Abstract: Mn(III) oxidation technology has attracted increasing interest in recent years because of its fast decontamination kinetics and second-pollution-free characteristic. Whether it can be used as a pre-oxidation step to enhance conventional coagulation process remains to be evaluated. Herein, an Fe-coagulation/sedimentation process combined with Mn(III) pre-oxidation (Mn(III)+C/S), hypochlorite pre-oxidation (Cl₂+C/S), and permanganate pre-oxidation (PM+C/S) was applied to treat simulated micro-polluted raw water. The removal performance of routine water quality indices (turbidity, dissolved organic carbon, total nitrogen, nitrate-nitrogen, ammonia-nitrogen, Pb(II), and Cr(VI)) and the emerging pollutants (acesulfame, carbamazepine, bisphenol S, and nano-ZnO) created by these three processes were researched. The mechanism of how Mn(III) pre-oxidation influences C/S was explored by identifying the transformation products of Mn(III), measuring the timely variation of flocs’ zeta potential and size, and scanning flocs’ micromorphology. Compared to Cl₂+C/S and PM+C/S, Mn(III)+C/S exhibited its superiority in removing dissolved organic carbon (72.9%), total nitrogen (31.74%), and emerging pollutants (21.78%–93.49%). The enhanced removal of these contaminants by Mn(III)+C/S found its explanation in the strong oxidation power of Mn(III) and the multiple roles of in-situ formed MnO₂ (e.g., flocculation core, adsorption co-precipitant, and densification agent). The acute toxicity tests confirmed that water treated by Mn(III)+C/S did not show a significant change in the associated toxicity. The findings of the present study indicate that Mn(III) oxidation technology shows great potential as an alternative to pre-oxidation technology of waterworks.

Keywords: pre-oxidation; enhanced coagulation; Mn(III); emerging pollutants; micro-polluted raw water

1. Introduction

In the past few decades, drinking water resources of many cities in China have been subject to varying degrees of pollution (micro-polluted raw water) [1–5], which threatens the safety of drinking water. The pollutants include ammonia nitrogen (NH₄⁺–N), dissolved organic materials (particularly non-acidic hydrophilic fraction), heavy metals, emerging pollutants (endocrine disrupting compounds (EDCs), pharmaceuticals and personal care products (PPCPs), taste and odor
compounds, and engineered nanomaterials), etc. It is difficult to remove them by the traditional coagulation–sedimentation–filtration–disinfection process, which subsequently results in a lot of problems, including the occurrence of colors, tastes, and odors, formation of disinfection byproducts (DBPs), and the increase of coagulant/chlorine demands [6–8]. Moreover, these risks become more highlighted for low-temperature raw water because of the low coagulation kinetics under cold conditions [9]. To improve the efficiency of coagulation and save coagulants, a mass of methods such as pre-oxidation [6], coagulant aids [10–12], high-efficient coagulant [13,14], etc. have been developed. Among these methods, pre-oxidation has attracted worldwide attentions because of its excellent effect on improving coagulation, easy operation, and low cost. In the pre-oxidation processes, oxidants such as chlorine are introduced at the beginning of the purification project to destroy hydrophilic organic compounds that stabilize dispersed colloids in the water and thus create favorable conditions for coagulation.

Chlorine, chlorine dioxide (ClO₂), ozone (O₃), permanganate (PM), and hydrogen peroxide (H₂O₂) are the commonly used oxidants for pre-oxidation to enhance coagulation. Ozone pre-oxidation has been used to assist coagulation to improve the removal of color, smell, algae, NH₄⁺–N, iron, and manganese [15]. However, the challenges associated with O₃ pre-oxidation, such as bromate and low-molecular-weight aldehydes, ketones, and organic acids (disinfection by-product precursors) [16] have been reported. Pre-oxidation with chlorine has been proved to be efficient in improving coagulation to eliminate soluble iron, manganese, sulfite, NH₄⁺–N, color, taste and odor compounds, and organic micro-pollutants [8,17]. However, there is a dark side of chlorine pre-oxidation—chlorine reacts with natural organic matters to produce a range of toxic DBPs [18,19]. ClO₂ can achieve the benefits of raw water pre-oxidation without forming significant levels of trihalomethane and haloacetic acid; it is gaining more popularity as an alternative to chlorine in drinking water treatment [20]. It is an effective oxidizer of iron and manganese, and an effective remover of color, taste, and odor of the source water [21,22]. Additionally, it is an effective killer of Cryptosporidium and Giardia, at shorter contact times than chlorine [23]. Yet, there are a few disadvantages to ClO₂ systems. ClO₂ is often used as only a primary disinfectant because of its low stability, undesirable taste, obnoxious odor, explosive properties, and formation of regulated inorganic DBPs [20]. Although the oxidation potential of H₂O₂ is greater than that of chlorine or ClO₂, the rate of its reaction or decomposition in water treatment at ambient temperature is very slow, so catalysts (transition metal salts, UV, or O₃) are often necessary [24]. The role of PM pre-oxidation in drinking water treatment is to remove taste and odor compounds, color, dissolved iron and manganese, and organic matters [25]. PM is also used to prevent biological growth by directly oxidizing cell material and destroying essential enzymes of bacteria, fungi, viruses, and algae [26]. The consumption of alkalinity from reactions between PM and natural organic matters is often a concern for plants practicing alum coagulation, which requires high alkalinity. As the PM solution is an intense purple color, to avoid increasing color and dissolved/precipitated manganese of the treated water, dosage of PM adopted in waterworks is usually low and long contact time is demanded. Therefore, it is of practical significance to develop green and efficient pre-oxidation technologies.

Recently, Mn(III) based-oxidation technologies (Mn(III)–OTs) have attracted increasing attention due to its high efficiency in degrading trace organic pollutants in water. It was found to oxidize micropollutants 5–6 orders of magnitude faster than those measured for permanganate alone, and 4 to 6 orders of magnitude faster than conventional advanced oxidation processes for water treatment [27]. Moreover, in-situ-formed manganese oxide (mainly in the form of MnO₂), after Mn(III) oxidation possesses a strong absorption capacity and displays a catalytic effect, which benefit the removal of pollutants through the subsequent coagulation and filtration process [28–32]. Mn(III) can be generated by the ionization of manganese acetate [33], metal oxide surface catalysis [34], reduction of Mn(VII) and Mn(IV) [27,35], Mn(II) electrolysis [36], high-energy radiation of Mn(II) [37], etc. Among them, S(IV) (including sulfite and bisulfite) reduction of permanganate is promising due to its mild operating conditions and economy. Due to the fast reaction kinetics of Mn(III) (finishing reactions within
several seconds), Mn(III)–OTs can be easily applied without changing the structure of water plants. On the basis of the above findings, we concluded that Mn(III)–OTs might act as an alternative to the pre-oxidation process.

To date, few studies have considered the potential of using Mn(III)–OTs to enhance the coagulation process. To address this point, this study evaluated the advantages of combining Mn(III) oxidation and coagulation to remove conventional contaminants (turbidity, dissolved organic carbon (DOC), total nitrogen (TN), nitrate nitrogen (NO$_3^-$–N), ammonia nitrogen (NH$_4^+$–N), lead (Pb$^{2+}$), hexavalent chromium (Cr(VI)), and emerging pollutants (micro organic pollutants and typical nanoparticle pollutants), and a comparison was made during enhanced coagulation with PM and chlorine. The mechanism of how Mn(III) oxidation influences the coagulation process was explored. The results have shown that the combination of Mn(III)–OT and conventional coagulation is beneficial and synergistic and this is described in detail as follows.

2. Materials and Methods

2.1. Preparation of Simulated Water

Raw water was collected from the Qiantang River and a predesigned substrate (acesulfame (ACE), carbamazepine (CBZ), bisphenol S (BPS), nano-ZnO) was artificially added. ACE, CBZ and BPS were chosen as representatives of trace emerging organic pollutants with different polarity. Nano-ZnO was used as a delegate of nanoparticle pollutants. The designed concentration of ACE, CBZ, BPS, and nano-ZnO referenced the reported value in previous works [38–40]. Table 1 shows the specific quality parameters of the simulated water.

<table>
<thead>
<tr>
<th>Index</th>
<th>Value</th>
<th>Index</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$–N (mg·L$^{-1}$)</td>
<td>0.41</td>
<td>NH$_4^+$–N (mg·L$^{-1}$)</td>
<td>0.53</td>
</tr>
<tr>
<td>HCO$_3^-$ (mg·L$^{-1}$)</td>
<td>25.42</td>
<td>Pb$^{2+}$ (mg·L$^{-1}$)</td>
<td>0.19</td>
</tr>
<tr>
<td>Cl$^-$ (mg·L$^{-1}$)</td>
<td>22.08</td>
<td>Cr(VI) (mg·L$^{-1}$)</td>
<td>0.18</td>
</tr>
<tr>
<td>Total phosphorus (TP, mg·L$^{-1}$)</td>
<td>0.13</td>
<td>Nano-ZnO (mg·L$^{-1}$)</td>
<td>0.10</td>
</tr>
<tr>
<td>TN (mg·L$^{-1}$)</td>
<td>1.16</td>
<td>CBZ (mg·L$^{-1}$)</td>
<td>0.05</td>
</tr>
<tr>
<td>Ca$^{2+}$ (mg·L$^{-1}$)</td>
<td>9.01</td>
<td>ACE (mg·L$^{-1}$)</td>
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</tr>
<tr>
<td>UV$_{254}$ (cm$^{-1}$)</td>
<td>0.03</td>
<td>BPS (mg·L$^{-1}$)</td>
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</tr>
<tr>
<td>pH</td>
<td>7.6</td>
<td>Turbidity (NTU)</td>
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</tr>
<tr>
<td>Temperature (°C)</td>
<td>19.0</td>
<td>Ionic strength (mol·kg$^{-1}$)</td>
<td>$1.4 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

2.2. Chemicals

FeCl$_3$, KMnO$_4$, Na$_2$SO$_3$, NaOH, MnSO$_4$, NaOCl, Pb(NO$_3$)$_2$, and K$_2$Cr$_2$O$_7$ (Cr(VI)) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) without further purification. Nano-ZnO (99.9%, 30 ± 10 nm), CBZ (≥98%), ACE (≥98%), and BPS (99%) were ordered from Aladdin Chemistry Co. Ltd. (Shanghai, China).

2.3. Coagulation Method for Simulating Waterworks Treatment Process

The coagulation jar tests were conducted on a program-controlled jar test apparatus (ZR4-4, Zhongrun Water Industry Technology Development Co. Ltd., Shenzhen, China). The mixing speed was maintained at 200 rpm (328.9 s$^{-1}$) for 2 min, and then decreased to 20 rpm (10.4 s$^{-1}$) for 20 min, with a subsequent 30 min sedimentation. FeCl$_3$ was chosen as the coagulant. In a typical run, the dosage of FeCl$_3$, KMnO$_4$, and chlorine (NaOCl) were, respectively, 20.0 mg·L$^{-1}$ (C(Fe$^{3+}$)/C(OH$^{-}$) = 15.7), 1.0 mg·L$^{-1}$, and 1.0 mg·L$^{-1}$ (as Cl$_2$), which was based on the actual water plants [41]. Mn(III) was generated in situ via a reaction of KMnO$_4$ with Na$_2$SO$_3$ with a molar ratio of 1:5, and the optimal dosage of KMnO$_4$ (15.0 mg·L$^{-1}$) and Na$_2$SO$_3$ (59.8 mg·L$^{-1}$) was screened out by pretests. All experiments
were conducted in triplets and the results were reported as mean ± standard deviation. For the convenience of subsequent discussion, the coagulation/sedimentation process was abbreviated as C/S, and C/S combined with Cl₂, KMnO₄, and Mn(III) pre-oxidation were abbreviated as Cl₂+C/S, PM+C/S, and Mn(III)+C/S, respectively. The experimental procedure is shown in Figure 1.

2.4. Analysis

Turbidity was measured by U.S. Hash 2100P Turbidimeter. Dissolved organic carbon (DOC) was determined by total organic carbon analyzer (TOC-VCPH, Shimadzu, Tokyo, Japan). A Hach DR6000 UV-Vis spectrophotometer was used to determine total nitrogen (TN) which adopted the alkaline potassium persulfate digestion-UV spectrophotometric method. Concentration of ammonia nitrogen (NH₄⁺-N) was determined by Nessler’s reagent spectrophotometry. Nitrate nitrogen (NO₃⁻-N) was analyzed by a Dionex ICS-2000 ion chromatography. Hexavalent chromium (Cr(VI)) and lead (Pb(II)) were quantified using a Perkin Elmer NexION 300 ICP–MS. For the detection of nano-ZnO, samples were pretreated by a high-speed centrifugation and acid digestion, and were then analyzed by ICP–MS. Zeta potential was determined using the Zetasizer Nano Series instrument (Malvern, UK). The floc morphology was visualized by using an FEI Quanta 650 FEG scanning electronic microscope (SEM). XPS was used to determine the oxidation state of Mn at the surface of the flocs. The anhydrous floc samples were collected by discarding supernatant of reaction solution at the end of the sedimentation process and were freeze-dried with the lyophilizer (Scientz-12N, Ningbo, China). For the determination of free Mn(II), the water sample was filtered with a 0.45 µm membrane before being analyzed by inductively coupled plasma mass spectrometry (ICP–MS).

The size variation of flocs involved in the above-mentioned experiments was measured with a laser particle size analyzer (Mastersizer 2000, Malvern, UK). To minimize breakage of flocs before measurement, the floc-containing water was fed into the laser diffractometer through a peristaltic pump (Longerpump, Baoding, China) equipped with a 6 mm inner diameter pipe at a flow rate of 25 mL·min⁻¹. The floc median diameter (d_{0.5}) served as the representative floc size.

The acute bio-toxicity evaluation was performed on a Microtox model 500 and followed the standard Microtox procedure outlined in Microtox system operating manual. The measurements of light output were carried out after 15 min, using the 81.9% screening test method. Toxicity was denoted using the luminescence inhibition rate, which was calculated according to Equation (1).

\[
\text{Luminescence inhibition rate (\%)} = \frac{[\%\text{Luminescence effect}]_0 - [\%\text{Luminescence effect}]_t}{[\%\text{Luminescence effect}]_0} \times 100\%
\] (1)
3. Result and Discussion

3.1. Mn(III) Pre-Oxidation Enhanced Coagulation and Sedimentation Process to Remove the Conventional Pollutants

Figure 2a presents removal performance of conventional pollutants in raw water by Mn(III)+C/S, PM+C/S, and Cl<sub>2</sub>+C/S. The removal rates of turbidity, DOC, TN, NH<sub>4</sub><sup>+</sup>–N, NO<sub>3</sub><sup>−</sup>–N, and TP by C/S were 94.3%, 40.0%, 8.4%, 32.7%, 2.0%, and 99.0%, respectively, while the removal rates of these pollutants by Mn(III)+C/S were 98.4%, 72.9%, 31.7%, 37.9%, 7.3%, and 100%, respectively. It could be seen that, compared to C/S, Mn(III)+C/S showed an obvious improvement in removal of DOC (32.9% increase) and TN (23.3% increase) but showed a subtle enhanced removal for turbidity, NH<sub>4</sub><sup>+</sup>–N, NO<sub>3</sub><sup>−</sup>–N, and TP. As compared to PM+C/S, we observed that the removal enhancement of turbidity, TN, NH<sub>4</sub><sup>+</sup>–N, and NO<sub>3</sub><sup>−</sup>–N were not significant (<5%) with C/S as a reference, and the highlighted performance was the removal of DOC (9.3% increase). The performance of Cl<sub>2</sub>+C/S was similar to that of PM+C/S, except for the NH<sub>4</sub><sup>+</sup>–N removal. NH<sub>4</sub><sup>+</sup>–N elimination by Cl<sub>2</sub>+C/S increased by 25.4% as compared to C/S, which was related to the reaction of chlorine and NH<sub>4</sub><sup>+</sup>–N. Thus, it could be concluded that Mn(III)+C/S showed advantages over Cl<sub>2</sub>+C/S and PM+C/S in the removal of DOC, TN, and NO<sub>3</sub><sup>−</sup>–N. By comparing the redox potentials of Mn(III) (1.51 V), KMnO<sub>4</sub> (0.58 V), and NaOCl (0.84V) under neutral conditions, we judged that the better removal of DOC and TN for Mn(III)+C/S might be partly attributed to the strong oxidizing power of Mn(III).

Compared to C/S, the removal of Cr(VI) and Pb(II) by Mn(III)+C/S, PM+C/S, and Cl<sub>2</sub>+C/S showed a certain degree of improvement (Figure 2a). It is well-established that heavy metal ion removal by C/S is mainly through co-precipitation with suspended colloidal particles such as surface adsorbates and co-precipitation with coagulant hydrolysates (for dissolved metal species) [45]. In addition, metal ions are often present in the form of complexation in raw water (for example, complexing with natural organic matters), which enhances their stability and migration in water. The oxidation of three pre-oxidants might break such complexation and thus enhance the co-precipitation removal of Cr(VI) and Pb(II) [46]. It is noteworthy that Mn(III)+C/S had the highest removal efficiency for Cr(VI) and Pb(II) (10.0%–12.2% higher than that of C/S alone). As the effect of pH can be excluded based on a similar pH variation for the four treatment processes (Figure 2b), the high oxidation potential of Mn(III) and newly formed MnO<sub>2</sub> (Figure A1 in Appendix A) were considered to make Mn(III)+C/S surpass PM+C/S and Cl<sub>2</sub>+C/S.

Figure 2. (a) Removal efficiency of conventional pollutants by C/S and C/S enhanced with Mn(III) pre-oxidation, KMnO<sub>4</sub> pre-oxidation, and chlorine pre-oxidation. (b) The final pH value of simulated water after treatment by different processes.
3.2. Removal of Emerging Micro-Pollutants by Mn(III)+C/S

3.2.1. Emerging Organic Pollutants

Figure 3 plots the removal of CBZ, BPS, and ACE by C/S, Mn(III)+C/S, PM+C/S, and Cl₂+C/S. C/S removed the three target organic pollutants poorly (<3.0%), which was consistent with the previous observation [47]. Differing from C/S, Mn(III)+C/S efficiently reduced these three pollutants (21.8%–93.5%). However, PM+C/S and Cl₂+C/S showed a limited removal of CBZ, BPS, and ACE (<10.0%). The secondary reaction rate constants of KMnO₄ and hypochlorous acid with CBZ, BPS, and ACE are reported to be slow ($10^{-4}$–$10^2$ M$^{-1}$·s$^{-1}$, [48–52]). Based on the dosage of KMnO₄ and NaClO, their apparent rate constants were calculated to be on the order of $10^{-9}$–$10^{-3}$ s$^{-1}$. Mn(III) was reported to oxidize a variety of organic matters at rate constants that ranged from $10^2$ s$^{-1}$ to $10^3$ s$^{-1}$ [27,53]). Such fast reaction kinetics resulted from the intramolecular ring electron transfer mechanism. Hence, the significant removal of CBZ, BPS, and ACE by Mn(III)+C/S resulted from the oxidation of Mn(III).

3.2.2. Nanoparticle Contaminant

Figure 4 presents the removal performance of nano-ZnO by Mn(III)+C/S, as well as the other three referenced processes. Mn(III)+C/S increased the removal rate from 21.2% (for C/S) to 86.1%. In contrast, PM+C/S and Cl₂+C/S showed a small elimination improvement (1.7%–9.8%) in comparison with C/S. The stability of nanoparticle contaminants in water is related to its own surface characteristics (organic coating, charging, etc.), natural organic matter, metal ions, solution pH, ionic strength, and other factors [54]. Given the positive correlation between the removal rate of nano-ZnO and the DOC removal efficiency, we speculated that oxidation of three oxidants destroyed the organic matters entrapped on the surface of nano-ZnO, causing its destabilization and facilitating its final removal [55]. Obviously, Mn(III) destroyed the organic coating more efficiently than KMnO₄ and chlorine.
3.3. Residual Mn in Treated Water

The transformation products of Mn(III) are Mn(II) and MnO₂ [27]. The generated MnO₂ can be effectively removed by the subsequent C/S process due to its good settleability. Whether the Mn(III)+C/S can “trap” Mn(II) is worthy of attention because of its high stability in water. As shown in Figure 5, the residual total Mn after treatment by Mn(III)+C/S was 0.017 mg·L⁻¹, which was lower than the guideline value of EPA (0.05 mg·L⁻¹) [56]. Notably, although the KMnO₄ dosage was only 1.0 mg·L⁻¹, the residual total Mn in the treated water of PM+C/S was 0.11 mg·L⁻¹, which was higher than the guideline value of 0.05 mg·L⁻¹. With regards to the Mn(III)+C/S and PM+C/S, the concentrations of residual Mn(II) after the sedimentation step were 0.002 mg·L⁻¹ and 0.04 mg·L⁻¹, respectively. This result suggests that Mn(III)+C/S would not bring any extra Mn(II) burden to the subsequent treatment unit and thus no additional steps are required.

3.4. Floc Characteristics

Dynamic Analysis of Floc Size in the Coagulation Process

As shown in Figure 6a, the raw water possessed a zeta potential (ζ) of −28.2 mV, which decreased to −10 mV after treatment by C/S. As to Mn(III)+C/S, PM+C/S, and Cl₂+C/S, the ζ values of treated
water were −5.1 mV, −11.4 mV, and −12.0 mV, respectively. \( \zeta \) is an important index to weigh the stability of colloidal particles. As the magnitude of \( \zeta \) indicates the degree of electrostatic repulsion between colloids, colloids are considered to be very unstable and tend to aggregate rapidly when the \( \zeta \) value of colloids locates in the range of (0~±5) mV. Based on this principle, colloids pre-oxidized by Mn(III) is more preferred for destabilization flocculation, as compared to those pre-oxidized by permanganate or chlorine. Figure 6b illustrates the size (represented by median equivalent diameter \( d_{0.5} \)) variation of flocs in different treatment processes. The biggest floc size was observed in Mn(III)+C/S (about 1000 µm after the end of the rapid mixing), indicating a fast floc growth and development. The increased floc \( d_{0.5} \) at the rapid mixing stage for PM+C/S and Cl2+C/S revealed that pre-oxidation by permanganate and chlorine also accelerated the floc growth. This meant that a short reaction time was needed in the slow mixing stage.

![Figure 6](image)

**Figure 6.** Time dependent profile of (a) zeta potential and (b) floc size at the coagulation stage for different processes.

The flocs produced in Mn(III)+C/S were sampled for XPS scanning to probe the participation of in-situ formed MnO2. Figure 7 shows the oxidation state of Mn at the Mn 2p core-level region. Two Mn 2p peaks were detected, Mn 2p\(_{3/2}\) peak at 641.58 eV and the Mn 2p\(_{1/2}\) peak was shown at 653.28 eV. The binding energy of Mn 2p with a spin-energy separation of 11.7 eV was in good agreement with the binding energy of MnO\(_2\) \([47,57]\), indicating that MnO\(_2\) was indeed generated in Mn(III)+C/S. The in-situ formed MnO\(_2\) could act as the nuclei for heterogeneous coagulation \([58]\). These MnO\(_2\) particles incorporated into flocs and complexes with hydrolysates of Fe\(_3^+\), endowing the flocs a good settleability and resistance of hydraulic shear. Therefore, in-situ formed MnO\(_2\) played an important role in Mn(III)+C/S.

![Figure 7](image)

**Figure 7.** XPS spectrum of flocs collected from Mn(III)+C/S.
To learn about the floc formation directly, the morphology of the flocs was characterized using SEM scanning. One can find that flocs of C/S and Cl$_2$+C/S were loose and amorphous (Figure 8a,c) while flocs of PM+C/S and Mn(III)+C/S were uniform and compact (Figure 8b,d). This might be due to the fact that there was in-situ formed MnO$_2$ for PM+C/S and Mn(III)+C/S. The MnO$_2$ particles played as flocculation cores which might induce different morphology of flocs.

Figure 8. SEM images of flocs collected from (a) C/S, (b) PM+C/S, (c) Cl$_2$+C/S, and (d) Mn(II)+C/S.

3.5. Acute Bio-Toxicity Evaluation

The acute toxicity of simulated water before and after treatment by different processes was investigated by the Vibrio fischeri light inhibition test. As shown in Table 2, the finished waters of C/S and PM+C/S, respectively, exhibited a luminescence suppression rate of $-0.01\%$ and $-1.63\%$, while the Cl$_2$+C/S-treated water showed an obvious increase of luminescence inhibition ($42.63\%$). Based on the USEPA test report of the Microtox Model 500 Biological Toxicity Tester [59,60], the standard deviation of the analysis results of common toxic substances is $\leq 10\%$ and a water sample with luminescence inhibition rate less than $20\%$ is considered to be of insignificant acute toxicity. We, thus, could conclude that treatment by C/S and PM+C/S hardly altered the acute bio-toxicity of raw water while the finished water of Cl$_2$+C/S faced the risk of acute bio-toxicity increase. This is consistent with several previous observations [61]. Treatment by Mn(III)+C/S yielded a luminescence suppression rate of $12.96\%$, indicating that there was no significant change of acute bio-toxicity. It is generally accepted that chlorination treatment of drinking water can cause the formation of toxic and mutagenic/carcinogenic by-products. This might explain the significant acute bio-toxicity increase of Cl$_2$+C/S-treated water. Given the weak luminescence inhibition caused by constituents in raw water and partial removal of these constituents by PM+C/S and Mn(III)+C/S, it is reasonable to infer that the oxidation products that remained in PM+C/S- or Mn(III)+C/S-treated water were of insignificant acute bio-toxicity.
Table 2. Light inhibition rate before and after treatment.

<table>
<thead>
<tr>
<th>Source of Sample</th>
<th>15 min Light Inhibition Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw water</td>
<td>-5.78%</td>
</tr>
<tr>
<td>C/S</td>
<td>-0.01%</td>
</tr>
<tr>
<td>KMnO₄+C/S</td>
<td>-1.63%</td>
</tr>
<tr>
<td>Cl₂+C/S</td>
<td>42.63%</td>
</tr>
<tr>
<td>Mn(III)+C/S</td>
<td>12.96%</td>
</tr>
</tbody>
</table>

4. Conclusions

This study indicates that Mn(III)–OT shows promise to act as a pre-oxidation step combined with a coagulation process. Overall, Mn(III)+C/S performed better than C/S, PM+C/S, and Cl₂+C/S at removing the investigated pollutants. Mn(III)+C/S especially showed an advantage over other three processes in term of eliminating DOC, TN, and the emerging micropollutants (ACE, BPS, CBZ, and nano-ZnO). The DOC removal rate of Mn(III)+C/S was 1.4–1.8 times higher than that of the other three processes, and 2.5–3.8 times higher for the TN removal rate. ACE, BPS, and CBZ could be efficiently removed by Mn(III)+C/S (21.8%–93.5%), contrary to their poor elimination by C/S, PM+C/S, and Cl₂+C/S (<10%). A total of 86.7% of the nano-ZnO particles were intercepted by Mn(III)+C/S, while the other three processes only showed interception rates less than 31.0%. Mn(III) pre-oxidation displayed a satisfactory enhanced effect on Fe-coagulation/sedimentation process due to the following reasons:

1. Mn(III) shows a stronger oxidation power than PM and hypochlorite at a neutral pH.
2. Disproportionation reaction of Mn(III) resulted in-situ formation of MnO₂ which could adsorb pollutants and then co-precipitate.
3. Mn(III) oxidation decreased electrostatic repulsion between the colloids and in-situ formed MnO₂ acted as the flocculation core, which made the flocs grow fast.
4. In-situ formed MnO₂ incorporated into the hydrolysate of Fe³⁺, to generate compact and easy settleable flocs.

Author Contributions: For Conceptualization, D.Y. and X.L.; Formal analysis, J.W. and X.L.; Methodology, Z.S., L.W., Q.W., and R.P.; Supervision, X.L.; Validation, D.Y.; Writing—original draft, D.Y., Z.S., and X.L.; Writing—review and editing, D.Y. and X.L.

Funding: This research was funded by the special S & T project on the treatment and control of water pollution (Grant No. 2017ZX07201-003), the Natural Science Foundation of Zhejiang Province (Grant No. LQ19E080023), the Major International (Regional) Joint Research Program of China (Grant No. 51761145022), and the National Key Research and Development Program of China (No. 2016YFC0400601, 2016YFC0400606).

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

In-situ formed MnO₂ was prepared by reducing KMnO₄ with a stoichiometric amount of MnSO₄ according to the following reaction:

$$3\text{Mn}^{2+} + 2\text{MnO}_4^- + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 4\text{H}^+ \quad (A1)$$

Carbonate was added to neutralize the formed H⁺. To minimize the influence of MnO₂ agglomeration, Cr(VI), and Pb(II), stock solutions were added instantly when KMnO₄ was completely consumed.
Figure A1. Removal efficiency of Cr(VI) and Pb(II) by in-situ formed MnO$_2$. Conditions: [Cr(VI)]$_0$ = 353.5 µg L$^{-1}$, [Pb(II)]$_0$ = 625.5 µg L$^{-1}$, and [MnO$_2$]$_0$ = 10.0 mg L$^{-1}$.

References

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