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# Elimination of $TiO_2$ nanoparticles with the assist of humic acid: Influence of agglomeration in the dissolved air flotation process

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## HIGHLIGHTS

- $TiO_2$ nanoparticles in the wastewater were eliminated with humic acid assisting by dissolved air flotation.
- Interaction mechanisms between $TiO_2$ nanoparticles and humic acid were investigated.
- Humic acid could improve the $TiO_2$ removal efficiency in flotation.
- Optimum operational conditions were determined.

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## ABSTRACT

With recent advances in nanotechnology, environmental and health consequences of nanomaterial disposal merit close attention. In the search for environmentally-friendly reagent, this study investigates the use of humic acid (HA) as an assist of dissolved air flotation (DAF) in the $TiO_2$ nanoparticle (TNP) elimination. To determine mechanisms of TNPs interacting with HA, surface modification experiments were firstly carried out; thereafter, laboratory scaled DAF tests were applied to remove TNPs with HA assisting. Results of surface modification experiments showed that the zeta potential of TNP suspension system had a reversal trend due to counter ions of TNP and anions offered by the HA stock solution. The surface modified suspension was not easy to restabilize because of the close combination of TNPs and HA through sphere linkages or hydrogen-bonded surface complexes. Agglomeration took place more readily along with increasing HA concentration in the optimum dosage range (7.8-9.15 mg/L DOC). The flotation performance revealed that HA could improve the DAF efficiency in the optimum dosage range of HA. The interaction between TNPs and HA ($Na^+$-humate), including surface charge neutralization (electrostatic interactions), sphere linkages or hydrogen-bonded surface complexes, hydrophobic interactions, and van der Waals interactions, played dominant roles.



## 1. Introduction

Manufactured nanomaterials have moved well beyond laboratory settings and are now found in a variety of commercial products. Titanium dioxide ($TiO_2$) is one of the most widely used nanomaterials in consumer products including sunscreens, cosmetics, paints and other products. $TiO_2$ nanoparticles (TNPs) can be introduced into the environment from processes such as mining, $TiO_2$-enabled product fabrication, product use, product recycling and disposal to the aquatic environment [1]. TNPs become problematic and are viewed as an emerging pollutant due to their neurotoxicity to animals, capability of causing oxidative stress in human cells and genetic instability in mice. After being released into the environment, TNPs have the potential to be transported in the subsurface [2]. Subsequently nanoparticles may get into groundwater and enter into the food web through bioaccumulation [3,4]. Over the last decade, given the environmental and ecological risk of aqueous TNPs, the TNP elimination from wastewater has received a certain degree of attention though more exploration is still greatly in need. For instance, Shen's research results demonstrated the feasibility of separating colloidal $TiO_2$ (particle size 30-70 nm) from an aqueous suspension by foam flotation. It was found that coulombic interaction between $TiO_2$ particle surface and the ionic collectors plays a dominant role in their system [5]. A group of researchers in Arizona State University have dedicated to the nanoparticle (including $TiO_2$ nanoparticles) removal by biosorption in both lab-scale study [6,7]

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and full-scale municipal wastewater treatment (WWT) application [8,9]. Possible mechanisms of nanoparticle sorption to active sludge were proposed, and the fate and biological effects of nanomaterials during treatment processes were explored. Their results also showed that, for 10 investigated representative WWT plants that used a range of unit processes, the effluent titanium concentration could be controlled beneath 25 μg/L.

Brown and black biopolymers associated with soil, sediment, and particles suspended in water, and consisting of material derived from the degradation of animals and plants, are referred to as humic substances. Humic acid (HA) is one of the main components of organic carbon in natural aquatic environments [10]. These substances are a mixture of weak-acid polyelectrolytes and organic macromolecules exhibiting a large range of molar-mass distribution, substances, and functionalities. The main functional groups present in a sample of HA are carboxylic acids, alcohols, phenols, carbonyls, phosphates, sulfates, amides, and sulfides, resulting in the interaction between HA and various metal ions, hydrated metal oxides, clay minerals and organic compounds [11–14].

In recent years, research on the HA assisting the flotation processes began to attract more and more attention [15–17]. However, the mechanisms involved have not been completely understood yet, particularly with reference to the phenomena observed in alkaline media [18]. Physical and chemical properties of HA endow it with a high potential value as the flotation assist, but it has not been applied in the nanoparticle elimination via dissolved air flotation (DAF). As the particle size becomes smaller, the surface-to-volume ratio increases and it becomes advantageous to use surface-dependent properties for separation. Since foam generated by adsorption of fine particles at the interfaces is the basic driving mechanism in many dynamic separation processes such as dissolved air flotation to clarify wastewater and effluents [19,20], it is interesting to deal with the nanoparticle suspension by flotation process.

This study aims at evaluating the feasibility of using HA as an assist to eliminate TNPs in wastewater. Experiments were divided into two parts: surface modification (agglomeration) experiments, and DAF tests. The former is to identify the possible interacting mechanism between TNPs and dissolved HA molecules, while the latter is to investigate the flotation performance of removing TNPs with the aid of HA.

## 2. Materials and methods

All chemicals used in this study were analytical reagent grade products. The water used for all experiments was produced by an AQUASOURCE system, where water was filtered for particles larger than 1 μm and de-ionized trough an ion exchange resin.

### 2.1. Origin and physicochemical characteristics of the TNP suspension

Nanoparticles used for these experiments are titanium dioxide ($TiO_2$, rutile, density 3.9 g·cm$^{-3}$ (20 °C), 15% w/w) 5-30 nm, supplied by Nanostructured & Amorphous Materials, Inc, U.S.A. The particle size distribution was determined by dynamic light scattering (DLS, Nanotrac NPA250 from Microtrac, Malvern Instruments Ltd, U.K.). The average diameter of the 5-30 nm TNP is 41.6 nm, a little beyond its diameter range (5-30 nm) due to the slight aggregation.

Transmission electron microscopy (TEM, JEOL 100CX, Japan) was applied for the morphology observation and particle size estimation of TNPs. The TEM photograph denotes that TNPs in the suspension are round in shape with a coating layer which may result from certain additives added for the well dispersion. The TEM image also shows a particle size range from about 30 nm to 70 nm, validating the size measurement of DLS.

**Table 1**
Physicochemical properties of TNP suspension (0.15% w/w).

| Item | Value | Item | Value |
|---|---|---|---|
| Turbidity/NTU | 23.2 | Si/ppm | ≤0.55 |
| Zeta potential/mV | 42.0 | Mg/ppm | ≤0.45 |
| pH (Temperature/°C) | 2.96 (22.4) | Ca/ppm | ≤0.60 |
| Conductivity/mS/cm | 0.832 | Pb/ppm | ≤0.002 |

Other physicochemical characteristics of the TNP suspension measured in the work and provided by the producer are summarized in Table 1. Turbidity was measured with a 2100N-IS Turbidimeter (Hach, U.S.A.); zeta potential was analyzed by electrophoresis with a Zetasizer 2000 (Malvern Instruments Ltd, U.K.); pH was measured at ambient temperature (around 22.4 °C) with a pH-539 pH-meter (WTW, Germany) and a SenTix 41 pH-electrode; and conductivity was measured with a LF 538 conductivity meter (WTW, Germany) and a Tetracon 325 probe. The TNP suspension in this study was set to be 0.15% w/w, and an ultrasonic bath (Branson ultrasonic) was applied for 15 min to enhance dispersion before use (prior to use).

### 2.2. Characteristics of HA and HA solution

A commercial sodium salt of HA (Carl ROTH, Germany) was used in this research. HA is the alkali soluble but acid insoluble fraction of humic substances [11]. The HA stock solution was prepared as follows: 1.0 g of HA powder was dissolved in 1 L of 0.1 mol/L NaOH solution, stirred for 6 h [21,22], and finally filtered through 0.45 μm membrane to remove residual non-dissolved HA powder. The amount of HA is related to its mass in general. The milligram of either its carbon content or the dried HA sample is usually used to give the concentration of HA solution in mg/L unit [21,23,24]. In this experiment, the HA concentration was determined by the TOC analyzer (Shimadzu corporation, Japan) with regard to dissolved organic carbon (DOC), mg/L DOC. This stock solution was diluted in surface modification experiments and DAF tests, and the relationship between DOC and the dilution factor is shown in Fig. 1, from which the HA concentration of the stock solution can be inferred as 391.7 mg/L DOC. An ultrasonic bath (Branson ultrasonic) was applied for 15 minutes to enhance dispersion before use.

The surfactant properties of HA have been recognized [25–27]. As a surface modifier of TNP and also flotation assist, HA may

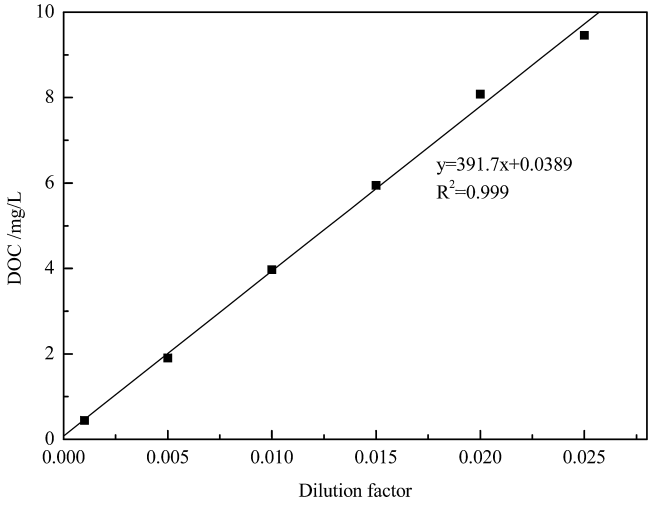


**Fig. 1.** DOC as a function of dilution factor of HA stock solution.