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CONTENTS

Aquatic environment

Applicable models for multi-component adsorption of dyes: A review
Babak Noroozi, George A. Sorial ····· 419

Effects of sludge dredging on the prevention and control of algae-caused black bloom in Taihu Lake, China
Wei He, Jingge Shang, Xin Lu, Chengxin Fan ····· 430

Distribution characteristics and source identification of polychlorinated dibenzo-*p*-dioxin and dibenzofurans, and dioxin-like polychlorinated biphenyls in the waters from River Kanzaki, running through Osaka urban area, Japan
Masao Kishida ····· 441

Pre-oxidation with $KMnO_4$ changes extra-cellular organic matter's secretion characteristics to improve algal removal by coagulation with a low dosage of polyaluminium chloride
Lei Wang (female), Junlian Qiao, Yinghui Hu, Lei Wang (male), Long Zhang, Qiaoli Zhou, Naiyun Gao ····· 452

Identification of causative compounds and microorganisms for musty odor occurrence in the Huangpu River, China
Daolin Sun, Jianwei Yu, Wei An, Min Yang, Guoguang Chen, Shujun Zhang ····· 460

Influences of perfluorooctanoic acid on the aggregation of multi-walled carbon nanotubes
Chengliang Li, Andreas Schäffer, Harry Vereecken, Marc Heggen, Rong Ji, Erwin Klumpp ····· 466

Rapid degradation of hexachlorobenzene by micron Ag/Fe bimetal particles
Xiaoqin Nie, Jianguo Liu, Xianwei Zeng, Dongbei Yue ····· 473

Removal of Pb(II) from aqueous solution by hydrous manganese dioxide: Adsorption behavior and mechanism
Meng Xu, Hongjie Wang, Di Lei, Dan Qu, Yujia Zhai, Yili Wang ····· 479

Cr(VI) reduction capability of humic acid extracted from the organic component of municipal solid waste
Barbara Scaglia, Fulvia Tambone, Fabrizio Adani ····· 487

Off-flavor compounds from decaying cyanobacterial blooms of Lake Taihu
Zhimei Ma, Yuan Niu, Ping Xie, Jun Chen, Min Tao, Xuwei Deng ····· 495

Pollutant concentrations and pollution loads in stormwater runoff from different land uses in Chongqing
Shumin Wang, Qiang He, Hainan Ai, Zhentao Wang, Qianqian Zhang ····· 502

Atmospheric environment

Influence of fuel mass load, oxygen supply and burning rate on emission factor and size distribution of carbonaceous particulate matter from indoor corn straw burning **(Cover story)**
Guofeng Shen, Miao Xue, Siye Wei, Yuanchen Chen, Bin Wang, Rong Wang, Huizhong Shen, Wei Li, Yanyan Zhang, Ye Huang, Han Chen, Wen Wei, Qiuyue Zhao, Bin Li, Haisuo Wu, Shu Tao ····· 511

Synergistic impacts of anthropogenic and biogenic emissions on summer surface O_3 in East Asia
Yu Qu, Junling An, Jian Li ····· 520

Effect of central ventilation and air conditioner system on the concentration and health risk from airborne polycyclic aromatic hydrocarbons
Jinze Lv, Lizhong Zhu ····· 531

Emission inventory evaluation using observations of regional atmospheric background stations of China
Xingqin An, Zhaobin Sun, Weili Lin, Min Jin, Nan Li ····· 537

An improved GC-ECD method for measuring atmospheric N_2O
Yuanyuan Zhang, Yujing Mu, Shuangxi Fang, Junfeng Liu ····· 547

Adsorption of carbon dioxide on amine-modified TiO_2 nanotubes
Fujiao Song, Yunxia Zhao, Qin Zhong ····· 554

Terrestrial environment

Factors influencing the contents of metals and As in soils around the watershed of Guanting Reservoir, China
Li Xu, Tieyu Wang, Wei Luo, Kun Ni, Shijie Liu, Lin Wang, Qiushuang Li, Yonglong Lu ····· 561

Photolysis of polycyclic aromatic hydrocarbons on soil surfaces under UV irradiation
Chengbin Xu, Dianbo Dong, Xuelian Meng, Xin Su, Xu Zheng, Yaoyao Li ····· 569

Sorption and transport studies of cetyl trimethylammonium bromide (CTAB) and Triton X-100 in clayey soil
Sivaram Harendra, Cumaraswamy Vipulanandan ····· 576

Environmental biology

Effects of soil water and nitrogen availability on photosynthesis and water use efficiency of *Robinia pseudoacacia* seedlings
Xiping Liu, Yangyang Fan, Junxia Long, Ruifeng Wei, Roger Kjelgren, Chunmei Gong, Jun Zhao ····· 585

Phytoremediation potential of charophytes: Bioaccumulation and toxicity studies of cadmium, lead and zinc
Najjapak Sooksawat, Metha Meetam, Maleeya Kruatrachue, Prayad Pokethitiyook, Koravisd Nathalang ····· 596

Sulfur speciation and bioaccumulation in camphor tree leaves as atmospheric sulfur indicator analyzed by synchrotron radiation XRF and XANES
Jianrong Zeng, Guilin Zhang, Liangman Bao, Shilei Long, Mingguang Tan, Yan Li, Chenyan Ma, Yidong Zhao ····· 605

Hydrocarbon biodegradation and dynamic laser speckle for detecting chemotactic responses at low bacterial concentration
Melina Nisenbaum, Gonzalo Hernán Sendra, Gastón Alfredo Cerdá Gilbert, Marcelo Scagliola, Jorge Froilán González, Silvia Elena Murialdo ····· 613

Environmental health and toxicology

Biogeochemical reductive release of soil embedded arsenate around a crater area (Guandu) in northern Taiwan using X-ray absorption near-edge spectroscopy
Kai-Ying Chiang, Tsan-Yao Chen, Chih-Hao Lee, Tsang-Lang Lin, Ming-Kuang Wang, Ling-Yun Jang, Jyh-Fu Lee ····· 626

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Pre-oxidation with $KMnO_4$ changes extra-cellular organic matter's secretion characteristics to improve algal removal by coagulation with a low dosage of polyaluminium chloride

Lei Wang (female), Junlian Qiao*, Yinghui Hu, Lei Wang (male), Long Zhang, Qiaoli Zhou, Naiyun Gao

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Abstract

Microcystis aeruginosa was used to study the effect of $KMnO_4$ pre-oxidation on algal removal through coagulation with polyaluminium chloride (PAC). $KMnO_4$ pre-oxidation improved the coagulation efficiency of algal at a low dosage of PAC. The optimal $KMnO_4$ feeding period was in the stationary growth phase of *Microcystis aeruginosa*. $KMnO_4$ traumatized the algal cells and stimulated cellular release of organic matter, contributing to the pool of extra-cellular organic matter (EOM). $KMnO_4$ also decomposed EOM, especially small molecular weight EOM. Lower concentrations of $KMnO_4$, such as 2 mg/L, induced algae cells to produce moderate amounts of new EOM with molecular weights of 11, 280, and 1500 kDa. These relatively large molecules combined easily with PAC, promoting coagulation and removal of algae. High concentrations of $KMnO_4$ lysed algae cells and produced much high-molecular-weight EOM that did not enhance flocculation by PAC at lower dosages.

Key words: $KMnO_4$; *Microcystis aeruginosa*; strength coagulation

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Introduction

As a result of human activities, nutrients like nitrogen and phosphorus are poured into water bodies continuously, causing eutrophication (Wang, 2005). Eutrophication may lead excessive growth of some kinds of algae such as blue algae, green algae, and diatoms, creating "water blooms". Water blooms lead to oxygen depletion, phycotoxin production, and high water turbidity. These factors can inhibit growth of fish, aquatic plants, and tiny aquatic organisms, eventually causing the aquatic ecosystem to fail and harm human health (Klemas, 2012). Physical, biological, and chemical methods are used to deal with water blooms. Physical methods include water diversion to solve eutrophication, gravity vibration, whirling, centrifugation to collect algae, removal of the algal after concentration and gradual dehydration (Shen et al., 2004), and ultrasonic irradiation to control cyanobacterial blooms. Physical methods involve a long processing period, large workload, high disposal cost, and can only be applied to small water bodies. Biological methods mainly make use of aquatic organisms to compete with algae. This biomanipulation method includes controlling algae with hydrophytes and fish (Drenner et al., 1997) and algal removal by efficient microorganism. Lambert et al. (1994) discovered that some microorganisms in water play an important role in biodegradation of algae and its poisonous byproducts. However, use of biological methods is rare due to their difficulty and risk of creating greater pollution. Although this pollution is not the traditional chemical pollution, it may harm the biotic structure and biodiversity of lakes.

Chemical methods are the most widely used algal inhibition technique around the world with a long and relatively complete history of development. The main merits of chemical methods are ease of operation, low cost, rapid killing of algae, and high efficiency. Qiao et al. (2011) indicated that chemical algae removal methods are considered cost-effective and user-friendly because the existing workflow is not significantly changed, and there is no increase in the amount of large-scale equipment (Shen et al., 2011). Chemical methods can be divided into coagulative precipitation (Pieterse and Cloot, 1997) and

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chemical oxidation methods. As a contingency measure for algae removal, coagulation is one of the most cost-effective methods to treat water blooms. Chen et al. (2009) concluded that coagulation is the key step in the water treatment process for algae removal. Currently the study on coagulation is mainly concentrated in the development of efficient, harmless, and economical coagulants. Wu et al. (2011) used diatomite as a coagulant aid and got good removal efficiency for algae. Polyaluminium chloride (PAC) has a better effect on the removal of organic matter than traditional aluminum coagulants, and consumes less alkalinity (Sinha et al., 2004). Use of PAC can cut the cost and production of sludge (Van Benschoten and Edzwald, 1990). In addition, the mechanism and influencing factors of algal coagulation have been investigated, such as the effect of algal extra-cellular organic matter (EOM) on algal removal (Qiao et al., 2011).

Coagulation together with chemical pre-oxidation with ferrate, Cl_2, O_3, $KMnO_4$, and so on can promote the coagulation and sedimentation, improving the filtration efficiency. Therefore, pre-oxidation is a common method for water treatment plants during high algal growth periods. Some scholars hold that pre-oxidation inactivates algae cells, making the algae easier to sediment (Wang et al., 2005). Others think that oxidizers oxidize organic matter that would otherwise obstruct flocculation (such as humic acid), and in this way the coagulation efficiency is improved. There are also some people who believe that agents like hydrated MnO_2 arising from $KMnO_4$ treatment can adhere on the surface of algae cells to increase the coagulation efficiency (Chen and Yeh, 2005).

$KMnO_4$ is usually used as an algaecide and disinfectant, but now more attention is paid to use it as a pre-oxidizer at low concentration to enhance coagulation. Petrusevski et al. (1996) found that $KMnO_4$ pre-oxidation can improve the clearance of algae and particulate matter compared to traditional methods with a coagulant only. He also found that during this process, the MnO_2, which is the reduction product from $KMnO_4$, plays an important role in adsorbing natural organic matter and some kinds of minerals. Chen and Yeh (2005) using scanning electron microscopy to study pre-oxidation of algae by $KMnO_4$ found that MnO_2 adheres to the surface of algae cells and increases the specific gravity of the cells, so the ability of flocs to sediment increases. However, a systematic study of the effect of pre-oxidation on coagulation of algae has not been performed. In particular, effects on EOM concentration, the molecular weight after pre-oxidation, and flocculation efficiency are poorly understood.

In this study, *Microcystis aeruginosa* was used as sample to investigate the optimal treatment conditions of $KMnO_4$ as a pre-oxidant for efficient coagulation of algae with PAC as the coagulating agent. This is because currently cyanobacterial bloom happens very frequently, especially the bloom whose preponderant algae is *Microcystis aeruginosa* draws people's attention most (Mohebbi et al., 2012). In addition, the effect of $KMnO_4$ pre-oxidation on the concentration, molecular weight of EOM, and coagulation efficiency of algae were examined.

1 Materials and methods

1.1 Materials

Microcystis aeruginosa (FACHB-912) was obtained from the Wuhan Institute of Hydrobiology (China) and cultivated by BG11. The components of BG11 medium are as follows (in g/L): $NaNO_3$1.5, $K_2HPO_4{\cdot}3H_2O$ 0.04, $MgSO_4{\cdot}7H_2O$ 0.075, $CaCl_2{\cdot}2H_2O$ 0.036, citric acid 0.006, ferric ammonia citrate 0.006, Na-EDTA 0.001, Na_2CO_3 0.02, and A5 solution 1 mL/L. While the formulations of A5 solution are as follow (in g/L): H_3BO_3 2.86, $MnCl_2{\cdot}H_2O$ 1.81, $ZnSO_4{\cdot}7H_2O$ 0.222, $CuSO_4{\cdot}5H_2O$ 0.079, $Na_2MoO_4{\cdot}2H_2O$ 0.39, and $Co(NH_3)_2{\cdot}6H_2O$ 0.049. Mother liquors of *Microcystis aeruginosa* were produced by cultivation in a constant temperature incubator at 25 ± 1°C. Illumination intensity in the incubator was 1500 Lux with a light-dark cycle of 12 hr:12 hr.

The $KMnO_4$ solution was prepared by dissolving $KMnO_4$ in distilled water at a concentration of 0.25 mg/mL. Fresh solutions were used. Because 680 nm is the maximal absorbance band of *Microcystis aeruginosa* cell suspensions (Liang et al., 2005), the concentration of protococcus cultures were determined by spectrophotometer (UV-1800, Shanghai Science Instrument Company Limited, China) at 680 nm. Algae were grown to stationary phase at a concentration of 2.32×10^9 cells/L, corresponding to optical density of algal culture suspension at 680 nm (OD_{680}) = 0.1, which concentration is extremely equal to the concentration of algae that causes bloom.

For preparation of EOM and EOM-free algal suspensionscells, the algal cells in stationary phase were centrifuged at 12,000 r/min for 5 min to separate algal cells from EOM. The supernatant containing EOM was collected and diluted with distilled water to a concentration appropriate for subsequent characterization techniques. The pelleted cells, free of EOM, were resuspended in 0.5% NaCl to OD_{680} = 0.1.

1.2 Pre-oxidation procedure and algal coagulation

For coagulation only, a flocculating agent was added to a 500 mL algae suspension in a 600 mL beaker. The mixture was stirred at 250 r/min for 3 min, and then at a slower speed of 30 r/min for 10 min. After static deflection for 1 hr, a sample was collected 2 cm below the surface for analysis.

For pre-oxidation only, to the 500 mL suspension, a specified amount of $KMnO_4$ was added. The suspension was stirred at 250 r/min for several minutes, and then left to pre-oxidize for specified time.

For coagulation with pre-oxidation, to the 500 mL suspension, 2 mg/L $KMnO_4$ was added firstly, after 1 hr of pre-oxidation, 30 mg/L PAC was add. Then follow the procedure of coagulation showed above.

1.3 Analysis methods

OD_{680} before and after flocculation, and the clearance of algae (r, %) was calculated according to following equation.

$$r = \frac{(OD_{680B} - OD_{680A})}{OD_{680B}} \times 100\% \quad (1)$$

where, OD_{680B} and OD_{680A} were the optical density values before and after flocculation, respectively.

A fluorometer (PAM, WALZ, Germany) was used to measure the amount of chlorophyll *a* (Ou et al., 2012). Dissolved organic carbon (DOC) was used as a measure of the EOM (Sugiyama et al., 2005). Stock solutions of algae and supernatants from algal cultures after flocculation were filtered through 0.45 μm membranes, and a TOC analyzer (V-CPN, Shimadzu, Japan) was used to measure the DOC. Samples were filtered through 0.45 μm membranes, and the molecular weight distribution of EOM was determined by gel chromatography (Lc-10ADVP, Shimadzu, Japan) (Dzherayan et al., 2008). A scanning electron microscope (SEM515, Royal Dutch Philips Electronics Ltd., Holland) was used to observe the effects of $KMnO_4$ on algae cells (Saruwatari et al., 2011).

2 Results and discussion

2.1 Coagulation removal of $KMnO_4$ pre-oxidized *Microcystis aeruginosa*

In preliminary experiments, PAC at different concentrations was used as a coagulant with algae in different growth periods (**Fig. 1**). The highest removal efficiency was obtained with PAC at 60 mg/L, delivered in the stationary growth phase (day 21). At low concentrations of PAC, algae were not effectively removed. Therefore, PAC at a concentration of 30 mg/L was chosen to study how $KMnO_4$ pre-oxidation promotes the coagulation and removal of algae at low PAC concentrations.

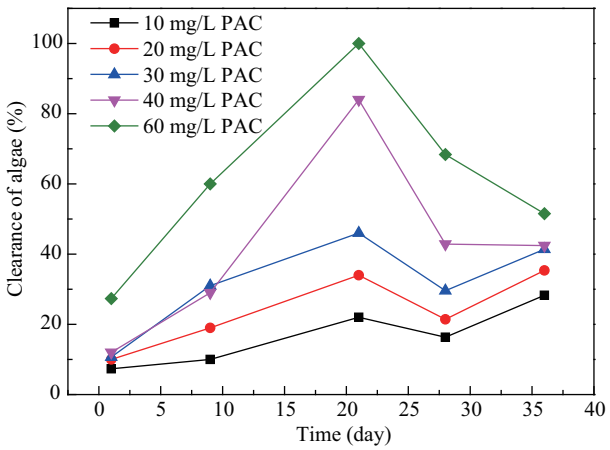

Fig. 1 Removal efficiency of algae with different concentrations of polyaluminium chloride (PAC) in different vegetation periods.

In addition, a strange phenomenon deserves special attention. At high concentrations of PAC, the removal efficiency of algal cells in the later period of algal growth decreased markedly, but at low concentrations of PAC, the decrease was not marked, even a rise could be seen. This may because that in the later period of algal growth, a lot of EOM will be secreted, EOM has two different kinds of functions on algal coagulation, one is to promote the coagulation as coagulant aid, the other one is to restrain the coagulation by battling for PAC with algae (Lei et al., 2010). We infer that for PAC with concentrations 10, 20 and 30 mg/L, the function of promoting works more than the function of restraining, so the removal efficiency of algae shows a increasing trend, but for 40 and 60 mg/L, the function of restraining surpasses the function of promoting. The detailed reasons still need further study.

Figure 2 shows the coagulation removal efficiency of algae and chlorophyll *a* in different vegetation periods with 30 mg/L PAC with or without pretreatment with 2 mg/L $KMnO_4$. Pre-oxidation improved the coagulation efficiency, especially during day 6 to day 36. On day 21, which was the stationary growth phase, the removal efficiency of algae and chlorophyll *a* reached 100% with pre-oxidation. In addition, the removal efficiency with 30 mg/L PAC was highest on day 21 day with or without $KMnO_4$ pre-oxidation. This result indicated that pre-oxidation can reduce the dosage of PAC greatly and improve the efficiency of coagulation. Zhou et al. (1997) used blue algae to carry out coagulation experiments and found that in the stationary growth phase, the flocculating agent strongly accelerated coagulation, and algal organic material played an important role. Therefore, we hypothesized that algal organic matter such as EOM may also play an important role in the pre-oxidation and coagulation processes.

2.2 Effect of $KMnO_4$ pre-oxidation on EOM concentration and molecular weight of algae solution

In order to clarify the how pre-oxidation affects the EOM pool to improve the coagulation and removal efficiency of algal cells, the concentration and molecular weight distribution of EOM after pre-oxidation were analyzed.

Figure 3 shows the change in EOM concentration (represented by DOC) of Protococcus solutions pre-oxidized with different $KMnO_4$ concentrations. At $KMnO_4$ concentrations below 4 mg/L, changes in the EOM concentration were not apparent as the $KMnO_4$ concentration increased. However, with $KMnO_4$ at 6 mg/L or higher, the EOM concentration increased substantially. A similar trend in EOM concentration occurred when the oxidation period was varied.

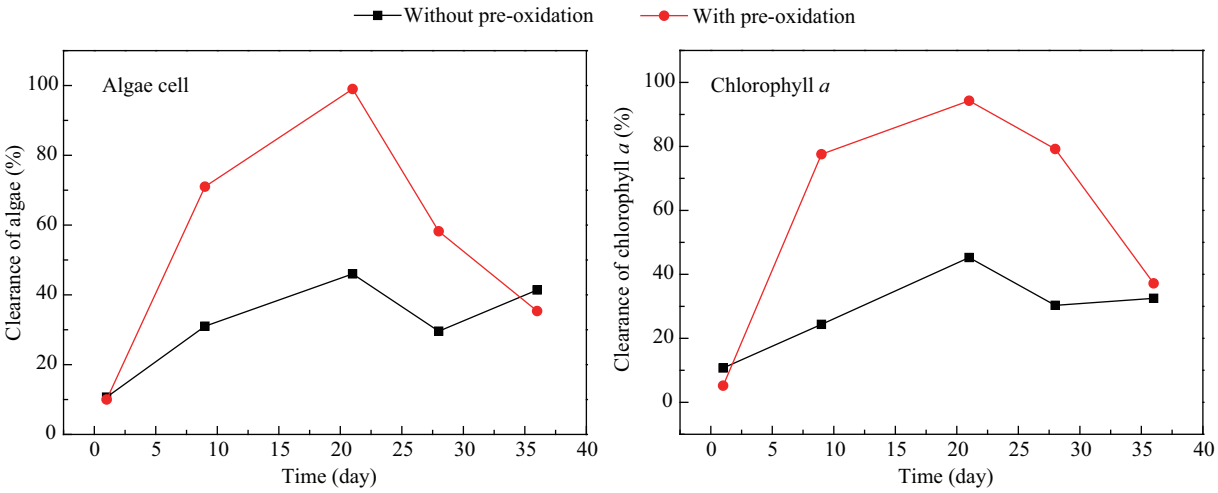

Fig. 2 Effect of $KMnO_4$ pre-oxidation on algae coagulation removal efficiency with 30 mg/L PAC in different vegetation periods.

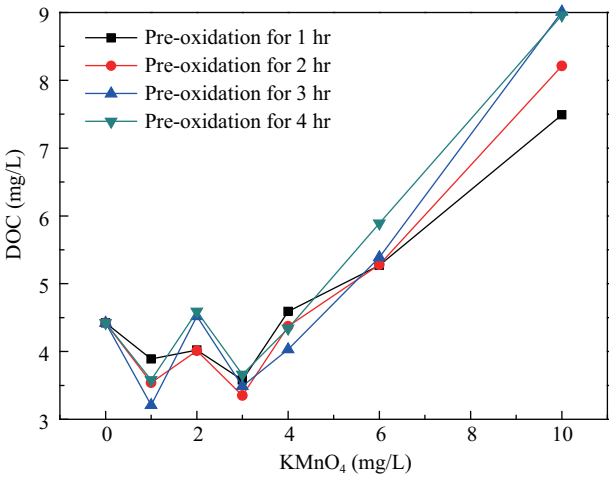

Fig. 3 Change curve of extra-cellular organic matter (EOM) concentration (represented by DOC) of protococcus solution pre-oxidized with different $KMnO_4$ concentrations.

$KMnO_4$ may impair algal cells and stimulate the secretion of EOM, leading to increased DOC. However, $KMnO_4$ also oxidizes EOM and decomposes the micro-molecular matter in EOM which may decrease the DOC. At low concentrations of $KMnO_4$, the DOC changes little. This may be the two contrasting effects of $KMnO_4$, promoting EOM secretion and decomposing EOM, cause the EOM concentration to fluctuate, thus when concentration of $KMnO_4$ change from 1 to 4 mg/L, change curve of DOC concentration shows no certain trend. To test this conjecture, we further analyzed the effect of $KMnO_4$ on algal cells without EOM and on pure EOM. In addition, here we should pay attention to the probability of the release of microcystin during the stimulating secretion of EOM by $KMnO_4$, although Ou et al. (2012) found appropriate dosage $KMnO_4$ can degrade the extra-cellular micorcystin. Therefore, studying the best amount of $KMnO_4$ to keep the relative integrity of algal cells to avoid secretion of large molecular microcystin should be carried out.

Figures 4 shows the change in DOC in algal solutions without EOM and in pure EOM solutions, pre-oxidized with different $KMnO_4$ concentrations. The concentration of DOC increased as the concentration of $KMnO_4$ increased (**Fig. 4a**). Because the EOM coating algal cells was removed in that experiment, the predominant function of $KMnO_4$ was to stimulate cells to secrete EOM. Thus, the more $KMnO_4$ was added, the more EOM was secreted, causing a corresponding increase in the DOC. In contrast, under different oxidation periods (1, 2, 3, 4 hr), the DOC steadily decreased as the $KMnO_4$ concentration increased (**Fig. 4b**). $KMnO_4$ contributes to degradation of EOM, especially degradation of the small molecular weight DOC, which can be oxidized to CO_2 causing a decrease in the DOC concentration. Because the molecular weight of EOM secreted by normal cells is probably small, the EOM can be oxidized to CO_2 easily. When treated with $KMnO_4$, damaged algae cells may release higher molecular weight EOM that is not thoroughly oxidized to CO_2. This would account for the results in **Fig. 4a**, where the DOC concentration increases with the $KMnO_4$ concentration.

The results of **Fig. 4** show that $KMnO_4$ acts on cells and EOM at the same time. When the dosage of $KMnO_4$ is low, the balance between stimulation of cells to secrete EOM and decomposition of EOM keeps the total amount of EOM almost unchanged. However, when the dosage of $KMnO_4$ is high, damage to algal cells is probably comparatively large, leading to greater secretion of EOM. As the amount of EOM secreted exceeds the amount oxidized, the total concentration of EOM begins to increase.

Numerous studies have indicated that the efficiency of coagulation relates to EOM, but it is not beneficial for coagulation if cells suffer serious damage and secrete superfluous EOM. Pivokonsky et al. (2006) reported that the influence of EOM on the efficiency of coagulation manifests itself in a manner similar to non-ionic polymers or anionic polyelectrolytes. At low concentrations, these compounds enhance particle removal efficiency by

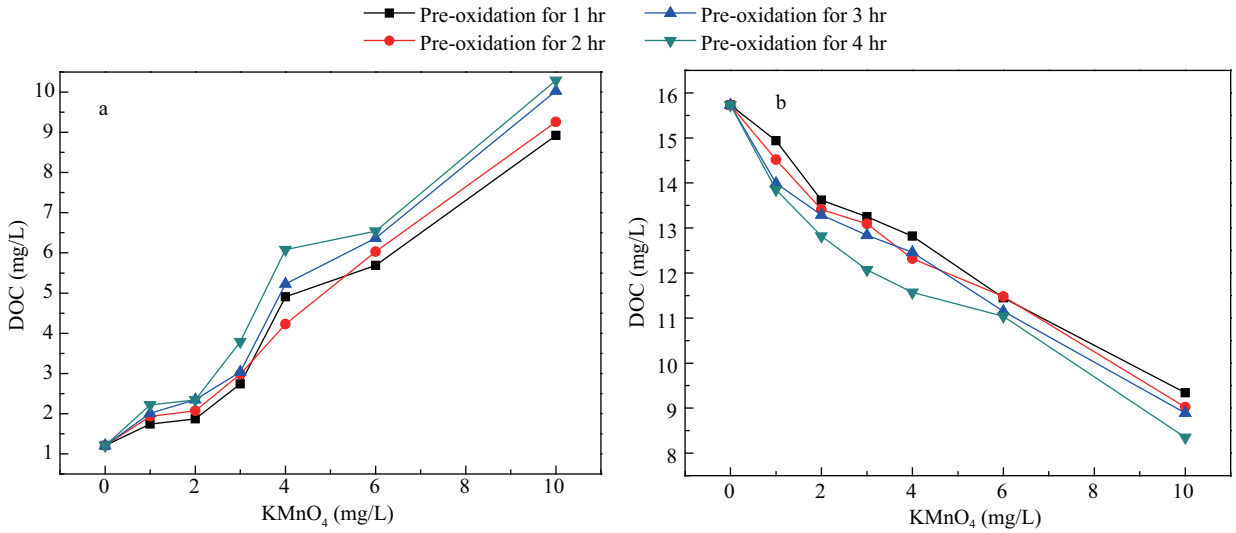

Fig. 4 Variation of DOC concentration in algae without EOM (a) and in pure EOM (b) solutions pre-oxidized with different $KMnO_4$ concentrations.

forming inter-particle bridges. In contrast, at higher concentrations, EOM inhibits coagulation of particles by increasing the negative charge on their surface, and hence, reduces contacts between particles. In the experiment, the concentration of EOM did not substantially change at low dosages of $KMnO_4$, but the efficiency of coagulation increased a lot. This is an interesting phenomenon. Some researchers have shown that hydrated MnO_2 from $KMnO_4$ acts synergistically with coagulants to improve the removal efficiency of algae. But considering the coagulating mechanism, the molecular weight of organic matter also can influence the coagulation efficiency (Pivokonsky et al., 2006; Bernhardt et al., 1985). Pivokonsky et al. (2006) pointed out that EOM with a molecular weight of 60 kDa appears to form complexes with Al(III) and Fe(III)-based coagulants, increasing the coagulant demand. Bernhardt demonstrated that higher molecular weight EOM compares with 10 kDa played a role in flocculation by reducing the required coagulant dose (Bernhardt et al., 1985). Based on these observations, we expect that although there is no remarkable change for EOM after pre-oxidization by low concentrations of $KMnO_4$, the molecular weight of EOM may change, thus influencing the coagulation efficiency. To evaluate this possibility, we further studied the molecular weight distribution of EOM after pre-oxidization with different concentrations of $KMnO_4$.

Figure 5 shows the molecular weight distribution of EOM from algae in the stationary phase before and after pre-oxidation with 2 and 6 mg/L $KMnO_4$. The EOM of algae in stationary phase comprised five fractions with molecular weights of about 200 Da, 2.2 kDa, 11 kDa, 280 kDa, and 1500 kDa (**Fig. 5a**). After pre-oxidation, the five EOM fractions in stationary phase persisted, but the relative abundance of the fractions changed. The relative abundance of the fractions with molecular weights of 200 Da and 2.2 kDa decreased from 27.6% and 42.1%, respectively, to 18.6% and 19.9%. The change may have arisen from $KMnO_4$-induced oxidation and decomposition of these two fractions to inorganic carbon. In contrast, the relative abundance of fractions with molecular weights of

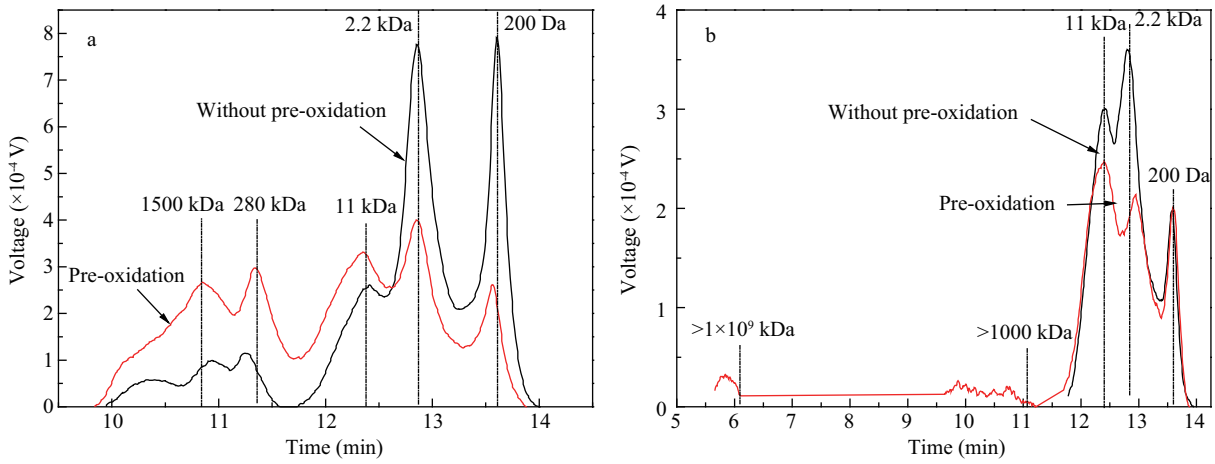

Fig. 5 Distribution of molecular weight of EOM before and after pre-oxidation by 2 mg/L (a) or 6 mg/L (b) $KMnO_4$.

11 kDa, 280 kDa, and 1500 kDa increased substantially. In particular, the 280 kDa molecular weight fraction increased from 5.3% to 21.8%. The increase of EOM fractions with relatively large molecular weights may have resulted from $KMnO_4$-induced damage to algal cells resulting in secretion of large molecular weight compounds. These larger molecules of EOM with molecular weight above 200 kDa easily combine with PAC, aiding coagulation (Henderson et al., 2006) and improving the efficiency of algae removal, possibly through adsorptive bridging.

After pre-oxidation with 6 mg/L $KMnO_4$, new material appeared with molecular weights above 200 kDa and even above 1×10^9 kDa (**Fig. 5b**). The latter molecular weight is too large to represent normal EOM, and may instead be cellular debris arising from destruction of algal cells by high concentrations of $KMnO_4$. Ma et al. (2012) have indicated that this outcome reduces the efficiency of coagulation.

To directly verify the different damage effects on algae cells from different concentrations of $KMnO_4$, we use stereoscan photography to observe cellular morphology after pre-oxidation with different $KMnO_4$ concentrations. Before pre-oxidation, the cytoderm and epicyte of algal cells were intact and the surfaces were smooth (**Fig. 6a**). After addition of $KMnO_4$, algae cells exhibited different degrees of damage (**Fig. 6b–d**). With $KMnO_4$ at 1 mg/L, tiny chasms appeared on the surface of algae cells, and some material exuded from the epicyte (shown by the arrow in **Fig. 6b**), but the cells maintained integrity. With $KMnO_4$ at 2 mg/L, the surface of the epicyte was no longer smooth. Exposure to the oxidizing agent stimulated the algal cells to secrete material (shown by the arrow in **Fig. 6c**), but the cells maintained integrity. When the amount of $KMnO_4$ increased to 6 mg/L, apparent ruptures were observed on the surface of cell with a lot of material flowing out (shown by the arrow in **Fig. 6d**). At this concentration, the algal cells were no longer spherical and appeared to be hollow.

A previous study found that the coagulation efficiency of severely damaged algae cells is low (Drikas et al., 2001). Takaara et al. (2007) also pointed out that material with excessively high molecular weight will adhere to coagulants and consume the dose of coagulant, which may reduce the efficiency of coagulation. According to our results with different EOM concentrations and molecular weight profiles, an appropriate concentration of $KMnO_4$, such as 2 mg/L, will stimulate algal cells to secrete desirable amounts of EOM with modest molecular weight, and at the same time, the relative integrity of cells will be maintained, thus favoring removal of algae by coagulation with a low dosage of PAC.

Chen and Yeh (2005) pointed that hydrated MnO_2 arising from $KMnO_4$ treatment has strong adsorption and can adhere on the surface of algae cells to change the zeta

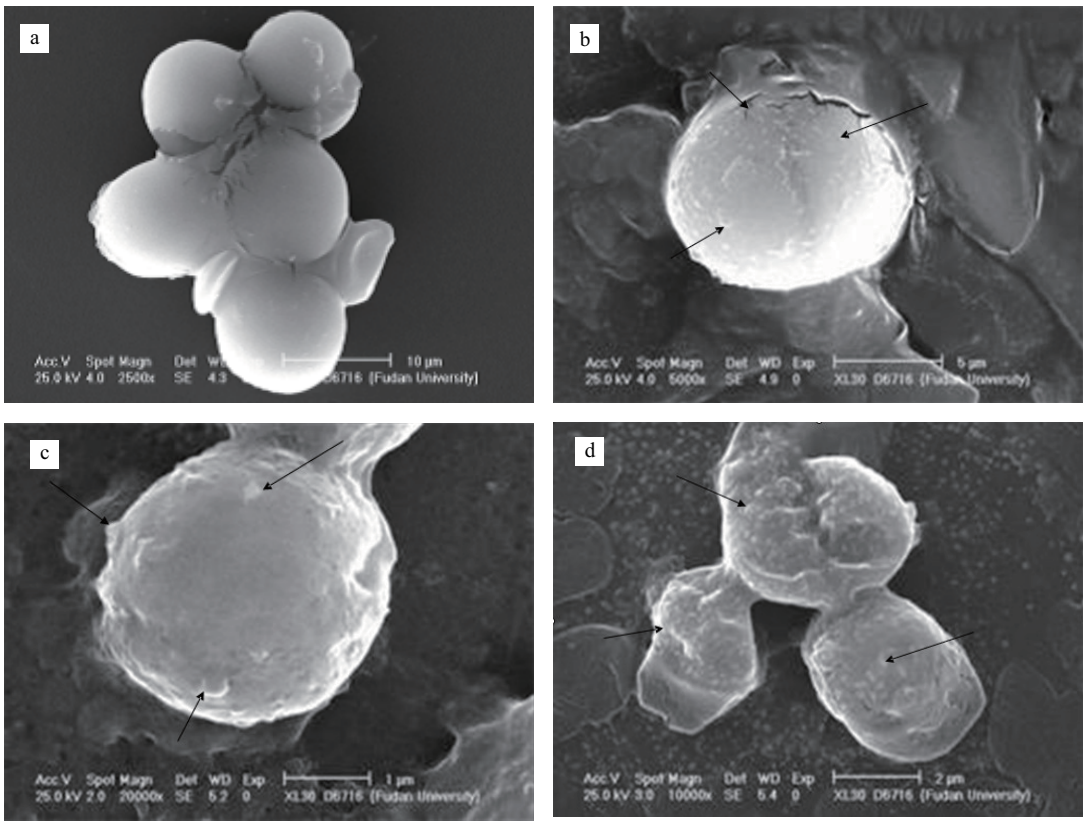

Fig. 6 Stereoscan photograph of algal cell influenced by different concentrations of $KMnO_4$. (a) protococcus; (b) $KMnO_4$ 1 mg/L; (c) $KMnO_4$ 2 mg/L; (d) $KMnO_4$ 6 mg/L.

potential of algae. And on the other hand, with the change of concentration of EOM after $KMnO_4$ treatment, the zeta potential of algae also changes. Therefore, we are trying to do some study on the corresponding effect on the zeta potential of EOM and algae.

3 Conclusions

According to the above-mentioned results and discussion, we can draw the following conclusions. (1) The use of low concentrations of $KMnO_4$ as a pre-oxidizer can improve the efficiency of removal of *Microcystis aeruginosa* by coagulation with low doses of PAC, and the optimal treatment period is during the stationary growth phase. (2) While $KMnO_4$ damages algae cells and stimulates cells to secrete more EOM, it can also oxidize and decompose existing EOM causing the concentration of EOM to decrease. When the amount of $KMnO_4$ is small (below 4 mg/L), the two contrasting effects of $KMnO_4$ cause the EOM concentration to fluctuate. When the amount of $KMnO_4$ increases to 6 mg/L or more, serious cell damage occurs and the rate of EOM secretion greatly exceeds the rate of EOM oxidation and decomposition, thus causing the EOM concentration to increase. (3) After pre-oxidation with 2 mg/L $KMnO_4$, although the EOM concentration does not change substantially and algae cells maintain relative integrity, algae cells are stimulated to secrete desirable amounts of EOM with modest molecular weights (e.g., 11, 280, 1500 kDa), thereby aiding coagulation at low dosages of PAC and improving removal of algae cells with remarkable efficiency.

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