



Properties of CuO nanoparticles–humic acid (CuONP–HA) flocs and subsequent effect on membrane fouling: Influence of aluminum species and solution pH



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ABSTRACT

The CuO nanoparticle (CuONP) is one of the most commonly-utilized groups of nanoparticles. The adsorption between CuONP and humic acid (HA) make it more complicated to remove both CuONP and HA from water. Results investigated from this study indicated that the properties of CuONP–HA flocs mainly depended on Al(III) species and solution pH. Al polymer (Al_p) and sol or gel species (Al_c) were appropriate for aggregating large and strong CuONP–HA flocs. Poly aluminium chloride (PAC) could aggregate more compact CuONP–HA flocs as solution pH increased and the largest CuONP–HA flocs (with size over $680\ \mu\text{m}$) was formed at solution pH of 8.0. These flocs influenced the performance of subsequent ultrafiltration membrane. In addition, aluminum species would influence the properties of CuONP–HA flocs, but show little effect on subsequent ultrafiltration membrane due to the special properties of nanoparticles.

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1. Introduction

Nanoscience and nanotechnology is widely considered as one of the most promising areas of scientific and technological development in many sectors (e.g., pharmaceutical, construction, energy, electronic medicine, and agriculture) for future decades [1]. It is widely agreed that this emerging technology will result in some socio-economic impacts as nanomaterials are being manufactured and utilized rapidly at an increasing rate. For example, engineered nanoparticles (ENPs) will inevitably be released into wastewaters and surface waters during manufacturing and waste disposal processes [2]. This may pose a health risk to aquatic and sediment organisms. ENPs could cause cell injury by damaging DNA, proteins and membranes due to their specific chemical and biological characteristics [3]. In addition, the ability of ENPs for penetrating the body and cells (e.g., via fluid-phase endocytosis and caveolae) would provide potential access for the nanoparticle-associated toxic pollutants to sites where they would not normally go [4].

ENPs generally exhibit different thermal, electronic, magnetic and optical properties from those of bulk ones because of quantum

size effect and so on. These features will shape quite different transport behavior of ENPs in unsaturated zone (e.g., vadose zone) and saturated media (e.g., aquifers) compared with the bulk ones [3]. When ENPs are released into natural water environments, they can absorb organic substances (e.g., humic acids (HA)) in aqueous solution, facilitating their transport into subsurface and ground-water environments [5].

The adsorption action between ENPs and HA would form ENPs–HA composite contaminants by the complex interplay, including electrostatic attractive and repulsive interactions, steric and van der Waals interactions. The complicated physicochemical characteristics of ENPs–HA composite contaminants were observed owing to the special interactions between HA and ENPs; this was thought to be differ from those known interactions involving soil minerals and organic compounds [6]. This would also result in the special performance of some common treating technologies for removing ENPs–HA composite contaminants. Both HA and ENPs can be partially removed by enhanced coagulation. For example, poly aluminium chloride (PAC) was able to directly precipitate HA over a broad pH range [7]. Alum coagulation could also achieve 20–80% variable removals of titanium ENPs, iron ENPs, zinc ENPs, nickel ENPs and silica ENPs [8]. In addition, enhanced coagulation combined with ultrafiltration (C-UF) seems to be an alternative to conventional drinking

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water treatment with higher removal efficiency and less membrane fouling [9]. Ultrafiltration (UF) membrane could block over 95% of nanoparticles, but membrane was severely fouled due to the aggravating cake resistance of nanoparticles [10].

The performances of enhanced coagulation and subsequent membrane filtration are significantly affected by floc properties, such as size, structure, and stability [11]. Large compact flocs have a higher settling rate that results in the treated water with lower turbidity [1], while small particles generally have lower removal efficiencies in solid/liquid separation process following flocculation [2]. Large and porous flocs will be beneficial to membrane filtration due to high permeability [12], while the fine and compact flocs would deteriorate the membrane flux [13].

The flocs properties are determined and influenced by the coagulant species, solution pH as well as the reaction between coagulant and contaminant etc. For example, the small and weak HA flocs were formed by monomeric and dimeric aluminum species [14], while sol or gel aluminum species formed large and strong HA flocs [15]. Larger HA flocs were formed under acidic coagulation pHs with less irregular boundaries or surfaces than those formed under neutral and alkaline coagulation pHs [16]. Therefore, the formation process of flocs as well as properties of ENPs should be considered to control the risk of ENPs.

Three coagulants were employed by Xu et al. to remove TiO₂ nanoparticles from water. They found the existed HA molecules played a significant role in the recovery of flocs by preventing the TiO₂ particles to aggregate together [17]. As TiO₂ flocs were broken by strong shear, the laden HA molecules on surface of TiO₂ particles were desorbed and then the fractal dimension of flocs decreased [18]. In addition, nano-sized primary particles contributed to the form of micro-flocs; this was also an important factor influencing the coagulation efficiency [19].

Amounts of papers have been focused on the coagulation of TiO₂ nanoparticles [17,20]. This technology, however, still need to be investigated to completely control the ENPs pollution. The flocs formation and properties of ENPs–HA composite contaminants were still unclear, partially due to the deviation of aggregation, transformation and dissolution behaviors from with the ENPs–HA systems. For example, Hu et al. found the deposition kinetics of magnetite nanoparticles pre-coated with HA was consistent with classic Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [21], indicating that nanoparticles suspended in water are colloids likeness system. However, Jones and Su discovered that the presence of both favorable and unfavorable Cu⁰⁰ nanoparticle interactions leads to significant deviation from DLVO theory [5]. These varied behaviors would lead to different formation processes and change the properties of ENPs–HA flocs, which would further impose an effect on the performance of coagulation and subsequent treatment processes. Few papers were reported related to these subsequent effects on performance of ultrafiltration membrane; this performance, however, is important to completely remove ENP from water with acceptable membrane fouling.

In this paper, CuO nanoparticles–HA (CuONP–HA) composite contaminant was treated by coagulation and C-UF process. CuONP is one of the most commonly-utilized groups of nanoparticles, which has emerged as potentially powerful materials in various technological applications such as antimicrobial preparations, heat transfer fluids semiconductors or intrauterine contraceptive device. Toxicity studies indicate that CuONP is more potent in both DNA damage and cytotoxicity than micrometer-sized particles [22]. As a result, their release into the environment may pose a risk to aquatic and sediment organisms [23].

The objectives of the present work are as follows: (1) to examine the influence of aluminum species and initial solution pH

on CuONP–HA flocs characteristics, and (2) to study the subsequent effect of CuONP–HA flocs on membrane fouling.

2. Materials and methods

2.1. Test water

CuONP (Kleiner new material Co. LTD, Huizhou) dispersions (size = 40 nm) were ultrasonicated twice in an ultrasonic bath (BaoDexxing Ultrasonic Co. LTD) for a cycle of 60 min (to make sure the CuONP could be dispersed homogeneous and effectively in the water sample). At the interval of the above two ultrasonic treatment processes, HA (10 mg/L) was added and mixed with CuONP dispersion under continuous magnetic stirring for 15 min to homogenize the dispersion. CuONP–HA was allowed to settle down and the sub-samples were removed from the supernatant at various time intervals to assess the stability of the dispersion.

CuONP–HA size was measured by Zetasizer 2000 (Malvern, UK). CuONP concentration and HA concentration were used to represent the content of CuONP–HA, which were measured by atomic absorption spectrophotometer TAS-990 (Beijing Purkinje General Instrument Co. Ltd., China) and TOC-VCPH analyzer (Shimadzu, Japan), respectively. The properties of water samples were: CuONP–HA size = 282.60 ± 36.80 nm, CuONP concentration = 4.00 ± 0.31 mg Cu/L, dissolved organic carbon (DOC) = 4.88 ± 0.52 mg/L, pH = 8.40, zeta potential = –13.7 mV.

2.2. Coagulants

PAC was used as coagulant for CuONP–HA removal. Stock AlCl₃ solution was prepared by dissolving 8.942 g of AlCl₃·6H₂O (A. R.) in 100 mL distilled water. Then, the predetermined dose of chemically pure Na₂CO₃ (A. R.) powder was slowly added to AlCl₃ solutions to obtain PAC solution with desired *B* (*B* = OH[−]/Al molar ratio) value at 1.0, 1.5 and 2.0. The aluminum species of three PAC samples (denoted as PAC₀₁, PAC₀₂ and PAC₀₃) were measured by a Al–Ferron timed complexation spectroscopy method [24]. The aluminum species can be classified as Al_a, Al_b and Al_c according to hydrolysis degree. The results are shown in Table 1.

2.3. Coagulation and subsequent ultrafiltration process

The coagulation test was conducted in 1.0 L plexiglass beakers using a conventional ZR4-6 laboratory stirrer jar-test apparatus. After coagulant addition, the synthetic test water (500 mL) was subjected to rapid mixing (200 rpm) for 2 min, followed by slow mixing (40 rpm) for 15 min. The coagulant dose was calculated as content of Al (mg/L).

After coagulation treatment, a dead-end batch UF unit was running in this study for subsequent ultrafiltration experiments. The coagulated water with flocs was transferred directly into a 0.3 L cylindrical filtration cell and filtered through ultrafiltration membrane under constant pressure of 150 kPa. An electronic balance (MSU5201S-000-D0, SARTORIUS AG GERMANY) connected to PC was employed to measure mass of the UF permeate. The mass data was recorded every 10 s and the flux decline with time was calculated to assess the membrane fouling. The

Table 1
The Al(III) species of PAC.

Coagulant	<i>B</i> value	Al _a (%)	Al _b (%)	Al _c (%)	Al _T (g/L)	pH
PAC ₀₁	<i>B</i> = 1.0	65.1	29.7	5.2	5.31	3.46
PAC ₀₂	<i>B</i> = 1.5	44.4	35.0	20.6	5.23	3.52
PAC ₀₃	<i>B</i> = 2.0	20.6	48.6	30.8	5.44	3.64

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