or salt addition (Table 1). Reagent grade chemicals were used except where noted.

### 2.2. Preparation of CB[8] usage solution

CB [8] was prepared and purified following the method described by Bi et al. [22]. Before the coagulation experiments, 2.5 g of CB [8] and 1.25 mmol NaCl was dissolved in 50 mL of deionized water under supersonication for 30 min to prepare CB [8] usage solution. Then, the mixture was centrifuged at 5000 r/min for 20 min to remove the suspended solids. The CB [8] concentration of the usage solution was calculated to be 6.6 mmol/L based on the difference between the total amount of CB [8] added and the residual CB [8]. To investigate the effects of salts on the solubility of CB [8], calcium, magnesium, and other sodium salts were introduced during the preparation of CB [8] usage solution through single-factor experiment. The amount of positive charges added to the usage solution were 25 mmol/L, the same for each kind of salt. Meanwhile, the coagulation performances of the CB [8] usage solutions were evaluated using the synthetic test water at pH 7.5 and 15 °C. The dosage of CB [8] was 0.3 mmol/L.

### 2.3. Coagulation and adsorption tests

The synthetic water was coagulated on a programmable jar tester (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China) using CB [8]. The coagulation procedure involved a rapid mixing at 250 r/min for 1.0 min, followed by a 15.0 min of flocculation at 75 r/min, and a 30.0 min settling. Water samples were taken from 2.0 cm below the water surface. Adsorption tests were conducted to determine the adsorption capacity of CB [8] under the same water quality conditions. 100 mL of the synthetic water was placed into 250 mL tubes. Then, 0.06 g of CB [8] was added to the tubes and stirred every 6 h. The mixtures were sampled before and after 24 h of the addition of CB [8]. Then the samples were centrifuged at 5000 r/min for 20 min to analyze the residual concentration of HA.

### 2.4. Effects of pH, CB[8] dosage, and salts on the removal of HA in coagulation/adsorption

The effects of pH, CB [8] dosage, and salts on the coagulation of HA were evaluated using single-factor experiments. The pH of the synthetic test water was adjusted using 0.1 mol/L HCl and 0.1 mol/L NaOH solutions. The dosage of CB [8] was maintained at 0.2 or 0.3 mmol/L except for the experiment investigating the effects of CB [8] dosage on HA removal. The effects of salts on the removal of HA in coagulation were examined by adding pre-determined amounts of stock solutions of 0.1 mol/L  $\text{CaCl}_2$ , 0.1 mol/L  $\text{MgCl}_2$ , or 1.0 mol/L NaCl to the synthetic test water as shown in Table 1. The values of all the parameters were selected based on the quality of actual seawater.

To evaluate the combined effects of salts on the removal of HA in coagulation, a mix of salts composed of 1.0 mmol/L  $\text{CaCl}_2$ , 8.0 mmol/L  $\text{MgCl}_2$ , and 0.4 mol/L NaCl were added to the synthetic water at

**Table 1**  
Synthetic water quality parameters and levels selected in single-factor experiments.

Factors	T (°C)	pH	HA (mg/L)	Turbidity (NTU)	Alkalinity (mmol/L)	Ca <sup>2+</sup> (mmol/L)	Mg <sup>2+</sup> (mmol/L)	Na <sup>+</sup> (mol/L)	Levels (mmol/L, except for pH)					
									(1)	(2)	(3)	(4)	(5)	(6)
pH	15	variable	5.0	4.5	1.2	0.5	0.4	0.006	6.5	7.5	8.0	8.5	9.0	–
Ca <sup>2+</sup>	15	7.5	5.0	4.5	1.2	variable	0.4	0.006	0.5	1.0	2.0	2.5	5.0	10.0
Mg <sup>2+</sup>	15	7.5	5.0	4.5	1.2	0.5	variable	0.006	0.4	2.0	4.0	8.0	20.0	40.0
Na <sup>+</sup>	15	7.5	5.0	4.5	1.2	0.5	0.4	variable	0.006	0.02	0.05	0.1	0.2	0.4
CB [8] dosage	15	7.5	5.0	4.5	1.2	0.5	0.4	0.006	0.05	0.1	0.2	0.3	0.4	0.45

pH 6.5–9.0. The initial concentration of HA, water temperature, and CB [8] dosage were maintained at 5.0 mg/L, 15 °C, and 0.2 mmol/L, respectively. Moreover, adsorption tests were conducted under the same water quality conditions following the method described in Section 2.3. Based on the difference between the removal rates of HA achieved in CB [8] coagulation and adsorption, the contribution of flocculation (a process wherein destabilized colloids grow up gradually and come out of the solution in the form of flocs) to the removal of HA was calculated.

### 2.5. Water quality and CB[8] structure analysis

HA concentration was determined using an UV–visible spectrometer (UV-1650PC, Shimadzu, Japan) following the method described by Yuan et al. [23]. The zeta potentials ( $\zeta$ ) of the CB [8] usage solution and the coagulated water were determined using a zeta meter (Nano-Z, Malvern, UK). pH was measured using a pH meter (Model 828, Thermo Electron Corporation, USA). The electrode was calibrated using buffers with a pH of 7.0 and 9.0. Turbidity residual in the settled water was determined using a turbidity meter (HI93703-11, Hanna, Italy). Scanning electron microscopy (SEM) (JSM-6490LV, JEOL Ltd., Japan) was used to observe the surface characteristics of CB [8]. The SEM samples were sputter-coated with gold prior to the scanning. Infrared analysis (1.0 mg HA/CB [8]/flocs mixed with 250.0 mg KBr) was performed using an IR spectrometer (IFS 55, Bruker, Germany) in transmission mode (200 scans collected at 2 cm<sup>-1</sup> resolution in the 4000–400 cm<sup>-1</sup> range). The primary FT-IR bands were assigned according to the method described by Gu et al. [24].

## 3. Results and discussion

### 3.1. Coagulation performance of CB[8] for HA removal

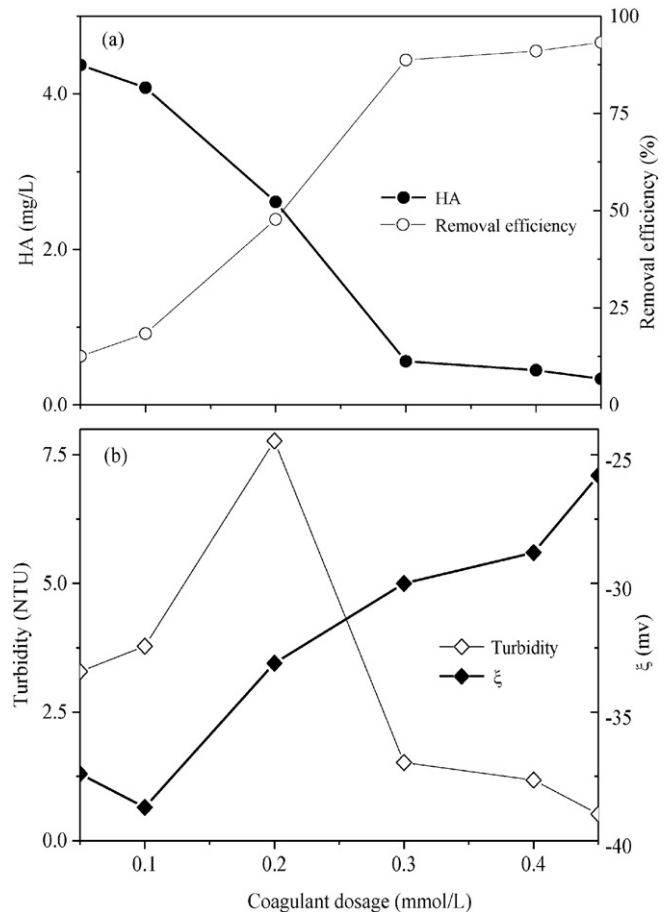
The effect of the CB [8] dosage on HA coagulation in the absence of added salts in the synthetic water (fresh water) was investigated at pH 7.5. It was determined that HA removal efficiency improved as the increase of CB [8] dosage. When the CB [8] dosage was less than 0.2 mmol/L, no flocs were observed during coagulation. The HA removal efficiency was less than 50% (Fig. 1a). When the CB [8] dosage was higher than 0.2 mmol/L, considerable amounts of flocs formed. At a CB [8] dosage of 0.3 mmol/L, the residual turbidity was approximately 1.5 NTU after sedimentation, corresponding to 89% of HA removal. The best value of HA removal of 93.3% was obtained when the CB [8] dosage was 0.45 mmol/L. The residual HA concentration of the settled water could be controlled within 0.33 mg/L. Meanwhile, the zeta potential of the coagulated HA increased gradually with increasing CB [8] dosage, indicating that the negative charges on the HA molecule was neutralized by the positive charges on the CB [8] surface. This results are consistent with existing literature data for inorganic coagulants, the hydrolysis products (with positive charges) of which can interact with HA with the formation of insoluble charge-neutralized products as well as an increase in the zeta potential [4,25].

The number of charges on both HA and CB [8] surfaces varied with pH [26], which might affect HA removal by coagulation. It was determined that as the solution pH decreased from 7.5 to 6.5, the zeta

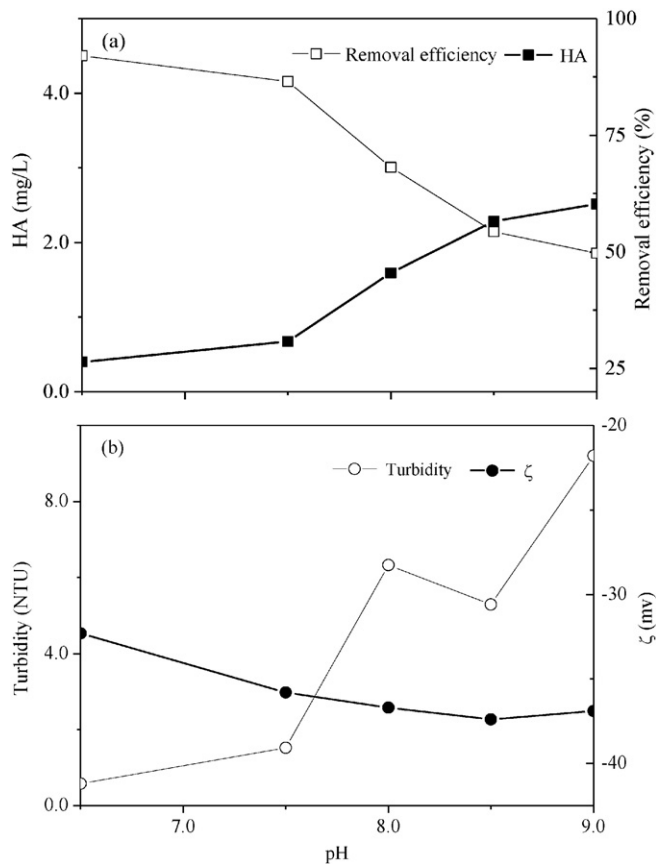
potential of the CB [8] usage solution increased from –1.2 to 0.43 mV. Moreover, the negative charge on the HA surface is low under acidic conditions [27]. Accordingly, HA removal was enhanced at pH 6.5; approximately 92% of the HA was removed, and the residual turbidity was 0.58 NTU after coagulation (Fig. 2). However, As the increase of solution pH, the number of negative charges on both the CB [8] and HA surfaces increased gradually, which led to a decrease in the charge neutralization effect during coagulation [28]. The HA removal efficiency was 54% at pH 8.5, indicating that CB [8] was ineffective in HA removal from fresh water under basic conditions.

### 3.2. Effects of salts introduced in CB[8] usage solution on the solubility and coagulation performance of CB[8]

In the presence of CaCl<sub>2</sub>, MgCl<sub>2</sub>, and NaCl, the solubility of CB [8] was 0.85, 0.86, and 0.88 g/(100 g H<sub>2</sub>O), respectively. These values were significantly higher than those obtained in the presence of Ca(NO<sub>3</sub>)<sub>2</sub>, Na(NO<sub>3</sub>)<sub>2</sub>, MgSO<sub>4</sub>, and MgSO<sub>4</sub> (Table 2), indicating that the type of



**Fig. 1.** Effects of the CB [8] dosage on HA coagulation (a) and the residual turbidity and zeta potential in the coagulated solution (b) at 15 °C. (pH = 7.5, HA = 5.0 mg/L).



**Fig. 2.** Effects of pH on HA coagulation performance (a) and the residual turbidity and zeta potential in the coagulated solution (b) at 15 °C (Coagulant dosage = 0.3 mmol/L, HA = 5.0 mg/L).

anions but not cations probably had an important effect on the solubility of CB [8]. Karcher et al. determined that neither the cation charge nor its complex stability with CB[n] had an obvious correlation with the solubility of cucurbituril [29]. Considering the zeta potential of CB [8] decreased in the presence of salts, inclusion complexes probably formed between CB [8] and the anions, and thus promoted the dissolution of CB [8]. Lee et al. [30] also determined that although the outer surface of CB [7] was somewhat positively charged, the inner surface of the cavity of CB [7] cavity was negatively charged. This finding is in consistent with the results obtained in our previous study [21].

The addition of salts also had a positive effect on HA removal by coagulation. When the CB [8] usage solution containing 12.5 mmol/L of

**Table 2**

Effects of salts introduced in CB [8] usage solution on the zeta potential, solubility, and HA coagulation performance of CB [8].

Type of salt	Content of salt (mmol/L)	ζ of CB [8] (mv)	Solubility (g/100 g H <sub>2</sub> O)	HA coagulation efficiency*			
				HA (mg/L)	Removal rate (%)	Turbidity (NTU)	ζ' (mv)
No salt added	–	16.7	0.61	1.87	62.5	5.7	–30.6
CaCl <sub>2</sub>	12.5	15.2	0.85	0.30	93.9	0.6	–1.8
Ca(NO <sub>3</sub> ) <sub>2</sub>	12.5	14.7	0.74	0.45	90.9	0.3	–3.0
MgCl <sub>2</sub>	12.5	8.8	0.86	0.45	90.9	1.0	–14.1
Mg(NO <sub>3</sub> ) <sub>2</sub>	12.5	9.6	0.80	0.97	80.7	1.8	–15.9
MgSO <sub>4</sub>	12.5	9.0	0.68	0.31	93.8	0.9	–5.9
NaCl	25.0	9.2	0.88	0.97	89.5	1.5	–26.9
NaNO <sub>3</sub>	25.0	11.9	0.56	0.67	86.7	0.6	–21.1
Na <sub>2</sub> SO <sub>4</sub>	12.5	7.9	0.76	0.57	88.6	2.9	–22.7

\* Coagulation condition: pH = 7.5, water temperature = 15 °C, HA = 5.0 mg/L, CB [8] dosage = 0.3 mmol/L.

CaCl<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, MgSO<sub>4</sub>, or MgCl<sub>2</sub>, more than 90% of the HA was removed by coagulation at pH 7.5, with a CB [8] dosage of 0.3 mmol/L. These removal efficiencies were significantly higher than the removal efficiency of 62.5% of the CB [8] usage solution prepared only with pure water (Table 2). Moreover, the residual turbidity of the settled water decreased considerably from 5.7 NTU to less than 1.0 NTU. Along with CaCl<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, MgSO<sub>4</sub>, and MgCl<sub>2</sub>, the addition of other salts in the CB [8] usage solution also improved HA coagulation. Given the high ionic strength of the CB [8] usage solution, the enhanced HA removal in the presence of cations might be due to the compression of the electrical double-layer [31].

Similar to clay surfaces, the HA surface has a negative static electric charge. When the CB [8] and salts are added in the coagulation process, the negative charge on the HA surface is neutralized, and the electrical double-layer is compressed, which decreases the stability of the HA. It has been proven that an increase in the number of positive charges on the coagulant increases the strength of the charge neutralization and electrical double-layer compression effects, resulting in a higher HA removal efficiency [5,32]. However, it should be noted that in this study, the decrease in the number of positive charges on the CB [8] surface with the introduction of salts did not inhibit HA removal by coagulation (Table 2). The charge neutralization and electrical double-layer compression effects contributed by the co-existing cations seem to be more obvious than that contributed by the CB [8].

### 3.3. Effects of salts in the synthetic seawater on HA coagulation

As discussed in Section 3.2, the effects of calcium, magnesium, and sodium salts on HA removal was primarily attributed to the double-layer compression effect of the cations introduced through the addition of CB [8] usage solution. In seawater, the salt contents are much higher. The effects of Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup> in the synthetic seawater (raw water) on HA coagulation were investigated further at pH 7.5 with a coagulant dosage of 0.2 mmol/L (Fig. 3). The HA removal efficiency increased considerably from less than 50%, corresponding to the raw water without Ca<sup>2+</sup>, to 86% when the Ca<sup>2+</sup> concentration of the raw water was 1.0 mmol/L. The residual HA concentration in the settled water was approximately 0.73 mg/L, which is lower than the suggested range (1.0–2.0 mg/L) for subsequent seawater desalination. Meanwhile, the zeta potential of the coagulated water was –7.7 mV (Fig. 3), providing further evidence that Ca<sup>2+</sup> helped to neutralize the negative charge on the HA, which led to an increase in the HA removal by coagulation and decrease in the residual turbidity.

However, when the Ca<sup>2+</sup> concentration of the raw water was higher than 2.5 mmol/L, the HA removal efficiency decreased slightly. Wang et al. also reported that HA removal efficiency tended to decrease when the concentration of Ca<sup>2+</sup> was above 1.6 mmol/L in the coagulation of HA-kaoline synthetic water with PACl [33]. This decrease could be due to a change in the electrical charge on the HA surface from negative to positive in water with a high salt content. Similar experimental results were obtained for Mg<sup>2+</sup>. The maximum HA removal efficiency of 85% was achieved when the Mg<sup>2+</sup> concentration of the synthetic water was 8.0 mmol/L (Fig. 3), and it decreased gradually to 76% when the Mg<sup>2+</sup> concentration was 40.0 mmol/L. Although Mg<sup>2+</sup> is much less efficient at enhancing HA removal than Ca<sup>2+</sup>, as previously reported by Wall and Choppin [31], the residual HA concentration and turbidity of the settled water were less than 1.2 mg/L and 0.5 NTU, respectively, for the synthetic water with Mg<sup>2+</sup> concentrations higher than 2.0 mmol/L.

The effect of Na<sup>+</sup>, which is the major cation in seawater, on HA removal by coagulation was not as obvious as those of Ca<sup>2+</sup> and Mg<sup>2+</sup>. When the Na<sup>+</sup> concentration of the raw water was 0.02, 0.1, and 0.4 mol/L, the HA removal efficiencies were 55%, 76%, and 80%, respectively (Fig. 3). Meanwhile, the zeta potential of the coagulated water increased gradually from –35 to –4.9 mV. The minimum Na<sup>+</sup> concentration required to rapidly coagulate HA is 0.05 mol/L. According

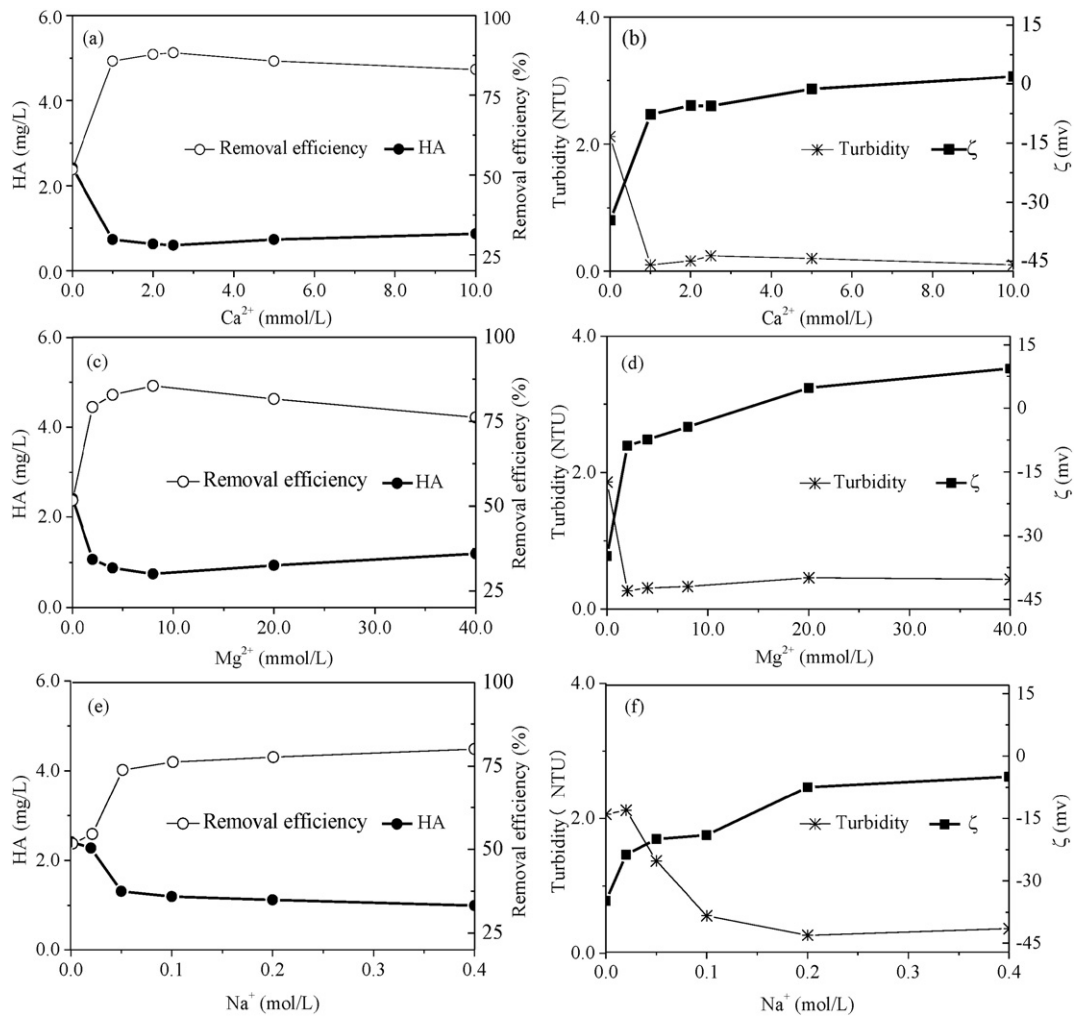


Fig. 3. Effects of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^{+}$  in the raw water on the coagulation performance of CB [8] (pH = 7.5, coagulant dosage = 0.2 mmol/L).

to Duan et al. [4], the net charge on the uncoagulated HA was the lowest in saline water and highest in deionized water. This finding is consistent with the results obtained in this study. Thus, it can be concluded that the presence of  $\text{Na}^{+}$  also enhanced HA removal by compressing the electrical double layer.

Most of the cations used in this study have small volumes, which aids their attachment to the HA surface and occupation of the surrounding space. The thickness of the diffusing layer is accordingly smaller and thus promotes HA removal by coagulation. When the HA and  $\text{Ca}^{2+}$  concentrations of the raw water were 5.0 mg/L and 1.0 mmol/L, respectively, the zeta potential of the coagulated water was  $-7.7$  mV, which is close to the value of  $-7.5$  mV obtained for the raw water with a  $\text{Na}^{+}$  concentration of 0.2 mol/L under the same coagulation condition. However, the HA removal efficiency obtained with the former kind of water was 86%, much higher than the efficiency of 78% obtained with the latter kind of water. This finding indicated that along with compressing the electrical double layer, multivalent cations, such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , might also react with reactive sites on both the surfaces of HA and CB [8], and accelerate the formation of flocs [5,32].

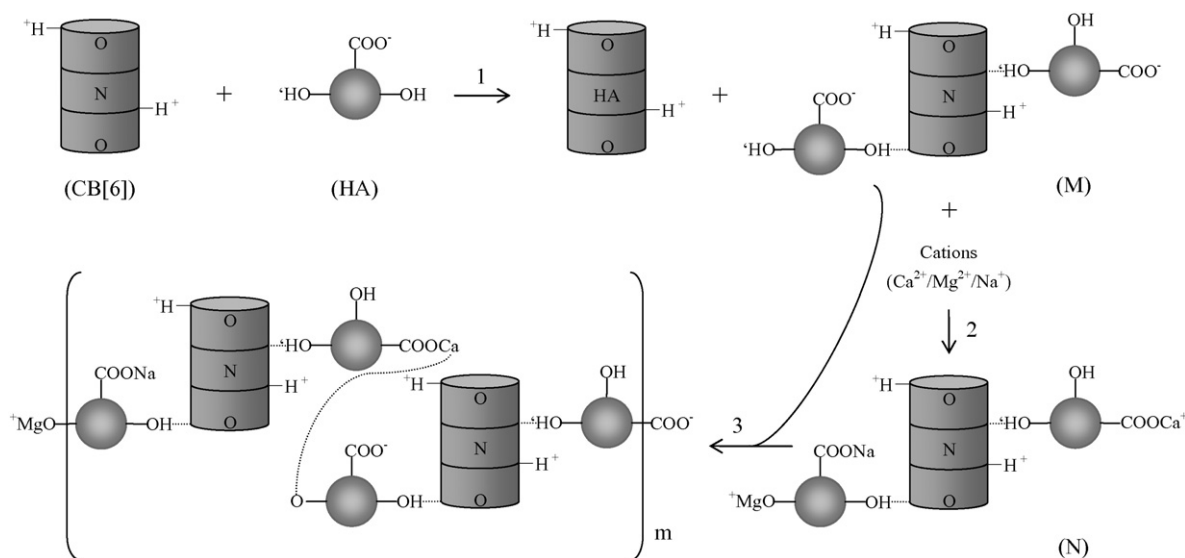
#### 3.4. Mechanism of HA coagulation by CB[8]

The experimental results discussed in Sections 3.1–3.3 indicate that when CB [8] is used as a coagulant, charge neutralization and electrical double-layer compression play important roles in destabilizing the HA, particularly for the seawater with high contents of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^{+}$  co-existing. The positive charges on the CB [8] structure might be

due to the protonation of nitrogen and oxygen to form  $=\text{N}-\text{H}^{+}$  and  $=\text{O}-\text{H}^{+}$  under neutral and acidic conditions (Fig. 4). Moreover, when the zeta potential of the HA solution was  $-33$  mV, considerable amounts of flocs could be observed during coagulation (Fig. 1b). This result indicated that along with charge neutralization and electrical double-layer compression, other factors, such as adsorption-bridge building effect, might also contributed to the destabilization of the HA.

The FT-IR spectra of HA and the flocs (HA + CB [8]) formed after coagulation were similar (Fig. 5a). No new peaks was observed in flocs' spectrum, indicating that HA coagulation by CB [8] is primarily a physical process. The bands at  $3430\text{ cm}^{-1}$ ,  $1727\text{ cm}^{-1}$ , and  $1620\text{ cm}^{-1}$ , which correspond to O–H stretching, C=O stretching, and N–H stretching, respectively, became stronger, indicating that the C=O oxygen and nitrogen in CB [8] probably formed hydrogen bonds with the phenolic hydroxyl ( $-\text{OH}$ ) and alcohol hydroxyl ( $-\text{OH}'$ ) groups on the HA molecule after coagulation, as shown in reaction 1 in Fig. 4. Under basic conditions, the relative amount of protonated  $-\text{OH}'$  was low, thus inhibiting the adsorption of HA on CB [8], which is in consistent with the experimental results presented in Section 3.1.

The hydrogen bond formed between CB [8] and HA is a typical type of 'bridge'. Both HA and CB [8] could also react with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  to form coordination bonds [16,34], which could promote particle growth (reactions 2 and 3, Fig. 4). However, peaks correspond to the formation of Ca–CB [8] and Mg–CB [8] bonds were not found in Fig. 5a. The flocculation and sedimentation of the HA occurred because super-aggregative structures are heavy enough to overcome Brownian motion formed. Meanwhile, as the porous structure of the flocs formed after coagulation



**Fig. 4.** Possible coagulation mechanism of CB [8] on HA removal. The up and bottom lines in the schematic structure of CB [8] stand for the adsorption points contributed to oxygen; two lines in the middle stand for adsorption points contributed to nitrogen. –OH and –OH<sup>+</sup> in the schematic structure of HA stand for phenolic and alcohol hydroxyl groups, respectively.

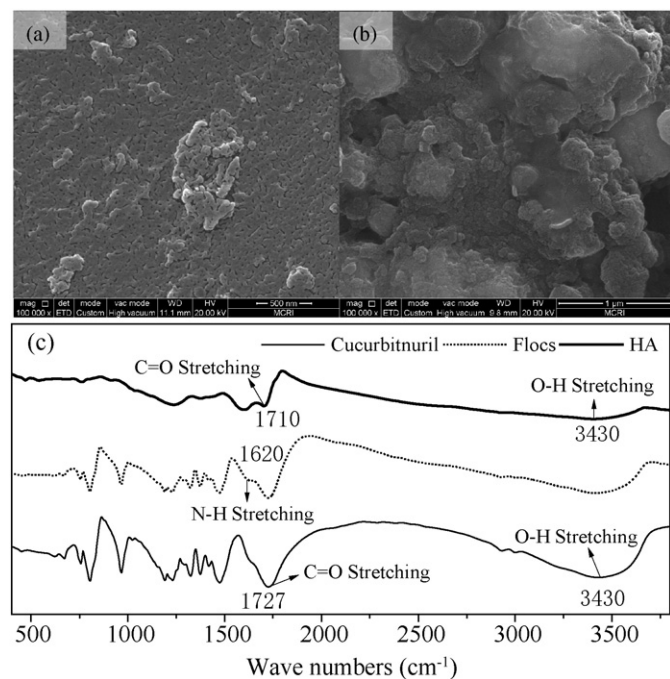
(Fig. 5b), part of the HA might also be removed by a net rolling-sweeping mechanism. In addition, the cucurbituril molecule has a hydrophobic cage-like structure (could not be directly observed from Fig. 5c) that can remove small HA molecular by forming inclusion complexes with them (Fig. 4). Accordingly, CB [8] exhibited a strong removal capacity for both low and high molecular weight HAs in the process of coagulation.

### 3.5. General discussion

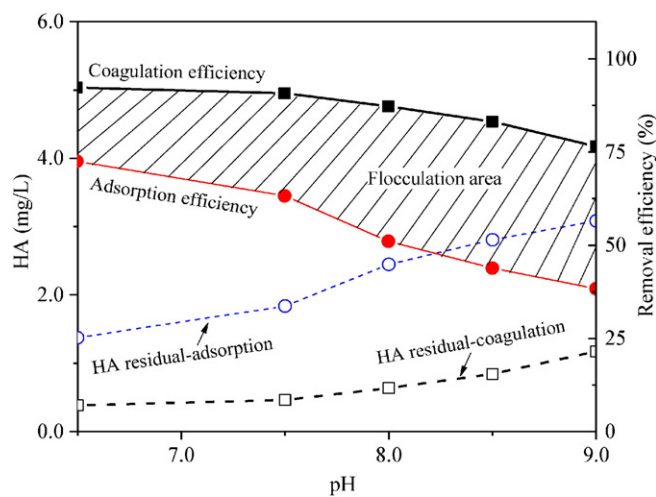
Compared with fresh water, the dissolved salt content in seawater is much higher. Although 0.2 mmol/L of CB [8] is ineffective in HA removal from synthetic fresh water at pH greater than 7.5, the addition of 1.0 mmol/L CaCl<sub>2</sub>, 8.0 mmol/L MgCl<sub>2</sub>, or 0.4 mol/L NaCl increased HA

removal efficiency from less than 50% to above 80%. However, for the real seawater, all the salts are co-existing. The HA removal efficiency by coagulation would be higher. Further study showed that approximately 90% of the HA was removed from the synthetic seawater with 1.0 mmol/L CaCl<sub>2</sub>, 8.0 mmol/L MgCl<sub>2</sub>, and 0.4 mol/L NaCl at pH 7.5 (Fig. 6). At pH 8.5, the removal efficiency decreased slightly to 83% which is higher than that of 75% achieved by 0.1 mmol/L alum under a similar water quality condition [4].

Adsorption tests using 0.2 mmol/L of CB [8] revealed that the residual HA concentration in the adsorbed solution was 1.8 mg/L at pH 7.5, which was much higher than that residual in the CB [8] coagulated water under the same water quality condition (Fig. 6). Compared with adsorption, the water flow velocity gradient was well controlled during coagulation. HA was destabilized in the rapid mixing process. The destabilized HA then aggregated to form visible flocs under the effects of electrical double-layer compression, adsorption charge neutralization, and hydrogen bond formation. Along with the HA adsorbed by CB [8], a significant amount of HA (an extra 20–40% at pH 6.5–9.0, Fig. 6) was removed by entrapment (sweep coagulation) after



**Fig. 5.** FT-IR spectra of the flocs, HA, and CB [8] (a), and the morphology characteristics of the flocs (b) and CB [8] (c) formed or used in coagulation.



**Fig. 6.** Effects of pH on the HA coagulation and adsorption performances of CB [8] from the synthetic seawater with 1.0 mmol/L CaCl<sub>2</sub>, 8.0 mmol/L MgCl<sub>2</sub>, and 0.4 mol/L NaCl co-existing (Coagulant/adsorbent dosage = 0.2 mmol/L, HA = 5.0 mg/L).

flocculation [25], which is probably the major reason for the obvious difference in the HA removal efficiencies of the CB [8] adsorbent and coagulant.

Considering the high HA removal efficiency in the normal seawater pH range of 7.5–8.3, CB [8] is proven to be a competitive coagulant for the pretreatment of seawater prior to desalination. However, it should be noted that this study has only investigated the coagulation performance of CB [8] and the effects of salts on HA removal from the synthetic seawater. The effects of other seawater quality parameters, such as temperature, turbidity, and alkalinity, on the HA removal of CB [8] was not considered. Meanwhile, the composition of the dissolved organic matter in the real seawater was different from HA, which might inhibit the application of present results in seawater coagulation. Notwithstanding its limitation, this study does suggest the coagulation performance and mechanisms of CB [8] hold true for the removal of HA with calcium, magnesium, and sodium salts co-existing in the raw water.

#### 4. Conclusions

To improve the removal efficiency of HA, the coagulation performance of CB [8] and the effects of salts on this process were evaluated in this study. It was determined that the type of anion had a significant effect on the solubility of CB [8]. When the CB [8] dosage was higher than 0.3 mmol/L, more than 89% of the HA was removed from the raw water at pH < 7.5. Under basic conditions, the removal of HA decreased significantly for the raw water in the absence of added salts. When the Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup> concentrations of the synthetic seawaters were 1.0 mmol/L, 8.0 mmol/L, and 0.4 mol/L, respectively, the HA removal efficiency increased from less than 50% to 86%, 85%, and 80%, respectively. Although charge neutralization and electrical double-layer compression played important roles in destabilizing the HA, the flocculation process was conducted before all the negative charges on the HA surface were neutralized by the coexisting cations and CB [8], which probably due to hydrogen bond formation during the coagulation process. Further in-depth analysis showed that HA coagulation with CB [8] is primarily a physical process. Compared with adsorption, an additional 20–40% of the HA was removed by CB [8] coagulation under the same water quality condition.

#### Acknowledgments

This research was supported by the National Natural Science Foundation of China (No. 21007050), Specialized Research Fund for the Doctoral Program of Higher Education (20106120120014), the Science and Technology Nova Program of Shaanxi (No. 2014KJXX-66), and the Natural Science Foundation of Shaanxi (No. 2009JQ7001).

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