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RESEARCH ARTICLE

Harmful algal bloom removal and eutrophic water remediation by commercial nontoxic polyamine-co-polymeric ferric sulfate-modified soils

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Abstract Harmful algal bloom has posed great threat to drinking water safety worldwide. In this study, soils were combined with commercial nontoxic polyamine poly(epichlorohydrin–dimethylamine) (PN) and polymeric ferric sulfate (PFS) to obtain PN-PFS soils for *Microcystis* removal and eutrophic water remediation under static laboratory conditions. High pH and temperature in water could enhance the function of PN-PFS soil. Algal removal efficiency increased as soil particle size decreased or modified soil dose increased. Other pollutants or chemicals (such as C, P, and organic matter) in eutrophic water could participate and promote algal removal by PN-PFS soil; these pollutants were also flocculated. During PN-PFS soil application in blooming field samples, the removal efficiency of blooming *Microcystis* cells exceeded 99 %, the cyanotoxin microcystins reduced by 57 %. Water parameters (as TP, TN, SS, and SPC) decreased by about 90 %. COD_{Mn}, PO_4-P, and NH_4-N also sharply decreased by >45 %. DO and ORP in water improved. Netting and bridging effects through electrostatic attraction and complexation reaction could be the two key mechanisms of *Microcystis* flocculation and pollutant purification. Considering the low cost of PN-PFS soil and its nontoxic effect on the environment, we proposed that this soil combination could be applied to remove cyanobacterial bloom and remediate eutrophic water in fields.

Keywords *Microcystis* · Poly(epichlorohydrin–dimethylamine) · Polymeric ferric sulfate · Soil · Flocculation

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Introduction

Cyanobacterial blooms frequently occur worldwide and pose great threat to drinking water safety by producing cyanotoxins and taste odors (Acuña et al. 2012; Zhang et al. 2013). *Microcystis* blooms are one of the most common cyanobacterial blooms in many countries, including China; Wuxi drinking water crisis in 2007 was caused by *Microcystis* blooms in Lake Taihu in East China (Liu et al. 2011). Purification of eutrophic water and inhibition of blooming algal growth in water resources are essential for cyanobacterial bloom control. However, such techniques are long-term investments for algal bloom management. Therefore, technologies should be developed for both emergent algal bloom removal and persistent improvement in water quality.

Thus far, many technologies have been developed for harmful algal bloom removal. Mechanical harvesting is a simple and safe method used in different lakes from various areas, but this method usually consumes much energy and increases the cost of algal disposal (Sim et al. 1988). Chemical reagents, such as $CuSO_4$, have been used in drinking water reservoirs to control

harmful algal bloom, and good results have been obtained (McKnight et al. 1983). However, studies have also revealed some risks; for example, excess Cu is harmful to other organisms (AWWARF 1987; Chorus and Bartram 1999). Light-shading method for harmful algal control is commonly used in small waters because shading materials are costly when used in large lakes (Chen et al. 2009a, b). In recent decades, algal flocculation using modified soil/clay materials, such as chitosan and *Moringa oleifera*, has been extensively investigated because of availability and flocculation efficiency (Li and Pan 2013; Pan et al. 2012, 2006). This method is also easy to use in lakes from different areas. However, much work is needed to prepare a properly modified material for large-scale field applications. *Moringa oleifera* is a natural material from plant seeds but lacks commercial production, which largely limited its wide application (Li and Pan 2013). Chitosan is also a quite expensive polymer (US$23,000/t) for use, and application of commercially produced chitosan may negatively affect the environment (Bautista et al. 2001). Thus, several nontoxic and inexpensive modified materials should be developed for soil/clay modification in harmful algal bloom removal.

Some algal cells, such as *Microcystis aeruginosa* (M.A.), are negatively charged in water and can easily bind to metals (e.g., Fe and Cu) and positively charged organic substances (Hadjoudja et al. 2011; Singh et al. 1998; Xue et al. 1988; Zou et al. 2006). The addition of positively charged metals, such as Al, into algal solutions can lead to cell aggregation (Johansson 2004). With the help of coiling, folding, or compression effect caused by net-shaped cationic polymers, we supposed that a cross-linking reaction may take place among cells, metals, and the polymers; then, the cell aggregation could lead to a steady flocculation process and many other pollutants could also be involved into the large algae flocs and coflocculated and biodegraded in the sediment. Both harmful algae cells and the pollutants in the water could be simultaneously removed or purified when the mechanism above functions in eutrophic waters. Poly(epichlorohydrin–dimethylamine) (PN or EPI-DMA), a commercial nontoxic cationic polyamine (Joo et al. 2003; Li et al. 2011), is relatively cheap and highly appropriate for extensive applications in the field. Polymeric ferric sulfate (PFS) is also a cheap iron-containing material used for water purification. In this study, PN was selected as the target net-shaped cationic polymers and PFS as the metal ion source. Both were mixed with soils to get a PN-PFS soil and used in harmful algae bloom treatment. The aim of this study was to develop a safe, economical, and efficient material for harmful algae bloom removal and eutrophic water remediation in the field.

Materials and methods

Materials

Soils were collected from the south offshore of Poyang Lake (116° 29′ 29.96″ E, 28° 54′ 53.54″ N), and the basic characteristics of soils are shown in Tables S1 and S2. M.A. cells were obtained from the Freshwater Algae Culture Collection of the Institute of Hydrobiology (FACHB-Collection, Wuhan, China). The M.A. cells were originally isolated from Lake Taihu (Jiangsu, China) and cultivated in BG11 medium (Gan et al. 2012). PN (MW 20 W) was purchased from Copolymer Chemical Corporation (Suzhou, China). PFS, polymeric aluminum ferric sulfate (PAFS), $NaNO_3$, KH_2PO_4, $NaHCO_3$, humic acid (HA), and salicylic acid (SA) were obtained from Shanghai Chemical Reagent Company. Other chemicals were of analytical grade.

Soil modification

The soil was dried at 100 °C and sieved through 100, 180, and 300 meshes. The soil (0.25 g) was first activated by HCl solution (pH 2.1, 3 mL) with magnetic stirring for 30 min. Before use, 0.04 g of PN and 0.04 g of PFS were added to the soil, and the mixture was diluted to 50 mL. The PN-co-PFS-modified soil mixture was finally applied in blooming water at a common dose of 40 mg/L (30.3 mg/L soil, 4.85 mg/L PN, and 4.85 mg/L PFS). The zeta potentials (Fig. 1) of the soil, PN-PFS soil, and *Microcystis* cells were measured on Malvern Zetasizer 2000.

Microcystis removal

In the experiments, the M.A. cells were diluted with BG11 medium or other experimental solutions from 2.97×10^9 to 6.0×10^9 cells/L. Modified soil was added to the M.A. cells in a 500-mL flask with constant stirring by using a glass stirring rod for 15 s. The middle water samples of the flask were collected at 15, 30, 45, 60, 90, and 120 min. During the experiments, the control group was set without the addition of modified soil, and all experimental groups were set in two parallels. To test the effects of N, P, C, and organic materials on *Microcystis* removal, we added KH_2PO_4, $NaNO_3$, $NaHCO_3$, HA, and SA to the M.A. cells with Milli-Q water before we added the modified soil. The following experimental procedure was performed the same as above.

Application

Surface water containing blooming *Microcystis* cells and other chemicals/pollutants was collected from a blooming lake in Nanchang City, Jiangxi Province, China (115° 55′ 57.35″ E, 28° 41′ 16.66″ N) in August 2014. The

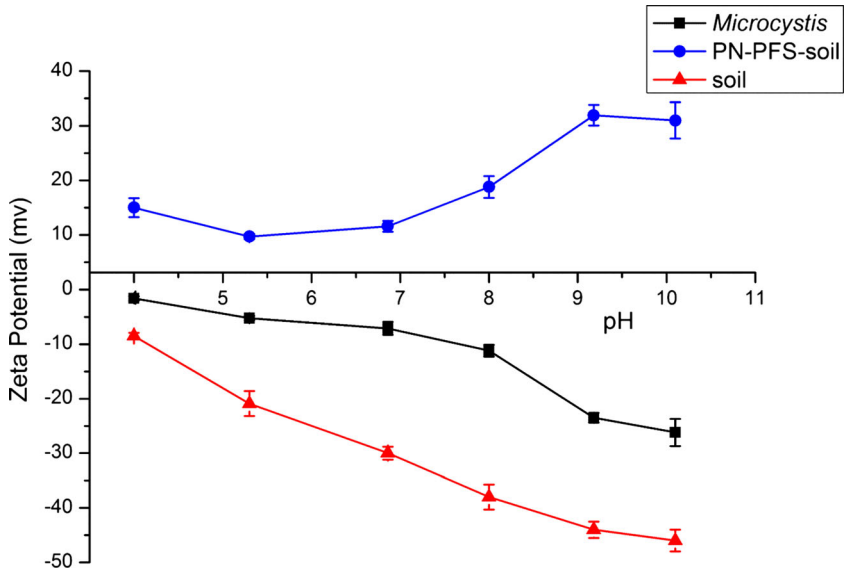


Fig. 1 Zeta potentials of *Microcystis* cells (3.02×10^9 cells/L), soil (40 mg/L), and PN-PFS soil (40 mg/L) at various pH values

application experiment was conducted in six longilineal glass cylinders (500 mL each) to simulate flocculation in a natural water column (three parallels for both control and experimental groups, Figs. S2 and S3). The density of *Microcystis* in the water was about 2.79×10^9 cells/L. PN-PFS-soil (40 mg/L) was added to water with constant stirring by using a glass stirring rod for 15 s. After 18 h, water parameters and *Microcystis* density in both control and experimental groups were analyzed.

Water analysis

Water temperature (T), pH, optical dissolved oxygen (ODO), specific conductance (SPC), and oxidation-reduction potential (ORP) were analyzed using a smart, field-ready water monitoring platform YSI-EXO (YSI Company, USA). Other water quality parameters, such as total phosphorus (TP), total nitrogen (TN), ammoniacal nitrogen (NH_3-N), and orthophosphate (PO_4-P), were analyzed as previously reported (Maske et al. 2010; Xu et al. 2008). An indirect competitive ELISA method described by Hu with a detection limit of 0.1 μg/L was also employed for cyanotoxin microcystins detection (Hu et al. 2008).

Results and discussion

Modified soil preparation and *Microcystis* removal

Microcystis removal by PN, PFS, soil (180 meshes), PN-soil, PFS-soil, PN-PFS-soil, and a soil comparison group PN-PFS soil (II) is illustrated in Fig. 2. Neither PN nor PFS alone in our experimental concentration (4.85 mg/L) exhibited an apparent flocculation effect on M.A. cells, but a slight aggregation effect was observed. The sorption characteristics of *Microcystis* species, such as M.A., are related to the chemical composition of the external surface with C, O, and P in proteins, polypeptides, and polysaccharides (Hadjoudja et al. 2011). *Microcystis* cells were negatively charged in natural water with pH of 6 to 10 because of these functional groups (Fig. 1). *Microcystis* cells could then bind with organic cations and ions, resulting in aggregation. However, the aggregation effect would not lead to flocculation without a proper gravity function. The addition of soil addresses this problem. After adding soil to the PN solution, the PN soil could steadily flocculate *Microcystis* (Fig. 2). The flocculation process by PN soil was largely accelerated with the help of PFS. The *Microcystis* removal rate of PN-PFS soil was much higher than that of PN soil, and the equilibrium time of the flocculation process of PN-PFS soil was much shorter than that of PN soil (from >120 to 45 min; Fig. 2). In general, the combination of inorganic flocculant (e.g., PFS) and organic polymer flocculant enhances netting and bridging effects, as well as the capture of pollutants via a cross-linking reaction (Shang and Zheng 2009). As a result, the synergistic effect increases flocculation efficiency; such effect has already been used in other wastewater treatment methods (Entry et al. 2003). In the present study, inorganic PFS, organic polymer PN, and soil were combined to flocculate *Microcystis* cells. Moreover, the scanning electron microscope (SEM) telegraphs are shown in Fig. 3 for demonstrating the state of *Microcystis* cells before and after PN-PFS soil treatment. A firm coiling, folding, or compression effect by netting and bridging functions of PN-PFS soil was observed; the *Microcystis* cells was captured tightly by the net-shaped polymers and flocculated to the sediment.

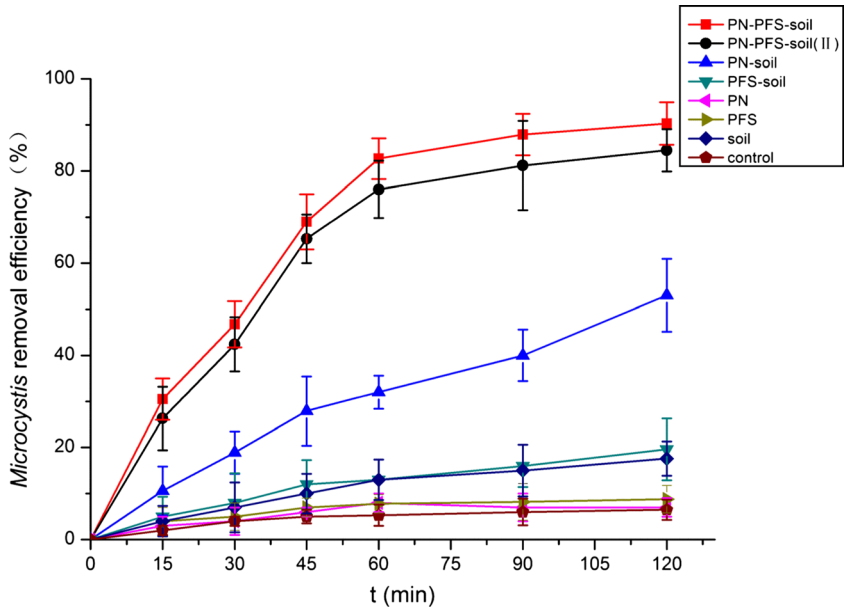


Fig. 2 *Microcystis* removal by soil, PFS, PN, and modified soils as PFS-soil, PN-soil, PN-PFS-soil, and PN-PFS soil (II) (2.97×10^9 cells/L *Microcystis*, 40 mg/L added substance), respectively

Another type of soil characterized by high organic matter content was also used as PN-PFS soil (II) for *Microcystis* removal. The results showed that the *Microcystis* removal efficiency by PN-PFS soil (II) was slightly lower than that of PN-PFS soil. When the experiment was repeated by changing PFS to PAFS, similar results were obtained (Fig. S1). The PN-PAFS soil showed an advantage over PN-PAFS soil (II). The difference in the removal efficiency may be ascribed to the soil characteristics. The soil in the experiment above contains more metals (e.g., Fe and Cu) than organic soil (II) (see Supporting Information). After acid activation was performed, the soil contained more metals that would generate more active sites for binding with algal cells. Although a previous study showed that high organic content of soil/mineral showed much advantage in organic adsorption because of more functional groups (Sathishkumar et al. 2010), this advantage was not observed during removal of algal cells in our experiment, in which these cells also contain many organic functional groups on the surface. Thus, netting and bridging effects through complexation (or binding reaction) by metals in soil or PFS with cells could be some of the key mechanisms for *Microcystis* removal.

Particle size and dosage effect on *Microcystis* removal

The soil particle size significantly influenced the removal of *Microcystis* cells (Fig. 4). The *Microcystis* removal efficiencies by soil from 180 and 300 meshes were much higher than that by soil from 100 meshes. A smaller particle size of soil indicates higher efficiency of *Microcystis* removal. The flocculation of *Microcystis* by modified soil mainly consisted of aggregation and deposition processes. At the same dose, the amount of particles of three different sizes of soil demonstrated the following order: 300 meshes >180 meshes >100 meshes. A large amount of soil particles resulted in more active sites for *Microcystis* binding, and more algal flocs were formed. Given the netting and bridging effects of PN-PFS soil, small algal flocs resulted in large algal flocs, which led to the deposition of *Microcystis*. However, in practical application, smaller particles resulted in high energy consumption and high cost; thus, large-scale application of modified soil was limited. For overall consideration of the algal removal efficiency and cost, 180-mesh soil was selected in the experiment.

The dose-dependent algal removal dynamics is shown in Fig. 5. The algal removal efficiency increased, and the removal equilibrium time was shortened, as the modified soil dose increased. During the addition of modified soil, negatively charged *Microcystis* cells were neutralized and deposited by positively charged PN-PFS soil. At a soil dose between 30 and 45 mg/L, almost all the algal cells were neutralized. A theoretical isoelectric point of the algal floc-soil system was observed around the dose of 40 mg/L (Fig. 6). As the addition of positively charged PN-PFS soil continued, the net charge of algal flocs with excess modified soil was positively charged. A repulsive interaction may occur between the positively charged algal flocs, which could obstruct algal aggregation and prolong deposition time. The *Microcystis* removal efficiency should decrease under these conditions, but this phenomenon was not observed when the modified soil dose was above the isoelectric point in our experiment (Fig. 5). The *Microcystis* cell removal efficiency improved as the dose of modified soil increased from 45 to 85 mg/L. This finding indicated that the netting and bridging effects resulting from the complexation reaction between modified soil and algal cells played an important role during the removal process. The aggregation effect from the complexation reaction may

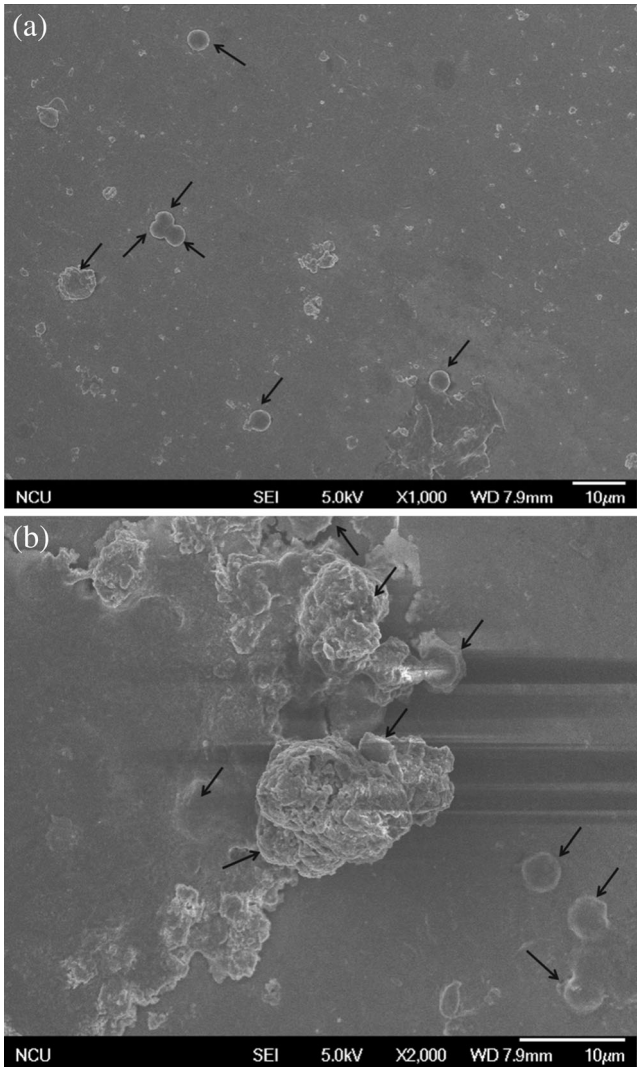


Fig. 3 SEM showing of *Microcystis* cells (**a**) before and (**b**) after PN-PFS soil treatment

overcome electrostatic repulsion, and the algal removal efficiency increased with the addition of positively charged modified soil. During application, a proper modified soil dose should be determined according to blooming algae cells density. Excess high dose of PN-PFS soil was not recommended. Previous study showed that Fe enrichment (as PFS addition in this study) in the water would stimulate *Microcystis* growth while not facilitate cyanotoxin microcystins production in the *Microcystis* cells (Sevilla et al. 2008; Xu et al. 2013). Excess PN-PFS soil addition may cause Fe enrichment in the water and stimulate the growth of *Microcystis* in the following year. Also, PN is a chemically synthesized polyamine containing C and N in it. After biodegradation in the sediment, PN would transform into nutrients as N and C for *Microcystis* growth. The use of excess PN also has a risk of stimulating *Microcystis* growth as well as increasing the COD_{Mn} of the water.

Effects of pH and temperature

The effects of pH on *Microcystis* removal are shown in Fig. 7. The *Microcystis* removal efficiency was correlated with the increase in pH. High pH conditions in the water will benefit *Microcystis* flocculation. In most blooming eutrophic waters, the pH level is >8, which can benefit algal flocculation by PN-PFS soil. Both positively charged functional groups (such as $[R\text{-}OH_2]^+$ and $[R\text{-}COOH_2]^+$) and negatively charged groups (such as $[R\text{-}O]^-$ and $[R\text{-}COO]^-$) are found in the algal surface. The amount of positively charged functional groups decreased when the pH of water increased. By contrast, the amount of negatively charged groups increased. Therefore, the net negative charge of algae increased as pH increased (Fig. 1). The charge state of the soil changed from negative to positive after modification, and the positive charge increased as the pH

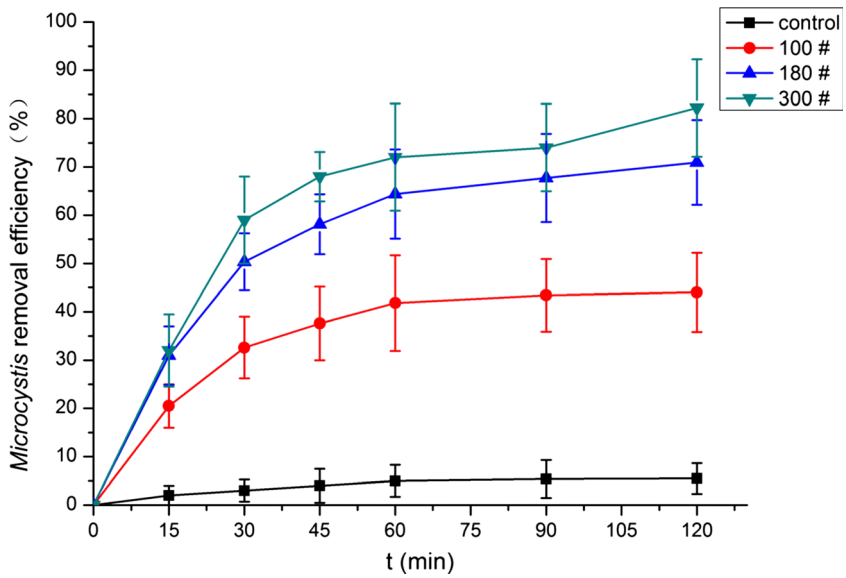


Fig. 4 *Microcystis* removal by PN-PFS soil of different soil particle sizes (3.17×10^9 cells/L *Microcystis*, 40 mg/L modified soil)

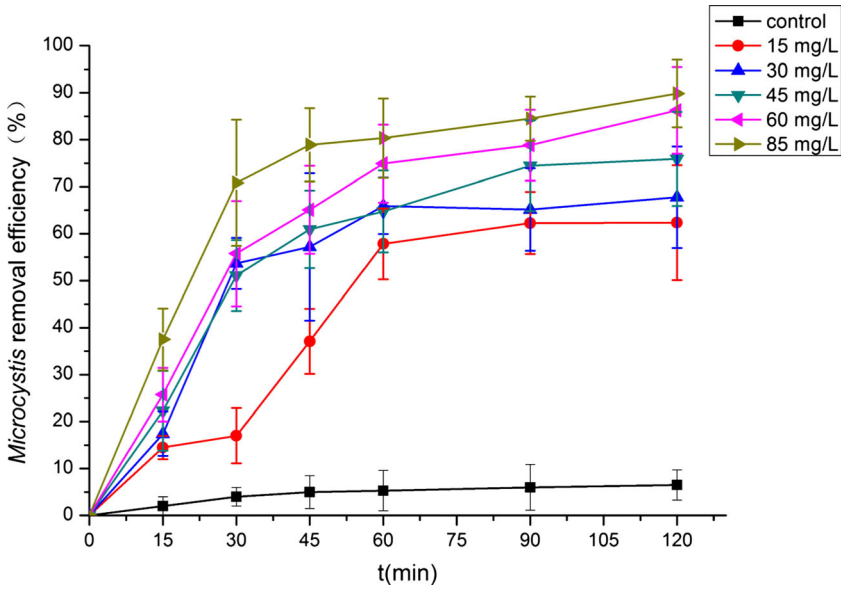


Fig. 5 *Microcystis* removal by PN-PFS soil of different doses (3.02×10^9 cells/L *Microcystis*)

elevated from pH 5.3 to pH 9.18 (Fig. 1). Consequently, the electrostatic attraction with negatively charged algal cells was enhanced, and the algal flocculation efficiency increased. Relatively high pH conditions were also suitable for Fe complexation and hydrate formation as $Fe(OH)_m{\cdot}nH_2O$ colloid. The small Fe hydrate from PFS or soil surface then generated large flocs to capture algal cells and flocculate them.

The effect of water temperature on *Microcystis* flocculation was similar to that of pH (Fig. 8). High temperature could increase efficiency of algal removal. Fe hydrate formation, binding, and complexation reaction between Fe and *Microcystis* cells, as well as cross-linking reaction among flocculants during the aggregation process, were accelerated by an increase in temperature. High temperature also decreases the viscosity of solutions, which can reduce drag around flocs by solutions during deposition (Wang et al. 2006). Algal aggregation and deposition were accelerated, which increased algal removal efficiency. However, unlike the effect of pH, high temperature shortened the equilibrium time of algal removal. The removal equilibrium times at 4, 37, and 28 °C were >120, 30, and 45 min, respectively. Cyanobacterial blooms broke out in summer or autumn, and water temperature was usually >28 °C. High temperature during the blooming season could benefit algal removal by PN-PFS soil.

Effects of N, P, C, HA, and SA in water

KH_2PO_4, $NaNO_3$, $NaHCO_3$, HA, and SA were selected to evaluate the effects of other pollutants in water (P, N, C, and organics in eutrophic water) on *Microcystis* removal by PN-

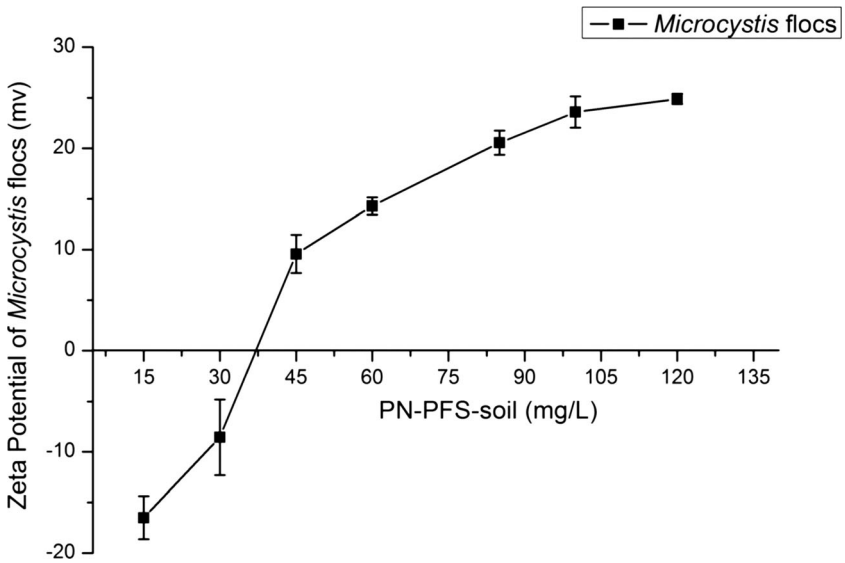


Fig. 6 Zeta potentials of *Microcystis* flocs with PN-PFS soil addition (3.02×10^9 cells/L *Microcystis*)

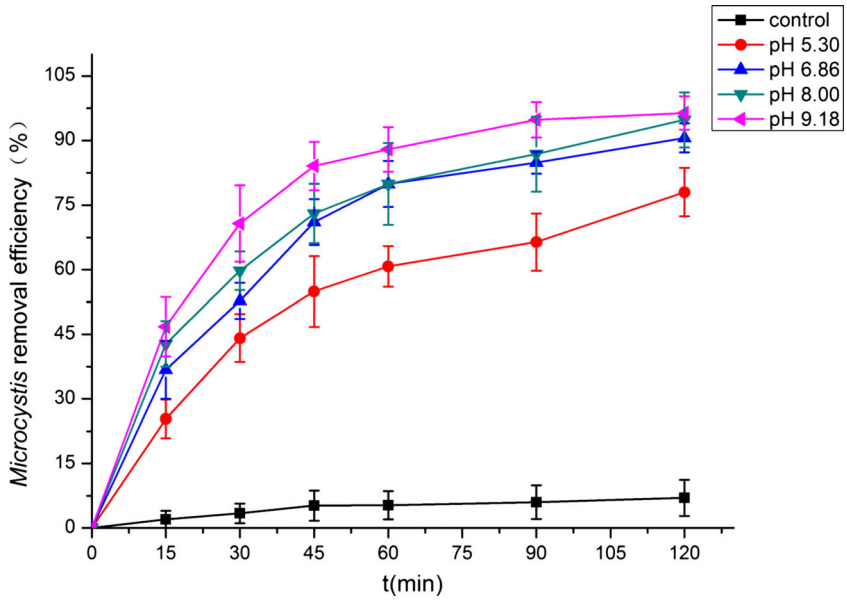


Fig. 7 *Microcystis* removal by PN-PFS soil at different pH levels (2.98×10^9 cells/L *Microcystis*, 40 mg/L modified soil)

PFS soil. The results are demonstrated in Fig. 9. The 0 group in these experiments was set by adding modified soil to *Microcystis* samples (*Microcystis* cells in Milli-Q water) without the addition of other chemicals. The experimental groups were established by replacing Milli-Q water with KH_2PO_4, $NaNO_3$, $NaHCO_3$, HA, or SA solution. The *Microcystis* removal efficiency in Milli-Q water (25 °C) of the 0 group was between 60 and 67 %, which was lower than that of the group in BG11 media (80 to 90 %) under the same experimental conditions (Figs. 7 and 8). This result suggested that chemical substances or other pollutants in natural water may play an important role in algal flocculation. The addition of C also increased the efficiency of algal removal (Fig. 9a). At a range of 2 to 50 mg/L, the *Microcystis* removal efficiency improved as the addition of C continued to increase. When the addition of C reached 200 mg/L, the *Microcystis* removal efficiency decreased. This result indicated an inhibitory effect caused by excess HCO_3^- input. A similar result was observed in the P addition group (Fig. 9b). At a concentration from 0.1 to 1.0 mg/L, the addition of P improved the *Microcystis* removal efficiency. When the P concentration was increased to 10 mg/L, the *Microcystis* removal efficiency decreased. The effect of N (NO_3-N) addition on *Microcystis* removal (Fig. 9c) was relatively different from the effects of C and P. The N addition did not show any significant effect on *Microcystis* removal at a wide concentration range (1 to 100 mg/L). The effects of hydrophobic HA (~3000 Da) and hydrophilic SA (138 Da) on *Microcystis* removal were also similar to those of C and P

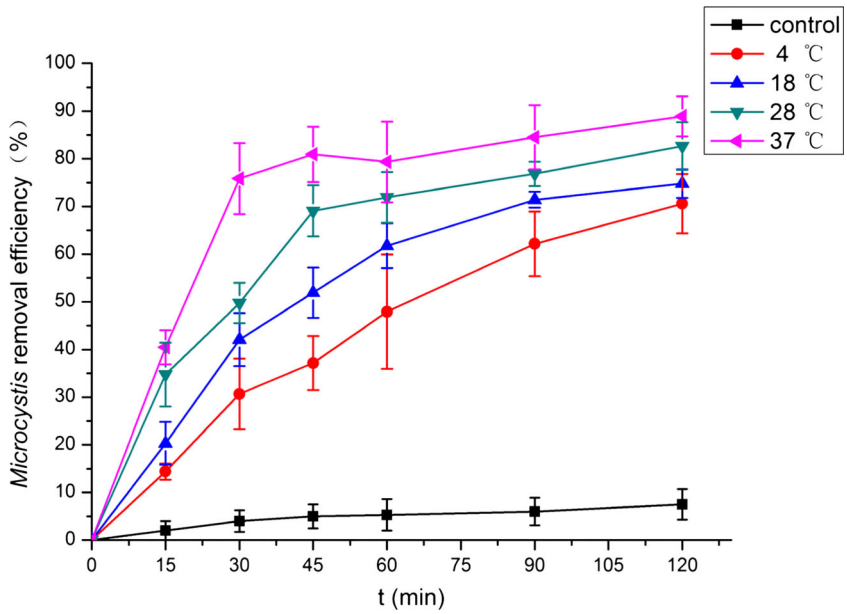


Fig. 8 *Microcystis* removal by PN-PFS-soil at different temperatures (3.02×10^9 cells/L *Microcystis*, 40 mg/L modified soil)

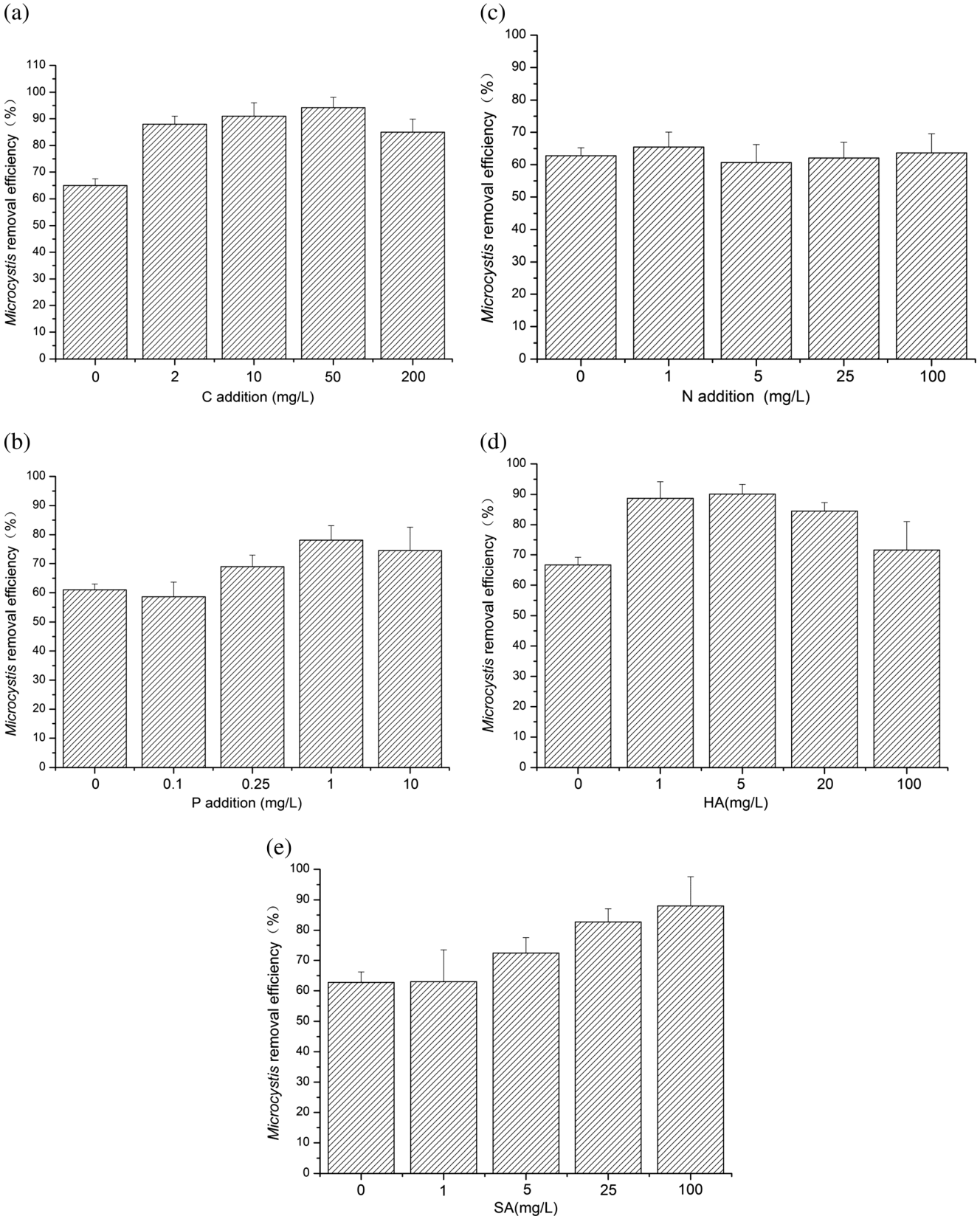
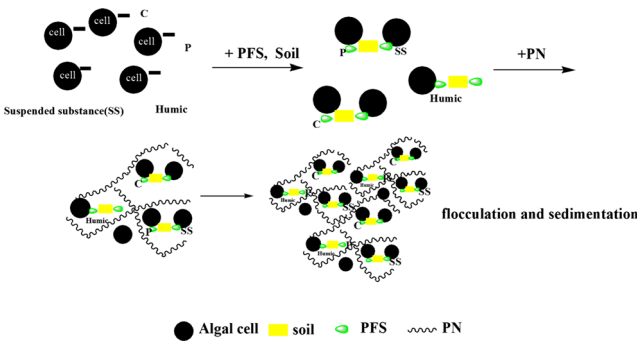


Fig. 9 *Microcystis* removal efficiency with addition of **a** C, **b** P, **c** N, **d** HA, and **e** SA (3.05×10^9 cells/L *Microcystis* density, 40 mg/L modified soil)

(Figs. 9d, e). The addition of both HA and SA below a certain concentration level increased the efficiency of algal removal.

Chemical substances in water, such as $H_2PO_4^-$, could hydrolyze PO_4^{3-}, resulting in a complexation reaction with metals in PFS or soil. Chemicals (e.g., HA and SA) also directly underwent a complexation reaction with Fe in PFS or soil (Fuentes et al. 2013). The complexation reaction resulted in a cross-linking reaction with the netting and bridging functions of PN-PFS soil to generate more netting and bridging sites for capturing and flocculating algal cells. The *Microcystis* removal efficiency then improved. However, under excess amounts of chemicals (such as $PO4^{3-}$ or HA at high concentrations), almost all of the Fe active points from PFS or soil underwent complexation to generate insoluble substances (e.g., $FePO_4$) and then deposit thereafter. The positively charged sites of modified soil were mainly occupied by PO_4^{3-} and HA^-. Flocs for algal cells were not formed, or insufficient positive charges were supplied for negatively charged algal cell neutralization (Edzwald and Tobiason 1999; Pan et al. 2006); thus, the algal removal efficiency decreased. The participation of these chemical substances or pollutants in algal cell flocculation also implicated that these pollutants (e.g., $PO4^{3-}$ or HA) were deposited to the sediments with algal flocs; as we observed that in the experimental group (P addition group, 1 mg/L) chosen randomly, the added pollutant P decreased by 44–58 % after the M.A. cells were removed by PN-PFS soil. Therefore, the concentrations of pollutants (such as C and P compounds) in water would decrease, and polluted water would be purified by PN-PFS soil (see Scheme 1). During application, the algae flocs containing various nutrients sank to the bottom of water column and were then biodegraded gradually in the sediment. However, there is a risk that part of the nutrients in the flocs may be released back to water column when the algae flocs began to collapse due to biodegradation process. Also, additional more nutrients and organics would be released into the overlying water when the sunken algae cells began to disintegrate (Ross et al. 2006). To block the nutrient diffusion from sediment to the overlying water, other supplementary measures were recommended. The study of Pan showed that after modified soil/sand



Scheme 1 Flocculation of blooming algae cells and pollutants in the water by PN-PFS soil

treatment, the capping layer addition would help to block the diffusion of nutrients from sediment to the overlying water chemically and reduce the resuspension of algal flocs (Pan et al. 2012). Also, the combination use of aquatic macrophytes would reduce the nutrients diffusion to overlying water and inhibit the growth and activity of harmful algae, offering a sustainable management of freshwaters (Chen et al. 2012; Hao et al. 2013).

Many inorganic nitrogenous compounds, such as $NaNO_3$ or KNO_3, are highly soluble in water and easily hydrolyzed into ions, including NO_3^-, Na^+, and K^+. No flocs for algal cells were formed through a complexation reaction. Thus, the presence of these substances in water did not affect *Microcystis* removal by PN-PFS soil (Fig. 9c). Complex pollutants exist in many blooming eutrophic waters in the field, which may be a positive or even advantageous factor for the application of PN-PFS soil in cyanobacterial bloom removal.

Application in natural water

The *Microcystis* density and water parameters of blooming water samples in control and experimental groups after 18 h are shown in Table 1. More than 99 % of blooming *Microcystis* was removed. And cyanotoxin microcystins was reduced by about 57 %. Microcystins were negatively charged when the pH level of the water was over 2.1 (Lawton et al. 2003). Moreover, an electrostatic attraction would take place between microcystins and positively charged modified soils. Also, Fe in PFS or soil could bind and absorb microcystins (Dai et al. 2012). TP in water decreased from 0.531 to 0.043 mg/L (reduced by 91.9 %), whereas PO_4-P decreased from 0.022 to 0.012 mg/L (reduced by 45.5 %). TN was reduced by 96.5 %, whereas the NO_3-N content in the

Table 1 Water characteristics of blooming water samples in PN-PFS soil experimental group (40 mg/L modified soil) and control group

	Control group	Experimental group
pH	7.41±0.084	7.74±0.104
T (°C)	28.6±0.152	26.5±0.118
Microcystis ($\times 10^7$ cells/L)	270±21.213	1.87±1.012
Microcystin (μg/L)	1.4±0.3	0.6±0.2
TP (mg/L)	0.531±0.006	0.043±0.012
PO_4-P (mg/L)	0.022±0.003	0.012±0.003
TN (mg/L)	19.717±6.535	0.690±0.048
NH_4-N (mg/L)	1.067±0.430	0.52±0.121
NO_3-N (mg/L)	0.104±0.019	0.097±0.031
COD_{Mn} (mg/L)	42.894±0.856	5.457±0.312
SS (mg/L)	273.333±23.352	3.667±1.756
ODO (mg/L)	4.02±0.092	7.87±0.131
SPC (μS/cm)	217.8±12.310	2.3±0.283
ORP (mv)	−14.5±6.252	127.3±15.059

experimental group was almost similar to that in the control group. Therefore, pollutants or chemicals in the water were also removed by PN-PFS soil when these pollutants participated in the algal flocculation. Other pollutants, such as NO_3-N, did not participate in flocculation, and PN-PFS-soil could not flocculate such substances in eutrophic water. The flocculation equilibrium time in natural blooming water was <15 min (Fig. S2). Almost all of the blooming *Microcystis* cells were removed within the first 15 min, which was relatively different from the data in a laboratory experiment conducted in Milli-Q water or chemical solutions (Figs. 2, 3, 4, 5, 6, 7, and 8; 80 to 90 % *Microcystis* removal within 120 min). Chemical substances in eutrophic water in the field were more complex than man-made chemical solutions, such as $NaHCO_3$ dissolved in Milli-Q water in our laboratory experiment. For example, the suspended substance (SS) concentration in the sampling water was very high (273.333±23.352 mg/L). The SS in the water was partly formed as small suspended colloids. The flocculation process continued, and the small colloids transformed into large ones, which could facilitate capture and flocculation of *Microcystis* cells. The SPC and COD_{Mn} of water also decreased mainly because of the coflocculation effect of phosphorous compounds or HA removal by modified soil. The increase in ORP may be attributed to the increase in ODO, which resulted from the reduction in blooming *Microcystis* cells in the water column. Our results were mainly obtained under static laboratory conditions, which is far different from that in the wild field. For example, in the wild lakes as Lake Taihu in China, the wind and waves sometimes mix the water and algae cells fiercely, which could pose a complicate impact on algae flocculation dynamic and efficiency (Wu et al. 2010). Thus, more environmental factors are still needed to be included in our future work. Considering the low cost of PN (US$1550/t) and PFS (US$250/t) and the nontoxic effects of these two substances on the environment, we found that PN-PFS soil exhibited great potential in cyanobacterial bloom removal and eutrophic water remediation in the field.

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