Colloids and Surfaces A 535 (2017) 96–104

Contents lists available at ScienceDirect

Colloids and Surfaces A

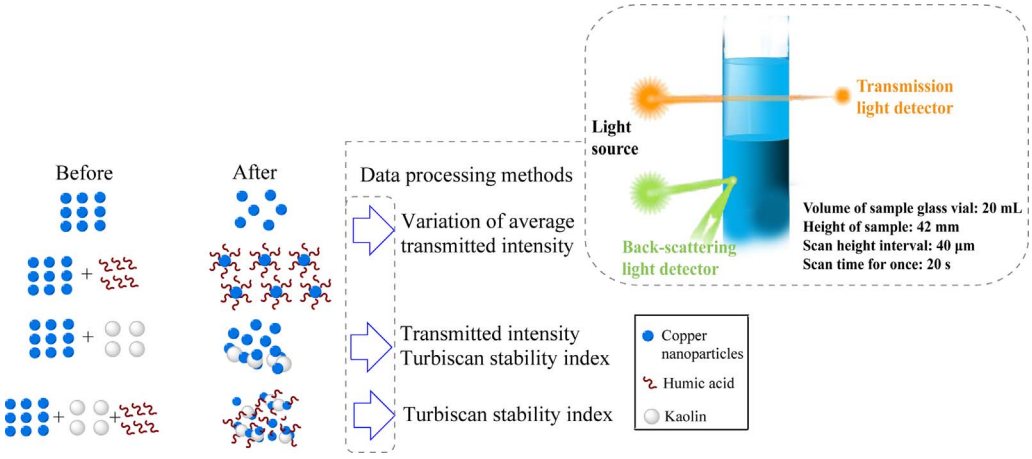
journal homepage: www.elsevier.com/locate/colsurfa

Application of Turbiscan in the homoaggregation and heteroaggregation of copper nanoparticles

Xuejiao Qi, Ya'nan Dong, Hongtao Wang*, Chen Wang, Fengting Li

State Key Laboratory of Pollution Control and Resource Reuse, Key Laboratory of Yangtze River Water Environment, Ministry of Education, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Turbiscan
Copper nanoparticles
Homoaggregation
Heteroaggregation
Kaolin

ABSTRACT

With the development of industries, copper nanoparticles (Cu NPs) have been abundantly discharged into natural water and may threaten the safety of aquatic environments. The stability (such as homoaggregation and heteroaggregation) of Cu NPs in aqueous phase may affect their toxicity. Turbiscan, including three kinds of data processing methods (transmitted intensity (T), variation of average transmitted intensity (ΔT) and Turbiscan stability index (TSI), were used to investigate the homoaggregation and heteroaggregation of Cu NPs with humic acid (HA) and kaolin in aqueous phase. T and TSI were used to analyze Cu NPs-kaolin and Cu NPs-HA-kaolin systems, respectively, whereas T and ΔT were used to analyze Cu NPs and Cu NPs-HA systems. Results showed that the stability of the system is influenced by the dissolution and sedimentation of Cu NPs, and the aggregation and sedimentation of Cu NPs, HA and kaolin. When pH is 4, the dissolution of Cu NPs is the main factor affecting the system stability. Kaolin may reduce the stability of system by sedimentation or impeding the dissolution of Cu NPs. When pH is 8, the aggregation and sedimentation of Cu NPs mainly affect the system stability. Kaolin renders the system unstable by promoting the aggregation of Cu NPs. In addition, HA improves the stability of the system by inhibiting the aggregation of Cu NPs and kaolin when pH = 4 and 8. Ionic strength reduces the

* Corresponding author.
E-mail addresses: hongtao@tongji.edu.cn, wanght010@gmail.com (H. Wang).

http://dx.doi.org/10.1016/j.colsurfa.2017.09.015
Received 19 June 2017; Received in revised form 9 September 2017; Accepted 11 September 2017
Available online 12 September 2017

stability of system by condensing electric double layer. Therefore, Turbiscan can be used to study both homoaggregation and heteroaggregation in a relatively long period (12 h), and three kinds of data processing methods can be applied based on the properties of the samples.

1. Introduction

Nanoparticles (NPs), such as copper nanoparticles (Cu NPs), titanium oxide nanoparticles (TiO_2 NPs), zinc oxide nanoparticles and cerium oxide nanoparticles have been widely used in worldwide industries, such as in cosmetics, lubricating oils and pesticides [1,2]. Approximately 10%-30% NPs were discharged into natural water in Asia, 3%-17% in Europe and 4%-19% in North America in 2013[3]. The amount of Cu NPs and CuO NPs used has recently reached 200 t/a [4]. Cu NPs may threaten the security of environment and human health [5], and can be toxic to fungus [6], aquatic and terrestrial plants [7,8], invertebrates [9], marine worms [10], mussels [10] and clams[11]. The toxicity and removal efficiency of Cu NPs are related to its fate and transportation in water and are affected by the concentration, ionic strength (IS), pH and presence of organic matter [12,13]. Therefore, it is necessary to investigate the migration and transformation of Cu NPs, including stability, aggregation, dissolution and precipitation, as well as the effects of ionic strength, pH and organic matters.

Environmental conditions, including pH, IS, natural organic matters (NOM) and other natural particles (such as kaolin and hematite), affect the stability and aggregation of NPs [14–19]. The pH affects the stability of NPs by influencing their electrical property [16,20]. High IS may improve the aggregation of NPs by condensing the thickness of the electric double layer [14,16]. NOM and clay particles can be adsorbed on the surface of NPs and affect the surface charge, thereby changing the stability [21–24]. Humic acid (HA) is a typical NOM, that affects the aggregation behavior of several NPs [25]. HA can reduce the removal efficiency of TiO_2 NPs and CuO NPs through electrostatic force of attraction, steric hindrances, and bridging effect [23,26]. HA possesses various structures and may cause different influences on the aggregation of NPs [27]. Kaolin, a clay material commonly found in natural water, can affect the aggregation behavior of NPs because of its varying electrical properties under different conditions [28]. In a previous study, kaolin was either sodium-modified to remove the calcium content [29] or was full dispersed [30].

To investigate the homoaggregation and heteroaggregation of NPs, three methods, namely, UV −spectrophotometry [31–33], dynamic light scattering (DLS) [15,24,34] and Turbiscan Tower have been used [35,36]. UV-spectrophotometry is often used to analyze samples with characteristic peaks and proper concentration range. It's usually used to study the homoaggregation in a single-phase system [14,16,18,37,38]. For heteroaggregation study, DLS is usually used to investigate the aggregation between NPs and kaolin by measuring the particle size. This method is applicable to systems wherein the size of NPs increases slowly and stabilizes within a short time, but is not appropriate for the measurement of large particles [22]. However, the particle size increases very quickly within a short time for most heterogeneous systems. Turbidimeter and laser diffraction (LD) can also be used to measure the stability of particles by measuring the turbidity and particle size, respectively [39–41]. Turbidimeter can only measure turbidity, and sometimes it's difficult to analyze stability based on turbidity [41]. LD can measure the particle size, and the heteroaggregation of nanoparticles can be determined according to the changes in their particle size. However, a continuous change in particle size cannot be measured by LD [39,40]. Turbiscan Tower can analyze the samples by evaluating the transmission light or back-scattering light. This device scans the samples every 40 μm and can obtain the data at different heights of the sample. Turbiscan can also be used to conduct long (> 12 h) continuous monitoring.

In this study, we tested Turbiscan on a typical ternary system. Turbiscan was used as the main method to analyze the homoaggregation and heteroaggregation of Cu NPs under different conditions. The effects of pH, IS, HA and kaolin were studied. We selected the most applicable data processing method to study the aggregation behavior of Cu NPs under different environment conditions.

2. Materials and methods

2.1. Chemicals

Cu NPs were purchased from Jingchun Biochemical Technology Company, Shanghai, China (Aladdin Reagent, C103843–50 G). The particle size of Cu NPs varies from 10 nm to 30 nm, and the purity is over 99%. Cu NP stock solution (500 mg/L) was prepared by adding 0.5 g Cu NPs into 1 L distilled water with ultrasonic treatment for 20 min. The Cu NP concentration used in this study was 10 mg/L, which was prepared by diluting the stock solution using distilled water.

HA was purchased from Sigma Aldrich Company (AR, 53680-10G). The main components and characteristics of HA used in this study were previously reported [42–44]. The main elements of HA are S, C, Fe and N. The weight-average molecular weight and number-average molecular weight of HA are 20,032 and 9787, respectively [42–44]. HA stock solution was prepared as follows: HA powder was first added into distilled water, and then the pH was adjusted to about 11.00 using 0.1 mol/L NaOH solution. Magnetic stirring was performed for 24 h to improve HA dissolution. Finally, the solution was filtered by 0.22 μm membrane and was stored at 4 °C. All the HA in the stock solution can pass through the membrane. The total organic carbon (TOC) of the 10 mg/L HA solution is about 4.5 mg/L. The desired TOC in this study (0.1 mg/L, 1 mg/L and 10 mg/L) was achieved through dilution.

Kaolin was purchased from Sinopharm, Shanghai, China (AR, 20020528). Given that IS was controlled by adding NaCl in this study, removing calcium was necessary to avoid interference. Sodium-modified method [29] was used to treat kaolin, and the process is shown in Fig. S1. The experimental concentration of kaolin is 50 mg/L.

NaCl was purchased from Sinopharm, Shanghai, China (AR). The desired concentrations (0, 0.1 and 1 mol/L) of NaCl were prepared by adding NaCl into distilled water. Three kinds of buffer, including $NaCH_3COO$-HCH_3COO (pH = 4, 5, 6), Na_2HPO_4-NaH_2PO_4 (pH = 7) and H_3BO_3-$Na_2B_4O_7$ (pH = 8, 9), were used to control the pH in this study. All reagents used to prepare the buffer were purchased from Sinopharm, Shanghai, China (AR).

2.2. Experiment 1: measurement of dissolved and sediment quantity and hydrodynamic diameter

In the absence of HA, 10 mg/L Cu NP suspension was prepared, and was filtered through 0.22 μm membrane to obtain the supernatant after 2 h. The concentration of Cu NPs in the supernatant was measured to find the concentration of dissolved copper. The dissolved quantity (DQ_{Cu}) of Cu NPs was calculated as Eq. (1). In the presence of HA, the sample was digested before measurement. To measure the total concentration of dissolved and suspending copper, the unfiltered suspension was digested after 2 h both in the absence and presence of HA. The sediment quantity (SQ_{Cu}) of Cu NPs was calculated as Eq. (2).

$$\text{Dissolved quantity of Cu NPs}(\%) = \frac{\text{concentration of dissolved Cu}}{\text{total concentration of Cu in initial suspension}} \quad (1)$$