



# The effects of extracellular polymeric substances on magnetic iron oxide nanoparticles stability and the removal of microcystin-LR in aqueous environments

Yangyang Yang, Jun Hou\*, Peifang Wang, Chao Wang, Lingzhan Miao, Yanhui Ao, Xun Wang, Bowen Lv, Guoxiang You, Zhilin Liu, Yongxu Shao

Key Laboratory of Integrated Regulation and Resources Development on Shallow Lakes of Ministry of Education, College of Environment, Hohai University, Nanjing 210098, People's Republic of China

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## ABSTRACT

The behaviors of nanoparticles rely on the aqueous condition such as natural organic matter (NOM). Therefore the presence of NOM would influence the interaction of nanoparticles with other substances possibly. Here, microcystin-LR (MC-LR) adsorption on iron oxide nanoparticles (IONPs) was studied in an aqueous solution with different types of NOM, including extracellular polymeric substances (EPS) from cyanobacteria and alginic acid sodium salt (AASS) from brown algae. Results revealed that EPS played an important role in stabilizing IONPs and in the toxin adsorption efficiency. The stability of IONPs was heavily depended on the concentration and type of NOM, which can affect the surface charge of IONPs significantly in solution. The enhanced stability of IONPs was due to the electrostatic interactions. Adsorption kinetics and isotherm studies confirmed that NOM can affect the IONPs' adsorption efficiency, and pseudo-second-order kinetics better explained this process. The removal efficiency for MC-LR decreased in the presence of NOM (Control > EPS-M1 > AASS > EPS-M9), indicating that NOM and MC-LR compete for limited adsorption sites. The presence of NOM in a eutrophic environment stabilized the IONPs while inhibiting the MC-LR removal efficiency. This investigation emphasized the negative effect of cyanobacterial EPS on the removal of microcystins when using magnetic separation technology. And this results could also be used to model the transportation of iron minerals carrying toxic substances in aqueous environment.

## 1. Introduction

Cyanobacterial blooms in fresh and coastal water are a great ecological problem because the mass algae growth compete to consume oxygen, leading to deteriorated water quality (Caron et al., 2010; Henderson et al., 2008). Moreover, the death of cyanobacteria releases microcystins (MCs) and anatoxins, which can cause severe human health problems such as nausea, vomiting, and liver damage due to long-term contact (El-Shehawey et al., 2012; Horst et al., 2014; Nishiwaki-Matsushima et al., 1992; Yoshizawa et al., 1990). Microcystin-LR (MC-LR) is frequently monitored as one of the most toxic byproducts of cyanobacteria (Antoniou et al., 2005; Carmichael, 1992). The World Health Organization (WHO) established a limit of  $1 \mu\text{g L}^{-1}$  for MC-LR to guarantee drinking water quality (WHO, 1998).

Meanwhile, the maximum concentration of MCs in Taihu Lake, China once reached up to  $16.23 \mu\text{g L}^{-1}$  during cyanobacterial blooms (Shi et al., 2015). Efforts at dealing with this problem include eliminating toxin-containing cyanobacteria and directly reducing cyanotoxins in eutrophic water systems. Many convenient and effective methods are applied to control cyanobacterial blooms. However, some of them have obvious drawbacks. Take herbicides as an example. The death of cyanobacteria could release MCs quickly, which could remain stable for a long time in aquatic environment (Jančula and Maršálek, 2011).

Nanoscale magnetic nanoparticles (NPs) such as ferric oxides, magnetite, and hematite have been widely applied to separate and remove various organic and inorganic contaminants from water due to their specific qualities such as low cost and recyclable (Lee and Walker, 2011; Hu et al., 2005; Liu, 2006; Peng et al., 2004). Recently, magnetic

Abbreviations: MC, microcystin; NPs, nanoparticles; IONPs, iron oxide nanoparticles; NOM, natural organic matter; EPS, extracellular polymeric substances; AASS, alginic acid sodium salt; WHO, World Health Organization; SEM, scanning electron microscope; HPLC, high performance liquid chromatography; SPE, solid-phase extraction; TOC, total organic carbon; HDD, hydrodynamic diameter; DLS, dynamic light scattering; PDI, polydispersity index; FTIR, Fourier transform infrared

\* Correspondence to: College of Environment, Hohai University, 1 Xikang Road, Nanjing 210098, China.

E-mail address: [huhjyhj@126.com](mailto:huhjyhj@126.com) (J. Hou).

separation has been employed to remove cyanobacteria and harvest algal biomass (Lim et al., 2012; Prochazkova et al., 2013a, 2013b; Chai et al., 2015; Seo et al., 2014). Therefore, it is important to investigate removing toxins with magnetic NPs. NPs have more reaction sites than other common adsorbents, such as activated carbon, due to their small particle size and high surface-to-volume ratio (Hu et al., 2005; Rajagopalan et al., 2006), which gives NPs a higher possibility to interact with other contaminants in surface water (Hartmann and Baun, 2010; Antoniou et al., 2005). The stability and distribution of magnetic NPs in surface water determine their interactions with other materials. The particle properties and water chemistry conditions both influence NPs distribution and stability. Adsorption of MCs onto iron oxide particles (IONPs) may also affect the fate and transport of these contaminants (Lee and Walker, 2011). Okupnik et al. (2015) reported that n-TiO<sub>2</sub> might act as a contaminant carrier in aqueous systems, because the discharged n-TiO<sub>2</sub> would possibly interact with other compounds in aquatic environments such as MC-LR. Furthermore, particle size affects adsorption (Okupnik et al., 2015), while NPs behaviors such as aggregation and settling may change in various environmental conditions and vice versa. For example, natural organic matter (NOM), which influences the fate of NPs in aqueous systems, has also been discussed (Miao et al., 2015; Gonzalez-Estrella et al., 2013; Li and Yu, 2014; Zhang et al., 2013).

In eutrophic aquatic ecosystems, cyanobacteria blooms result in mass production of extracellular polymeric substances (EPS), which are heterogeneous organic compounds. This complex mixture is mainly excreted and secreted by *Microcystis* cells (Xu et al., 2016a). The death of cyanobacteria cells will also increase the concentration of EPS in aqueous system. Protein and polysaccharides are the main components of EPS, therein polysaccharides takes up nearly 50% of the total EPS (Sheng et al., 2010; Xu et al., 2013a; Hou et al., 2017). The range of NOM concentration that most effectively influences the NPs stability is still under discussion, and the type of NOM is also important (Lee and Walker, 2011; Zhang et al., 2013; Louie et al., 2015; Miao et al., 2015). For example, our previous study (Miao et al., 2015) investigated the role of biofilm EPS can enhance the stability and dissolution of CuO nanoparticles. And interaction mechanisms influenced by different NOM were obtained. What's more, EPS extracted from cyanobacteria can greatly hinder the aggregation of inorganic colloids (Xu et al., 2016b). However, to the best of our knowledge, the role of EPS in the adsorption of MC-LR onto IONPs in aqueous systems was rarely known. The aim of the present work was to elucidate the effect of NOM on the aggregation and sedimentation behaviors of hematite (Fe<sub>2</sub>O<sub>3</sub>) nanoparticles and further studied how the adsorption behaviors of cyanobacterial toxins (MC-LR) on hematite (Fe<sub>2</sub>O<sub>3</sub>) nanoparticles were affected in the presence of various NOM. Different types of NOM, such as cyanobacterial EPS and algal EPS were selected and investigated in batch aggregation, sedimentation and adsorption studies. Adsorption kinetics experiments were conducted to verify the adsorption mechanism. The relation between NPs stabilization and MC-LR removal efficiency in the presence of NOM was also discussed in this study. To our knowledge, this work was the first study that evaluated the contributions of EPS on the stability of IONPs and the removal efficiency of MC-LR when using magnetic separation technology.

## 2. Materials and methods

### 2.1. Preparation of IONPs and determination

A Malvern Zetasizer Nano ZSP (UK) was applied to determine the size distribution and surface charge of IONPs (maghemite nanoparticles,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, 544884-5G, Sigma-Aldrich Trading Co., Ltd., Shanghai). During the measurement for the hydrodynamic particle size, automatic attenuator was applied to adjust the transmission light intensity, and adjustment was stopped until light intensity that the detector measures below 500 kcps. The point of zero charge of IONPs was

measured by an automatic titrator (Malvern MPT-2, UK). A 200 mg L<sup>-1</sup> IONPs stock suspension was prepared by adding 0.1 g of nanopowder in 0.5 L of Milli-Q water (18 M $\Omega$  cm<sup>-1</sup>, pH 7  $\pm$  0.1), which was ultrasonicated (25 °C, 15 min, 250 W) to make the suspension homogenous before use. The morphology of IONPs was observed by scanning electron microscopy (SEM, Hitachi S-4800).

### 2.2. MC-LR acquisition and determination

Standard MC-LR (high performance liquid chromatography (HPLC)-grade; purity  $\geq$  95%, purchased from Agent Technology Co., Ltd.) isolated from *Microcystis aeruginosa* was diluted with HPLC-grade methanol to make a 1 mg L<sup>-1</sup> MC-LR stock solution and stored at -20 °C before use.

To reach the detection limit, a preconcentration of MC-LR was applied on an XBridge LC C18 via solid-phase extraction (SPE) (5  $\mu$ m, 4.6  $\times$  150 mm HPLC column, XBridge Systems, Inc., Mountain View, CA, USA). The MC-LR concentration was measured by HPLC using a 2489 UV/Visible detector (Waters, Milford, MA, USA) at 238 nm. The column oven temperature was set to 35 °C with a 10  $\mu$ L injection volume. The mobile phase consisted of 0.1% formic acid in water (solvent A, 40%) and in HPLC-grade methanol (solvent B, 60%). The elution peak for the target toxin appeared around 8.5 min. And the standard curve ( $R^2 > 0.999$ ) for MC-LR concentration was obtained ranging from 1 to 500  $\mu$ g L<sup>-1</sup> to ensure minimal system error (Wang et al., 2016).

### 2.3. Organic matter preparation

The EPS used in this experiment were extracted from *Microcystis aeruginosa* 1343 (M1) and 905 (M9) following the method described by Gao et al. (2015). Namely, the cell suspension in the early logarithmic phase was homogeneously dispersed by sonication (100 W, 30 s) and then centrifuged (1500 rpm, 5 min; H2050R-1, Xiangyi, Hunan, China) to remove the culture medium. The cells were re-suspended and centrifuged again (14,000 rpm, 20 min) to obtain the supernatant as raw EPS. Alginate sodium salt (AASS) from brown algae (Sigma-Aldrich, St. Louis, MO) representing the natural polysaccharides was added to deionized water. And then all the EPS solution and AASS solution were filtered with a 0.22  $\mu$ m membrane, and preserved at 4 °C. The total organic carbon (TOC) concentration of the NOM stock solution was measured using a TOC analyzer (Liqui TOC II, Elementar, Germany) before experiment. The concentration of NOM used in this study was TOC concentration. The content of MC-LR in the EPS solution was also measured to guarantee whether the intrinsic toxin was detectable in the solution and results indicated that the concentration of MC-LR was under the detection limit.

### 2.4. Stability and aggregation of IONPs

The settling kinetics experiments were conducted in beakers at pH 7 (NaCl, 5 mM). After adding aliquot of NOM, MC-LR, NaCl and IONPs stock solutions to cuvettes to reach the final MC-LR concentration at 25  $\mu$ g L<sup>-1</sup> and IONPs at 100 mg L<sup>-1</sup>. The final NOM concentration was set at 0, 1, 10 and 50 mg L<sup>-1</sup>. The stability and aggregation kinetics of IONPs were monitored during the whole experiment. In the settling experiments, each solution was added into a vial in turns and mixed (40 W, Vertex QL-901, Kylin-Bell) for less than 3 s, then the suspension were transferred to the cuvette immediately and quantified by a UV-vis spectrometer (TU-1901, Persee, China) due to a peak at 500 nm in the visible range continuously. The remaining suspended fraction was obtained by normalizing the absorbance ( $A/A_0$ ) to better understand the aggregation/sedimentation tendency. Where the  $A_0$  represents the initial absorbance at time 0 and  $A$  at the time  $t$ , respectively. The settling ability indicates the stability of aggregated IONPs in aqueous solution. In the aggregation kinetics studies, the hydrodynamic diameter (HDD) of IONPs was measured continuously by dynamic light scattering (DLS)

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