



How heavy metals impact on flocculation of combined pollution of heavy metals–antibiotics: A comparative study



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ABSTRACT

Previous research found that certain types of heavy metals could play a “bridge” role in promoting removal of antibiotics in flocculation, but details (i.e. under what conditions and how heavy metals wielded this effect) were not clear. To investigate this point, two sorts of combined pollution [Cu(II)–tetracycline and Zn(II)–sulfadiazine] were selected in synthetic wastewaters for flocculation, to give a comparative study. A flocculant with high capacity to coordinate with heavy metals was applied. The flocculation performance declared that, Cu(II) improved removal of coexisted antibiotic molecules whereas Zn(II) did not. Analyses of macro- and micro-scopic properties of flocs demonstrated that, (i) tightly binding of the flocculant with heavy metals, and (ii) strong coordination of heavy metals–antibiotics when the two contaminants were suitably matched according to Hard–Soft–Acid–Base theory and steric effect, were two factors for heavy metals to perform the “bridge” role, and to achieve high co-removal efficiencies of both contaminants. The finding had operational significance for both promoted removal of antibiotics with the coexistence of heavy metals and mutual promotion in the removal of the combined contaminants from water.

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1. Introduction

The co-removal of heavy metals and antibiotics has attracted increasing concern in view of the threat of combined pollution of these two sorts of contaminants in livestock or centralized industrial wastewater [1]. On the one hand, both the contaminants are extensively employed as growth promoters in livestock farming, whereas most of them cannot be absorbed and are finally excreted to the environment [2,3]. On the other hand, one sort of wastewater containing heavy metals is quite possible to be mixed with another sort of wastewater from pharmaceutical industries containing antibiotics, with the promotion of centralized industrial wastewater treatment [4]. Circumstantial evidences have exhibited that the treatment of combined pollution of heavy metals and antibiotics is more difficult than that of traditional contaminants [5,6]. Consequently, much attention has been given to effective control of such kind of pollution recently [7–9].

As a facilely operated and highly cost-effective technique, flocculation is widely applied in many wastewater treatment works [10–13]. Especially, when biomass-based flocculants are employed, this method further enjoys a benefit of environmental-friendliness

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[14–17]. However, insufficient reports on flocculation of combined pollution of heavy metals and antibiotics are available through an overview of literatures [18–20]. This phenomenon may be attributed to the flocculation difficulties resulting from the complicated environmental behaviors of complex species formed by heavy metals and antibiotics as reported [5,6]. Despite this, when such complexation effect is not considered temporarily to make the problem easier and the two sorts of contaminants are just separately analyzed, one can find that flocculation of the organic components (antibiotics) is more difficult than that of the inorganic ones (heavy metals): Heavy metals, usually being strong electron acceptors, could be eliminated in flocculation *via* introducing strong electron donors, such as mercapto, carboxyl and phosphonate groups, onto the flocculants backbones according to previous studies [21–23]; but organic antibiotic molecules are not able to be easily removed by flocculation due to their complicated structures or variable physicochemical properties [18], as no study has reported efficient flocculation of wastewaters containing antibiotics alone.

Differently, it has been found in authors' previous work that the flocculation efficiency of tetracycline (TC) could be significantly enhanced with the co-existence of Cu(II) [19]. Therein, Cu(II) played a “bridge” role connecting the flocculant and TC, by coordination with both components. From this viewpoint, it seems that heavy metals–antibiotics complex species could be recognized to

promote, rather than to hinder, the flocculation. Nevertheless, this deduction from only one case is inappropriate, because a number of inconsistent results on adsorption of antibiotics have demonstrated that heavy metals could either be positive or negative to the removal efficiencies [24,25]. Therefore, a more fundamental understanding on under what conditions and how heavy metals play the “bridge” role to promote the removal of antibiotics in flocculation is needed, which has been rarely discussed to date. If it is known how to manually adjust flocculation conditions to improve the synergistic removal of antibiotics by heavy metals, an advantages would emerge: the promoted removal of antibiotics would be obtained with the coexistence of heavy metals and mutual promotion in the removal of the combined contaminants would be thus achieved.

The overall objective of this study was to investigate how flocculation conditions such as pH, dosage, type and initial concentration of contaminants impacted the “bridge” role of heavy metals to promote the removal of antibiotics. A biomass-based flocculant (mercapto-modified chitosan, denoted as MAC) with high capacity to coordinate with heavy metals was used here. Two systems of synthetic combined-polluted wastewater, including Cu(II)-TC and Zn(II)-Sulfadiazine (SDZ), were employed to give a comparative study. All these contaminants were commonly available heavy metals or antibiotics in both real livestock and centralized industrial wastewaters [26,27].

2. Materials and methods

2.1. Materials

The flocculant, MAC, was synthesized according to previous report [22] as described in Supporting Information Fig. S1 and Text S1. Its characterization methodologies, including Fourier transform infrared (FTIR), ^1H nuclear magnetic resonance (^1H NMR), X-ray diffraction (XRD) and zeta potential (ZP) measurements, are provided in Supporting Information Text S2. The spectroscopy characterization results of MAC are extensively discussed in Supporting Information Figs. S2–S4 and Text S3. According to the ^1H NMR spectra, the substitution degree (SD) of mercapto groups was calculated to approximate 170%. Such high SD indicates the large potential to coordinate with heavy metal ions.

CuSO_4 , ZnSO_4 , HCl aqueous solution, and NaOH were purchased from Sinopharm Chemical Reagent Co., Ltd. TC and SDZ were purchased from Sigma–Aldrich Chemical Co., and their chemical structures and selected physicochemical properties are depicted in Supporting Information Fig. S5. Secondary deionized water was used in all experiments.

2.2. Flocculation experiments

Standard jar tests were conducted in flocculation experiments at room temperature. Before each test, the stock solution of MAC was always freshly prepared by dissolving 0.5 g of MAC into 100 mL of water, and pH of synthetic wastewater was adjusted to a pre-designed value by adding dilute HCl or NaOH aqueous solution. The investigated synthetic wastewater in this work included binary combined contaminants of Cu(II)-TC and Zn(II)-SDZ, as well as single contaminant of Cu(II), TC, Zn(II) and SDZ, respectively.

After adding a known volume of MAC stock solution into the synthetic wastewater, the jar tests were made up of three stages: (i) 2.5 min of rapid mixing at 200 rpm, (ii) 7.5 min of slow mixing at 50 rpm, and finally (iii) 30 min of floc sedimentation without mixing. The settling time was determined from preliminary tests,

as flocculation equilibrium could be reached within this period. After that, samples were collected at a depth of approximate 2 cm in the supernatant for contaminants' concentration determination. Each measurement was triplicated.

Residual concentration (RC) of certain contaminant was applied to assess flocculation efficiency of MAC. RC of Cu or Zn was measured by a GBC Savant AA atomic adsorption spectrophotometer; RC of TC or SDZ was measured by a Mapada UV3100-PC UV-Vis spectrophotometer. ZP was measured by a Malvern Nano-Z Zetasizer.

2.3. Floc properties analysis

Macroscopic properties of flocs in water, including particle size and fractal dimension (D_F), were analyzed on-line according to previous literature [28] by a Malvern Mastersizer 3000 Light Scattering System. D_F , of which the definition and calculation method were described in authors' previous work in detail, signified the space-filling capacity of flocs [29]. Generally, larger D_F values represented more compacted flocs which were more favorable in flocculation owing to smaller total volumes and easier handling.

Floc breakage and regrowth experiments were also conducted to investigate the properties of flocs. After the fast and slow mixing steps (2.5 min at 200 rpm and 7.5 min at 50 rpm) as programmed in jar tests, the suspension was exposed to an enhanced shear (200, 150, 100 or 50 rpm) for further 2.5 min for floc breakage, followed by another slow mixing at 50 rpm for 2.5 min.

After withdrawn from the bottom of jars, the flocs were vacuum freeze-dried to prevent the change of functional groups as much as possible. Then, microscopic properties of flocs in dried form, i.e. type and intensity of interactions among different components in flocs, were characterized by FTIR and X-ray photoelectron spectroscopy (XPS) on a Bruker Tensor-27 FTIR spectrometer and a ULVAC-PHI 5000 VersaProbe XPS spectrometer, respectively.

3. Results and discussion

3.1. Surface charge properties of MAC and contaminants

It is widely accepted that surface charge properties of a flocculant and a contaminant are of notable importance for predicting and understanding charge interactions between the two components in flocculation [30]. Hence, ZP–pH profiles of MAC and contaminants in this work were measured and illustrated in Fig. 1.

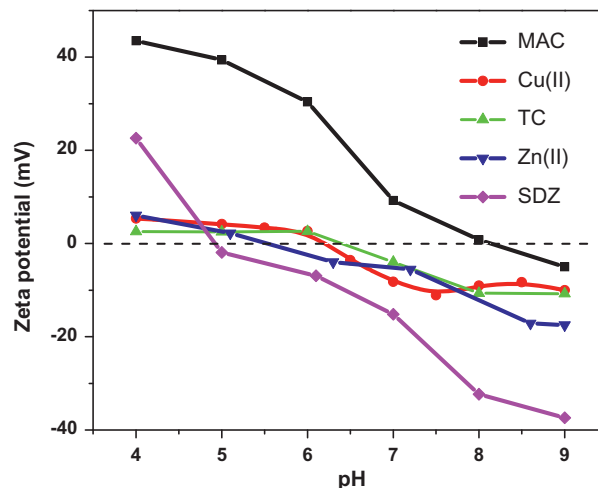


Fig. 1. ZP–pH profiles of MAC (■), Cu(II) (●), TC (▲), Zn(II) (▼) and SDZ (◆) solutions.

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