Chemical Engineering Journal 300 (2016) 245–253

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Removal of *Microcystis aeruginosa* by UV-activated persulfate: Performance and characteristics

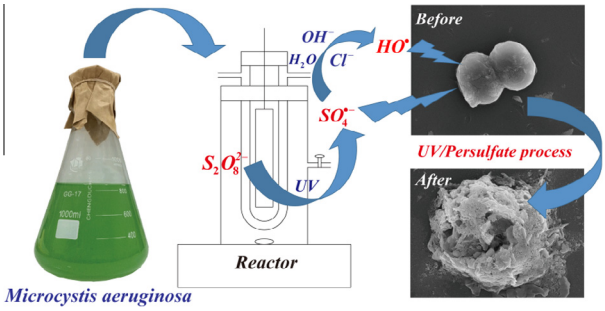
Zongping Wang [a,b], Yiqun Chen [a,b], Pengchao Xie [a,b,*], Ran Shang [c,*], Jun Ma [d]

[a] School of Environmental Science and Engineering, Huazhong University of Science and Technology (HUST), Wuhan 430074, China
[b] Key Laboratory of Water and Wastewater Treatment (HUST), MOHURD, Wuhan 430074, China
[c] Department of Sanitary Engineering, Faculty of Civil Engineering and Geosciences, Delft University of Technology, P.O. Box 5048, 2600 GA Delft, The Netherlands
[d] State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China

HIGHLIGHTS

- UV-activated persulfate was firstly applied to remove *Microcystis aeruginosa*.
- Sulfate and hydroxyl radicals contributed to the effective algae removal.
- Release and mineralization of algal organic matter were detected.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 December 2015
Received in revised form 21 April 2016
Accepted 24 April 2016
Available online 25 April 2016

Keywords:
Microcystis aeruginosa
Ultraviolet
Persulfate
Cell integrity
Algal organic matter

ABSTRACT

Cyanobacteria blooms in source waters have become a worldwide issue for drinking water production. UV-activated persulfate (UV/PS) technology was firstly applied to remove cultivated *Microcystis aeruginosa* (*M. aeruginosa*) in bench scale. The presence of persulfate significantly enhanced both cytoclasis and algal organic matter mineralization compared with UV-C inactivation alone. Around 98.2% of algal cells were removed after UV/PS process treatment for 2 h at a dosage of PS being 1500 mg/L (approximately 6 mM). Both sulfate and hydroxyl radicals were proven to contribute to the removal of algae and the loss of cell integrity. The cultivated *M. aeruginosa* in death growth phase were found to be more vulnerable to UV/PS treatment than those growing in log phase, thus a significant lower dosage of PS is needed to achieve the desired removal efficiency. This study suggested a novel application of UV/PS process in the removal of algae in source waters due to the high degradation efficiency of both algal cells and their derived organic matter.

1. Introduction

In recent decades, harmful algal blooms have frequently occurred in source waters such as lakes, rivers and reservoirs associated with eutrophication throughout the world [1–4]. *Cyanobacteria*, a prominent and ubiquitous issue, has attracted worldwide attention among the harmful algal blooms. Along with excessive algal cells, the algal organic matter (AOM) including extracellular organic matter (EOM) and intracellular organic matter (IOM) generated via metabolic excretion always cause serious water problems [5]. The AOM produced by some specific *Cyanobacteria* genera including *anabaena*, *microcystis*, *planktothrix*, etc. has been proven to comprise taste- and odor-substances, such as

* Corresponding authors at: School of Environmental Science and Engineering, Huazhong University of Science and Technology (HUST), Wuhan 430074, China (P. Xie).
E-mail addresses: pengchao.x@gmail.com (P. Xie), r.shang@tudelft.nl (R. Shang).

http://dx.doi.org/10.1016/j.cej.2016.04.125
1385-8947/

2-methylisoborneol and geosmin [6], and a wide range of toxic intracellular metabolites being suggested to cause both acute and chronic effects on hepatocyte and central nervous system of aquatic organisms and biomagnify [7–10]. Moreover, algal cells and AOM have been reported to be important precursors of vast disinfection by-products (DBPs) including traditional trihalomethanes (THMs), haloacetic acids (HAAs) and emerging nitrogenous DBPs (N-DBPs) containing high genotoxicity and carcinogenicity [11–13].

However, the conventional drinking water treatment plant only shows limited removal efficiency on algal cells due to electrostatic repulsion, surface hydrophilicity and steric effects [14–16]. The residual cells after sedimentation could adhere to the filter material surface subsequently causing filter clogging, penetrate into the water supply pipe network, and finally impair the drinking water quality [17]. It should be noted that the dissolved AOM generated via metabolic excretion is even more difficult than algal cells to be removed by using traditional coagulation–sedimentation–filtration process [18], which may adversely affect conventional water production via inhibition of coagulation [19,20].

Activated persulfate (PS) oxidation has been studied as an alternative conventional advanced oxidation process (AOP) in water treatment [21–23]. The AOP using PS is mainly achieved by the formation of reactive sulfate radical ($SO_4^{\cdot-}$, E^0 = 2.65–3.1 V) through the decomposition of PS by heat, transit metals, light, microwave or ultrasound [24–26]. Similar to hydroxyl radical ($HO^{\cdot}$, E^0 = 1.8–2.7 V), electron-transfer is expected to be a vital reaction when $SO_4^{\cdot-}$ is used to degrade organic pollutants [27]. However, $SO_4^{\cdot-}$ is more selective in comparison with hydroxyl radical in general, thus might be more effective in the degradation of some organic pollutants in the presence of radical scavengers [27]. Particularly, PS activated by zerovalent iron was recently used for disinfection of ballast water and achieved a result that the species of marine phytoplankton could be inactivated by such a process without generating harmful byproducts [28]. However, to our knowledge, activated PS technology has not been utilized for algae removal in source waters.

Among the known PS-activation processes, ultraviolet (UV) radiation at 254 nm can activate the PS to generate $SO_4^{\cdot-}$ through Eq. (1) with a quantum yield of 0.7 mol E/s [29], and the other main chemical interactions subsequently take place are summarized in Eqs. (2)–(5) [30].

$$S_2O_8^{2-} \xrightarrow{UV} 2SO_4^{\cdot-} \quad \phi = 0.7 \tag{1}$$

$$SO_4^{\cdot-} + OH^- \rightarrow SO_4^{2-} + HO^{\cdot} \quad k = 6.5 \times 10^7\ M^{-1}\ s^{-1} \tag{2}$$

$$SO_4^{\cdot-} + H_2O \rightarrow HSO_4^{2-} + HO^{\cdot} \quad k = 8.3\ M^{-1}\ s^{-1} \tag{3}$$

$$OH^{\cdot-} + S_2O_8^{2-} \rightarrow S_2O_8^{\cdot-} + OH^- \quad k = 1.4 \times 10^7\ M^{-1}\ s^{-1} \tag{4}$$

$$OH^{\cdot-} + SO_4^{\cdot-} \rightarrow HSO_5^- \quad k = 1 \times 10^{10}\ M^{-1}\ s^{-1} \tag{5}$$

Furthermore, UV process has been applied to suppress algae growth in many cases accompanied by chlorophyll bleaching and inhibition of metabolic activity [31–35]. Therefore, the UV radiation can be regarded as one of the feasible techniques to activate the PS for drinking water treatment applications.

In the present study, the performance of UV-activated PS (UV/PS) process on algae removal has been investigated using *Microcystis aeruginosa* (*M. aeruginosa*), a most abundant and common occurring cyanobacteria specie [36]. Additionally, variations in the characteristics of AOM during the UV/PS treatment were identified to further recognize the plausible by-products within the oxidation process.

2. Materials and methods

2.1. Materials

The *M. aeruginosa* (No. FACHB-909) was purchased from the Institute of Hydrobiology, Chinese Academy of Sciences, and laboratorial cultivated in a light growth incubator (Guohua Electric Co., Ltd., China). The *M. aeruginosa* was incubated under the specific growth conditions (25 ± 1 °C with a light–dark cycle of 12 h:12 h) in BG-11 media [37]. The algae solutions in log phase were harvested and diluted using ultrapure water (18.5 MΩ cm) produced from a water purifier (PCDX-J, Pincheng Co. Ltd, China). Then a final cell density of 1×10^6 cell/mL was achieved for the experiments, which mimics to the practical density in harmful algal blooms [38].

All chemicals used in the experiments were of analytical reagent grade at least. Sodium persulfate ($Na_2S_2O_8$), sodium hydroxide, hydrochloric acid, methanol (MeOH) and tert-butylalcohol (TBA) were obtained from Sinopharm Chemical Reagent Co., Ltd., China. Powdered $Na_2S_2O_8$ was added to the prepared *M. aeruginosa* solutions to achieve designated concentrations of PS each time. Solution pH was subsequently adjusted to be 7.0 which is around the pH of natural water by using HCl and NaOH at a concentration of 0.1 M.

2.2. Experimental reactor and procedures

Algae removal experiments were carried out in a cylindrical Pyrex reactor (600 mL effective volume) with a low-pressure UV lamp (254 nm, 23 W, GPH 436T5L/4, Philips Electronics Ltd., The Netherlands) (Fig. S1). An immersion well made of high purity quartz was placed inside the glass reactor. The UV lamp was fixed inside the immersion well. Cooling water was pumped through the thin annular zone of the immersion well to prevent overheating of the reaction solutions. In order to achieve a stabilized radiation intensity (measured to be 1.25 mW/cm^2 in average by the reported method [39]), the lamp was always switched on for 15 min before being placed into the reactor. A magnetic stirring apparatus at a speed of 200 rpm was used to homogenize the solutions throughout the experiments. Samples were collected via the sampling port at specific time intervals. To evaluate the reaction mechanisms in the UV/PS system, MeOH and TBA were added as scavengers for hydroxyl and sulfate radicals. Each batch of experiment was carried out in triplicate. As the formed $SO_4^{\cdot-}$ could be scavenged by high concentrations of $S_2O_8^{2-}$ and Cl^- from BG-11 media and HCl solution (Section 3.2), the presence of anions including NO_3^- and HCO_3^- at concentrations as usual in natural waters was expected to play little role in the removal of algal cells (Fig. S2). Thus, the impacts of co-existing anions would not be further discussed in the following sections.

2.3. Analytical methods

The cell concentration of *M. aeruginosa* was measured using an UV–visible spectrophotometer (U-3100, Hitachi, Japan) at a wavelength of 681 nm since the optical density at 681 nm (OD_{681}) is linearly correlated with counted cell number by microscope within the experimental range [40,41]. Thus, the removal efficiency of algal cells (ρ, %) can be calculated using Eq. (6).

$$\rho = \frac{(OD_{681_0} - OD_{681_t})}{OD_{681_0}} \times 100\% \tag{6}$$

where OD_{681_0} and OD_{681_t} were the optical density values at 0 min and t min.