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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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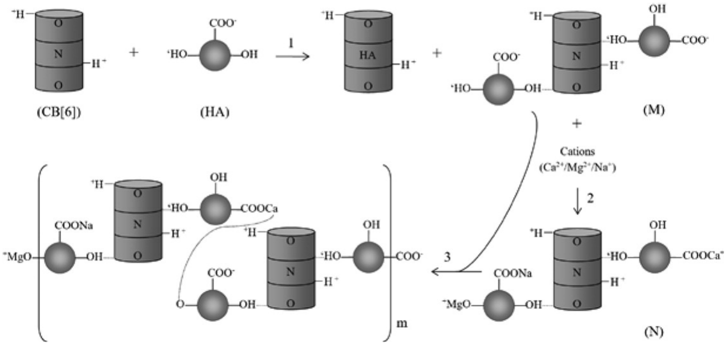
HIGHLIGHTS

- 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



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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 Ca^{2+}, 8.0 mmol/L of Mg^{2+}, and 0.4 mol/L of 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.

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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rivers [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 $AlCl_3$, $FeCl_3$, 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 μm 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 Cl_2 disinfection processes are used in the plant. To avoid the destruction of residual 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, Na^+, Mg^{2+}, and 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 $CaCl_2$, 0.1 mol/L $MgCl_2$, 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 $CaCl_2$, 8.0 mmol/L $MgCl_2$, and 0.4 mol/L NaCl were added to the synthetic water at