



Comparison of coagulation and magnetic chitosan nanoparticle adsorption on the removals of organic compound and coexisting humic acid: A case study with salicylic acid

Ning Wang^a, Zhenghe Xu^{a,*}, Weiying Xu^{a,b,*}, Jing Xu^c, Yingying Chen^a, Min Zhang^a

^a School of Water Conservancy and Environment, University of Jinan, Jinan 250022, PR China

^b Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Science, Chinese Academy of Science, No. 18 Shuangqing Road, Haidian District, Beijing 100085, PR China

^c School of Water and Soil Conservation, Beijing Forestry University, Beijing 100083, PR China

HIGHLIGHTS

- High MW and hydrophobic fractions were mainly removed by coagulation.
- MCS, although efficient in removing SA, was not desirable in removal of HA.
- SA co-existed with HA imposed inhibitory effect for their removals in individual adsorption/coagulation process.
- Hybrid MCS-alum system could increase the OMs removal efficiencies and final floc sizes.
- The adsorption of SA/HA onto MCS was a physical and multilayer adsorption.

ARTICLE INFO

Keywords:

Magnetic chitosan
Coagulation
Compound pollution
Competitive adsorption
Synergistic effect

ABSTRACT

Removals of salicylic acid (SA) and humic acid (HA) in individual and bi-component systems by coagulation employing aluminum sulfate (alum) and adsorption using magnetic chitosan (MCS), were comparatively investigated in this study. In single-component system, alum at sufficient dose (12.0 mg/L), although efficient in removing HA, was not desirable in removal of SA. Conversely, higher SA removal rate in the adsorption process was achieved due to its superior adsorption tendencies and size-exclusion effects than that of HA. Moreover, individual SA/HA by MCS adsorption fit with Freundlich isotherm model, indicating a multilayer adsorption process. In the bi-component system, the SA and HA removal rates were observed to decrease to varying extents. Dynamic floc sizes during coagulation processes were studied using a laser diffraction particle sizing device. The results demonstrated high molecular weight (MW) HA-Al(III) complex could grow into enough large size and consequently tended to separate in water; while more coagulants (> 14.0 mg/L) were required in the bi-component system compared with individual HA water when the system emerged obvious flocs, which was associated with the discrepancy of charge neutralization and competition of adsorption sites. For sole adsorption, the reaction between HA and MCS was faster than that of SA, and parts of adsorption sites were preoccupied by HA and thereby result in the low SA removal efficiency. Furthermore, combination of alum and MCS could significantly enhance organic matter removal, and alum with low dose of 8.0 mg/L coupled with MCS could evidently improve flocs settlement performance and increase the floc sizes.

1. Introduction

As the population and economic development increases, water quality is greatly impacted by anthropogenic processes with the synthetic organic compounds (SOCs) from industrial production and household consumption extensively discharged into aquatic

environment [1,2]. These organic pollutants typically include pharmaceuticals, personal care products, industrial chemicals from consumer products and pesticides [3]. The recent commercialization of SOC-containing products has raised concerns about their possible accumulation and fate into the source waters [1,4]. For instance, some SOC in potable water could potentially lead to increased risk of heart

* Corresponding authors at: School of Water Conservancy and Environment, University of Jinan, Jinan 250022, PR China (W. Xu).
E-mail addresses: xu4045@126.com (Z. Xu), stu_xuwy@ujn.edu.cn (W. Xu).

<https://doi.org/10.1016/j.cej.2018.04.131>

Received 4 February 2018; Received in revised form 17 April 2018; Accepted 19 April 2018

Available online 22 April 2018

1385-8947/ © 2018 Elsevier B.V. All rights reserved.

attacks, organ damage, mental health, and cancer [5,6]. Therefore, it is vital that effective water treatment processes are employed to remove the organic contaminants, and thus ensure that any potential human health risks are mitigated prior to consumption.

The solubility of organic matter (OM) in aquatic environment can be altered in the presence of hydrolyzing metals through formation of insoluble complexes or adsorption on amorphous metal hydroxides [7]. This effect, termed coagulation and flocculation, is used as the most common and economically feasible water treatment technology [8]. Formation of polyhydroxy-complexes of Al, the most commonly used coagulant, and adsorption of the OM to the amorphous Al hydroxides are thought to be responsible for coagulation and precipitation of OM [9]. However, this conventional water treatment process is not designed to purposefully eliminate the SOC contaminants [10]. Neither Al nor Fe coagulants are capable of removing all OM in solution independent of the total metal concentration, which might indicate the presence of a certain OM fraction that can be regarded as “non-coagulated” [11,12]. High molecular weight (MW) OM fractions tend to be more aromatic and possess high electrostatic potential, which can be efficiently removed by coagulation and have lower coagulant demand due to the high charge density. Low MW fractions have small radii, tend to be more hydrophilic and some of them present negligible charge density, which are considered difficult to remove by coagulation [13,14]. For facilities that employ hydrolyzing metal salts for coagulating this nonremovable fraction may be problematic when removal regulations have to be met.

Furthermore, the aquatic environment is complex and consists of a wide variety of organic compounds, including those from the decomposition of plant and animal materials and natural dissolved organic matters (DOM) [15], such as humic substance. Humic acid (HA), which can be regarded as supramolecular assemblies of several thousands of different organic molecules, is a major concern in water treatment, since it often contributes not only to offensive taste and odors but also to formation of carcinogenic byproducts, such as trihalomethanes and halo acetic acids, that can form during chlorination [16,17]. Additionally, the high diversity and complexity of natural DOM also constitute a challenge for the water and wastewater treatment, as it has a crucial role for the transformation and fate of coexisting SOCs by modifying their surface properties and consequently their stability throughout the water treatment. It has been claimed that DOM generally contributes to various complexation processes with the harmful SOCs, and these interactions are expected to affect the distribution, transport and mobility of contaminants in waters [18,19]. Previous study of Cho et al. [20] claimed that the DOMs are known to enhance the apparent aqueous solubility of hydrophobic organic contaminants and lead to more serious pollution. It has also been proved that DOM could enhance the transport of some persistent organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) to aquatic organisms [21]. In spite of the presence of various components in practical feeds, lab-based experiments have tended to primarily focus on the targeted contaminant like bisphenol, 2,4-D, and sulfamethoxazole, thus neglecting the influence of the inorganic salts and natural dissolved DOM inevitably present [22,23]. A clear understanding of the influence of DOM on the character and transport mechanisms of the coexisted SOC in aquatic environment is still lacking, which is expected to seriously influence the OM removing during water treatment process.

Since conventional water treatment processes have not been designed to and cannot effectively remove the SOCs, novel water treatment material has gained much interest in resolving this issue. Chitosan (CS), as the only cationic polysaccharide existed widely in nature, has been used in pharmaceuticals, food, environmental protection and agriculture, etc [24]. It is a partial deacetylation of chitin and can be easily modified due to the presence of the amine ($-NH_2$) and hydroxyl ($-OH$) groups [25]. Chen et al. [26] obtained the zirconium cross-linking Fe_3O_4 -CS microspheres, showing that the product has higher adsorption capacity for Cr(VI) (280.97 mg/g) at pH 4.0 and 25 °C. Fan

et al. [27] prepared Fe_3O_4 -CS nanoparticles by high-gravity reactive precipitation method, experimental results shown that the product has better adsorption effect for Pd^{2+} (79.24 mg/g). The CS/kaolin/ Fe_3O_4 magnetic microspheres was successfully fabricated by Ma et al. [28], and the material was used as adsorbents for removal of ciprofloxacin (CIP) from an aqueous solution. These published literatures have proven magnetic chitosan (MCS for short) has relatively strong adsorption capacity of OMs and metal ions such as methylene blue [29], Cu^{2+} [30], etc, which the results of the above studies gave valuable insight into the study on the adsorption properties of modified CS. Besides, all the studies mentioned above are conducted in single-component adsorption system with test solutions containing one pollutant, using MCS. Nevertheless, the adsorption performance (equilibrium, kinetics and thermodynamics process) of target pollutant may have discrepancy in the single-component or multi-component system. To our knowledge, the adsorption performance and mechanism by MCS have not been clearly elucidate for natural DOM and SOC in the single-component or bi-component system.

The aim of the present work is thus to comparatively assess the removabilities of synthetic OM and natural DOM in the single-component and bi-component systems. Salicylic acid (SA) as a typical SOC, which presents a serious environmental hazard due to its high toxicity and tendency to accumulate in the environment, was utilized as a model contaminant in this study [31], and HA is selected to represent the natural DOM. Conventional coagulation and adsorption with lab-prepared MSC as well as their combined processes were employed to remove the OM in individual SA/HA and mixed SA-HA waters. Additionally, coagulation dynamic and adsorption degradation kinetic were systematically investigated to develop a mechanism understanding of coagulant/MCS-NOM-SA interactions in the single-component and bi-component systems.

2. Materials and methods

All reagents were of analytical grade and used without further purification. Chitosan with a deacetylation degree of 80–95%, SA and glutaraldehyde were purchased from Sinopharm Chemical Reagent Co. Ltd, China. HA was purchased from Aladdin Industrial Co. Table 1 shows the physicochemical properties of SA and HA. Distilled water was used throughout the study.

2.1. Coagulation experiments

Standard jar tests were conducted on a program-controlled jar-test apparatus at room temperature. 1000 mL of test water was transferred into a beaker and involved three stages: a 90 s rapid mix at 200 rpm to disperse the coagulant evenly, a 15 min at 40 rpm coagulation stage, and 30 min settling stage. Finally, the water samples were collected from 3 cm below the surface, and zeta potential (ZP) was measured by Zetasizer Nano ZS 90 (Malvern Instruments, UK). For spectrometric measurements, SA and HA absorbance values are 295 and 254 nm, respectively. In order to avoid interference between the two organic compounds in the mixed solution, SA and HA were separated by precipitation at pH 1.5 using a 1 M HCl solution. The study has proved that HA was precipitated under acidic conditions, whereas SA was stable in the solution [15]. After the sample was precipitated for 24 h, it was filtered through 0.45 μ m membrane filter. Then, the filtered humic substance was rinsed in 0.1 M NaOH solution, and HA-dissolved solution was collected. The filtrates and SA-dissolved solution was analyzed for UV_{295} value with no further treatment; the pH of HA-dissolved solution was adjusted to pH 7 with 1 M HCl, and then UV_{254} value was analyzed.

2.2. Synthesis of magnetite (Fe_3O_4) nanoparticles

Currently, there are many chemical methods for preparing Fe_3O_4 ,

Download English Version:

<https://daneshyari.com/en/article/6579080>

Download Persian Version:

<https://daneshyari.com/article/6579080>

[Daneshyari.com](https://daneshyari.com)