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ABSTRACT: A novel disinfection method with recyclable magnetic nanoparticles is presented to optimize the traditional method with metal ions upon virus contamination. In this study, magnetic nanoparticles with permanently confined micelle arrays (Mag-PCMA) were coated with Ag^+, Cu^{2+}, and Fe^{3+} via sorption to increase the ζ potential from negative to positive. Three types of Mag-PCMA coated with different metal ions (Mag-PCMA-MI) were mixed with a model virus, MS-2, to evaluate their disinfection ability. MS-2 removal by Mag-PCMA-MI was influenced by the concentration of Mag-PCMA-MI and contact time. The MS-2 removal efficiency reached 99% with 0.5 g/L Mag-PCMA-Ag after 30 min. Removal with Mag-PCMA-MI remains stable under most environmental conditions (e.g., water hardness and the presence of natural organic matter), except for a change in pH, which decreases removal efficiency (0.43% for Mag-PCMA-Ag, 0.35% for Mag-PCMA-Cu, and 0.28% for Mag-PCMA-Fe) for an increase in pH from 6 to 8. The reuse of Mag-PCMA-MI can be achieved by simply rinsing the nanoparticles with deionized water to remove the inactivated virus after disinfection, and the removal efficiency remains >99.8% for all three Mag-PCMA-MI after five continuous cycles, highlighting the recyclability of the process.

KEYWORDS: virus contamination, metal ion adsorption, recyclable magnetic nanoparticles, drinking water treatment, disinfection
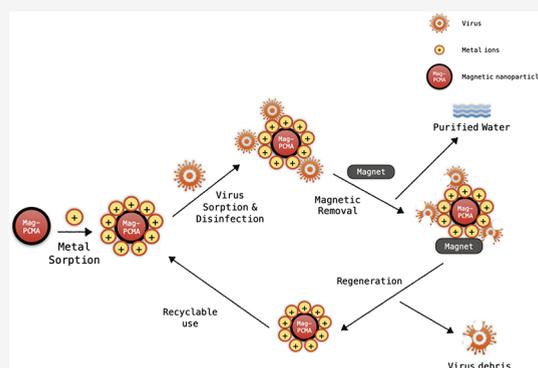
1. INTRODUCTION

The worldwide spread of COVID-19 has made the disinfection of viruses one of the hottest research topics since 2020. As one of the major sources of microbial contamination in water, viruses have spawned much concern in wastewater treatment due to their potential for spreading diseases. The World Health Organization (WHO) has reported that several types of water-transmitted viruses, including DNA viruses (e.g., adenovirus and herpesviruses) and RNA viruses (e.g., astrovirus, rotavirus, norovirus, and other caliciviruses), can spread disease through water, resulting in an increase in the threat to human health.[1] For example, several enteric viruses, including norovirus, rotavirus, sapovirus, astrovirus, and adenovirus, have been recognized as being the main causes of nonbacterial acute gastroenteritis, and they have been detected in tap water, especially in some developing countries.[2−4] In recent years, many outbreaks of water-transmitted viruses have been reported around the world due to fecal contamination, making it a major concern for public health, as hundreds of people were involved in each case. In April and May 2018, more than 500 patients were infected with hepatitis E virus due to an outbreak in Halisohor, Bangladesh, caused by the fecal contamination of water.[5] Another large gastroenteritis outbreak that occurred in northern Greece in 2019 was later identified as a waterborne norovirus outbreak.[6] Given the fact

that many viruses can survive in water for several weeks to months and are infectious even when highly diluted,[7,8] seeking efficient methods to remove viruses from water is a high priority in water treatment.

Traditional microfiltration or ultrafiltration methods in drinking water treatment plants are not effective for the removal of viruses in the water due to their size (~0.01−0.1 μm).[8,9] Other conventional disinfection methods, such as chlorination, ozonation, or ultraviolet radiation, may produce disinfection byproducts[10−12] or require a high maintenance cost,[13] which are major concerns during practical applications. In contrast, metal ions used as disinfectants have the advantages of good effectiveness without the formation of byproduct(s) and low operating costs. Metal ions can be attracted to the negatively charged surface of viruses through electrostatic interaction and then destroy DNA, RNA, or the enzymes to inactivate target microorganisms.[14,15] Some studies have shown that many metal ions, such as Ag^+ and Cu^{2+}, are
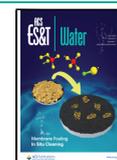
effective disinfectants for both DNA and RNA viruses.[16] However, the residual metal ions in the water after disinfection may be a major concern, as metal ions at concentrations beyond a certain level are toxic to humans or ecological receptors. To address this issue, some improvement in the disinfection method with metal ions has been made, such as the combination with other disinfectants to reduce the concentration of metal ions[17] or the use of metal nanoparticles, such as silver nanoparticles,[18] photocatalytic TiO_2,[19] and nanosized ZnO,[20] instead of dissolved metal ions. However, many issues must be addressed before the improved methods can be put to practical use. For example, some metal nanoparticles such as TiO_2 and ZnO cannot inactivate target microorganisms effectively without the help of visible light irradiation, which will increase the energy consumption and maintenance cost for the disinfection system.[19,20] In addition, the removal of nanoparticles from the water after disinfection is another concern, as the nanoparticles will also generate environmental risk if they are discharged into the natural environment without efficient treatment. Thus, research on the optimization of disinfection with metal ions is still necessary to achieve a high efficiency, reduced environmental effects, and ease of operation.

To optimize the method for the disinfection of viruses with metal ions, as well as to reduce the cost, energy consumption, and environmental risk, a novel magnetic nanoparticle with permanently confined micelle arrays (Mag-PCMA) was coated with metal ions through sorption and used to disinfect and remove target viruses under different environmental conditions. Mag-PCMA have been used to remove a wide range of contaminants, including persistent organic pollutants, emerging contaminants, and even oxyanions such as nitrate, phosphate, perchlorate, and others.[21−27] However, this is the first time they have been used for disinfection of waters with viruses. In contrast to previous disinfection methods in which the waterborne viruses are exposed to the metal ions or to metallic nanoparticles, the proposed method uses adsorption of the metal ions on the surface of magnetic nanoparticles, and then the magnetic nanoparticles coated with metal ions (Mag-PCMA-MI) are used for disinfection. In this way, the novel magnetic nanoparticles can retain the disinfection ability of the metal ions and can be easily removed from the water with an external magnetic field after treatment. After one removal cycle, the magnetic nanoparticles can be regenerated and reused for several continuous cycles by simply being rinsed with water, which makes this method suitable for sustainable use.

2. MATERIALS AND METHODS

2.1. Materials. *Escherichia* bacteriophage MS-2 was selected as the target virus in this study, as it has been used as a surrogate for pathogenic RNA viruses in many studies to evaluate the efficacy of disinfection technology, because it is harmless to humans and is easy to propagate, store, and quantify.[28,29] *Escherichia coli* C-3000 was used as the host of MS-2. Both MS-2 and *E. coli* C-3000 were purchased from ATCC. Silver nitrate, copper sulfate, iron nitrate, nitric acid, sulfuric acid, sodium hydroxide, sodium chloride, and calcium carbonate were purchased from Fisher Scientific. The magnetic nanoparticle, Mag-PCMA, was synthesized using the method developed in our previous studies,[21−27] and the maghemite [iron(III) oxide] nanoparticles (30 nm in diameter) used for synthesis were purchased from Alfa Aesar. In brief, the Mag-

PCMA was prepared by a three-step procedure. First, maghemite iron(III) oxide nanoparticles were negatively activated by dispersing the magnetic nanoparticles in a tetramethylammonium hydroxide solution under constant stirring, overnight. Next, a cationic surfactant, 3-trimethoxysilyl propyl octadecyl dimethylammonium chloride, was deposited onto the activated magnetite surface while the suspension was being constantly stirred. In the end, tetraethyl orthosilicate was attached to the trimethoxysilyl groups of the surfactants through covalent bonds to cross-link the surfactant onto the magnetic iron core. All of the steps were performed at room temperature. All chemicals were used as received without further purification. All solutions were prepared with deionized water (18 MΩ cm) from a Barnstead NANOpure Diamond Water Purification System.

2.2. Synthesis and Characterization of Mag-PCMA Coated with Metal Ions (Mag-PCMA-MI). Various types of metal ions were adsorbed onto Mag-PCMA to enhance the electrostatic interaction between nanoparticles and MS-2 for disinfection, as both the Mag-PCMA and MS-2 are negatively charged in a neutral environment (the ζ potential of Mag-PCMA is approximately −30 mV,[21] and the isoelectric point of MS-2 is 3.5[30]). Ag^+, Cu^{2+}, and Fe^{3+} were selected for the preparation of nanoparticles to compare their disinfection ability on the target virus and their cost. In this study, 50 mg of Mag-PCMA was exposed to different concentrations of metal ion solutions (Ag^+, Cu^{2+}, and Fe^{3+}, 20−150 mg/L) in 20 mL vials for sorption at room temperature. After sorption reached equilibrium, the Mag-PCMA-MI were separated with a hand-held magnet, and samples were collected from the supernatant to measure the concentration of metal ions via an Agilent 7900 (Agilent Technologies) inductively coupled plasma mass spectrometer (ICP-MS). The concentration of metal ions adsorbed onto Mag-PCMA can be calculated and used to develop the relationship between the ζ potential and the concentration of adsorbed positive charges. Mag-PCMA-MI were then washed twice with deionized water and dried in the oven at 75 °C for 24 h. Dried nanoparticles were dispersed in water again, and the dispersion was used for ζ potential analysis by a Malvern Zetasizer.

2.3. Removal of MS-2 with Mag-PCMA-MI. MS-2 was mixed with different concentrations of the various Mag-PCMA-MI (0.5−2.5 g/L) in a 20 mL glass vial for disinfection and removal. Samples were collected at various contact times (0.5, 1, and 2 h) and passed through a 0.22 μm Millipore filter for measurement. The removal process was performed in a pH 6.0 environment adjusted via a phosphate-buffered saline solution. The concentration of infectious MS-2 in each sample was determined by a double-layer agar plaque assay.[31] In brief, the sample was diluted properly, and then 100 μL of the diluted sample was mixed with 100 μL of the *E. coli* host at exponential phase and 5 mL of melted tryptic soy agar (with 0.75% agar) that was kept in a 45 °C water bath. The mixture was then poured onto the tryptic soy agar plate (with 1.5% agar) immediately, and the agar plate was incubated at 37 °C for 24 h. The number of plaques on the agar plate was then counted, and the concentration of MS-2 was calculated and measured as plaque-forming units (PFU) per milliliter.

Different environmental conditions, including the pH, water hardness, concentration of Cl−, and natural organic matter (NOM), were evaluated to explore their possible influence on the efficacy of removal by Mag-PCMA-MI. The pH of the deionized water was adjusted from 6 to 8 using 0.1 M NaOH,

and a phosphate-buffered saline solution was added to maintain a stable pH. To adjust the water hardness from soft to hard, 50 and 100 mg/L $CaCO_3$ were used. Different concentrations of Cl^- (1−100 mg/L) were added to the mixture to explore the possible influence of Cl^- on removal. This could be especially important for Mag-PCMA-Ag, as the combination of free Cl^- and adsorbed Ag^+ on Mag-PCMA may affect the removal efficacy. In addition, humic acid (HA) at different concentrations (0, 1, and 10 mg/L) was added to the system to explore the influence of NOM.

2.4. Regeneration and Reuse of Mag-PCMA-MI. Regeneration and reuse of Mag-PCMA-MI were investigated in this study. A suspension of MS-2 (2.2×10^6 PFU/mL) was exposed to 2.5 g/L Mag-PCMA-Ag, Mag-PCMA-Cu, or Mag-PCMA-Fe for 1 h to achieve sufficient removal. After removal by an external hand-held magnet, the Mag-PCMA-MI were then rinsed two or three times with deionized water to remove the inactivated virus from the surface and reused for another removal cycle immediately. Deionized water was used in the washing step because the magnetic nanoparticles with metal ions are very sensitive to the pH of the environment, and a more basic pH would decrease their ζ potential, weakening the electrostatic interaction between the nanoparticles and target viruses (Table S1). The continuous removal and regeneration cycles were repeated five times. Samples were collected in each cycle, and the concentration of MS-2 was measured with a double-layer agar plaque assay.

2.5. Data Analysis. All tests in this study were performed in triplicate, and analysis of variance (ANOVA) was used to test the significance of the results. A p value of <0.05 was considered to be statistically significant. The p values of each test are listed in Table S2.

3. RESULTS AND DISCUSSION

3.1. Sorption-Based Characterization of Mag-PCMA by Metal Ions. The ζ potential is an important indicator that reflects the stability of nanoparticle dispersions. Previous studies have shown that the ζ potential of ∼30 nm Fe_2O_3 nanoparticles is negative when the pH is >4.[32] To attract negatively charged MS-2 in neutral environments, the surface of Mag-PCMA was modified to be positively charged using different concentrations of Ag^+, Cu^{2+}, and Fe^{3+}. The metal ion solutions were individually mixed with Mag-PCMA to adsorb the metal ions. After sorption reached equilibrium, the relationship between the ζ potential of Mag-PCMA-Ag, Mag-PCMA-Cu, and Mag-PCMA-Fe and the amount of adsorbed positive charges was explored. The amount of adsorbed positive charges can be calculated with the concentration of adsorbed metal ions on Mag-PCMA and the charge number for each metal ion (eq 1):

[adsorbed positive charges]

$$= \text{[adsorbed metal ions]} \times \text{charge number} \quad (1)$$

The relationships between the ζ potential and adsorbed positive charges with data from the three systems are shown in Figure 1, and the linear relationship in Figure 1 can be described by eq 2:

$$\zeta \text{ potential} = K_{MI}\text{[adsorbed positive charges]} + b \quad (2)$$

where K_{MI} (volt liter per equivalent) is the coefficient of relationship and b (millivolts) equals the ζ potential of Mag-
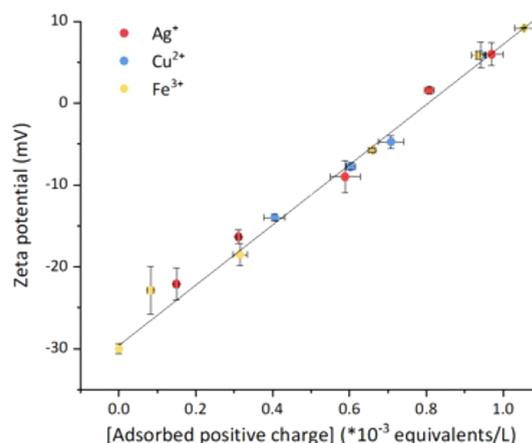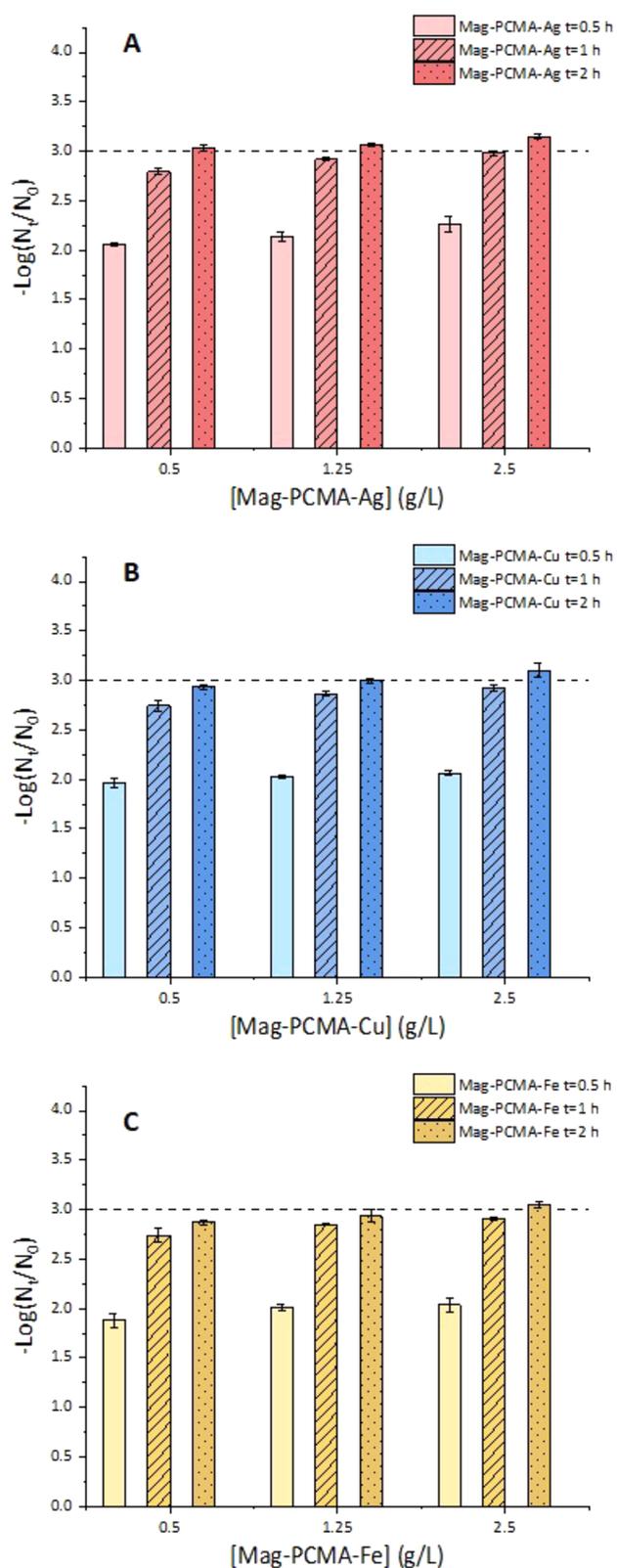

Figure 1. Relationship between the concentration of the positive charge and ζ potential. Red plots refer to the data from sorption of Ag^+ by Mag-PCMA, blue plots to those from sorption of Cu^{2+}, and yellow plots to those from sorption of Fe^{3+}.

PCMA with no metal ions on the surface. Based on Figure 1, the K_{MI} is 37.895 V L equiv^{-1} and b is −30 mV ($R^2 = 0.9862$).

On the basis of the relationship in Figure 1 and the corresponding K_{MI} and b, as well as the relationship between the concentration of adsorbed metal ions and positive charges (eq 1), the minimum concentration of adsorbed metal ions needed to convert the ζ potential of Mag-PCMA from negative to positive can be calculated. For Ag^+, the value is 7.9×10^{-4} equiv/L. For Cu^{2+}, it is 3.9×10^{-4} equiv/L. For Fe^{3+}, it is 2.6×10^{-4} equiv/L. Due to the limitation of the available sorption sites on the surface of Mag-PCMA, there is a maximum sorption capacity that reflects the maximum adsorbed concentration of each metal ion under a specific condition. The maximum sorption capacity for Ag^+, Cu^{2+}, and Fe^{3+} by Mag-PCMA was calculated on the basis of the Langmuir isotherm equation, and the calculation results as well as the R^2 for each system are listed in Table S3. Within the range between the minimum and maximum adsorbed concentration mentioned above, one can control the ζ potential of Mag-PCMA-MI by adjusting the concentration of metal ions adsorbed to Mag-PCMA using eqs 1 and 2.

3.2. Effectiveness of Disinfection of MS-2 by Three Types of Mag-PCMA-MI. Three types of Mag-PCMA-MI with different adsorbed metal ions (i.e., Mag-PCMA-Ag, Mag-PCMA-Cu, and Mag-PCMA-Fe) with similar ζ potentials were used for the removal of MS-2, and the concentration of infectious virus after removal was measured. The removal efficiency is defined in terms of the log removal value [removal efficiency = $-\log(N_t/N_0)$, where N_t is the number of MS-2 at time t and N_0 is the initial number of MS-2 (1.6×10^6 PFU/mL in this study)]. The concentration of MS-2 in the control remains stable during the removal process, as there is no disinfectant or *E. coli* host in the aqueous environment that may result in a decrease or increase in MS-2 concentration, respectively. Figure 2 presents the relationship between the removal efficiency and concentration of Mag-PCMA-MI at different contact times. According to Figure 2, the removal ability of three Mag-PCMA-MI at the same concentration and contact time decreases in the following order: Mag-PCMA-Ag > Mag-PCMA-Cu > Mag-PCMA-Fe. The main reasons are the mechanisms of the removal process include both electrostatic interaction between positively charged Mag-PCMA-MI and

Figure 2. Relationship between the concentration of (A) Mag-PCMA-Ag, (B) Mag-PCMA-Cu, and (C) Mag-PCMA-Fe and the removal efficiency at different contact times [the dashed line refers to the equation $-\log(N_t/N_0) = 3.0$, with a high removal efficiency of 99.9%].

negatively charged MS-2 (at pH 6) and the destruction of the host-cell receptor or the nucleic acid of MS-2 by the adsorbed

metal ions on the surface of Mag-PCMA (Figure 3).[15] Because the ζ potential of the three Mag-PCMA-MI are quite close (11.5 eV for Mag-PCMA-Ag, 11.9 eV for Mag-PCMA-Cu, and 11.7 eV for Mag-PCMA-Fe), the difference in electrostatic interaction between three Mag-PCMA-MI and MS-2 is not significant. Thus, the slight difference in removal efficiency among the three Mag-PCMA-MI is mainly due to the disinfection ability of adsorbed metal ions on Mag-PCMA. Although the disinfection mechanism of metal ions on viruses is not yet fully understood, it is believed that the inactivation of viruses by free metal ions is mainly due to the combination with amino acids and prevention of RNA replication, and that disinfection capacity is proportional to the concentration of metal ions.[33,34] On the basis of the relationship between the concentration of adsorbed metal ions and ζ potential, to achieve the same ζ potential, more Ag^+ needs to be adsorbed on Mag-PCMA than Cu^{2+} or Fe^{3+}. As a result, a higher concentration of adsorbed Ag^+ will lead to more MS-2 being inactivated by Mag-PCMA-Ag than by Mag-PCMA-Cu and Mag-PCMA-Fe during the removal process. In addition, previous studies have shown that free Ag^+ is a better disinfectant than Cu^{2+} or Fe^{3+}, as less free Ag^+ is needed to achieve the same disinfection effectiveness compared to the amounts of other metal ions.[29] Thus, Mag-PCMA-Ag can disinfect MS-2 more effectively than Mag-PCMA-Cu or Mag-PCMA-Fe due to the difference in the disinfection ability of free metal ions.

The concentration of magnetic nanoparticles and contact time are two major factors that determine the removal efficiency of MS-2. As shown in Figure 2, for all three types of Mag-PCMA-MI, the removal efficiency increased with the concentration of Mag-PCMA-MI at any contact time. With more Mag-PCAM-MI added to the system, there will be more adsorbed metal ions in the water, which will both increase the amount of positive surface exposed to MS-2, thus strengthening the electrostatic interaction, and inactivate more MS-2 to reduce the concentration of viable virus. The contact time is another factor that determines the removal efficiency of MS-2. As shown in Figure 2, for all three types of Mag-PCMA-MI, the removal efficiency increased with the Mag-PCMA-MI contact time at any concentration, indicating that the disinfection processes are time-dependent. Although a small fraction of metal ions will leach into the water after removal (0.8% of adsorbed Ag^+, 0.6% of adsorbed Cu^{2+}, and 0.9% of adsorbed Fe^{3+}), the concentration of residual metal ions can be maintained below a safe level by adjusting the amount of metal ions coated onto Mag-PCMA during the sorption process.[35] The residual metal ions in the water can also serve as a long-term disinfectant during the distribution of treated water to prevent target viruses from growing again.[36] Thus, the removal of MS-2 with Mag-PCMA-MI should not lead to additional environmental effects.

3.3. Influence of Environmental Conditions on Viral Disinfection. *3.3.1. pH.* The influence of pH on the removal process with different Mag-PCMA-MI was evaluated by adjusting the pH from 6 to 8 with 0.1 M NaOH. As shown in Figure 4A, the removal efficiency of all three Mag-PCMA-MI decreased with an increase in pH, and the decrease was more significant for Mag-PCMA-Ag than for Mag-PCMA-Cu or Mag-PCMA-Fe. The decrease in log 10 reduction from pH 6 to 8 is 0.52 for Mag-PCMA-Ag, 0.46 for Mag-PCMA-Cu, and 0.38 for Mag-PCMA-Fe. The most likely reasons are that the change in pH will not only influence the conformation of
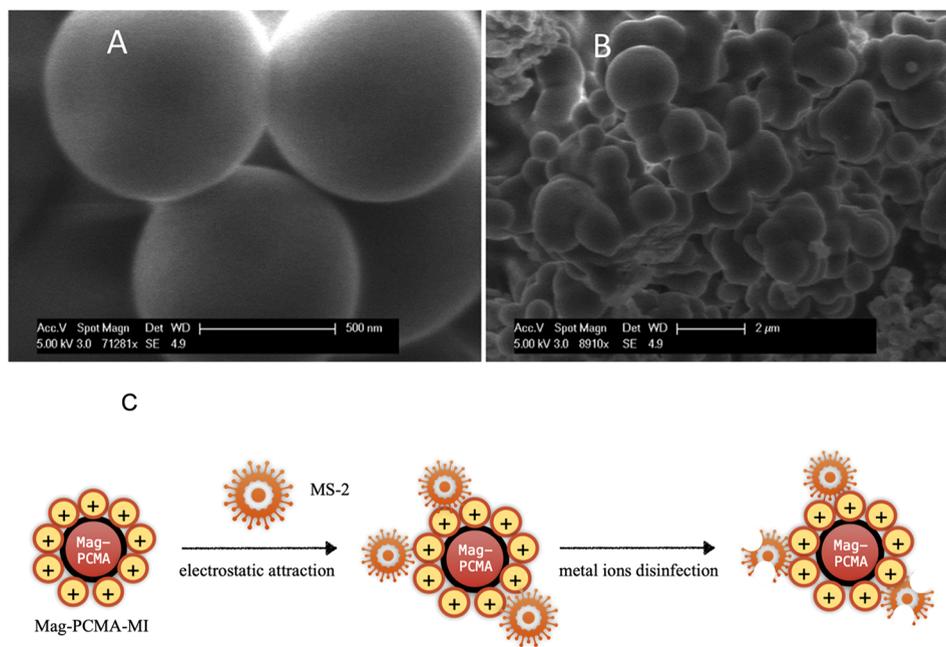
Figure 3. (A) Scanning electron microscopy (SEM) images of Mag-PCMA at 71281× and (B) SEM images of Mag-PCMA at 8910×[26] (adapted with permission from ref 26. Copyright 2013 American Chemical Society.) (C) Schematic representation of the disinfection mechanism with Mag-PCMA-MI.

the virus and its susceptibility to disinfection but also determine the speciation of adsorbed metal ions, thus weakening the removal ability.[16,37,38] In addition, the decrease in the level of adsorbed free metal ions will lead to a decrease in the ζ potential, thus weakening the electrostatic interaction. The influence of increasing OH^- concentration is more significant for Mag-PCMA-Ag than Mag-PCMA-Cu or Mag-PCMA-Fe, indicating that Mag-PCMA-Fe is more stable under variable environmental conditions than Mag-PCMA-Ag or Mag-PCMA-Cu.
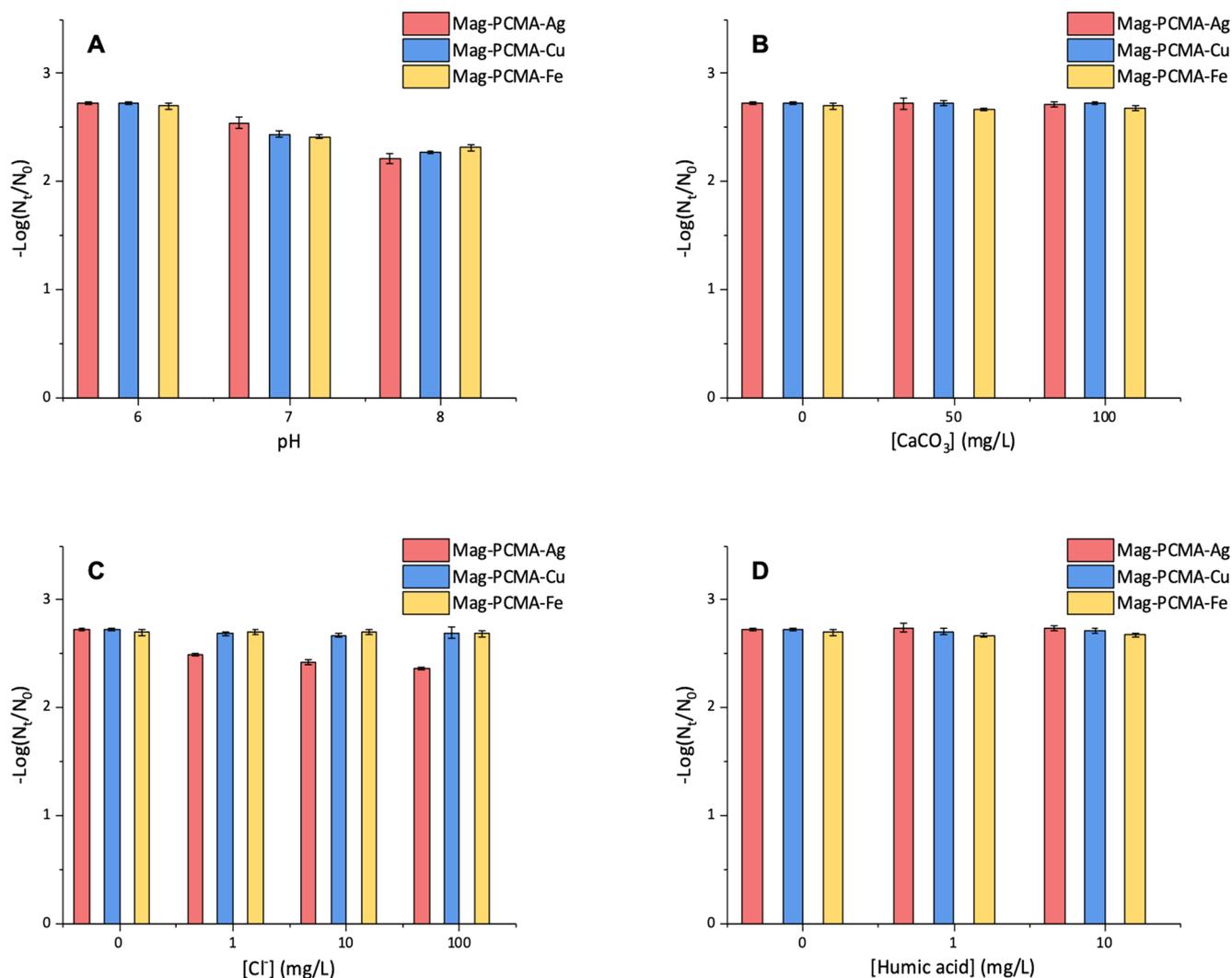
3.3.2. Water Hardness. Different concentrations of $CaCO_3$ (0−100 mg/L) were added to the system to simulate a soft or hard water condition, and the influence of water hardness on the removal process was evaluated. As shown in Figure 4B, no significant influence on the removal efficiency of MS-2 was observed with all three Mag-PCMA-MI (*p* value test in Table S2). This is mainly because the speciation of adsorbed Ag^+, Cu^{2+}, and Fe^{3+} did not change substantially with the addition of $CaCO_3$.[39,40] Thus, the removal ability of all three Mag-PCMA-MI remained stable with a change in the hardness of the water.

3.3.3. Cl⁻ Concentration. The influence of Cl^- at different concentrations (0−100 mg/L) was also evaluated to determine if there would be a change in the removal efficiency for the three Mag-PCMA-MI, as Cl^- is one of the common constituents in water. According to the results depicted in Figure 4C, the presence of Cl^- had no influence on the removal process with Mag-PCMA-Cu or Mag-PCMA-Fe, as the adsorbed Cu^{2+} and Fe^{3+} are not influenced by Cl^-. However, Mag-PCMA-Ag will be affected by Cl^-, as Cl^- can combine with Ag^+ and form AgCl on the surface, thus reducing the concentration of available Ag^+ and weakening the removal of MS-2. As the concentration of Cl^- increased from 0 to 100 mg/L, the log 10 reduction with Mag-PCMA-Ag decreased from 2.73 to 2.37. However, the removal efficiency still remains above 99% (>2 in log 10 reduction) even with a high Cl^-

concentration, indicating that this method is quite stable with a change in the natural environment.

3.3.4. NOM. NOM, which is derived from decaying plant and animal matter, is one of the main constituents in many environmental and drinking supply water sources and is a major factor that must be considered in water treatment. In this study, humic acid was used as a representative of NOM and different concentrations of humic acid (0−10 mg/L) were added to the system for evaluation. As shown in Figure 4D, no significant influence on removal efficiency was observed for any of the three Mag-PCMA-MI (*p* value test in Table S2). Although HA could form complexes with Fe^{3+}, Cu^{2+}, and Ag^+, and the metal ion−HA complexes are not so toxic compared to free ions,[41−43] the affinity is quite limited in the HA concentration range considered in this study (0−10 mg/L). Thus, the influence of humic acid on the removal process is negligible.

3.4. Regeneration and Reuse of Mag-PCMA-MI. The removal efficiency of three Mag-PCMA-MI in each regeneration cycle was measured and is shown in Figure 5. The removal efficiency decreased slightly for all three types of Mag-PCMA-MI (a decrease of 0.20 in log 10 for Mag-PCMA-Ag, 0.19 for Mag-PCMA-Cu, and 0.15 for Mag-PCMA-Fe), mainly due to the inevitable mass loss during the regeneration of nanoparticles by the external magnet, as well as the mass loss that occurred during the washing step. Because the number of nanoparticles is one of the main factors that determine the disinfection effectiveness, the mass loss will lead to a decrease in the removal efficiency during the continuous regeneration cycles. However, the removal efficiency remains at a high level even after five cycles (2.79 for Mag-PCMA-Ag, 2.76 for Mag-PCMA-Cu, and 2.78 for Mag-PCMA-Fe), indicating that the reusability of all three Mag-PCMA is very promising. The concentration of viable MS-2 in the rinsing water during each regeneration cycle is negligible, as previous studies have shown that MS-2 can be effectively inactivated by free metal ions

Figure 4. Influence of different (A) pH values, (B) water hardness values, (C) Cl⁻ concentrations, and (D) NOM concentrations on the removal of MS-2 by three types of Mag-PCMA-MI.
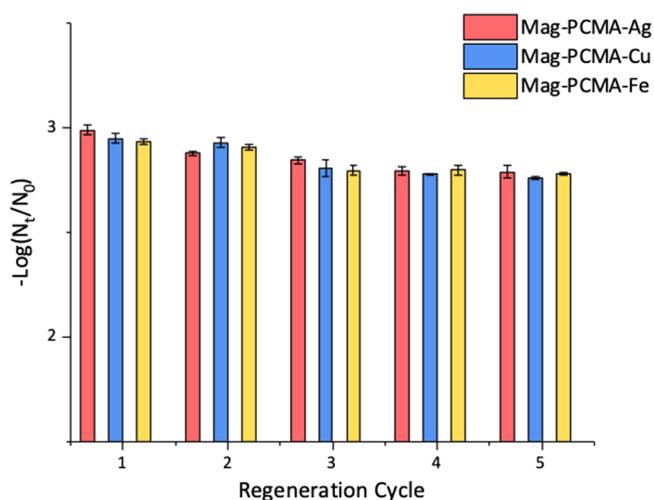
Figure 5. Removal efficiency of MS-2 by three types of Mag-PCMA-MI after five regeneration cycles.

within a short contact time;[16] thus, most of the MS-2 attached to Mag-PCMA-MI will be inactivated by the adsorbed metal

ions during the removal process. Therefore, no additional environmental risk will arise during the regeneration cycles.

4. CONCLUSION

In this study, a novel method for disinfecting and removing viruses from water was explored and evaluated by using magnetic nanoparticles coated with metal ions. The negatively charged Mag-PCMA can be positively charged by adsorbing different metal ions, and the ζ potential has a linear relationship with the concentration of adsorbed positive charge, which is determined by both the number of positive charges in each metal ion and the adsorbed concentration of metal ions. The minimum adsorbed concentration of the metal ion needed to convert the ζ potential from negative to positive for Mag-PCMA-MI can be calculated with a linear relationship. The Mag-PCMA-MI were then used to explore the removal of MS-2 from the water. All three Mag-PCMA-MI achieved very good viral removal efficiencies with proper concentrations and within a short contact time (a log 10 reduction of >2.8 with a 2 h contact time). The differences in removal ability among Mag-PCMA-Ag, Mag-PCMA-Cu, and Mag-PCMA-Fe were mainly due to the removal mechanisms, which can be attributed to a combination of electrostatic attraction by the

positively charged Mag-PCMA-MI and the destruction of viral structure caused by adsorbed metal ions on Mag-PCMA. Although Mag-PCMA-Ag can achieve better removal efficiency than Mag-PCMA-Cu and Mag-PCMA-Fe with a similar ζ potential, the difference in the removal efficiency among these three Mag-PCMA-MI is not significant (e.g., the difference in removal efficiency between 2.5 g/L Mag-PCMA-Ag and Mag-PCMA-Fe after 3 h is merely 0.02%). Thus, Mag-PCMA-Fe is a competitive option for the removal process when considering the cost of each metal ion.

Various environmental conditions, including the pH, water hardness, presence of Cl^-, and NOM, were evaluated to explore the possible influence on the removal process with three Mag-PCMA-MI. No obvious influence was observed with a change in water hardness or NOM concentration, as the presence of $CaCO_3$ and humic acid will not change the speciation of adsorbed metal ions and thus will not influence the removal ability. The pH does have a significant influence on the removal process. With an increase in pH, the removal efficiency decreased noticeably for all three Mag-PCMA-MI, as the change in pH will influence the interaction between the protein of MS-2 and the metal ions. The presence of Cl^- will not influence the removal with Mag-PCMA-Cu or Mag-PCMA-Fe but will influence the disinfection process with Mag-PCMA-Ag, as Cl^- can combine with the adsorbed Ag^+ and form AgCl, thus weakening the disinfection ability of Ag^+. Although some change in the environmental conditions will lead to a decrease in the removal efficiency, the removal efficiency of MS-2 with three Mag-PCMA-MI remains high, indicating that this disinfection method is quite stable.

The reusability of Mag-PCMA-MI was evaluated in this study to explore the sustainability of this method by regenerating and reusing the three Mag-PCMA-MI for five continuous removal cycles. Although the removal efficiency decreased slightly during the five cycles due to incomplete recovery of Mag-PCMA-MI, the removal efficiency remained above 2.75 of log 10 reduction, indicating the reuse of Mag-PCMA-MI is very promising. Compared to conventional disinfection methods for viruses, this method with metal ion-coated Mag-PCMA has several advantages. First, the free metal ions are fixed to the surface of Mag-PCMA and can be removed by an external magnet simultaneously, thus reducing the potential risk caused by free metal ions left in the treated water after disinfection. In addition, no extra removal process is needed to deal with the residual metal ions after disinfection as they can be maintained within a safe level, which will simplify the disinfection process. Second, several metal ions can provide very good disinfection, which can be used alternatively to avoid the resistance of target microorganisms after long-term application. Third, the Mag-PCMA-MI can be reused for several cycles, which makes this method quite sustainable. Thus, this method is very promising for practical use in the future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.2c00026.

Relationship between the pH and ζ potential of three Mag-PCMA-MI, statistical analysis of results, and calculation of the maximum sorption capacity of Ag^+, Cu^{2+}, and Fe^{3+} by Mag-PCMA (PDF)

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Notes

The authors declare no competing financial interest.

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