



Removing Malachite Green and Leucomalachite Green From Freshwater and Seawater With Four Water Treatment Agents

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Malachite green (MG) residue in aquatic environments can adversely affect food chains. To solve this problem, many adsorbents have been developed to remove MG from aqueous solutions. These adsorbents exhibit benefits in different aspects such as low cost, nontoxicity, and environment friendliness. Zeolite, oyster shell powder (OSP), humic acid (HA), and Chlorine dioxide (ClO₂) are widely used agents for water purification, indicating their potential to remove MG from both freshwater and seawater. Liquid chromatography tandem mass spectrometry was performed as a valid analytical method for measuring MG and its metabolite leucomalachite green (LMG). The analysis examined linearity, specificity, accuracy, precision, and limit of quantification. We found that three agents—zeolite, OSP, and HA—have high affinity for MG and LMG in both freshwater and seawater because of their physicochemical properties; ClO₂ exhibited even greater efficiency for MG and LMG degradation due to its oxidation capacity. The MG removal efficiency of zeolite, OSP and HA in freshwater was 100%, 87.52%, and 100%, respectively. In the MG-containing seawater, the removal efficiency of zeolite, OSP and HA was 95.24%, 6.57%, and 89.36%, respectively. The LMG removal efficiency of zeolite, OSP and HA in freshwater was 100%, 53.56%, and 100%, while in seawater, the LMG removal efficiency of zeolite, OSP and HA was 100%, 62.70%, and 84.65%, respectively. ClO₂ treatments in both freshwater and seawater expressed 100% removal efficiency. The adsorption capacity of three water agents in MG-containing freshwater decreased in the order: zeolite = HA > OSP; in MG-containing seawater: zeolite > HA > OSP. Whereas the adsorption capacity of three water agents in LMG-containing freshwater decreased in the order: zeolite = HA > OSP; in LMG-containing seawater: zeolite > HA > OSP. In this study, four water treatment agents are reported to remove MG and LMG from freshwater and seawater, indicating their potential for reducing the amount of hazardous MG and LMG residue in aquatic environments.

Keywords: malachite green (MG), leucomalachite green (LMG), adsorbent, chlorine dioxide (ClO₂), liquid chromatography tandem mass spectrometry (LC-MS/MS)

INTRODUCTION

Water pollution, in the form of hazardous artificial substances, directly or indirectly influences biological systems and the environment. Malachite green (MG) is traditionally known as a dye, also a synthetic parasiticide, used in the aquaculture industry. It can kill protozoa and fungi and to prevent the economic losses associated with parasites (Alderman, 1985; Srivastava et al., 2004). However, MG is an illegal parasiticide because the use of one of its metabolites—leucomalachite green (LMG)—harms aquatic animals, including damaging immune and reproductive systems and promoting carcinogenesis (Bills and Hunn, 1976; Meyer and Jorgenson, 1983; Mitrowska et al., 2005).

Although MG has been banned in aquaculture, its residue and metabolite LMG remain in freshwater and seawater present a substantial challenge because MG is a recalcitrant compound that resists normal biodegradation. According to the 2002/657/EC, a minimum required performance limit (MRPL) of 2 µg/kg was established for both MG and LMG in aquaculture products (Chain, 2016). However, the residue and metabolite of MG in the water environment are neglected by people, it remains to be confined that the concentration and limits of MG and LMD in the freshwater or seawater by food control authorities. Studies have developed various methods, including biodegradation and the use of nanoparticles or natural materials (Baek et al., 2010; Wang et al., 2014; Zhou et al., 2015; Lima et al., 2017; Li et al., 2018), to partially remove MG. For instance, polymer composites have been used in MG removal, such as sodium alginate/SBAC composite beads, polymer-marine biomass based nanocomposite, and lignocellulose biomass composite biosorbent, which perform high removal efficiency in solution (Khan et al., 2019; Das et al., 2020; Sarojini et al., 2022). Although such methods reduce MG in various aqueous solutions, whether they can be applied to freshwater or seawater to remove MG remains unclear. Besides the challenges in the removal efficiency of freshwater or seawater, the cost, price, and eco-friendly materials are still under-investigated.

MG removal presents challenges in aquatic environments, which are complex because of their composition, pH, and temperatures; this is especially true in high-salinity seawater. Water treatment agents, such as zeolite, oyster shell powder (OSP), and humic acid (HA), have been frequently used in water purification because they are environment friendly, nontoxic, inexpensive (Wu et al., 2010; Zhang et al., 2015; Wei et al., 2018); such qualities indicate the potential of these adsorbents for removing MG from both freshwater and seawater.

This study developed novel approaches for the removal of MG from both freshwater and seawater; these approaches employ four water treatment agents, zeolite, OSP, HA, and ClO₂. The advantages of these four agents are as follows:

(1) Zeolite is a polar adsorbent with a high affinity for bacteria (Milenkovic et al., 2017), and a multicavity substance with strong electrostatic force for adsorption (Arbuznikov et al., 1998; Rhodes, 2016). Zeolite is abundant with

aluminosilicates. The adsorbent properties of zeolite have made it useful for removing heavy metal ions and dyes (Wang and Ariyanto, 2007; Han et al., 2010). The adsorption kinetics of malachite green by zeolite have been proposed, which are pseudo-first-order, pseudo-second-order, and diffusion models (Wang and Ariyanto, 2007). Han et al. (2010) also demonstrated that spent zeolite could be reused after microwave irradiation for 10 min at 160 W, suggesting that zeolite is a low cost and eco-friendly material to remove the malachite green.

(2) Oyster shell powder (OSP) is commonly used as a fertilizer for soil improvement in agriculture and as a filter material for water recycling and aquaculture (Huh et al., 2016). OSP can adsorb heavy metals such as Cd and Cr (Wu et al., 2014; Alidoust et al., 2015; Fan et al., 2015; Jung et al., 2016). OSP (CaCO₃ microparticles) absorbs metal ions through ion exchange in three steps: 1) absorption of metal ions on the porous surface; 2) precipitation of the metal ions on the surface; and 3) formation of heavy metal complex nucleation and crystals on the surface (Xu et al., 2021). In addition to metal ions, calcined oyster shells are also used as an eco-friendly and low-cost effective adsorbent for anionic dye removal from water (Inthapanya et al., 2019). However, it remains unclear whether OSP has potential function to remove malachite green.

(3) Humic acid (HA) can be used for chelation to react with cations and remove heavy metals used in aquaculture (Musani et al., 1980; Livens, 1991a; Zhou et al., 2015). It is composed of an aromatic nucleus surrounded by carboxylic and phenolic substitutes arranged in a motif. Due to its hydrophobic structure and abundance of hydrophilic groups, HA has a high affinity for organic compounds, such as cationic dyes, because of hydrophobic interactions, ion exchange, π - π interactions, and hydrogen bonds (Luo et al., 2007). It has been demonstrated the adsorption kinetics, equilibrium, and adsorption thermodynamics for the removal of cationic dye (methylene blue (MB) by using HA-modified expanded perlite (HA/EP) (Luo et al., 2014).

(4) Chlorine Dioxide (ClO₂) is an oxidant, which used for disinfection in water purification because of its capacity for strong oxidation reactions (Volk et al., 2002). MG has been reported to react with some oxyanions, suggesting its potential to be degraded through ClO₂ oxidation (Alderman and Clifton-Hadley, 1993; Mohammed et al., 2010). ClO₂ has been demonstrated to degrade the triaryl methane dye-Brilliant Blue-R by its oxidation capacity (Nadupalli et al., 2019), leading to a possibility that MG (N-methylated diaminotriphenylmethane industrial dye) might be degraded by ClO₂.

To our knowledge, no research has employed liquid chromatography tandem mass spectrometry (LC-MS/MS) to analyze the capacity of these four agents to remove MG and LMG from freshwater and seawater. Our study is the first to report the use of these alternative water treatment agents for the successful removal of MG and LMG.

MATERIALS AND METHODS

Experimental Water

To assess the removal efficiency of MG and LMG in water samples without any interferences, the double distilled water from Ultra Analytic; ELGA, pH7.4) was used as freshwater samples (salinity 0‰). Seawater (pH 8.4; salinity 34 ± 1 ‰) was collected from the aquatic animal culture room of the Department of Aquaculture at National Taiwan Ocean University. The seawater was filtrated by 0.22 μm filter and autoclaved under 121°C for 20 min prior to experiments. Both water samples were examined and no detectable MG and LMG in water.

Experimental Water Treatment Agents

White zeolite was purchased from Gih-Hwa Enterprise, Taiwan. The composition of zeolite is 68.9% SiO_2 , 13.5% Al_2O_3 , 0.2% MgO , 4.26% CaO , 1.6% Na_2O , 2.2% K_2O , and 0.1% P_2O_5 . OSP is consisted by 95.99% CaCO_3 , 0.69% SiO_2 , 0.42% Al_2O_3 , 1.83% Fe_2O_3 , 0.52% SO_3 , and 0.54% MgO . It was purchased from a commercial store. HA is consisted by 71.2% HA, 9.6% fulvic acid, 10.0% ash, and 9.2% water. It was purchased from Gih-Hwa Enterprise, Taiwan. Finally, the ClO_2 was purchased from Taiwan Pulp & Paper Corporation.

Analytical Method Validation

The technique of analytical method validation was adapted from those used in previous studies (Halme et al., 2004; Mitrowska et al., 2005; Halme et al., 2007) and included analyses of linearity, specificity, accuracy, precision, and limit of quantification (LOQ). All procedures for measuring MG and LMG residue in freshwater and seawater were evaluated in accordance with the guidelines of the Taiwan Food and Drug Administration (<https://www.fda.gov.tw/>).

Chemicals and Reagents

MG ($\text{C}_{46}\text{H}_{50}\text{N}_4\cdot 3\text{C}_2\text{H}_2\text{O}_4$, purity: 96.9%) was purchased from Sigma-Aldrich. LMG ($\text{C}_{23}\text{H}_{26}\text{N}_2$, purity: 98%) was purchased from Sigma-Aldrich. MG-d₅ ($\text{C}_{29}\text{H}_{22}\text{D}_5\text{N}_5\text{O}_7$, purity: 99.6%) and LMG-d₅ ($\text{C}_{23}\text{H}_{21}\text{D}_5\text{N}_2$, purity: 99.8%) were purchased from Witega and were used as the internal standards for MG and LMG, respectively.

Zeolite, Oyster Shell Powder, and Humic Acid Treatment for Malachite Green and Leucomalachite Green Removal From Freshwater and Seawater

Three water treatment agents (200 mg/L), zeolite, OSP, and HA, were added individually to 50 ml freshwater or seawater-containing 1 mg/L MG or LMG, vortex until dissolved and then stand in bench at room temperature. 20 μl of sample was collected at day 0 as control and at day 1, 2, 4, 7, 14, 30, 60, and 90 from each treatment group. The collected samples were analyzed by LC-MS/MS and MG or LMG concentration were calculated by the following formula. C_{initial} and C_{final} indicate the concentration of control and treatment water samples, respectively. The adsorption capacity was expressed as follows:

$$\text{Removal (\%)} = \left(\frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}} \right) * 100\%$$

$$\text{Adsorption capacity (AC) (mg/g)} = \frac{(C_i - C_f) * V}{Ws (g)}$$

AC is the adsorption capacity, C_i (mg/l) and C_f (mg/l) are the concentration of MG or LMG before and after treatment, respectively, V (l) is the solution volume of MG or LMG, and Ws (g) is the concentration of three water agents (200 mg/L).

Liquid Chromatography Tandem Mass Spectrometry

A high-performance liquid chromatography tandem mass spectrometer consisting of an Agilent 1100 Series HPLC (Agilent, Germany) and an API 4000 Q-Trap mass spectrometer (Applied Biosystems, Canada) with electrospray ionization was employed for analysis. MG, LMG, MG-d₅, and LMG-d₅ were detected through LC-MS/MS using multiple reaction monitoring for mass transitions of m/z 329.5→313.4, 331.2→239.3, 334.0→318.3, and 336.0→239.2, respectively. After optimization, the working MS parameters were as follows: flow rate of 800 $\mu\text{L}/\text{min}$, positive polarity, curtain gas pressure of 10 psi, ion source gas pressure of 50 psi, ion spray voltage of 5500 V, and temperature of 500°C. All data were analyzed using Analyst 1.4 software.

Statistical Analyses

Data were analyzed through one-way analysis of variance with a subsequent Scheffe test, with statistical significance was defined as ($p < 0.05$).

RESULTS

Analytical Method Validation for Malachite Green and Leucomalachite Green

The method of analyzing MG and LMG was validated in accordance with the guidelines of the Taiwan Food and Drug Administration and was applied to all LC-MS/MS measurements, those of linearity, specificity, accuracy, and precision, and to the LOQ by LC-MS/MS. All of the measurements are presented in the Supplementary Figures S1, S2 and Supplementary Tables S1–S5.

Zeolite, Oyster Shell Powder, and Humic Acid for Malachite Green Removal From Freshwater and Seawater

To test whether zeolite, OSP and HA could efficiently remove MG from freshwater, we treated MG containing freshwater (initial MG conc. 1300.0 ± 70.0 $\mu\text{g}/\text{L}$) with 200 μl of each water agents and PBS as control group. Then samples were collected at 1, 2, 4, 7, 14, 30, 60, and 90 days post treatment. In day 1, the conc. of MG is significantly reduced (zeolite: 19.3 ± 2.3 $\mu\text{g}/\text{L}$; OSP: 675 ± 16.4 $\mu\text{g}/\text{L}$; HA: 165.6 ± 4.9 $\mu\text{g}/\text{L}$), compare to control group (1002.6 ± 70.0 $\mu\text{g}/\text{L}$, $p < 0.05$; Table 1). At day 30, the concentration of MG is not detectable in Zeolite and HA group. In total, After 90 days, 100%,

TABLE 1 | Concentrations of MG ($\mu\text{g/L}$) in freshwater after treating with three agents (200 mg/L) at observation point during 90 days.

Agents	Time (day)								
	0	1	2	4	7	14	30	60	90
Control	1300.0 \pm 70.0 ^A	1002.6 \pm 41.1 ^{B_a}	991.6 \pm 5.5 ^{BC_a}	925.6 \pm 5.5 ^{BCD_a}	890.0 \pm 22.5 ^{CDE_a}	882.0 \pm 16.1 ^{DE_a}	814.6 \pm 8.0 ^{E_a}	689.0 \pm 1.7 ^{F_a}	654.6 \pm 9.4 ^{F_a}
Zeolite		19.3 \pm 2.3 ^{A_d}	15.8 \pm 0.6 ^{B_d}	13.7 \pm 0.0 ^{BC_c}	13.9 \pm 1.2 ^{BC_c}	11.7 \pm 0.0 ^{C_c}	N.D.	N.D.	N.D.
OSP		675.0 \pm 16.4 ^{A_b}	672.3 \pm 29.7 ^{A_b}	604.6 \pm 33.5 ^{AB_b}	563.3 \pm 43.8 ^{B_b}	278.0 \pm 3.0 ^{C_b}	196.3 \pm 27.5 ^{C_b}	83.4 \pm 2.8 ^{D_b}	81.7 \pm 4.1 ^{D_b}
HA		165.6 \pm 4.9 ^{A_c}	71.3 \pm 9.7 ^{B_c}	41.5 \pm 4.5 ^{C_c}	27.7 \pm 3.4 ^{CD_c}	15.7 \pm 0.8 ^{D_c}	N.D.	N.D.	N.D.

(1) Data are means \pm S.D.

(2) N.D. means not detectable.

(3) Mean in the same row with the different letters (A, B, C) are significantly different ($p < 0.05$).(4) Mean in the same column with the different letters (a, b, c) are significantly different ($p < 0.05$).(5) Control pH: 6.03 \pm 0.01, Zeolite pH: 6.75 \pm 0.02, Oyster shell powder: 12.66 \pm 0.01, HA: 6.15 \pm 0.01.**TABLE 2** | The removal efficiency (%) of 1000 $\mu\text{g/L}$ of MG in freshwater treated with three agents (200 mg/L) at observation point during 90 days.

Agents	Time (day)							
	1	2	4	7	14	30	60	90
Zeolite	98.0 \pm 0.2 ^{C_a}	98.4 \pm 0.0 ^{BC_a}	98.5 \pm 0.0 ^{B_a}	98.4 \pm 0.1 ^{B_a}	98.6 \pm 0.0 ^{B_a}	100.0 \pm 0.0 ^{A_a}	100.0 \pm 0.0 ^{A_a}	100.0 \pm 0.0 ^{A_a}
OSP	32.6 \pm 1.6 ^{C_c}	32.2 \pm 3.0 ^{C_c}	36.5 \pm 3.5 ^{C_b}	36.7 \pm 4.9 ^{C_b}	68.4 \pm 0.3 ^{B_b}	75.9 \pm 3.3 ^{B_b}	87.9 \pm 0.4 ^{A_b}	87.5 \pm 0.6 ^{A_b}
HA	83.4 \pm 0.4 ^{E_b}	92.8 \pm 0.9 ^{D_b}	95.6 \pm 0.4 ^{C_a}	96.8 \pm 0.3 ^{BC_a}	98.2 \pm 0.0 ^{B_a}	100.0 \pm 0.0 ^{A_a}	100.0 \pm 0.0 ^{A_a}	100.0 \pm 0.0 ^{A_a}

(1) Data are means \pm S.D.(2) Mean in the same row with the different letters (A, B, C) are significantly different ($p < 0.05$).(3) Mean in the same column with the different letters (a, b, c) are significantly different ($p < 0.05$).**TABLE 3** | Concentrations of MG ($\mu\text{g/L}$) in seawater after treating with three agents (200 mg/L) at observation point during 90 days.

Agents	Time (day)								
	0	1	2	4	7	14	30	60	90
Control	1100.0 \pm 20.0 ^A	772.3 \pm 42.7 ^{B_a}	761.6 \pm 30.9 ^{BC_a}	733.0 \pm 16.0 ^{BC_a}	689.3 \pm 16.2 ^{C_a}	569.6 \pm 6.4 ^{D_a}	441.6 \pm 16.9 ^{E_a}	319.6 \pm 7.5 ^{F_a}	167.3 \pm 5.5 ^{G_a}
Zeolite		265.0 \pm 7.0 ^{A_c}	224.3 \pm 7.5 ^{B_d}	181.6 \pm 14.4 ^{C_c}	179.0 \pm 2.6 ^{C_c}	171.3 \pm 17.7 ^{C_c}	131.3 \pm 5.5 ^{D_c}	45.0 \pm 0.8 ^{E_b}	7.9 \pm 0.0 ^{F_b}
OSP		710.3 \pm 41.6 ^{A_b}	696.3 \pm 13.4 ^{A_b}	619.6 \pm 22.4 ^{AB_b}	589.0 \pm 16.5 ^{B_b}	491.6 \pm 10.5 ^{C_b}	358.6 \pm 37.9 ^{D_b}	356.0 \pm 8.1 ^{D_a}	156.3 \pm 3.0 ^{E_a}
HA		421.0 \pm 11.1 ^{A_b}	339.6 \pm 17.9 ^{B_c}	233.3 \pm 24.7 ^{C_c}	152.3 \pm 9.0 ^{D_c}	150.0 \pm 10.5 ^{D_c}	134.3 \pm 19.3 ^{D_c}	68.5 \pm 2.3 ^{E_b}	17.8 \pm 2.6 ^{F_b}

(1) Data are means \pm S.D.(2) Mean in the same row with the different letters (A, B, C) are significantly different ($p < 0.05$).(3) Mean in the same column with the different letters (a, b, c) are significantly different ($p < 0.05$).(4) Control pH: 8.64 \pm 0.01, Zeolite pH: 8.72 \pm 0.01, OSP: 10.40 \pm 0.01, HA pH: 8.13 \pm 0.01.

87.52%, and 100% of the MG had been removed by the zeolite, SOP, and HA, respectively (Table 2). As shown in Supplementary Figure S3, the adsorption capacity of three water agents in MG-containing freshwater were calculated as following: 65.0 mg/g for zeolite, 60.9 mg/g for OSP, and 65.0 mg/g for HA. These results suggest that zeolite and HA have a good adsorption capacity for MG in freshwater among the three tested agents.

In the seawater samples, we treated MG-containing seawater (initial MG conc. 1100.0 \pm 20.0 $\mu\text{g/L}$) with 200 μl of each water agents and PBS as control group. Then samples were collected after 1, 2, 4, 7, 14, 30, 60, and 90 days. In day 1, the conc. MG in seawater is significantly reduced by zeolite (265.0 \pm 7.0 $\mu\text{g/L}$) and HA (421.0 \pm 11.1 $\mu\text{g/L}$), compare to control group (772.3 \pm 42.7 $\mu\text{g/L}$; Table 3). After 90 days, the MG removal rates of zeolite, OSP, and HA were 95.2%, 6.57%, and 89.36%, respectively (Table 4). As shown in Supplementary Figure S3, the adsorption capacity of

three water agents in MG-containing seawater were calculated as following: 54.6 mg/g for zeolite, 47.1 mg/g for OSP, and 54.1 mg/g for HA. This suggests that the adsorption ability of zeolite and HA is poorer in high-salinity seawater than in freshwater; by contrast, OSP efficiently removes MG from seawater.

Zeolite, Oyster Shell Powder, and Humic Acid for Leucomalachite Green Removal From Freshwater and Seawater

To investigate whether zeolite, OSP, and HA could effectively remove LMG from freshwater, freshwater containing 836.3 \pm 25.5 $\mu\text{g/L}$ LMG was treated with the agents. We collected samples at 1, 2, 4, 7, 14, 30, 60, and 90 days after treatment. As shown in Table 5, in the zeolite-treated samples, the amount of residual LMG had significantly decreased after 30 days. After 60 days, the

TABLE 4 | The removal efficiency (%) of 1000 µg/L of MG in seawater treated with three agents (200 mg/L) at observation point during 90 days.

Agents	Time (day)							
	1	2	4	7	14	30	60	90
Zeolite	65.6 ± 0.9 ^{E_a}	70.5 ± 0.9 ^{CDE_a}	75.5 ± 0.3 ^{C_a}	73.6 ± 2.1 ^{CD_a}	69.9 ± 3.1 ^{DE_a}	70.2 ± 1.2 ^{DE_a}	85.9 ± 0.2 ^{B_a}	95.2 ± 0.0 ^{A_a}
OSP	8.0 ± 5.3 ^{AB_c}	8.5 ± 1.7 ^{AB_c}	15.4 ± 3.0 ^{A_c}	14.5 ± 2.4 ^{A_b}	13.6 ± 1.8 ^{AB_b}	18.7 ± 8.6 ^{A_b}	0.0 ± 0.0 ^{B_c}	6.5 ± 1.8 ^{AB_b}
HA	45.4 ± 1.4 ^{F_b}	55.4 ± 2.3 ^{F_b}	68.1 ± 3.3 ^{D_b}	77.9 ± 1.3 ^{BC_a}	73.6 ± 1.8 ^{BCD_a}	69.5 ± 4.3 ^{CD_a}	78.5 ± 0.7 ^{B_b}	89.3 ± 1.5 ^{A_a}

(1) Data are means ± S.D.
 (2) Mean in the same row with the different letters (A, B, C) are significantly different (p < 0.05).
 (3) Mean in the same column with the different letters (a, b, c) are significantly different (p < 0.05).

TABLE 5 | Concentrations of LMG (µg/L) in freshwater after treating with three agents (200 mg/L) at observation point during 90 days.

Agents	Time (day)								
	0	1	2	4	7	14	30	60	90
Control	836.3 ± 25.5 ^A	58.8 ± 4.6 ^{B_a}	30.5 ± 2.0 ^{BC_a}	20.3 ± 0.3 ^{C_a}	9.2 ± 0.3 ^{C_a}	7.2 ± 1.0 ^{C_a}	6.2 ± 0.4 ^{C_a}	5.8 ± 0.6 ^{C_a}	3.4 ± 1.1 ^{C_a}
Zeolite		10.1 ± 2.0 ^{A_c}	8.9 ± 1.1 ^{A_c}	7.7 ± 2.7 ^{C_c}	2.3 ± 0.3 ^{B_c}	1.6 ± 0.2 ^{B_c}	0.6 ± 0.0 ^{B_c}	N.D.	N.D.
OSP		55.1 ± 0.8 ^{A_a}	22.9 ± 0.4 ^{B_b}	15.7 ± 1.0 ^{C_{ab}}	6.5 ± 0.8 ^{D_b}	4.7 ± 0.2 ^{DE_b}	3.1 ± 0.2 ^{DE_b}	3.0 ± 0.0 ^{DE_b}	1.6 ± 0.1 ^{E_a}
HA		36.0 ± 1.4 ^{A_b}	21.6 ± 1.3 ^{B_b}	12.2 ± 1.7 ^{C_{bc}}	7.1 ± 0.6 ^{D_b}	3.6 ± 0.2 ^{DE_b}	0.9 ± 0.0 ^{E_c}	N.D.	N.D.

(1) Data are means ± S.D.
 (2) N.D. means not detectable.
 (3) Mean in the same row with the different letters (A, B, C) are significantly different (p < 0.05).
 (4) Mean in the same column with the different letters (a, b, c) are significantly different (p < 0.05).
 (5) Control pH: 6.65 ± 0.01, Zeolite pH: 7.16 ± 0.01, OSP pH: 12.66 ± 0.01, HA pH: 6.89 ± 0.01.

TABLE 6 | The removal efficiency (%) of 1000 µg/L of LMG in freshwater treated with three agents (200 mg/L) at observation point during 90 days.

Agents	Time (day)							
	1	2	4	7	14	30	60	90
Zeolite	82.7 ± 3.4 ^{AB_a}	70.6 ± 3.8 ^{BC_a}	61.9 ± 13.4 ^{C_a}	74.4 ± 3.7 ^{BC_a}	77.1 ± 3.5 ^{BC_a}	89.6 ± 1.0 ^{AB_a}	100.0 ± 0.0 ^{A_a}	100.0 ± 0.0 ^{A_a}
OSP	6.3 ± 1.3 ^{D_c}	25.0 ± 1.5 ^{C_b}	22.6 ± 5.1 ^{C_b}	29.2 ± 9.2 ^{C_b}	34.6 ± 3.9 ^{BC_c}	49.6 ± 3.4 ^{AB_b}	47.3 ± 5.1 ^{AB_b}	53.5 ± 2.8 ^{A_b}
HA	38.7 ± 2.4 ^{BCD_b}	29.3 ± 4.5 ^{CD_b}	40.0 ± 8.5 ^{BC_{ab}}	23.16.5 ^{D_b}	49.5 ± 3.9 ^{B_b}	84.7 ± 0.8 ^{A_a}	100.0 ± 0.0 ^{A_a}	100.0 ± 0.0 ^{A_a}

(1) Data are means ± S.D.
 (2) Mean in the same row with the different letters (A, B, C) are significantly different (p < 0.05).
 (3) Mean in the same column with the different letters (a, b, c) are significantly different (p < 0.05).

TABLE 7 | Concentrations of LMG (µg/L) in seawater after treating with three agents (200 mg/L) at observation point during 90 days.

Agents	Time (day)								
	0	1	2	4	7	14	30	60	90
Control	847.3 ± 16.9 ^A	52.5 ± 0.2 ^{B_a}	26.9 ± 0.6 ^{C_a}	25.0 ± 0.6 ^{CD_a}	12.4 ± 0.3 ^{CDE_a}	8.4 ± 0.8 ^{CDE_a}	5.5 ± 0.3 ^{DE_a}	5.4 ± 0.2 ^{DE_a}	3.7 ± 0.2 ^{E_a}
Zeolite		28.4 ± 3.5 ^{A_b}	8.0 ± 0.1 ^{B_c}	4.5 ± 0.3 ^{BC_c}	3.3 ± 0.1 ^{C_c}	1.0 ± 0.0 ^{C_b}	0.8 ± 0.0 ^{C_c}	0.5 ± 0.0 ^{C_c}	N.D.
OSP		23.1 ± 2.0 ^{A_b}	13.9 ± 2.8 ^{B_b}	11.2 ± 4.2 ^{B_b}	8.7 ± 1.6 ^{BC_b}	1.7 ± 0.1 ^{CD_b}	1.5 ± 0.0 ^{D_b}	1.4 ± 0.0 ^{D_b}	1.4 ± 0.1 ^{D_b}
HA		56.1 ± 0.8 ^{A_a}	12.2 ± 2.7 ^{B_{bc}}	7.1 ± 1.4 ^{BC_{bc}}	2.3 ± 0.1 ^{C_c}	1.1 ± 0.0 ^{C_b}	1.0 ± 0.0 ^{C_{bc}}	0.6 ± 0.0 ^{C_c}	0.5 ± 0.0 ^{C_c}

(1) Data are means ± S.D.
 (2) N.D. means not detectable.
 (3) Mean in the same row with the different letters (A, B, C) are significantly different (p < 0.05).
 (4) Mean in the same column with the different letters (a, b, c) are significantly different (p < 0.05).
 (5) Control pH: 8.69 ± 0.01, Zeolite pH: 8.68 ± 0.01, OSP pH: 10.46 ± 0.01, HA pH: 8.03 ± 0.01.

TABLE 8 | The removal efficiency (%) of 1000 µg/L of LMG in seawater treated with three agents (200 mg/L) at observation point during 90 days.

Agents	Time (day)							
	1	2	4	7	14	30	60	90
Zeolite	45.8 ± 6.7 ^E _a	69.9 ± 0.6 ^D _a	81.8 ± 1.5 ^{BC} _a	73.4 ± 1.1 ^{CD} _a	87.8 ± 0.5 ^B _a	84.9 ± 0.9 ^B _a	90.0 ± 0.2 ^B _a	100.0 ± 0.0 ^A _a
OSP	55.9 ± 3.9 ^{ABC} _a	48.2 ± 10.6 ^{BC} _a	55.0 ± 17.1 ^{ABC} _a	29.8 ± 13.0 ^C _b	79.1 ± 1.1 ^A _b	73.3 ± 0.7 ^{AB} _c	72.8 ± 0.7 ^{AB} _c	62.7 ± 3.8 ^{AB} _c
HA	0.0 ± 0.0 ^C _b	54.5 ± 10.0 ^B _a	71.3 ± 5.9 ^{AB} _a	81.5 ± 0.8 ^A _a	86.9 ± 1.0 ^A _a	80.5 ± 0.5 ^A _b	88.1 ± 0.2 ^A _b	84.6 ± 0.4 ^A _b

(1) Data are means ± S.D.

(2) Mean in the same row with the different letters (A, B, C) are significantly different ($p < 0.05$).

(3) Mean in the same column with the different letters (a, b, c) are significantly different ($p < 0.05$).

TABLE 9 | Concentrations of MG (µg/L) in freshwater after treating with various concentrations of ClO₂ at observation point during 14 days.

	ClO ₂ (mg/L)	Time (day)					
		0	1	2	4	7	14
(A) Concentrations of MG in freshwater	Control	1253.3 ± 15.2 ^A	1213.3 ± 94.5 ^A _a	1190.0 ± 69.2 ^A _a	1186.6 ± 72.3 ^A _a	1133.3 ± 47.2 ^A _a	973.3 ± 75.2 ^B
	1		667.0 ± 8.6 ^A _b	498.0 ± 13.1 ^B _b	90.7 ± 5.1 ^C _b	5.6 ± 0.3 ^D _b	N.D.
	5/10/25		N.D.	N.D.	N.D.	N.D.	N.D.
Control pH: 6.03 ± 0.01, 1 mg/L ClO ₂ pH: 3.66 ± 0.01, 5 mg/L ClO ₂ pH: 2.54 ± 0.01, 10 mg/L ClO ₂ pH: 2.28 ± 0.01, 25 mg/L ClO ₂ pH: 1.93 ± 0.01							
(B) Concentrations of MG in seawater	Control	1017.0 ± 67.5 ^A	990.6 ± 69.2 ^A _a	819.0 ± 30.4 ^{AB} _a	761.6 ± 84.5 ^B _a	636.0 ± 20.0 ^C _a	567.0 ± 8.8 ^D
	1		456.0 ± 17.3 ^A _b	322.6 ± 19.4 ^B _b	87.3 ± 6.4 ^C _b	5.2 ± 0.3 ^C _b	N.D.
	5/10/25		N.D.	N.D.	N.D.	N.D.	N.D.
Control pH: 8.64 ± 0.01, 1 mg/L ClO ₂ pH: 7.75 ± 0.01, 5 mg/L ClO ₂ pH: 7.53 ± 0.01, 10 mg/L ClO ₂ pH: 7.26 ± 0.01, 25 mg/L ClO ₂ pH: 6.64 ± 0.01							
(C) Concentrations of LMG in freshwater	Control	887.6 ± 15.3 ^A	58.1 ± 1.9 ^B	23.3 ± 1.5 ^C	20.9 ± 2.9 ^C	10.6 ± 2.6 ^C	6.6 ± 0.1 ^C
	1/5/10/25		N.D.	N.D.	N.D.	N.D.	N.D.
Control pH: 6.65 ± 0.01, 1 mg/L ClO ₂ pH: 3.72 ± 0.01, 5 mg/L ClO ₂ pH: 2.86 ± 0.01, 10 mg/L ClO ₂ pH: 2.50 ± 0.01, 25 mg/L ClO ₂ pH: 2.05 ± 0.01							
(D) Concentrations of LMG in seawater	Control	1056.6 ± 15.2 ^A	63.2 ± 3.6 ^B	25.1 ± 1.9 ^C	22.0 ± 0.7 ^C	9.8 ± 1.2 ^C	6.5 ± 0.4 ^C
	1/5/10/25		N.D.	N.D.	N.D.	N.D.	N.D.

Control pH: 8.69 ± 0.01, 1 mg/L ClO₂ pH: 8.05 ± 0.01, 5 mg/L ClO₂ pH: 7.76 ± 0.01, 10 mg/L ClO₂ pH: 7.74 ± 0.01, 25 mg/L ClO₂ pH: 6.90 ± 0.01

The double line was used to distinguish four independent experiments.

(1) Data are means ± S.D.

(2) N.D. means not detectable.

(3) Mean in the same row with the different letters (A, B, C) are significantly different ($p < 0.05$).

(4) Mean in the same column with the different letters (a, b, c) are significantly different ($p < 0.05$).

concentration of LMG was lower than the limit of detection. Moreover, OSP reduced the concentration of LMG to 836.3 ± 25.5 µg/L by day 1 and 1.6 ± 0.1 µg/L by day 90. HA also gradually reduced the concentration of LMG over 90 days. A comparison of the efficiency of the three agents (Table 6) revealed that zeolite was the most effective at removing LMG from freshwater, followed by OSP and then HA. As shown in Supplementary Figure S3, the adsorption capacity of three water agents in LMG-containing freshwater were calculated as following: 41.8 mg/g for zeolite, 41.7 mg/g for OSP, and 41.8 mg/g for HA. The results suggest that zeolite, OSP, and HA may be effective treatment agents for removing LMG from freshwater.

In the seawater test, we added LMG at a concentration of 847.3 ± 16.9 µg/L to seawater before treatment with zeolite, OSP, or HA. We collected samples at 1, 2, 4, 7, 14, 30, 60, and 90 days after

treatment. Table 7 indicates that, compared with the negative control, zeolite, OSP, and HA resulted in significantly less LMG in seawater; the removal rates are listed in Table 8. As shown in Supplementary Figure S3, the adsorption capacity of three water agents in LMG-containing seawater were calculated as following: 42.3 mg/g for zeolite, 42.3 mg/g for OSP, and 42.3 mg/g for HA.

Chloride Dioxide for Malachite Green Degradation From Freshwater and Seawater

ClO₂ is a common disinfectant used in drinking-water processing. To investigate whether ClO₂ could degrade MG, we added MG to samples of freshwater at a concentration of 1253.3 ± 15.2 µg/L before treatment with various ClO₂ (1, 5, 10,

or 25 mg/L) concentrations. We then collected freshwater samples at 1, 2, 4, 7, and 14 days after treatment. As shown in **Table 9A**, the concentration of MG is detectable when water sample treated with 1 mg/L ClO_2 , and gradually diminished over 14 days. Once samples treated above 5 mg/L ClO_2 , the MG is degraded and is lower than the limit of detection limit. A comparison of MG removal rates indicates that in the concentrations of ClO_2 (5, 10, 25 mg/L) result in a greater capacity for MG degradation from freshwater (**Supplementary Table S6**).

In the seawater test, we treated seawater containing 1017.0 ± 67.5 $\mu\text{g/L}$ MG with various concentrations of ClO_2 (1, 5, 10, or 25 mg/L) and then collected samples at 1, 2, 4, 7, and 14 days after treatment. Similar to those in the freshwater tests, the samples treated with 1 mg/L ClO_2 exhibited less MG after 14 days, and in the other samples (5, 10, and 25 mg/L ClO_2), the concentration decreased below the limit of detection (**Table 9B** and **Supplementary Table S7**). These results indicate that ClO_2 efficiently degrades MG from seawater.

Chloride Dioxide for Leucomalachite Green Degradation From Freshwater and Seawater

To further determine whether ClO_2 could also degrade LMG from freshwater and seawater, the LMG-containing freshwater (887.6 ± 15.3 $\mu\text{g/L}$) and seawater (1056.6 ± 15.2 $\mu\text{g/L}$) were treated with various concentrations of ClO_2 (1, 5, 10, or 25 mg/L). Samples were collected at 1, 2, 4, 7, and 14 days after treatment. In the freshwater and seawater samples, the concentration of LMG was lower than the limit of detection at every time point (**Table 9C,D**), indicating that ClO_2 degrades LMG from freshwater and seawater highly effectively (**Supplementary Tables S8, S9**).

DISCUSSION

Performance of Zeolite, Oyster Shell Powder, and Humic Acid in Adsorbing Malachite Green and Leucomalachite Green

Adsorbents are considered effective for removing MG and LMG from aquatic environments. Many adsorbents, such as magnetic nanocomposites, coffee waste, and chitosan, can efficiently eliminate MG from wastewater and aquaculture water (Baek et al., 2010; Wang et al., 2014; Lima et al., 2017; Li et al., 2018; Arumugam et al., 2019).

The adsorption capacity of zeolite depends on its cavity structures and the charges of its inner and outer surfaces (Altun et al., 1998). Crini (2006) demonstrated that zeolite has ion-exchange capacity. Wu et al. (2010) indicated while the influent concentration of MG was 50 mg/L, the maximum adsorption quantity reached 23.55 mg/g by using a fixed-bed column. In our study, zeolite removed 100.00% of MG from freshwater within 30 days and 95.24% of MG from seawater within 90 days. Moreover, zeolite removed 100.00% of LMG

from freshwater within 60 days and 100.00% of LMG from seawater within 90 days. These results demonstrate that zeolite is highly effective in adsorbing MG or LMG; this effectiveness may be due to MG being a cationic dye and LMG being adsorbed by the surface cavities of the zeolite (Arbuznikov et al., 1998; Rhodes, 2016).

OSP has a cavity structure and exhibits mild alkaline properties in aqueous solutions; thus, it can react with water contaminants to form coordination complexes or precipitants for water purification (Boyd and Massaut, 1999). We discovered that OSP was less effective at removing MG and LMG than were zeolite and HA, but this might have been caused by OSP's high affinity for anionic dye (Inthapanya et al., 2019), resulting in a low affinity to cationic dye MG; however, LMG might be adsorbed by the cavities in the structure of the OSP.

HA consists of anionic functional groups, such as carboxylic group and phenolic groups, which become polyanionic in aqueous solutions to form stable complexes with metals (Thanabalasingam and Pickering, 1986; Livens, 1991b; Bowley et al., 2016). Zanini et al. (2006) proposed that MG is adsorbed because of the hydrophobicity and electrostatic force of HA. In our study, HA removed 100.00% of the MG from freshwater within 30 days and 89.3% of the seawater MG within 90 days. Moreover, zeolite removed 100.00% of the LMG from freshwater within 60 days, and 84.6% from seawater in 90 days. These results indicate that HA is efficient at removing MG and LMG for both freshwater and seawater and that such efficiency may be mediated by its physicochemical properties, such as its polyanionicity, hydrophobicity, and electrostatic force.

Inexpensive, nontoxic adsorbents are optimal for removing MG and LMG from water. In this study, we examined three agents—zeolite, OSP, and HA; these agents can effectively remove both MG and LMG, exhibit favorable adsorption efficiency, and cost little. Nevertheless, their effectiveness may be limited by their saturation capacity or their ability to be recycled; studies are currently investigating the recycling of such adsorbents (Han et al., 2010).

Oxidation by ClO_2 Is Effective for Malachite Green and Leucomalachite Green Degradation From Freshwater and Seawater

ClO_2 is often used for disinfection in water purification (Volk et al., 2002) and degrades pesticide residues from vegetables or fruits through its oxidation capacity (Wei et al., 2018; Calvo et al., 2019). During oxidation, ClO_2 is photodegraded into nontoxic metabolites, including H_2O , NaCl, ClO_2 , and carbohydrates, and it is beneficial for environmental protection (Costilow et al., 1984). We propose that ClO_2 can be used for the degradation of MG or LMG from freshwater and seawater in aquaculture because of its oxidation capacity. Our results indicate that, compared with zeolite, OSP, and HA, ClO_2 treatment degrades MG and LMG with higher efficiency, even at low concentrations.

Effect of Seawater Salinity on Malachite Green and Leucomalachite Green Removal

The salinity of freshwater and seawater affects MG removal efficiency. Seawater salinity is complex, and cations such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Sr^{2+} and anions such as Cl^- , SO_4^{2-} , Br^- , HCO_3^- (CO_3^{2-}), and F^- are present. We found that the efficiency of OSP for removing MG from seawater ($6.57\% \pm 1.83\%$) was lower than that from freshwater (<limit of detection), suggesting that the complexity of the salinity of seawater may reduce the adsorption capacity of OSP. Moreover, the pH of the OSP-treated seawater increased, possibly because of the dissociation of the powder, thereby influencing adsorption efficiency. Moreover, OSP reacts with ions in seawater to form coordination complexes or precipitants, resulting in low MG removal efficiency (Xu et al., 2021). Furthermore, zeolite and HA demonstrate great efficiency for removing MG from freshwater than from seawater. Compared with HA and OSP, zeolite is most efficient in removing LMG from both freshwater and seawater. These results suggest that, in various aquatic environments, MG and its metabolite LMG differ in their affinities for adsorbents. In sum, the determinants of the efficiency of MG and LMG removal from seawater are ion concentrations and pH values.

Reversible Malachite Green–Leucomalachite Green Reaction After Treatment With Three Agents

MG was detected after days 7 in seawater containing LMG and zeolite, 14 days in seawater containing LMG and OSP, and 7 days in seawater containing LMG and HA. This suggests that LMG may be oxidized by the air within the zeolite cavities, the HCO_3^- (CO_3^{2-}) of OSP, or a reaction with an oxygen-containing group of HA, thereby reverting to MG. By contrast, no MG was detected in freshwater containing LMG, suggesting that the high ion exchanges of seawater affect the removal efficiency of MG; by contrast, complete removal occurs in freshwater. In summary, these findings suggest that a functional composite material

comprising zeolite, OSP, HA, and ClO_2 could be used to remove MG and LMG from various aquatic environments.

CONCLUSION

In this study, we demonstrated that four agents: zeolite, OSP, HA, and ClO_2 , can remove MG and LMG from both freshwater and seawater; ClO_2 is the most effective, followed by zeolite, HA, and OSP. Our results suggest that these agents can be used in water purification treatment to reduce the concentrations of hazardous MG or LMG residue in both freshwater and seawater.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

Y-RL: methodology, formal analysis, and manuscript writing; Y-FH: formal analysis and manuscript revision; C-YH, H-TH, Z-HL, A-TL, and Y-SW: methodology and formal analysis; and F-HN: supervision.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fenvs.2022.906886/full#supplementary-material>

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