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Removal of Algae, and Taste and Odor Compounds by a Combination of Plant-Mineral Composite (PMC) Coagulant with UV-AOPs: Laboratory and Pilot Scale Studies

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Featured Application: The proposed combined plant-mineral composite coagulant with UV-AOPs can be applied to remove taste and odor compounds and its precursor (algae) in the drinking water system.

Abstract: The seasonal occurrence of algae blooms in surface waters remains a common problem, such as taste and odor (T&Os), the risk of disinfection by-products (DBPs), and disturbance to water treatment systems. The coagulation efficiency of plant-mineral composite (PMC) coagulant followed by UV-based advanced oxidation processes (UV-AOPs; UV/H_2O_2 and UV/Cl_2) was evaluated for removal of algae, turbidity, dissolved organic matters, and taste and odor compounds in lab-scale and pilot-scale tests. In the lab-scale test, coagulation process with 20 mg/L of PMC shows high removal efficiency of turbidity (94%) and algae (99%) and moderate removal efficiency of UV_{254} (51%) and geosmin (46%). The pilot test results also show good removal efficiency of turbidity (64%), chlorophyll-a (96%). After PMC coagulation process, the major water factors, which affected the performance of UV-AOPs (i.e., UV transmittance (85–94%), and scavenging factor (64,998–28,516 s^{-1})), were notably improved, and further degradation of geosmin and 2-methylisoborneol (2-MIB) was achieved in both lab-and pilot-scale tests of the UV-AOPs. The UV/H_2O_2 process shows higher removal efficiency of geosmin and 2-MIB than the UV/Cl_2 process because of the pH effect. The results confirmed that the PMC-based coagulation followed by UV/H_2O_2 process could be an effective process for the removal of algae, geosmin, and 2-MIB.

Keywords: advanced oxidation process; algae; coagulation; geosmin; 2-MIB; plant-mineral composite coagulant

1. Introduction

Harmful algae bloom problems are becoming more serious with increasing frequency and quantity in the aquatic environment [1]. Especially in drinking water sources in Korea, the problem is significant because of the impact of the harmful algal on the water treatment performance [2]. An algal bloom event results in the release of geosmin, 2-methylisoborneol (2-MIB) and taste and odor (T&O)

compounds from the algal cells during and after bloom events. The toxic and/or odorous metabolites produced by these blooms impact the drinking water quality. Odors of organic compounds produced by algae are characterized as earthy and musty/camphorous. Odors of such compounds can be easily sensed by the human nose even at extremely low concentrations, e.g., concentrations as low as 4.0 and 8.5 ng/L for geosmin and 2-MIB, respectively [3].

Various mitigation methods for algae and T&O problems have been examined, including coagulation, filtration, potassium permanganate, chlorine and ozone treatments [4–6]. Among those processes, the coagulation stage is recommended for removal of algae to ensure minimal impact on subsequent processes and prevent the release of the toxic or T&O compounds from cell destruction [7]. However, some of the most commonly used coagulants (e.g., aluminum salts) have disadvantages, such as production of harmful sludge and residuals in the treated water, which can be harmful to human health [8,9].

In practice, owing to the variability in water quality and low degradability of certain compounds, achieving the desired water quality by using a single conventional method for removal of algae, geosmin, and 2-MIB is difficult. Implementation of nontoxic and easy-to-use treatment methods to protect drinking water from algal-bloom-related problems is needed. Therefore, the water industry is exploring alternatives to replace Al-based coagulants and ways to strengthen methods that combine coagulation and advanced oxidation processes (AOPs). One effort that has been made in this context is the investigation of the use of a new coagulant that is based on a plant–mineral composite (PMC) for water treatment [10], which was selected to reduce the aluminum sludge and residuals and evaluated for treatment of algae and dissolved organic matters (DOMs) in a lab-scale batch system and a pilot-scale flowing system (109 m^3/h). The pilot facility was installed at a water intake station from Han-river in Korea. The PMC-based coagulant consists of mixtures of indigenous plant extracts (e.g., *Camellia sinensis*, *Quercus acutissima*, and *Castanea crenata*) and minerals (e.g., loess, quartz porphyry, and natural zeolite) [10]. In reservoir water treatment, PMC performance was found to be effective in removing chlorophyll-a (88–98%), phytoplankton (84–92%) and zooplankton [11]. Moreover, about 70% removal efficiency of turbidity and suspended solids was also reported in the reservoir water [11]. In the present study, the algae and its metabolite removal efficiencies in the drinking water system of PMC based coagulation process were evaluated. For the case that required higher removal efficiency of T&O compounds, UV based AOPs, i.e., UV/H$_2$O$_2$ and UV/Cl$_2$ processes, were also evaluated as a following processes of the PMC coagulation process. The geosmin and 2-MIB removal efficiencies could be enhanced through several options like simultaneous application of various AOPs, achieving safety and subsequent suitability of the drinking water [12,13]. UV-based AOPs are well-established processes which have been implemented worldwide and have distinct benefits for simple installation and small footprint.

The aim of this study was (1) to evaluate the PMC for removal of algae, turbidity, dissolved organic matter and mechanism of coagulation; (2) to evaluate the combination process of PMC coagulation with UV-based AOPs to remove T&O compounds.

2. Materials and Methods

2.1. Reagents and Materials

All reagents used were of analytical grade, unless mentioned otherwise. Geosmin (>97%) and 2-MIB (>98%) dissolved in methanol were purchased from Dalton Pharma Services (Toronto, ON, Canada) and diluted in deionized water for further use. Sulfuric acid (98.08%) and hydrogen peroxide (H$_2$O$_2$; 30 wt % solution) were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan) and Sigma-Aldrich Korea (Seoul, Korea), respectively. HCl (30%) and sodium chloride (>99%) were purchased from Duksan Chemical Co., Ltd. (Ansan, Korea). The PMC-based coagulant that consisted of silicate (20%), barleystone (20%), loess (10%), kaolin (3%), sericite (3%), and zeolite (4%) and extracts

from chestnut (6.5%), sawtooth oak (6.5%), green tea plant (6.5%), persimmon (6.5%), ash tree (6.5%), and pine (6.5%) volume% was from MCE Korea and K-water (Hongseong-gun, Korea).

2.2. Experimental Procedure

2.2.1. Lab-Scale Experiment

Raw water was collected at the pilot plant site (Han River, South Korea). The raw water was stored at 4 °C immediately after collection. The jar test experiment was conducted at 22 to 25 °C.

Anabaena sp. (AG10279) was obtained from the Korean Type Culture Collection (KTCC). *Anabaena* sp. was cultured in a 250 mL Erlenmeyer flask with a BG-11 media and under culture conditions of a constant temperature of 25 °C, light exposure for 12 h (150 $\mu mol \cdot m^{-2} \cdot s^{-1}$) and dark intervals for 12 h with a shaking speed of 150 rpm. To examine the algae removal efficiency of the PMC-based coagulant, a known amount of *Anabaena* sp. culture was mixed with raw water collected from the Han River. A water sample for lab-scale tests was prepared by injecting *Anabaena* sp., into the raw water collected from the influent of the pilot system. To ensure stable algae concentration, we monitored the optical density at 680 nm (OD_{680}) of the test water using a spectrophotometer [14]. The OD_{680} of the sample solution was stable after 6 h, and the initial concentration of chlorophyll-a was measured as 97.1 mg/m^3. Other parameters of the tested water are listed in Table 1.

Table 1. Water quality parameters of raw water used in the lab-scale and pilot-scale tests.

Parameters	Lab-Scale Test	First Pilot-Scale Test	Second Pilot-Scale Test
Turbidity (NTU)	4.6	1.1	15.6
DOC (mg/L)	3.4	0.9	0.8
UV$_{254}$ (cm^{-1})	0.034	0.015	0.027
pH	7.8	6.9	6.7
chlorophyll-a (mg/m^3)	97.1	0.5	0.7
Target chemicals	134.6 ng/L geosmin 159.0 ng/L 2-methylisoborneol (2-MIB)	100.0 ng/L geosmin 80.0 ng/L 2-MIB	100.0 ng/L geosmin 80.0 ng/L 2-MIB

The coagulation process was conducted using a programmable jar tester to determine the optimum dose of PMC for the removal of algae, turbidity, and organic matters from the incident water of the pilot system. The PMC was added to 1 L of raw water in a 1 L beaker. The addition of PMC was followed by rapid mixing at 140 rpm for 1 min, then slow mixing at 40 rpm for 59 min. These conditions were determined to simulate the pilot-system. After allowing the contents in the beaker to settle for 30 min, samples for water quality measurements were collected from approximately 3 cm below the water surface. Varying PMC-based coagulant dose, with five levels (0, 5, 10, 20, 40, and 70 mg/L) were evaluated for algal cells, turbidity, dissolved organic carbon (DOC), and UV$_{254}$ removal. The zeta potentials of the coagulated samples with varying doses of coagulant were also measured.

The photodegradation experiments were carried out using a bench-scale quasi-collimated beam apparatus [15] equipped with two 11-W low-pressure lamps (Philips, Amsterdam, The Netherland), which primarily emit light at 253.7 nm. A 50 mL geosmin and 2-MIB aliquot was placed in a Petri dish at a depth of about 0.786 cm [15–17]. The solution was stirred using a cross-shaped stirring bar with a diameter of 1 cm to ensure that it was homogenously exposed to UV light, and the solution is well mixed in the system. The UV irradiance (mW/cm^2) was determined using the peroxide actinometry method with a calibrated radiometer equipped with a UV 254 detector (UVX Radiometer; UVP, Upland, CA, USA) at the height of the surface of the Petri dish [15,17]. The average incident irradiance across the surface of the solution was determined using a Petri factor and a reflection factor [15].

2.2.2. Pilot-Scale Experiment

Pilot-scale experiments were conducted in a water treatment plant (WTP) intake station during late spring (April and May) and summer (July), which takes raw water from Han-river in Korea.

To examine the coagulation efficiency of PMC-based coagulant at pilot-scale (109 m^3/h), varying doses of the PMC-based coagulant (0, 10, 20, 30, and 40 mg/L) were evaluated for chlorophyll-a, turbidity, and UV_{254} removal. Online chlorophyll-a concentration measurement was carried out using a PLC automatic control system (Namyangju, Korea). The concentrations of chlorophyll-a in the raw water ranged from 2.3 to 156 mg/m^3.

After the PMC-based coagulation process, the treated water was branched to conduct the UV AOPs experiments. The flow rate in UV system was around 1.8 m^3/hr, and geosmin, 2-MIB were spiked into the influent of the UV reactor. The UV reactor was a LPA15 system with one low-pressure amalgam lamp rated at 871.8 mJ/cm^2. The contaminant and oxidant (i.e., hydrogen peroxide and chlorine) stock solutions were injected into the UV influent pipe through separate injection ports. The effluent sampling port was sufficiently far downstream from the injection ports to ensure that the stream was well mixed before reaching the sampling port and that representative samples were collected. The schematic design of the combined treatment is shown in Figure 1.
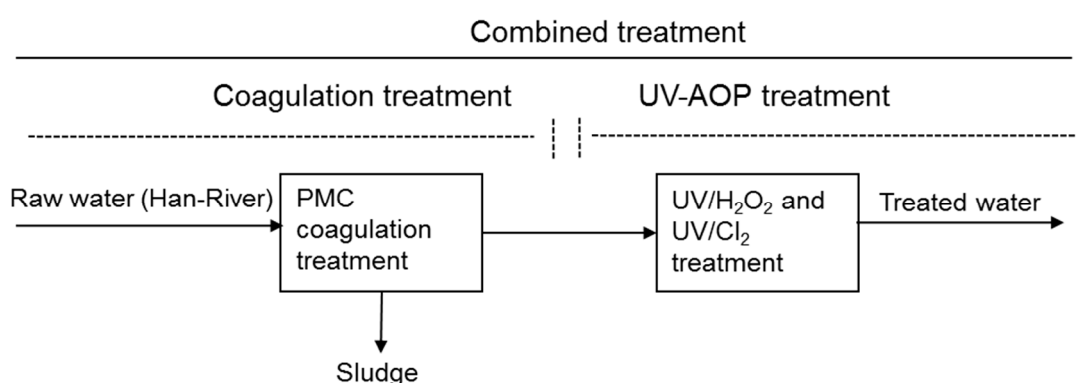

Figure 1. Schematic design of the combined treatment, plant-mineral composite (PMC) coagulation treatment followed by UV-based advanced oxidation processes (UV-AOP) treatment.

2.3. Analysis

Turbidity was measured using a Hach 2100 N Turbidimeter (Hach Company, Loveland, CO, USA). A total organic carbon (TOC) analyzer (Dong-il SHIMADZU Corp., Seoul, Korea) was used to measure the DOC of samples after filtration through a cellulose acetate membrane (pore size: 0.45 μm). A spectrophotometer (Cary 50 Probe, Varian Australia Pty, Ltd., Melbourne, Australia) was used to measure the UV_{254} of samples after filtration through a membrane (pore size: 0.45 μm). A pH meter (Thermo Fisher Scientific Inc., Singapore, Singapore), which was calibrated daily using standards of pH 4.0, 7.0, and 10.0, was used to measure the pH of the water samples. A microscope was used to count the algal cells. A zeta-potential & particle size analyzer (Otsuka Electronics Co., Ltd., Osaka, Japan) was used to determine the zeta potential of the coagulant.

The concentrations of geosmin and 2-MIB were determined using a gas chromatograph equipped with a Polaris Q ion-trap mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). Separation of different compounds was achieved using a J&W CP-Sil 5 CB MS column (length: 30 m; internal diameter: 0.25 mm; film thickness: 0.25 μm; Agilent Technologies, Santa Clara, CA, USA). The GC oven temperature was held at 40 °C for 2 min, increased by 7 °C min^{-1} to 200 °C, which was held for 2 min. Helium at a constant flow rate of 1 mL min^{-1} was used as the carrier gas. The split vent was opened for 3 min after the injection. The electron impact ionization modes were as follows: ion source temperature of 230 °C; the transfer line temperature of 280 °C; solvent delay time of 5 min; electron energy of 70 eV. The full scan mass spectra were obtained at a mass-to-charge ratio scan ranging from 50 to 350 amu to determine appropriate masses for selected ion monitoring [18].

A colorimetric method for the determination of peroxidase with *N,N*-diethyl-*p*-phenylenediamine (DPD) was used to determine the concentrations of H_2O_2 and chlorine using a DR/2500 spectrophotometer

(Hach, Loveland, CO, USA) at 530 nm. The spectrophotometer was calibrated using 10 mL of water sample as a blank. A 10 mL water sample pipetted into a sample cell. Then, one DPD free chlorine Powder Pillow was added and mixed well. After adding 25 μL (1 g/L peroxidase stock solution) of peroxidase reagent, the chlorine concentration measured in mg/L. For the H_2O_2, the chlorine result was divided by two [19–21].

3. Results and Discussion

3.1. PMC for Algae and Organic Matters Removal, Lab-Scale

Figure 2 shows the removal efficiency of algae and turbidity as a function of varied PMC-based coagulant dose from 0 to 70 mg/L at 22 to 25 °C. Overall, the degradation tendencies of algae and turbidity were similar. The removal efficiencies of both algae and turbidity tended to increase with increasing PMC dose up to 20 mg/L, with further increase in the PMC dose decreasing the algae and turbidity removal efficiency. The highest removal of algae was found to be 98% at 20 mg/L PMC. For the case of turbidity, the removal efficiency was around 94% at 20 mg/L PMC, but it was decreased to 83.4% at 70 mg/L PMC. It was implied that particles repelled each other due to the strong electrostatic repulsion forces caused by adsorbed polycations, as reported earlier in [22]. The algae removal efficiencies achieved with the PMC were approximately 10 to 19% higher than those reported in previous work using Al-based [2].
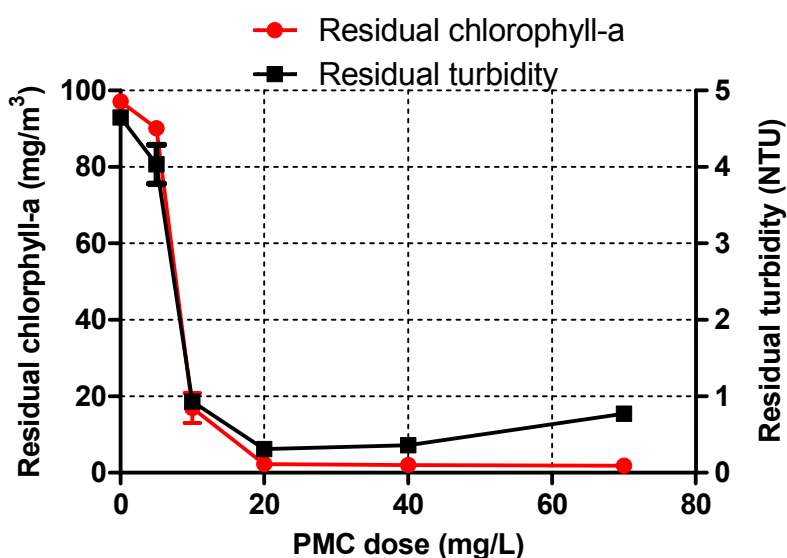

Figure 2. Concentration of chlorophyll-a and residual turbidity after removal with varying doses of the PMC-based coagulant (0, 5, 10, 20, 40, and 70 mg/L).

Figure 3 shows the removal efficiency of UV_{254} and DOC as a function of initial dose of the PMC. UV_{254} and DOC are parameters for monitoring the dissolved organic matter (DOM) removal and controlling coagulant doses in water supply systems for the removal of TOC [23]. The initial UV_{254} and initial concentration of DOC were 0.034 cm^{-1} and 3.4 mg/L, respectively.

In the coagulation process, the removal efficiency of both parameters, i.e., UV_{254} and DOC, increased with increasing PMC dose (Figure 3). At 20 mg/L PMC, the UV_{254} and DOC removals were found to be 51% and 14%, respectively. The higher UV_{254} removal efficiencies than the DOC removal indicates that hydrophobic and large aromatic compounds were preferentially removed via the coagulation process [24]. Ghernaout et al. [25] also reported that small aliphatic compounds do not absorb UV light because they lack conjugated double bonds, and therefore are not detected through UV_{254} measurements. This finding is in agreement with those of previous studies [25–27].
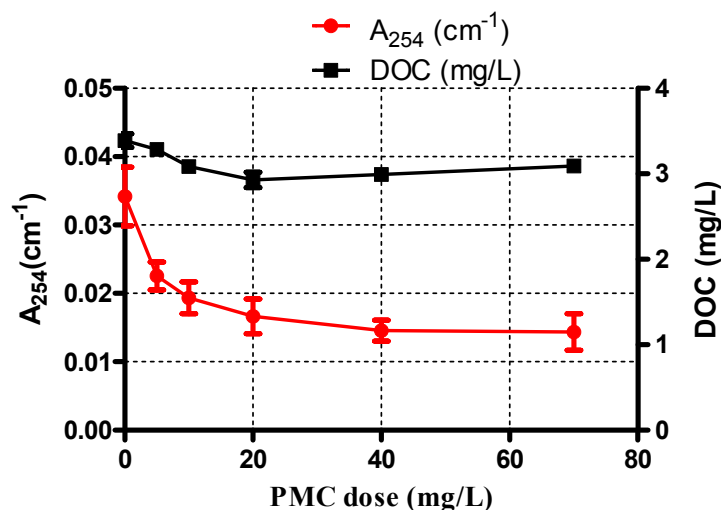
Figure 3. Removal of UV$_{254}$ and dissolved organic carbon (DOC) at the laboratory-scale using varying doses of the PMC-based coagulant (0, 5, 10, 20, 40, and 70 mg/L).

3.2. Zeta Potential of PMC

The zeta potential of the test water at varying PMC-based coagulant doses was determined to investigate the mechanism of turbidity and algae removal. With increasing PMC dose from 0 to 70 mg/L, the zeta potential was increased from −26.3 mV to +27.1 mV (Figure 4). This could be explained by the highly positive charge of the PMC stock solution (+44.86 mV). The isoelectric point was found to be around 20–40 mg/L PMC dose, which range is close to the optimum PMC dose for the algae and turbidity removal, i.e., 20 mg/L (Figure 4). This result indicates that the charge neutralization could be the major removal mechanism of algae and turbidity in coagulation process [28]. At the PMC dose higher than 20 mg/L, the reversal of the solution charge from negative to positive could lead to restabilization of the particles. The particles could repel each other, owing to strong electrostatic repulsion forces caused by the adsorbed polycations [22]. Moreover, algae bio-colloids are known to carry negative surface charges at most pH levels [29]. Thus, the high algae removal efficiencies of the PMC can be attributed to the mechanisms of charge neutralization and mutual attraction between the negatively charged algae and the positively charged components of the PMC-based coagulant (i.e., zeolite, barley stone, and loess) [10].
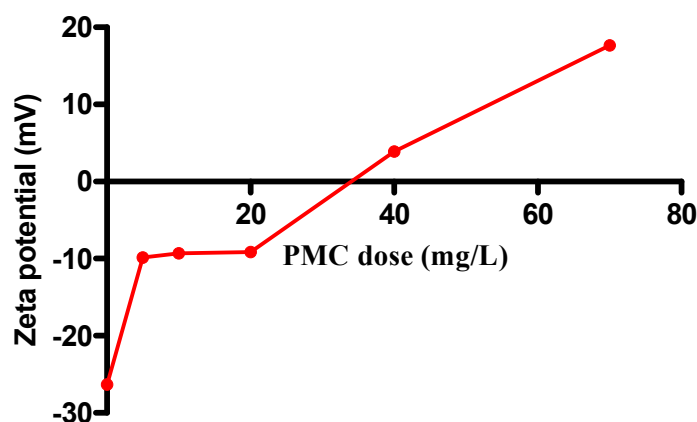

Figure 4. Effect of PMC-based coagulant dose (0, 5, 10, 20, 40, and 70 mg/L) on Zeta potential.

3.3. pH and Alkalinity

The changes in solution pH and alkalinity after coagulation with various PMC-based coagulant doses are shown in Figure 5. The initial pH of the raw water was approximately 7.8. The jar test was conducted with varying doses of the PMC-based coagulant, and the effect of PMC dose on the pH of the test water was evaluated. It was observed that the test water pH decreased after addition of the PMC-based coagulant. Increasing the PMC dose decreased the pH and alkalinity of the test water. The pH decreased to approximately 7.0 at the optimum PMC-based coagulant dose, which indicates that the alkalinity consumption of the PMC coagulant is less than that of alum-based chemical coagulants [30,31].
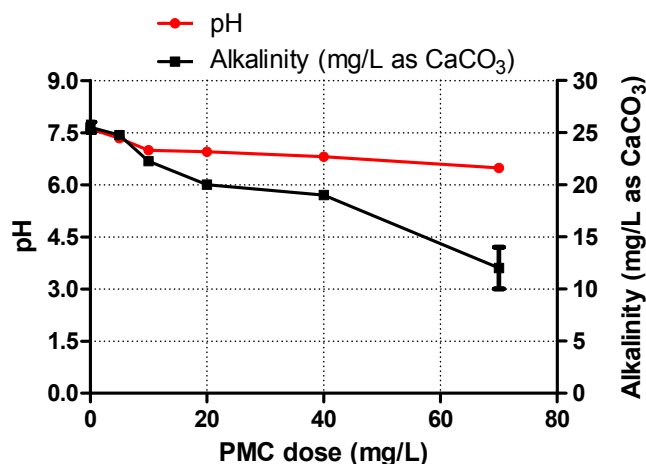

Figure 5. Effect of coagulant dose on pH and alkalinity with varying doses of the PMC coagulant (0, 5, 10, 20, 40, and 70 mg/L).

3.4. PMC for Geosmin and 2-MIB Removal

The geosmin and 2-MIB removal efficiencies of the different PMC doses were investigated. In the coagulation process, PMC-based coagulant was injected up to 70 mg/L. The removal efficiency of geosmin and 2-MIB increased with increasing the PMC dose in both processes (Figure 6). The removal efficiency of geosmin and 2-MIB at 20 mg/L of PMC was approximately 46% and 37%, respectively. The removal efficiencies were higher for geosmin than for 2-MIB. This was attributed to the flatter structure and solubility of geosmin than 2-MIB [1].
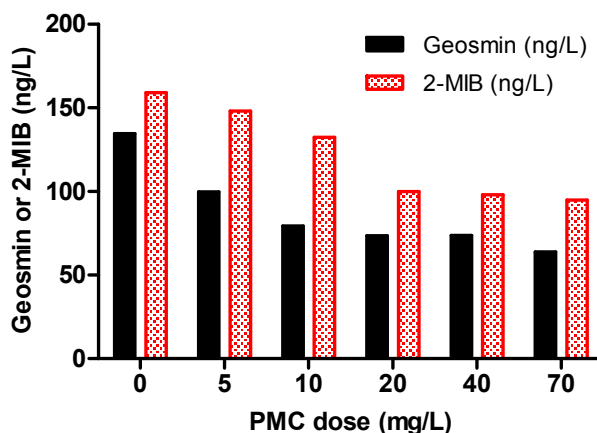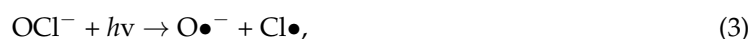

Figure 6. Trends in geosmin and 2-methylisoborneol (2-MIB) removal by PMC processes at the lab-scale (initial geosmin concentration = 134.58 ng/L; initial 2-MIB concentration = 159.02 ng/L; PMC dose: 0, 5, 10, 20, 40 and 70 mg/L).

From the results in Figure 6, it was found that PMC coagulation process could remove some geosmin and 2-MIB, and PMC shows higher removal efficiency of geosmin (46%) and 2-MIB (37%) than other chemical coagulant reported in previous studies [32,33]. After the PMC coagulation, the residual geosmin and 2-MIB was found to be about 73.63 and 99.85 ng/L, respectively. However, the average threshold of geosmin and 2-MIB concentrations is approximately 10 ng/L [34], thus further removal of geosmin and 2-MIB is still needed. Therefore, to enhance the removal efficiency of these compounds a PMC-based coagulation process followed by AOP process was carried out.

3.5. UV/H_2O_2 and UV/Cl_2 for T&O Removal, Lab-Scale

This study investigated two different UV based AOPs, i.e., UV/H_2O_2 and UV/Cl_2 processes, to enhance the geosmin and 2-MIB removal efficiencies after the PMC-based coagulation process. Both of the processes are known to generate hydroxyl radical ($\bullet$OH), which reacts non-selectively with a wide range of organic and inorganic compounds, by the photolytic decomposition of H_2O_2, HOCl, and OCl^- [35] as following equations:

$$H_2O_2 + h\text{v} \rightarrow 2\bullet OH, \tag{1}$$

$$HOCl + h\text{v} \rightarrow \bullet OH + Cl\bullet, \tag{2}$$

$$OCl^- + h\text{v} \rightarrow O\bullet^- + Cl\bullet, \tag{3}$$

$$O\bullet^- + H_2O \rightarrow \bullet OH + OH^-. \tag{4}$$

For the case of the UV/Cl_2 process, it is known that there are formation of reactive chlorine species (i.e., Cl$\bullet$, $Cl_2^-\bullet$, and ClO$\bullet$), but it was reported that OH$\bullet$ is a primarily radical species to the degradation of taste-and-odor compounds as compared to reactive chlorine species which are formed in the UV/Cl_2 process [36].

Treatment in the presence of algae species using oxidation processes has drawbacks such as undesirable toxins and taste and odor compounds [37,38]; therefore, the AOPs were applied after the coagulation process with the optimum PMC dose, i.e., 20 mg/L. In addition, since AOPs performance is significantly affected by DOC and UV_{254} level [39], higher performance of AOPs is expected after the coagulation with the PMC-based process.

Figure 7 shows the geosmin and 2-MIB removal with the UV/Cl_2 and UV/H_2O_2 processes. UV doses were varied as around 200, and 700 mJ/cm^2, and oxidant dose was 5 mg/L. The initial pH of the test water was approximately 6.9, but it was increased to 7.4 after the injection of 5 mg/L of Cl_2 because of the basic pH of sodium hydrochloric acid solution and low buffer system of tested water (alkalinity = 27.5 mg/L as $CaCO_3$). No pH change was observed after the injection of H_2O_2.

In both processes, the removal efficiency of geosmin and 2-MIB increased as UV dose increased. The removal of geosmin and 2-MIB in the processes could be explained by the $\bullet$OH formation and reaction with those compounds. It is known that geosmin and 2-MIB are not photo-reactive compounds [12] but highly reactive with $\bullet$OH ($k_{OH, geosmin}$ = 7.8 × 10^9 M^{-1}·s^{-1} and $k_{OH,2\text{-MIB}}$ = 5.1 × 10^9 M^{-1}· s^{-1}) [40].

At the same UV dose of 700 mJ/cm^2, the UV/H_2O_2 process shows higher removal efficiency (87.2% of geosmin and 71.4% of 2-MIB) than UV/Cl_2 process (62% of geosmin and 38% of 2-MIB). This result could be explained by the speciation of free chlorine (HOCl and OCl^-) with pKa 7.5. At the condition of pH higher than 7.5, OCl^- is the predominant species, and it is known that the $\bullet$OH scavenging rate by OCl^- ($k_{OH,OCl-}$ = 8.80 × 10^9 M^{-1}·s^{-1}) is much higher than H_2O_2 ($k_{OH, H2O2}$ = 2.7 × 10^7 M^{-1}·s^{-1}) and HOCl ($k_{OH,HOCl}$ = 8.46 × 10^4 M^{-1}·s^{-1} [41]; therefore, it is reported that the removal efficiency of geosmin and 2-MIB in the UV/H_2O_2 process could be higher at pH above 7 than the UV/Cl_2 process [36].

Between the two compounds, geosmin removal efficiency was higher than 2-MIB in both processes. This is because geosmin has higher reactivity with $\bullet$OH than 2-MIB.
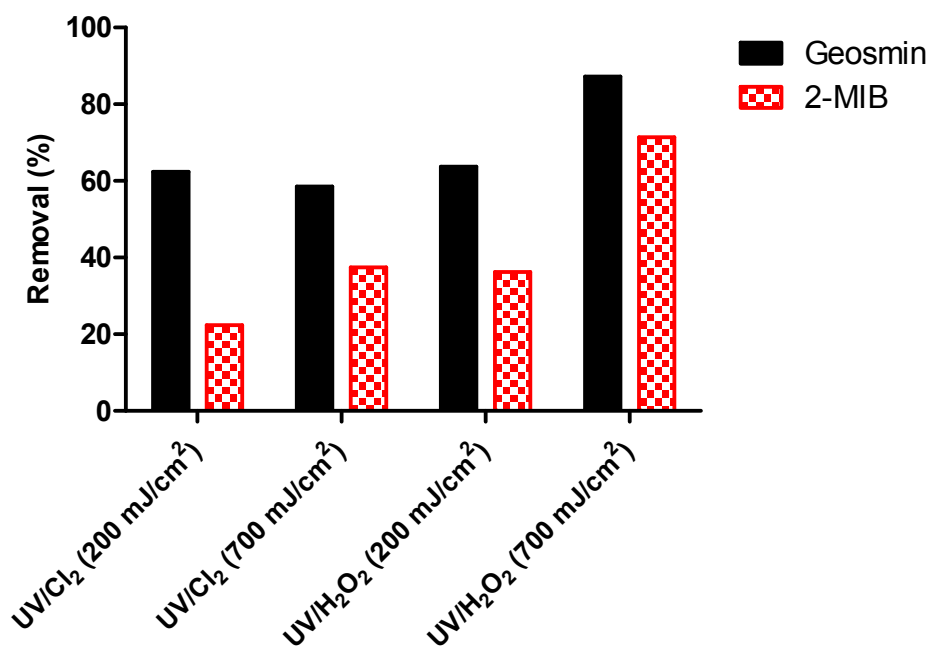
Figure 7. Trends in geosmin and 2-MIB removal by the UV/Cl$_2$, and UV/H$_2$O$_2$ processes at the lab-scale (initial geosmin concentration: 134.58 ng/L; initial 2-MIB concentration: 159.02 ng/L; UV dose: 0, 200, and 700 mJ/cm^2; Cl$_2$ dose: 5 mg/L; H$_2$O$_2$ dose: 5 mg/L; initial pH: 6.9).

3.6. Coagulation Test in Pilot Scale

The pilot-scale PMC-based coagulation experiments were conducted with varying doses of PMC (from 10 to 40 mg/L) at 109 m^3/h flow rate. The algae removal performance of the PMC-based coagulant in the pilot-scale tests is shown in Figure 8. The chlorophyll-a removal efficiencies in the pilot-scale tests were found to be from 78.0–96.0%, 80.0–98.7%, 90.0–99.6% and 78–95% (depending on the period of experiment) at PMC-based coagulant doses of 10, 20, 30, and 40 mg/L, respectively (Figure 8). The removal trends of algae and turbidity were similar. The coagulation process with PMC showed good algae removal efficiencies in the pilot-scale tests.

Figure 9 shows the turbidity and UV$_{254}$ data before and after PMC coagulation process. The raw water turbidity was varied from 1.6 to 11.8 turbidity (NTU). The turbidity removal efficiencies in the pilot-scale tests were found to be from 33.3–41.4%, 41.2–77.4%, 48.3–84.0% and 36.7–78.9% (depending on the period of experiment) at PMC doses of 10, 20, 30, and 40 mg/L, respectively (Figure 9a). Additionally, the average UV$_{254}$ removal efficiencies in the pilot-scale tests were approximately 35.6–45.7%, 41.4–48.9%, 36.7–62.4%, and 42.6–57.6% (depending on the period of experiment) at PMC doses of 10, 20, 30, and 40 mg/L, respectively (Figure 9b). Moreover, the turbidity removal efficiency of the coagulation process increased as the level of turbidity increased. Even though the turbidity removal efficiency was not as high as the lab-scale test, the turbidity level after treatment was low.

The optimum PMC-based coagulant dose was 20 mg/L for all levels of turbidity in the lab-scale tests. However, the optimum dose for the pilot-scale tests was varied depending on the level of turbidity from 20–30 mg/L, which is 10 mg/L higher dose than the lab-scale. The maximum levels of turbidity of the test water were 4.6 and 11.8 NTU for the lab-scale and pilot-scale tests, respectively. Further increase in PMC dose (40 mg/L) decreases the turbidity removal efficiency. This indicates the occurrence of charge reversal which causes the particles in the test water to be positively charged during the coagulation process and therefore the particles start to restabilize at high PMC coagulant doses. Similarly, chemical coagulants, such as polyaluminium chloride have been reported to decrease turbidity removal efficiencies at doses above the respective optimum doses [42–44]. The turbidity

removal was higher in the lab-scale than the pilot-scale test at the optimum dose of PMC (20–30 mg/L). For instance, in case of the turbidity of 4.7 NTU, the removal efficiency in the lab scale was 93.4% but the obtained value from the pilot-tests was approximately 70.2%. Even though the turbidity removal efficiency was not as high as the lab-scale test, the turbidity level after treatment was low. The optimum PMC doses difference for the turbidity removal efficiency in the lab-scale test and pilot-scale tests could be due to the differences in the water matrices. Therefore, a PMC dose of 30 mg/L was used for the removal of both T&O compounds in the pilot-scale tests.

Figure 8. Concentrations of chlorophyll-a before and after coagulation using the PMC-based coagulant in the pilot-scale tests (PMC dose: 10, 20, 30, and 40 mg/L).

3.7. UV/H$_2$O$_2$ and UV/Cl$_2$ Process in Pilot Scale

The oxidation of geosmin and 2-MIB in the UV/H$_2$O$_2$ and UV/Cl$_2$ processes was evaluated after the PMC coagulation process with PMC dose of 30 mg/L. For the UV based AOPs, background water characteristics are significantly important for removal efficiency of target compounds. As mentioned in Section 3.6, after coagulation process using PMC, the water quality was notably increased as follows: DOC (1.3 → 0.8 mg/L), UV$_{254}$ (0.0695 → 0.0272 cm^{-1}), and turbidity (31.1 → 15.6 NTU). To predict the performance of UV-based AOPs, the scavenging factor could be an indicator for ●OH water background demand (s^{-1}). The scavenging factors were measured before and after the PMC treatment (Figure S1). As expected, the scavenging factor was notably decreased after PMC treatment (64998 → 28516 s^{-1}). The UV transmittance was increased (85 → 4%). This could be explained by the decreased DOC and UV$_{254}$ after the PMC process because DOMs are the main water constituents considered in the estimation of ●OH scavenging rates in natural waters [16]. Moreover, removal of turbidity could increase the performance of UV based AOPs because turbidity causing particles can

act as a 'screen' that reduces the amount of light reaching H_2O_2 or Cl_2; therefore, those oxidants do not receive sufficient UV photons for ●OH production [12].
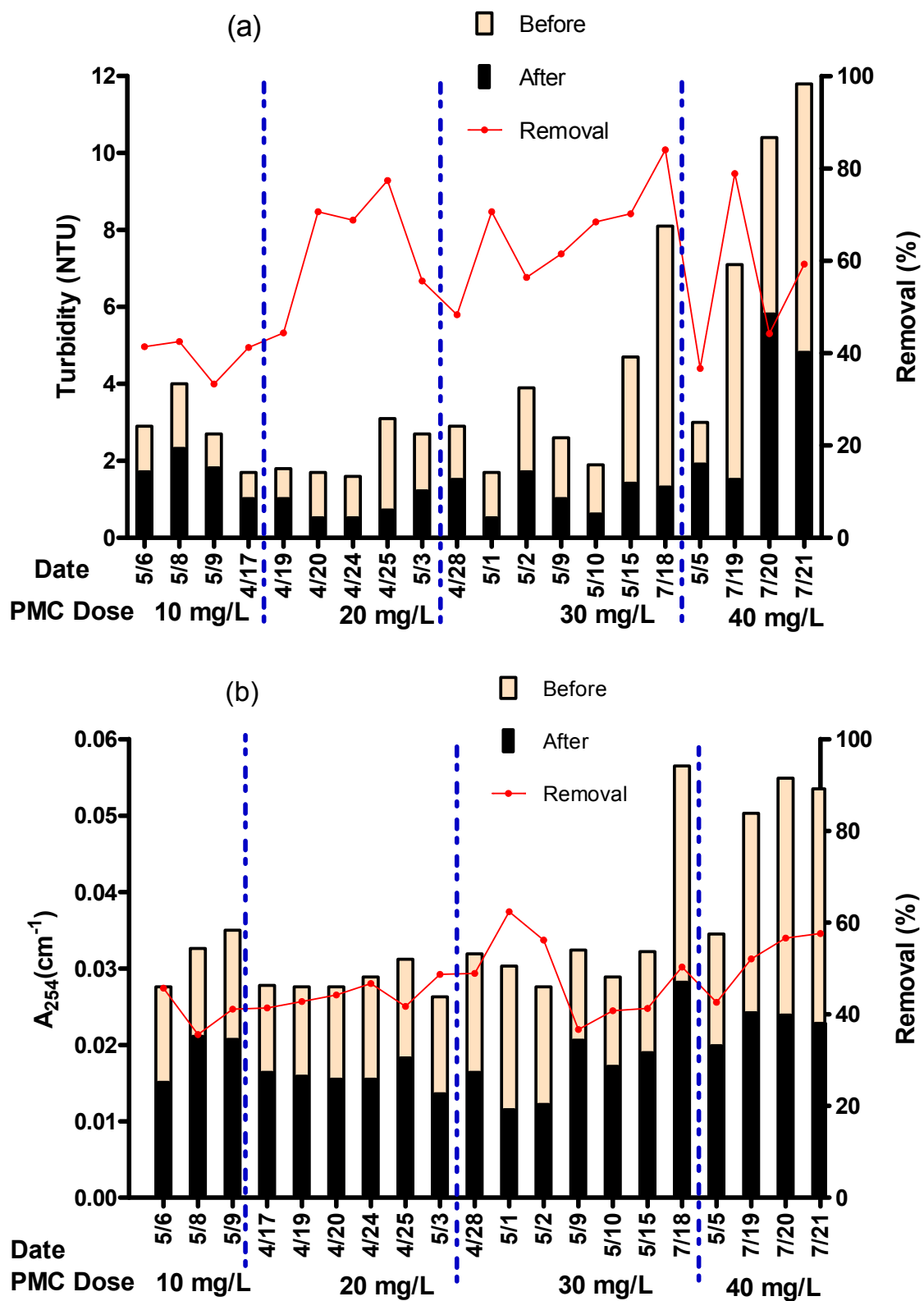

Figure 9. Removal of turbidity (**a**) and UV_{254} (**b**) with varying doses of the PMC-based coagulant in the pilot-scale tests (10, 20, 30, and 40 mg/L).

Since there was no geosmin and 2-MIB issue during pilot-tests, we could not verify the removal of those compounds in the PMC coagulation process. Instead, we split the PMC treated water from the main line flow (109 m^3/h) into the smaller flow rate (1.8 m^3/h) for the spiking test of taste and odor compounds in UV/H$_2$O$_2$ and UV/Cl$_2$ for AOPs. Figure 10 shows the degradation of geosmin and 2-MIB by UV alone, UV/H$_2$O$_2$, and UV/Cl$_2$ processes with varying concentrations of H$_2$O$_2$ and Cl$_2$ (0, 2, 5, and 10 mg/L). The change in geosmin and 2-MIB concentration by UV direct photolysis was not significant, but it was significantly decreased by injection of H$_2$O$_2$ and Cl$_2$. Interestingly, the removal efficiency of both of the compounds in the UV/H$_2$O$_2$ process increased with increasing H$_2$O$_2$ dose, but the UV/Cl$_2$ process had a lower removal at a higher Cl$_2$ dose. One plausible reason is the pH change by the injection of Cl$_2$. Similar to the lab test, the pH values were constant at 6.7 in the UV/H$_2$O$_2$ process; however the pH levels of the test water after the injection of 2, 5, and 10 mg/L chlorine were 6.9, 7.5, and 7.9, respectively. As mentioned in previous Section 3.5, the performance of the UV/Cl$_2$ process is highly dependent on pH and could be decreased at the higher pH than pH 7 because of higher scavenging effect by OCl$^-$ than by HOCl. From this result, the PMC/UV/H$_2$O$_2$ process can suggested as effective treatment process for geosmin and 2-MIB.
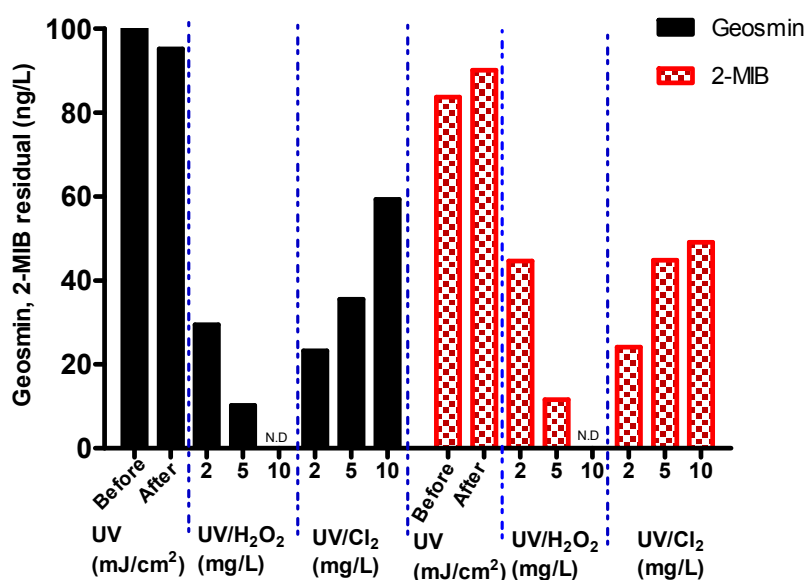

Figure 10. Degradation of geosmin and 2-MIB by UV, UV/H$_2$O$_2$, and UV/Cl$_2$ processes in the pilot-scale test (PMC dose: 20 mg/L; UV dose: 871.8 mJ/cm^2; Cl$_2$ dose: 2, 5, and 10 mg/L; H$_2$O$_2$ dose: 2, 5, and 10 mg/L).

The concentrations of geosmin and 2-MIB in the surface water were successfully reduced using the UV/H$_2$O$_2$ process. Lower than average taste and odor threshold of geosmin and 2-MIB (10 ng/L) was achieved in the UV/H$_2$O$_2$ process with >5 mg/L H$_2$O$_2$.

These results emphasize that UV-based AOPs are applicable at the water intake stage when algae and turbidity are successfully removed using PMC. However, it is true that the performance of UV-based AOPs will be increased if the processes are installed after filtration process of the main water treatment processes. This is because the UV-based AOPs are highly dependent on the UV transmittance.

4. Conclusions

In this study, the coagulation efficiency of the PMC-based coagulant and the algae, geosmin, and 2-MIB removal efficiencies of the combined application of this coagulant with UV-based AOPs were investigated. The coagulation efficiency of the PMC-based coagulant was high in both the lab-scale and pilot-scale tests. In the lab-scale test, the removal efficiency of PMC showed 98%

of the high initial algae concentration (97.1 mg/m^3) and more than 94% of the turbidity removal. The geosmin and 2-MIB removal by the PMC coagulation process was found to be 45% and 37%, respectively. However, the level of residual T&O compound was above the threshold. In the pilot-scale test, coagulation process using PMC showed 64% and 96% of the average turbidity and chlorophyll-a removal efficiencies, respectively. For the PMC-based coagulation combined with UV/H$_2$O$_2$ and UV/Cl$_2$ processes, the change in geosmin and 2-MIB concentration by UV direct photolysis was not significant, but it was significantly decreased after the injection of H$_2$O$_2$. Complete degradation of geosmin and 2-MIB was achieved when the H$_2$O$_2$ (oxidant) dose was increased to 10 mg/L. The UV/H$_2$O$_2$ process was superior to the UV/Cl$_2$ process in both the lab-scale and pilot-scale experiments. It was also observed that water quality parameters such as turbidity reduced the efficiency of the oxidation process. Thus, it was concluded that combining the PMC-based coagulant with UV/H$_2$O$_2$ processes is an efficient coagulation process for the removal of T&O compounds and the producers of such compounds (algae). Further research is needed to optimize the combination of AOP with different coagulation options for different water matrices. A cost-comparison analysis with other coagulants is also required.

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