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The interaction between effluent organic matter fractions and $Al_2(SO_4)_3$ identified by fluorescence parallel factor analysis and FT-IR spectroscopy

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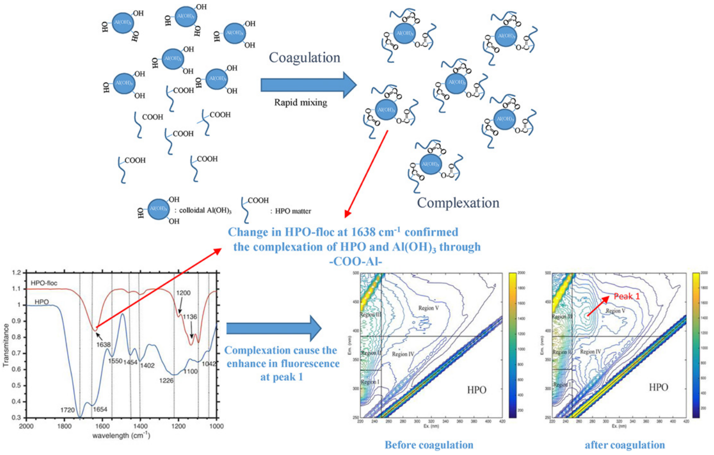
GRAPHICAL ABSTRACT



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ABSTRACT

Colloidal organic matter (OC fraction), hydrophobic organic matters (HPO fraction), transphilic matters (TPI fraction) have been extracted and fractionated from Effluent Organic Matter (EfOM). FT-IR spectroscopy and Fluorescence Excitation-Emission Matrix parallel factor (EEM-PARAFAC) analysis have been performed to characterize the chemical structure of fractions. The coagulation performance of EfOM fractions with $Al_2(SO_4)_3$ was investigated in terms of turbidity reduction and dissolved organic carbon (DOC) removal. FT-IR spectroscopy and Fluorescence have also been introduced to identify the interaction between fractions and $Al_2(SO_4)_3$. The results showed the main component in different fractions and that HPO fractions can be representative of natural organic matter (NOM), whereas OC fractions is representative of EfOM. The dissolved organic matters (DOMs) like HPO fraction showed better removal efficiency during coagulation. The relationship between zeta potential and DOC removal suggested that the coagulation mechanism of EfOM fractions were different. A new intensity peak showed up in Region V and the enhancement of Fluorescence intensity in humic-like substance exhibited after coagulation, which due to the complex with aluminum salts. The –COO–Al asymmetric stretch in FT-IR spectroscopy confirmed the complexation between aluminum salts and carboxyl groups. As the interaction

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of Effluent Organic Matter can cause enhancement in fluorescence intensity, fluorescence-EEM was not an appropriate method to evaluate the coagulation performance of secondary effluent with aluminum salts.

1. Introduction

Due to population growth, periodic droughts, and increasing contamination of both surface and ground water, the reuse of advanced treated wastewater is considered as an important component of sustainable wastewater management practices worldwide [1–3]. Effluent Organic Matter (EfOM) in wastewater treatment plant (WWTP) is consist of natural organic matter (NOM), soluble microbial products and contaminants of emerging concern [4,5] and has been shown to exhibit a contradictory effect towards various aquatic organisms and adverse effects to human health, like reducing bioavailability of metal ions to organisms by binding with inorganic [5,6], fouling adsorbents and membranes [4] and containing precursor for disinfection by-product formation [7,8]. Therefore, advanced treatment technologies of EfOM are in urgent need. Coagulation has been commonly employed in advanced treated wastewater treatment process to remove contaminants, such as DOC, suspended solids (SS), total phosphorus (TP) and specific UV absorbance (SUVA) [9,10], and control the formation of disinfection byproducts (DBPs) [8,11]. As studies reported, coagulation could reduce trihalomethanes (THMs) concentration by removing hydrophobic acid precursor and aromatic protein [8], and was effective at removing genotoxic DBP precursors [11].

Effects of characteristics, like functional group and chemical structure of dissolved organic matter (DOM), on coagulation efficiency during coagulation have been studied and a contradictory result has been shown. Shi et al. [12] reported that humic acid can be removed efficiently by coagulation with UV_{254} removal of more than 80% and similar results have also been reported by Xue et al. [13] and Matilainen et al. [14], that hydrophobic fractions are removed more efficiently than hydrophilic fractions. However, the study of Liu et al. [9] showed that fulvic acid-like and humic acid-like substance were removed inefficiently, according to EEM fluorescence spectra and DOC removal of raw effluent and this result have also been gained by Cui et al. [10]. The contradictory phenomenon may due to the effect of interaction between DOM and coagulants on fluorescence spectra. Fluorescence as a potential monitoring tool have been commonly applied in recycled water system [15] to acquire fluorescence identification of sewage-derived dissolved organic matter [16–18] and interaction of metal ions and dissolved organic matter [6,19]. Many researches have been done to investigate binding properties between metals and DOM [6,19–21], and it has been known for many years that diamagnetic ions such as Al^{3+},Mg^{2+},Ca^{2+} and Cd^{2+} can quench, enhance or have little effect on humic-like and fulvic-like fluorescence [20]. Fluorescence studies of humic acid and fulvic acid complexation with aluminum have demonstrated that the interaction of aluminum and organic acid can enhance fluorescence at low pH (pH = 3–5) [12,19,20], but studies at neutral pH are limited. Studies have suggested that aluminum ions appeared to have no impact on sewage wastewater fluorescence [15,22], while recently an investigation on the effect of metal ions on fluorescence of soluble microbial products from wastewater treatment plant demonstrated that the intensities decreased with the increasing Al^{3+} concentration [6].

In summary, the conclusion about removal efficiency of hydrophobic fraction are different, and few studies have targeted the effect of aluminum on wastewater fluorescence at neutral pH during coagulation. The objective of this work was to investigate the effect of aluminum hydrolysis products on wastewater fluorescence at neutral pH and the interaction of different organic fractions with coagulants. Secondary effluent sampled from WWTP was fractionated into three fractions by resin, according to molecular weight and hydrophobicity, and were treated with aluminum salt coagulant ($Al_2(SO_4)_3$). The efficiency of DOC, UV_{254} and turbidity removal were measure to understand the coagulation treatability of contaminants and zeta potential was measure to judge coagulation mechanism. Spectroscopy approaches like fluorescence EEM and FT-IR were applied to identify fluorescence components of different fractions and study the interaction of aluminum with DOM.

2. Materials and methods

2.1. Isolation and characterization of EfOM fractions

2.1.1. Secondary effluent

About 125 L treated wastewater was obtained from Longwangzui wastewater treatment plant in Autumn (Wuhan, China). Samples were firstly through micro-filtration (JX1812C-34D, GE, American) system to remove suspended matter and biomass, and then concentrated into approximately 200 mL by reverse osmosis (RO) system (SG1812C-34D, GE, American) and evaporation (RE52CS-1, YaRong, Shanghai). The concentrate was stored in refrigerator and prepared for extraction procedure.

2.1.2. Extraction procedure

EfOM isolation and extraction was conducted according to the methods described by Leenheer [23] and Kim [24] with minor modifications. After RO system, the concentrated sample was put into dialysis bags (3500–5000 Da, Spectrum Labs, American) and the bag was stirred in 5 L beaker which is full of 0.1 mol L^{-1} HCl solution. Keep stirring and change the HCl solution in beaker every day. The sample in dialysis bag was freeze dried and got colloidal organic matter (OC fraction). The dialysate in beaker was pumped through DAX-8 resin (Supelite ™, Sigma-Aldrich, Germany) and XAD-4 resin (Amberlite®, Sigma-Aldrich, Germany), which were both pre-cleaned using 0.1 mol L^{-1} NaOH, deionized water, and 0.1 mol L^{-1} HCl, in series to isolate hydrophobic organic matters (HPO fraction), transphilic matters (TPI fraction). Using acetonitrile solution (75% acetonitrile/25% deionized water, v/v) the HPO and TPI were extracted from the resins. The organics were freeze-dried after evaporating acetonitrile.

2.2. Batch jar test

2.2.1. Synthetic test water

Colloids, HPO, and TPI fractions obtained in Section 2.1.2 were dissolved with 0.01 mol L^{-1} NaOH as stock solution. The stock solutions were prefiltered with 1.2 μm glass fiber filters (Whatman GF/C, United Kingdom) to remove coarse materials. Before each coagulation experiment, appropriate amount of stock solution was added and diluted to total organic carbon (TOC) about 5 mg L^{-1} and aliquots of the stock solutions were diluted into a background electrolyte solution containing 29.9 mg L^{-1} $CaSO_4$, 49.8 mg L^{-1} $NaHCO_3$, 26.8 mg L^{-1} $MgSO_4$ and 2.0 mg L^{-1} KCl to prepare different synthetic surface waters [25]. The pH was adjusted to about 7 with 0.1 mol L^{-1} NaOH and 0.1 mol L^{-1} HCl with pH meter (Starter 3C, OHAUS, U.S.A). In order to investigate the effect of ionic strength on coagulation performance, 1 mol L^{-1} NaCl was used to provide three different ionic strengths: 0 mM L^{-1} NaCl, 2.5 mM L^{-1} NaCl and 5 mM L^{-1} NaCl.