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Removal of antibiotics from water in the coexistence of suspended particles and natural organic matters using amino-acid-modified-chitosan flocculants: A combined experimental and theoretical study

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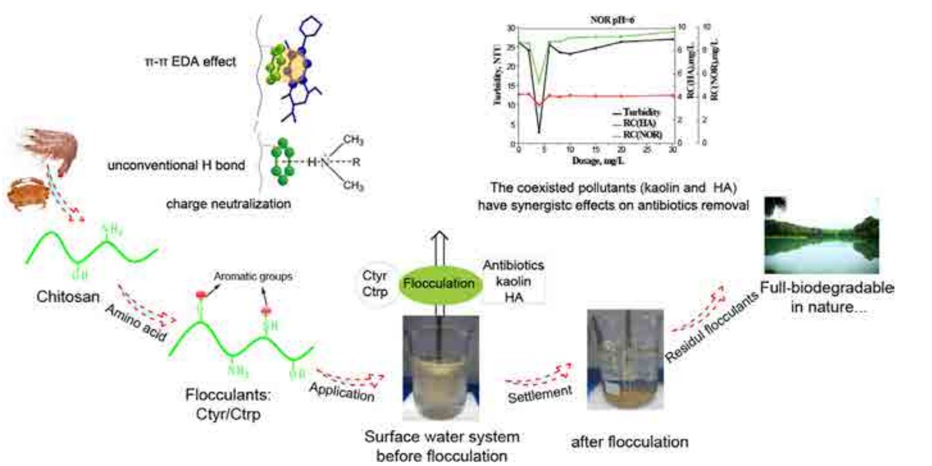
HIGHLIGHTS

- Novel amino-acid-modified-chitosan flocculants are employed to remove antibiotics.
- Effects of different structures of amino acids and antibiotics are investigated.
- Correlation analysis shows coexisted kaolin and HA have synergistic removal effect.
- Theoretical DFT calculation clarifies the interactions in molecular level.

GRAPHICAL ABSTRACT



Removal of antibiotics from water in the coexistence of suspended particles and natural organic matters using environmental-friendly amino-acid-modified-chitosan flocculants.

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ABSTRACT

Contamination of trace antibiotics is widely found in surface water sources. This work delineates removal of trace antibiotics (norfloxacin (NOR), sulfadiazine (SDZ) or tylosin (TYL)) from synthetic surface water by flocculation, in the coexistence of inorganic suspended particles (kaolin) and natural organic matter (humic acid, HA). To avoid extra pollution caused by petrochemical products-based modification reagents, environmental-friendly amino-acid-modified-chitosan flocculants, Ctrp and Ctyr, with different functional aromatic-rings structures were employed. Jar tests at various pHs exhibited that, Ctyr, owning phenol groups as electron donors, was favored for elimination of cationic NOR (~50% removal;

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Surface water
Environmental behavior
DFT calculation

optimal pH: 6; optimal dosage: 4 mg/L) and TYL (~60% removal; optimal pH: 7; optimal dosage: 7.5 mg/L), due to π–π electron donator-acceptor (EDA) effect and unconventional H-bonds. Differently, Ctrp with indole groups as electron acceptor had better removal rate (~50%) of SDZ anions (electron donator). According to correlation analysis, the coexisted kaolin and HA played positive roles in antibiotics' removal. Detailed pairwise interactions in molecular level among different components were clarified by spectral analysis and theoretical calculations (density functional theory), which are important for both the structural design of new flocculants aiming at targeted contaminants and understanding the environmental behaviors of antibiotics in water.

1. Introduction

In recent years, increasing interest has been addressed to the risk of drinking water contamination caused by pharmaceutical compounds, of which antibiotics are one large class [1–3]. According to previous literatures [4,5], the excessive use of antibiotics in medical industry and intensive livestock farming has resulted in the pollution of several of the world's surface water sources, which further affects the quality of subsequently treated drinking water [6,7]. Generally, since the removal of antibiotics is not primarily considered in the design of drinking water treatment processes, antibiotics can hardly be removed in conventional drinking water treatment plants. Besides, as real surface waters often contain suspended particles (generating turbidity) and natural organic matters (NOMs, producing UV_{254}), the transport and transformation behaviors of antibiotics are more complex due to their interactions with suspended particles and NOMs. Consequently, the difficulty of the removal of antibiotics is further enhanced [8].

Previous studies [9,10] have listed a wide range of chemical and physical methodologies for organic compounds removal, including oxidation, flocculation/coagulation, adsorption, extraction, membrane techniques, etc. Among aforesaid techniques, flocculation [11–13] is an efficient and widely employed surface water treatment method because of its low cost, facile operation and simple apparatus required [14]. Among various types of flocculants, eco-friendly natural polymer flocculants, which own benefits of high cost-effectiveness, inexpensiveness, wide source, non-polluting and biodegradability [15–18], have attracted extensive attention. Chitosan [15,19], generated from the deacetylation of chitin, is one of such sort of natural polymers. Generally, in order to improve the flocculation efficiency for practical application, chemical modification on chitosan is necessary to introduce desired functional groups onto the molecular backbones [19–21].

However, the potential problem associated with most chemically modified chitosan flocculants lies in the fact that traditional use of petrochemical products-based modification reagents may result in extra pollution. Both residual modification reagents and the corresponding derivatives produced from the degradation of modified chitosan are quite possible to represent health hazards [22,23]. From this viewpoint, it is particularly meaningful to use alternative environmental-friendly reagents for chemical modification of chitosan, in order to avoid secondary pollution. According to previous study [24,25], amino acids, which are totally biodegradable and biocompatible modification reagents, can provide such approach. Meanwhile, according to our recent work [26], the flocculant owing aromatic rings have demonstrated improved removal rates of antibiotics due to the existence of π–π stacking [27] of aromatic rings between the flocculant and antibiotics. Therefore, amino acids with aromatic rings structure would be preferred. Additionally, chitosan-based products modified by various amino acids with different structures may lead to different performances, which is also an interesting topic that has not been studied and reported systematically yet.

In the current paper, according to the aforementioned analysis, two novel amino acids (L-tryptophan and L-tyrosine owing indole and phenol groups, respectively) modified chitosan flocculants (denoted as Ctrp and Ctyr, respectively) were synthesized. They were then applied to flocculate three sorts of synthetic surface water, in which the targeted antibiotic contaminant was norfloxacin (NOR), sulfadiazine (SDZ) or tylosin (TYL), in the coexistence of model suspended particles (kaolin) and model NOM (humic acid, denoted as HA). How (1) different structures of amino acids and antibiotics and (2) the coexistence of kaolin and HA impacted on the flocculation performance systematically studied at different pHs and flocculant dosages. Finally, the flocculation mechanism was explored in detail by Zeta potential (ZP)-dosage profiles, Fourier transform infrared (FTIR), X-ray photoelectron (XPS) spectra, and density functional theory calculation.

2. Materials and methods

2.1. Materials

Ctrp and Ctyr were synthesized in a similar way through a single-step process as depicted in Fig. 1(a) and Supporting information Text S1. HA was purchased from Aladdin Industries Co. NOR, SDZ and TYL (structures shown in Fig. 1(b)) were purchased from Dalian Meilun Biotechnology Co., Ltd., Amino acids (L-tryptophan and L-Tyrosine), kaolin (mean diameter: ~1 μm), polyaluminum chloride (PAC, $[Al_2(OH)_nCl_{6-n}]_m$, n = 3.6–5, m < 10, Al_2O_3 content > 28%), polyacrylamide (PAM, weight-average molecular weight: 3×10^7 g/mol) and other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. Distilled water was used in all experiments.

Due to the large differences in the molecular structures of three antibiotics, their physical and chemical characteristics varied significantly and were listed in Table S1.

According to pK_a values, species distribution of antibiotics' molecules/ions, which affects interactions between flocculants and antibiotics, were calculated [28,29] and illustrated in Supporting information Fig. S1.

2.2. Characterization of Ctrp and Ctyr

The characterization methodologies of Ctrp and Ctyr included FTIR spectra, X-ray diffraction (XRD), ^1H nuclear magnetic resonance (^1H NMR), elemental analysis, and ZP measurements, as described in Supporting information Text S2.

2.3. Flocculation experiments

Synthetic surface water containing antibiotics in the coexistence of kaolin and HA was used in standard jar tests conducted on a six-place programmed paddle mixer (MY3000-6B, Wuhan Meiyu Instrument Co., Ltd.) at room temperature. In addition to 10 mg/L of antibiotic as the targeted contaminant, kaolin (30 mg/L, provid-