

Research Article

Oxidative Transformation of Controlled Substances by Manganese Dioxide

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This study investigated the oxidative transformation of four controlled substances (ketamine, methamphetamine, morphine, and codeine) by synthesized MnO_2 ($\delta\text{-MnO}_2$) in aqueous environments. The results indicated that ketamine and methamphetamine were negligibly oxidized by MnO_2 and, thus, may be persistent in the aqueous environment. However, morphine and codeine were able to be oxidized by MnO_2 , which indicated that they are likely naturally attenuated in aqueous environments. Overall, lower solution pH values, lower initial compound concentrations, and higher MnO_2 loading resulted in a faster reaction rate. The oxidation of morphine was inhibited in the presence of metal ions (Mn^{2+} , Fe^{3+} , Ca^{2+} , and Mg^{2+}) and fulvic acid. However, the addition of Fe^{3+} and fulvic acid enhanced codeine oxidation. A second-order kinetics model described the oxidation of morphine and codeine by MnO_2 ; it suggested that the formation of a surface precursor complex between the target compound and the MnO_2 surface was the rate-limiting step. Although the target compounds were degraded, the slow TOC removal indicated that several byproducts were formed and persist against further MnO_2 oxidation.

1. Introduction

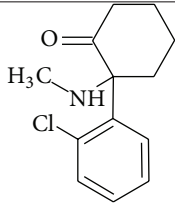
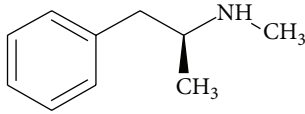
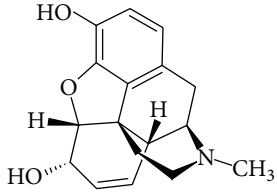
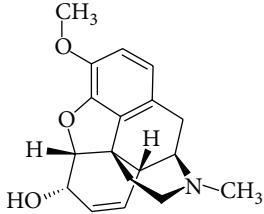
The presence of pharmaceuticals in aqueous environments is an important environmental issue because conventional wastewater treatment plants (WWTP) do not remove them, resulting in their release into the environment [1, 2]. Controlled substances are one type of pharmaceuticals commonly used in hospitals. Besides their medical applications, controlled substances are also used illicitly and abusively. These substances can be classified as antidepressants, stimulants, and hallucinogens based on their effects on the central nervous system. In addition, these compounds can cause significant toxicity after prolonged exposure because they are chemically and biologically active [3].

Ketamine, methamphetamine, morphine, and codeine are four controlled substances and have been detected in various waterbodies in different countries. For example, they were detected in hospital effluents (maximum concentrations of 10,000, 260, 1,240, and 378 ng/L, resp.), and ketamine, methamphetamine, and codeine were detected in river water

in Taiwan (maximum concentrations of 341, 405, and 57 ng/L, resp.) [4, 5]. Boleda et al. [6] reported that morphine and codeine were detected at concentrations of up to 81 and 397 ng/L, respectively, in WWTP effluents in Spain. Hummel et al. [7] investigated the occurrence of morphine and codeine in Germany and found that both of these compounds were present in river water (Rhine water) (78 ng/L; 94 ng/L), WWTP influents (820 ng/L; 540 ng/L), and effluents (110 ng/L; 260 ng/L). In addition, Castiglioni et al. [8] investigated the occurrence of morphine and methamphetamine in Italy and Switzerland, maximum concentrations of 204 and 16 ng/L, respectively, in the WWTP influent and 55 and 4 ng/L, respectively, in the WWTP effluent. The release of these controlled substances into the aqueous environment may endanger aquatic life and result in ecosystem contamination.

Natural attenuation (hydrolysis, redox reaction, sorption, photolysis, and biodegradation) is considered to be one of the most important pathways for removing contaminants from the aqueous environment and is the most economically

TABLE 1: Physicochemical properties of ketamine, methamphetamine, morphine, and codeine.

	Molecular formula	Molecular weight (g/mol)	pKa	Solubility (mg/mL)	Structure
Ketamine	C ₁₃ H ₁₆ ClNO	237.7	7.5 ^b	250	
Methamphetamine	C ₁₀ H ₁₅ N	149.2	9.9 ^a	NA	
Morphine	C ₁₇ H ₁₉ NO ₃	285.3	9.85 ^b (phenol group)	60	
Codeine	C ₁₈ H ₂₁ NO ₃	299.4	9.8 ^b	434.8	

^a[19], ^b[20].

feasible method for further attenuation of treated wastewater [9]. However, very limited information is currently available regarding the environmental fates of these four controlled substances (ketamine, methamphetamine, codeine, and morphine), and the oxidative transformation of these four controlled substances by manganese oxide (MnO₂) has not been previously investigated. MnO₂ is abundant in natural sediments and soils and has been reported to possess a powerful oxidative capacity for removing phenol, aniline, aliphatic amine, and triazine in aquatic environments through oxidation and sorption [10, 11].

The objective of this study was to investigate the oxidative transformation of four controlled substances (ketamine, methamphetamine, morphine, and codeine) by synthesized MnO₂ (δ -MnO₂) in an aqueous environment. Several critical environmental factors that may affect the MnO₂ oxidation rate were studied, including the MnO₂ loading, initial compound concentration, and solution pH. In addition, the effects of cosolutes (metal ions (Mn²⁺, Fe³⁺, Ca²⁺, and Mg²⁺) and natural organic matter) on MnO₂ oxidation were investigated, and total organic carbon removal and oxidative transformation byproducts were studied.

2. Experimental Setup

2.1. Chemicals. Morphine, codeine, and ketamine were purchased from Sigma-Aldrich (St. Louis, MO, USA).

Methamphetamine was purchased from the US Pharmacopial Convention (USP). Without any further purification, the purities of all drugs were greater than 95%. All other stock solutions were prepared in deionized water at concentrations of 500–1,000 mg/L and were stored at 4°C in a refrigerator. Other chemicals were purchased from Merck Millipore (Guyancourt, France), Avantor Performance Materials (Phillipsburg, NJ, USA), Sigma-Aldrich (St. Louis, MO, USA), and Nacalai Tesque (Kyoto, Japan) with purities greater than 85% (Table S1 in Supplementary Material available online at <http://dx.doi.org/10.1155/2015/364170>). The physicochemical properties of ketamine, methamphetamine, codeine, and morphine are listed in Table 1.

2.2. Synthesis of Manganese Dioxide. δ -MnO₂ was synthesized according to the methods of Murray [12]. First, 80 mL of 0.1 M KMnO₄ and 160 mL of 0.1 M NaOH were added to 1.64 L of N₂-sparged reagent water, and 120 mL of 0.1 M MnSO₄ was added to the solution while continuously stirring. After the MnO₂ particles settled, the supernatant solution was replaced with deionized water until the conductivity of the MnO₂ suspension was less than 2 μ S-cm⁻¹. The final volume of the MnO₂ solution was adjusted to 1 L, and then the solution was stored at 4°C.

2.3. Chemical Analysis. High-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) was

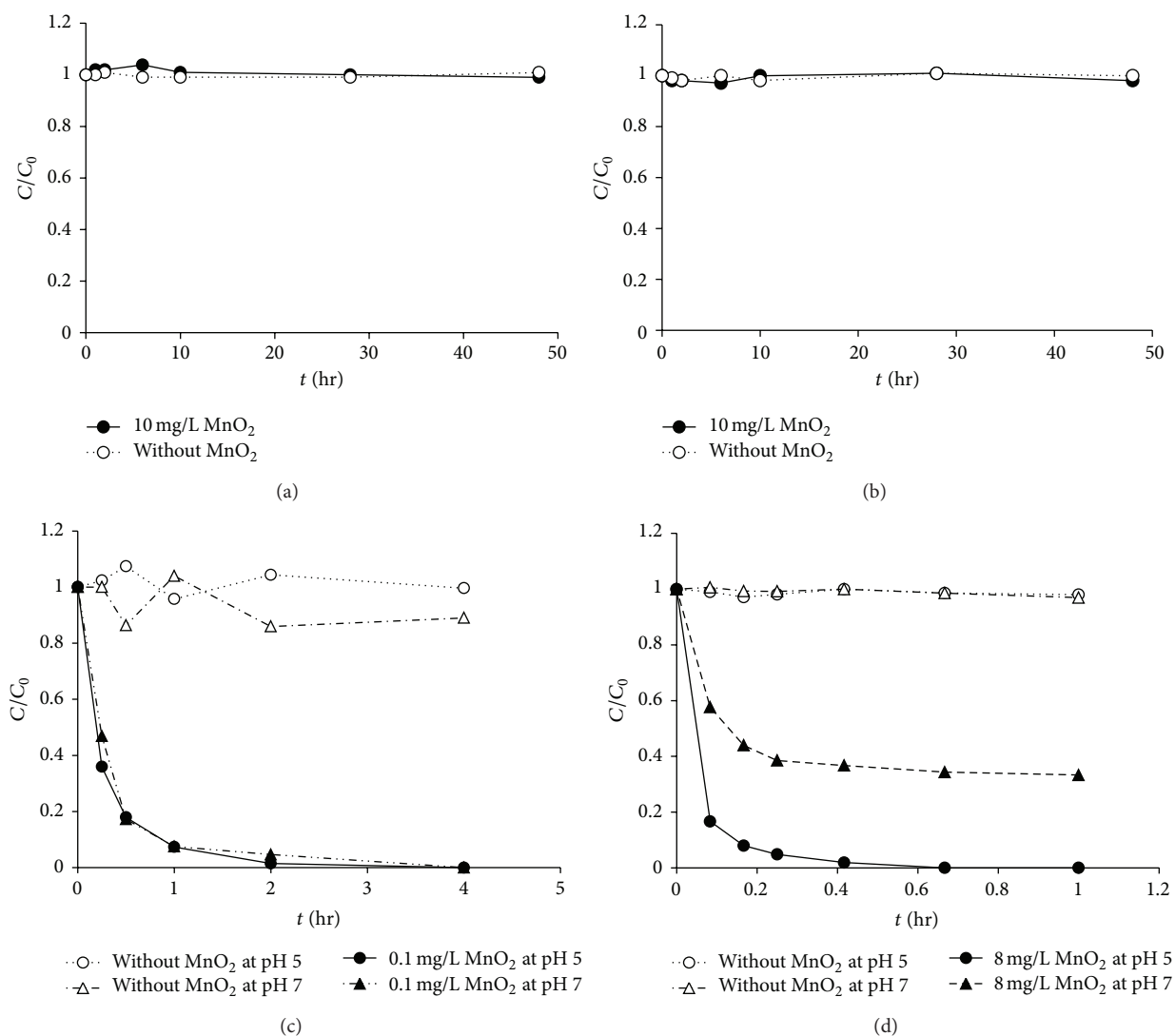


FIGURE 1: Oxidation of the four controlled substances by MnO_2 : (a) ketamine at pH 5, (b) methamphetamine at pH 5, (c) morphine, and (d) codeine (compound concentration = $100 \mu\text{g/L}$, ionic strength = 10 mM).

used to analyze the concentrations of the four target controlled substances. The HPLC module consisted of a pump (Agilent 1200 Series Binary Pump), degasser (Agilent 1200 Series Micro Vacuum Degasser), and autosampler (Agilent 1200 Series Autosampler). The analytes were determined using chromatography with a ZORBAX Eclipse XDB- C_{18} column ($150 \times 4.6 \text{ mm}$, $5 \mu\text{m}$ particle size) and a flow rate of 1 mL min^{-1} . Mobile phases A and B consisted of 0.05% formic acid with 10 mM ammonium acetate in DI water and methanol, respectively.

2.4. Oxidation of Controlled Substances. MnO_2 oxidation experiments were conducted using 250 mL screw-cap amber glass bottles with aluminum foil septa at room temperature (22°C). The solution pH was controlled using a 10 mM acetate buffer (pH 4 and 5), 4-morpholinepropanesulfonic acid (MOPS) (pH 6 and 7), 2-(cyclohexylamino)ethanesulfonic acid (CHES) (pH 9), and a phosphate buffer (pH 9). In

addition, NaCl (0.01 M) was added to maintain an appropriate ionic strength.

The volume of the reactor was fixed at 100 mL . The reaction aliquots were collected (1 mL) and quenched using two different methods: the filtration quenching method and the reductant quenching method. In the reductant quenching method, oxalic acid (0.5 g/L) was added to desorb the target compound from the MnO_2 surface. The filtration quenching method can only detect target compounds dissolved in solution, not those adsorbed on the surface of manganese dioxide.

2.5. Analysis of Oxidative Byproducts. To analyze the oxidative byproducts of codeine, an Agilent LC-ESI-MS/MS combined with a ZORBAX Eclipse XDB- C_{18} column ($150 \times 4.6 \text{ mm}$, $5 \mu\text{m}$ particle size) was used to perform quantitative analyses. Three steps were required to analyze the byproducts. First, the electron-spray ionization (ESI) detector

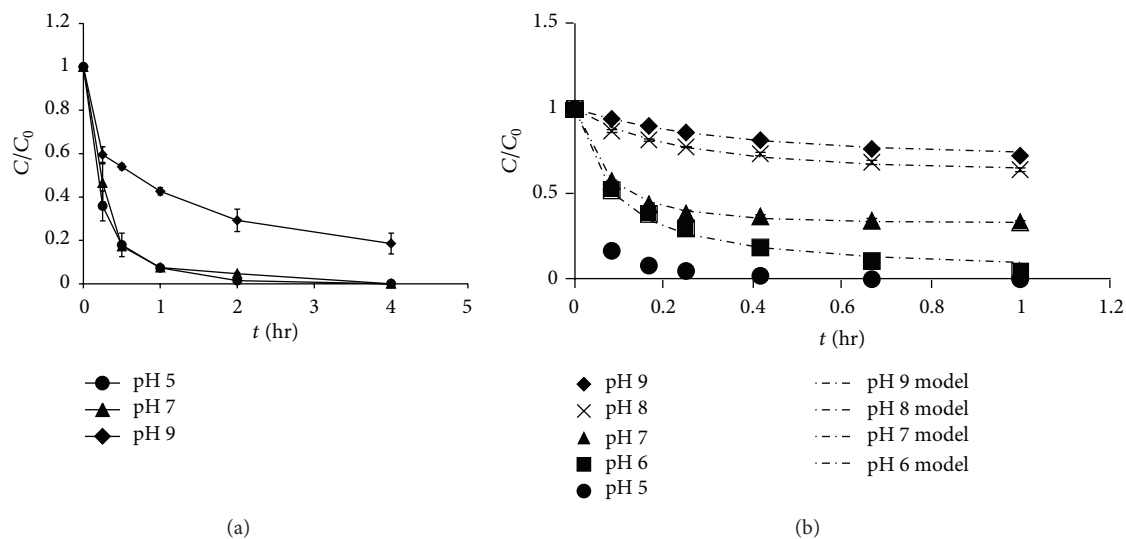


FIGURE 2: Effect of solution pH on the oxidation of controlled substances by MnO_2 : (a) morphine (with $100 \mu\text{g/L}$ MnO_2) and (b) codeine (with 8 mg/L MnO_2) (morphine and codeine = $100 \mu\text{g/L}$, pH = 7, and ionic strength = 10 mM) (the second-order kinetic model developed by Zhang et al. [11] was fitted to describe the codeine oxidation).

was operated to obtain a full mass spectrum scan (Q1 scan) ranging from 50 to 600. Then, the selected sample was compared with the control sample to determine the possible oxidative byproduct. Second, the multiple-reaction monitoring transition mode (MRM) was used to optimize the parameters for MS/MS detection, including the declustering potential (DP), collision energy (CE), and collision cell exit potential (CXP). Third, the LC parameters were optimized to separate the analyte, including the mobile phase, flow rate, and injection volume.

3. Results and Discussion

Background tests (hydrolysis and adsorption) were performed before the MnO_2 oxidation experiment. The four controlled substances remained stable in the water at all tested pH conditions (pH 4 and 5 for ketamine and methamphetamine; pH 5, 7, and 9 for morphine; and pH 5, 6, 7, 8, and 9 for codeine) (Figure S1). No obvious differences were observed between the filtration quenching method and the reductant quenching method (Figure S2) and no measurable adsorption by MnO_2 was observed by the four controlled substances.

The MnO_2 experiments revealed that ketamine and methamphetamine were persistent and were not oxidized by 10 mg/L MnO_2 . However, morphine and codeine were oxidized by MnO_2 , indicating that they may undergo attenuation in natural soil and sediment environments (Figure 1). Based on the kinetic model reported by Zhang et al. [11], the oxidation of morphine and codeine follows second-order kinetics with adsorption as the rate-limiting step. The second-order kinetics of this process are shown in (1), where k_1 , k_{-1} , and k_2 present the adsorption rate constant of the compound by MnO_2 , the desorption rate constant of the compound by MnO_2 , and the electron transfer rate constant,

respectively. Because the adsorption reaction is considerably slower than the electron transfer reaction, the amount of target compound (morphine and codeine) adsorbed on MnO_2 but unreacted would be negligible for detection as observed by the experiments. Consider

$$-\frac{dC}{dt} = \frac{k_1 k_2 [S_{\text{rxn}} - (C_0 - C)] C}{k_{-1} + k_2} = k'' [S_{\text{rxn}} - (C_0 - C)] C. \quad (1)$$

3.1. Effects of pH. An initial environmentally relevant concentration was selected for the four controlled drugs ($100 \mu\text{g/L}$). Ketamine and methamphetamine remained stable against MnO_2 oxidation (4 mg/L) at pH 4 and 5 for 48 h (Figure S3). However, the degradation behaviors of morphine and codeine were different from that of ketamine and methamphetamine. In this study, different MnO_2 loadings were used for morphine and codeine ($100 \mu\text{g/L}$ MnO_2 for morphine and 8 mg/L MnO_2 for codeine) because morphine is oxidized by MnO_2 much more readily than codeine. The results showed that morphine and codeine exhibited lower degradation rates as the solution pH decreased (Figure 2). Morphine was >99%, 91.5%, and 82% degraded at pH 5, 7, and 9, respectively (reaction time = 4 h, $MnO_2 = 100 \mu\text{g/L}$). Codeine was >99%, 96%, 67%, 36%, and 28% degraded at pH 5, 6, 7, 8, and 9, respectively (reaction time = 1 h, $MnO_2 = 8 \text{ mg/L}$). Previous studies indicated that the oxidation of compounds by synthesized MnO_2 is a surface reaction and that the surface charge of MnO_2 is negative (point of zero charge (PZC) of MnO_2 was 2.25) [12, 13]. Therefore, the intensity of the negative MnO_2 charge increased as the pH increased from 5 to 9. This increase caused the MnO_2 surface to become more hydrophilic and subsequently reduced the number of accessible active sites for the target compound because of obstruction from the nearby water molecules,

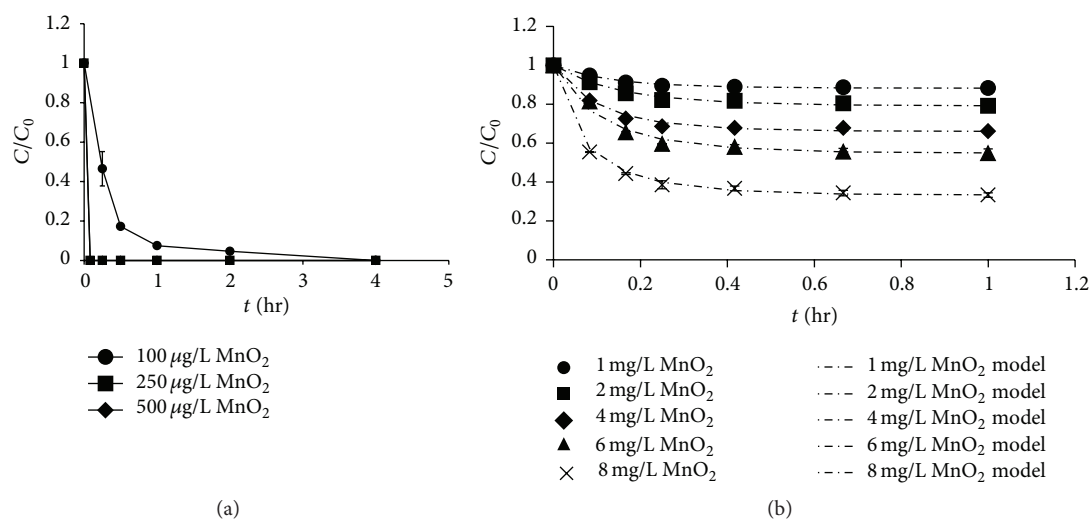


FIGURE 3: Effect of MnO₂ loading on the oxidation of controlled substances by MnO₂: (a) morphine and (b) codeine (morphine and codeine = 100 $\mu\text{g/L}$, pH = 7, and ionic strength = 10 mM) (the second-order kinetic model developed by Zhang et al. [11] was fitted to describe the codeine oxidation).

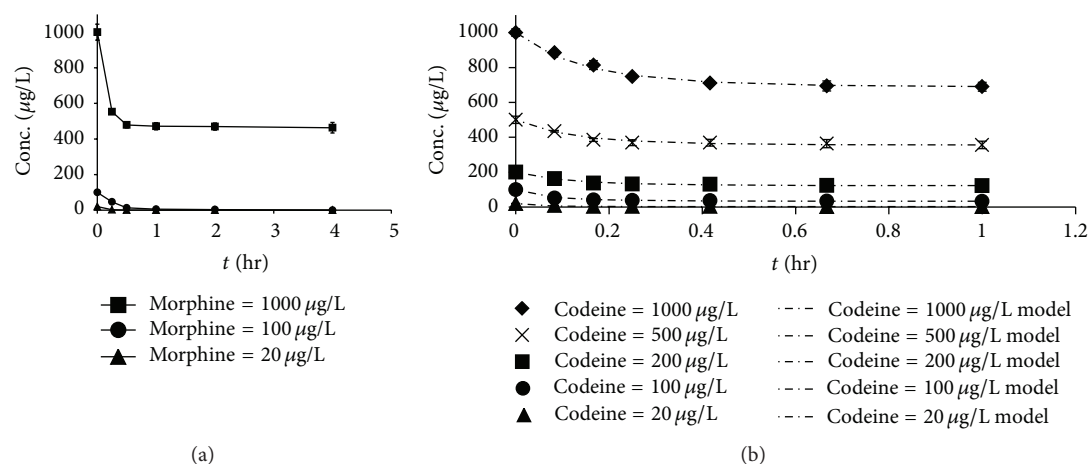


FIGURE 4: Effect of initial compound concentration on the oxidation of controlled substances by MnO₂: (a) morphine (with 100 $\mu\text{g/L}$ MnO₂) and (b) codeine (with 8 mg/L MnO₂) (pH = 7, ionic strength = 10 mM) (the second-order kinetic model developed by Zhang et al. [11] was fitted to describe the codeine oxidation).

which further reduced the reaction rate [14]. Lin et al. [15] also demonstrated that the ability of MnO₂ to oxidize organic compounds is pH-dependent. Furthermore, Stumm and Morgan [16] reported that the MnO₂ reduction potential decreased from 0.99 V to 0.76 V when the pH increased from 4 to 8. Zhang and Huang [17] also reported that more surface species are produced at lower pH that subsequently react with the reductants. In addition, Klausen et al. [18] indicated that protons are required to dissociate the reaction product Mn(II) from the MnO₂ (Mn(IV)) mineral surface $((1/2)\text{Mn}^{\text{IV}}\text{O}_{2(\text{s})} + 2\text{H}^+ + \text{e}^- \rightleftharpoons (1/2)\text{Mn}^{2+} + \text{H}_2\text{O})$. Therefore, a higher solution pH may result in a lower degradation rate.

3.2. Effect of MnO₂ Loading. The results showed that ketamine and methamphetamine were still present after MnO₂

oxidation for 48 hrs unless the MnO₂ loading reached 750 mg/L (Figure S4). High MnO₂ loading (750 mg/L) indicates that ketamine and methamphetamine are not degraded by natural MnO₂ in soils and sediments. For morphine and codeine, higher MnO₂ loadings resulted in a faster oxidation rate (Figure 3). The degradation rates of morphine by 250 and 500 $\mu\text{g/L}$ MnO₂ were faster than that by 100 $\mu\text{g/L}$ MnO₂. Similarly, when MnO₂ increased from 1 mg/L to 8 mg/L, the degradation efficiency of codeine increased from 12% to 65% in 1 h. Zhang et al. [11] reported that a precursor complex between the organic compound and MnO₂ is formed before electron transfer reaction occurs during the redox reaction. These two steps (precursor complex formation and electron transfer reaction) were hypothesized to be rate-limiting steps and to influence the reactivities of organic compounds and MnO₂. Thus, the oxidation of organic compounds by MnO₂

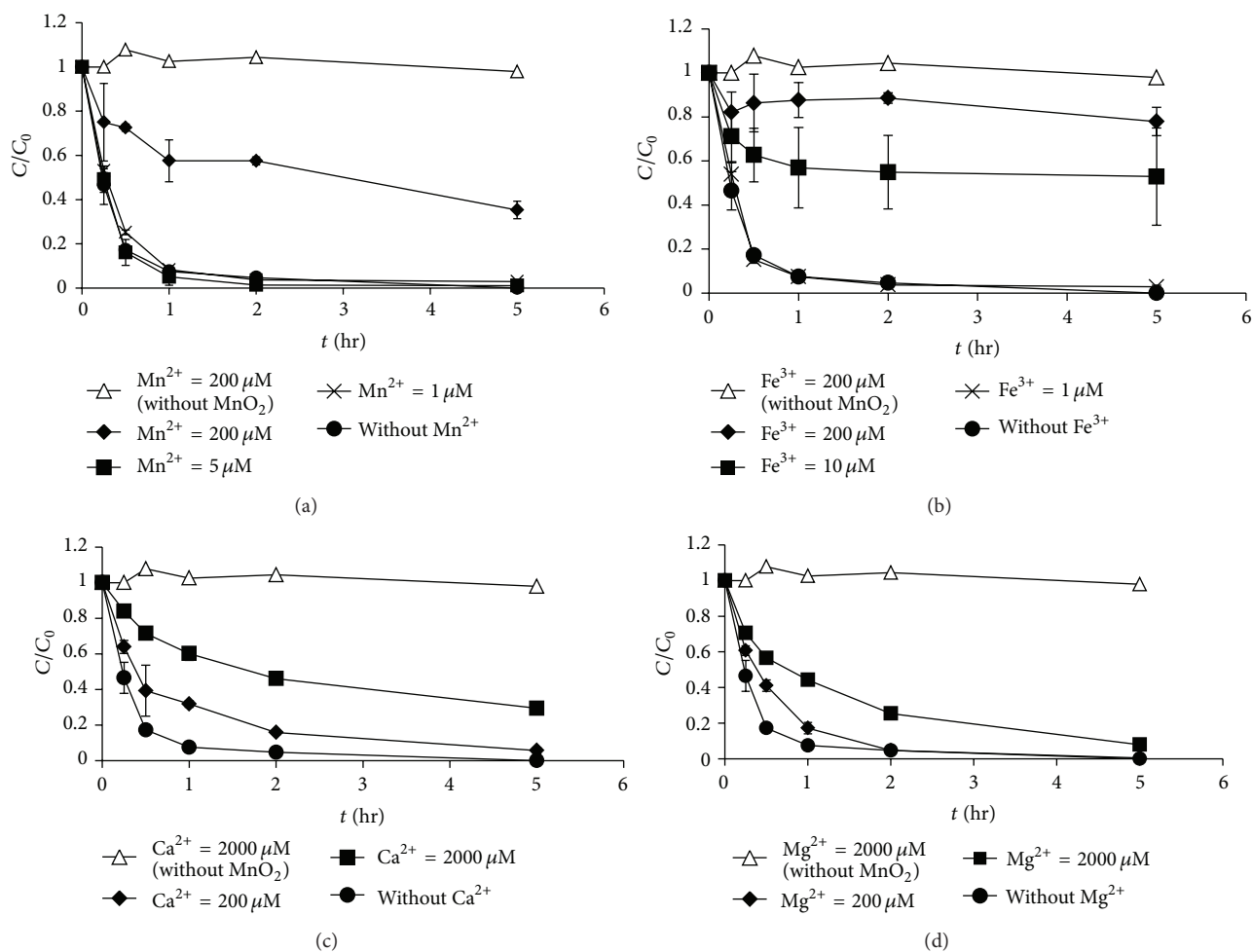


FIGURE 5: Effect of metal ions on the oxidation of morphine by MnO_2 : (a) Mn^{2+} , (b) Fe^{3+} , (c) Ca^{2+} , and (d) Mg^{2+} (MnO_2 loading = $100 \mu\text{g/L}$, initial morphine concentration = $100 \mu\text{g/L}$, $\text{pH} = 7$, and ionic strength = 10 mM).

resulted from surface reactions between the MnO_2 and compounds [10]. Consequently, when the MnO_2 concentration increased, the potential for contact between the target compounds and MnO_2 increased and resulted in the reaction. Furthermore, Zhang and Huang [17] reported that higher MnO_2 concentrations offer more active surface sites, which resulted in an increase in the rate of precursor complex formation.

3.3. Effects of the Initial Compound Concentration. It has been hypothesized that the formation of a surface complex is the rate-limiting step in the oxidation of morphine and codeine by MnO_2 . The formation rate of such a surface complex is affected by the MnO_2 loading, solution conditions (pH and ionic strength), and the initial concentration of the target compound. In this study, the initial compound concentration (morphine and codeine) range was 20 to $1,000 \mu\text{g/L}$. The results showed that increasing compound concentrations resulted in decreased degradation efficiency (Figure 4) when the MnO_2 loading and pH were fixed. A higher compound concentration could result in self-competition for the fixed

number of active sites on the surface of MnO_2 , thereby decreasing the removal rate of morphine and codeine [11].

3.4. Effects of Metal Ions. The effects of metal cations (Mn^{2+} , Fe^{3+} , Ca^{2+} , and Mg^{2+}) on the oxidation of morphine and codeine by MnO_2 were investigated (Figures 5 and 6). Previous studies showed that dissolved cations in real water matrices may inhibit the degradation of compounds by MnO_2 [11, 17]. Our results showed a similar phenomenon, in which the coexistence of metal ions resulted in an inhibitory effect on the oxidation of morphine and codeine by MnO_2 (except for the effect of Fe^{3+} on the oxidation of codeine). The degradation of morphine by MnO_2 was inhibited more when the concentrations of the metal cations (Mn^{2+} , Fe^{3+} , Ca^{2+} , and Mg^{2+}) increased. For example, as the Mn^{2+} concentration increased from 1 to $200 \mu\text{M}$, the degradation efficiency of morphine decreased from 99.0% to 65.7% in 4 h . However, when the Ca^{2+} concentration increased from 200 to $2,000 \mu\text{M}$, the degradation efficiency decreased from 94.3% to 70.6% . Similarly, the degradation efficiency of codeine decreased when the metal cation concentrations (Mn^{2+} , Ca^{2+} ,

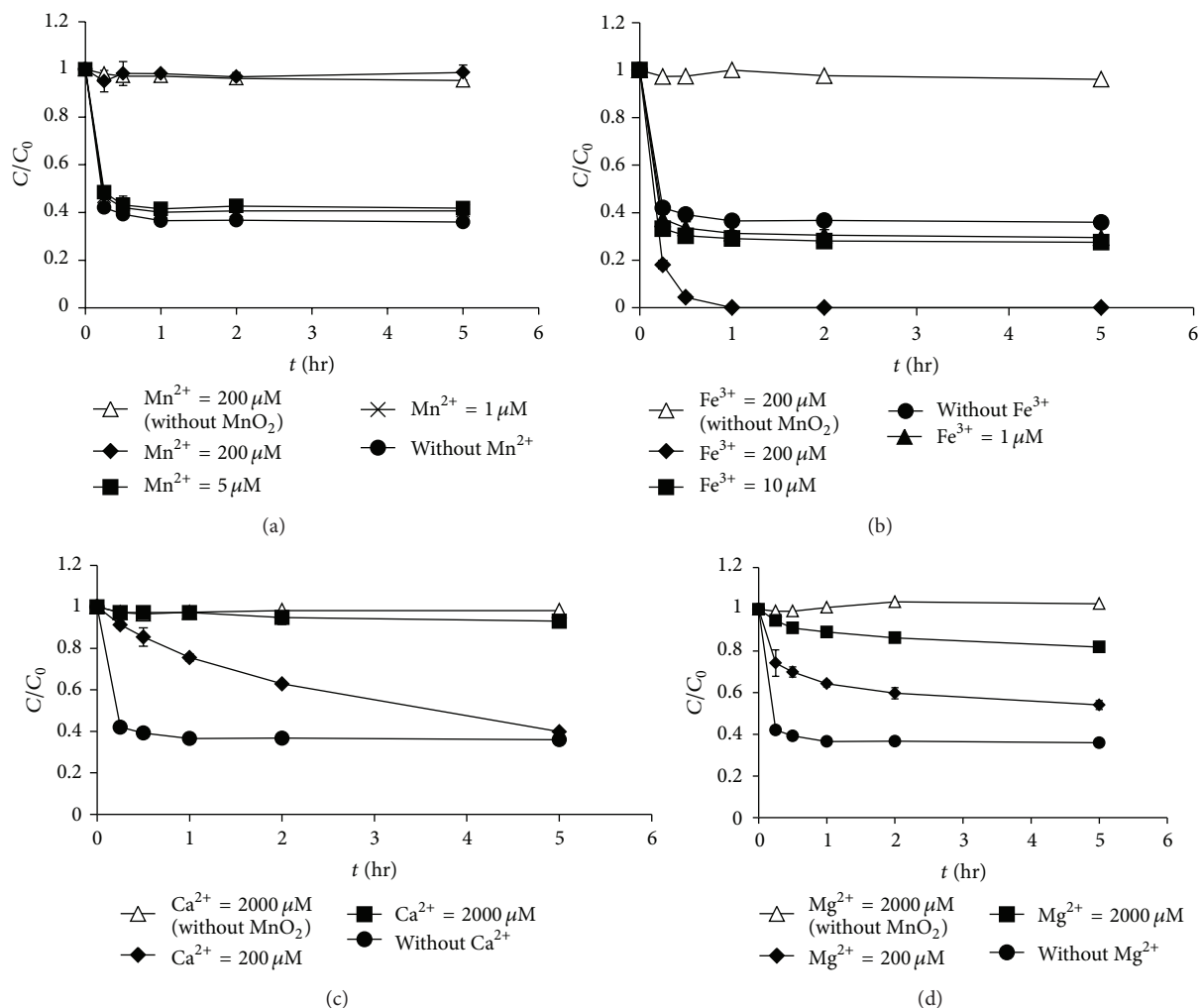


FIGURE 6: Effect of metal ions on the oxidation of codeine by MnO₂: (a) Mn²⁺, (b) Fe³⁺, (c) Ca²⁺, and (d) Mg²⁺ (MnO₂ loading = 8 mg/L, initial codeine concentration = 100 μg/L, pH = 7, and ionic strength = 10 mM).

and Mg²⁺) increased. However, the opposite phenomenon was observed regarding the effects of Fe³⁺ on the degradation of codeine (Fe³⁺ enhanced the degradation efficiency of codeine by MnO₂). As the Fe³⁺ concentration increased from 1 to 200 μM, the degradation efficiency of codeine increased from 54.6% to 100%. One possible explanation for this result is that the addition of FeCl₃ at pH 7 could result in coagulation of MnO₂ particles, which might reduce the codeine concentration in the solution. The induced coagulation is more likely to occur at the higher MnO₂ loading (8 mg/L) applied for codeine. Further investigations should be performed to understand the detailed mechanisms of Fe³⁺ toward codeine degradation by MnO₂.

3.5. Effects of Natural Organic Matter. Natural organic matter (NOM) is present in aqueous environments and is also a factor that may influence the oxidation efficiency of MnO₂ [18]. In this work, fulvic acid (FA) was used to represent the NOM in the natural environment. The effects of FA on the oxidation of morphine and codeine by MnO₂ are shown in

Figure 7. Results showed that FA decreased the degradation efficiency of morphine, potentially because FA competes with target compounds to the active surface hydroxyl groups of MnO₂, resulting in slowing the removal of morphine [21]. In contrast, greater concentrations of FA resulted in slightly greater codeine removal. This result implied that FA did not compete with codeine for the same reactivity sites on MnO₂. Another possibility is that the presence of FA might facilitate some aggregation of the MnO₂ particles under the experimental conditions used for codeine (with 8 mg/L MnO₂). In the absence of MnO₂, FA alone did not react with morphine or codeine (Figure 7), which indicated that the interaction between FA and the target compound (morphine or codeine) did not result in the removal of the target compound.

3.6. Total Organic Carbon (TOC) and Oxidative Byproduct Analysis. The results obtained for the removal of TOC help determine whether the target compounds were mineralized

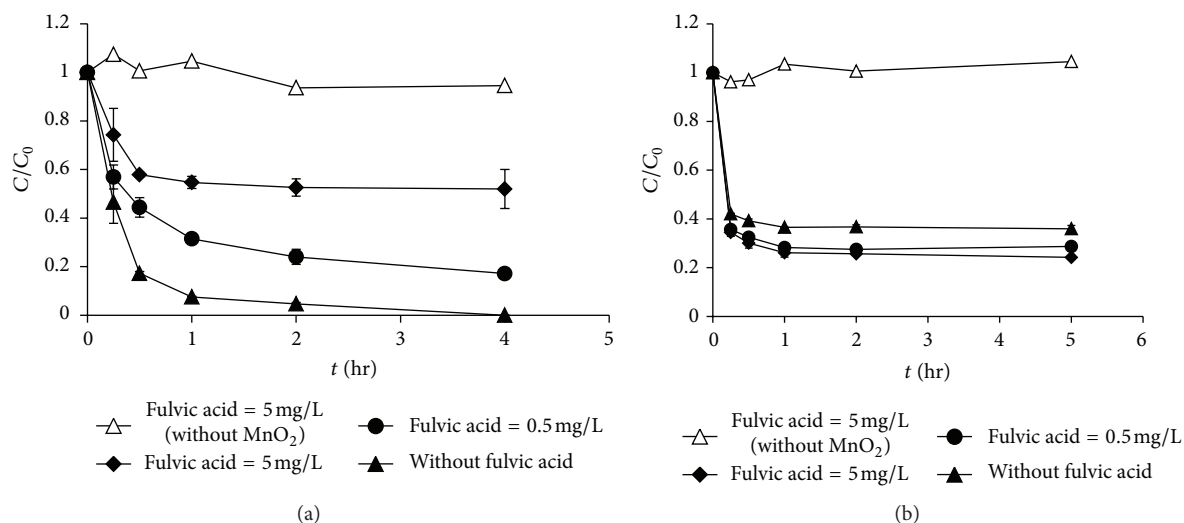


FIGURE 7: Effect of fulvic acid on the oxidation of (a) morphine (with $100 \mu\text{g/L MnO}_2$) and (b) codeine (with 8 mg/L MnO_2) (compound concentration = $100 \mu\text{g/L}$, $\text{pH} = 7$, and ionic strength = 10 mM).

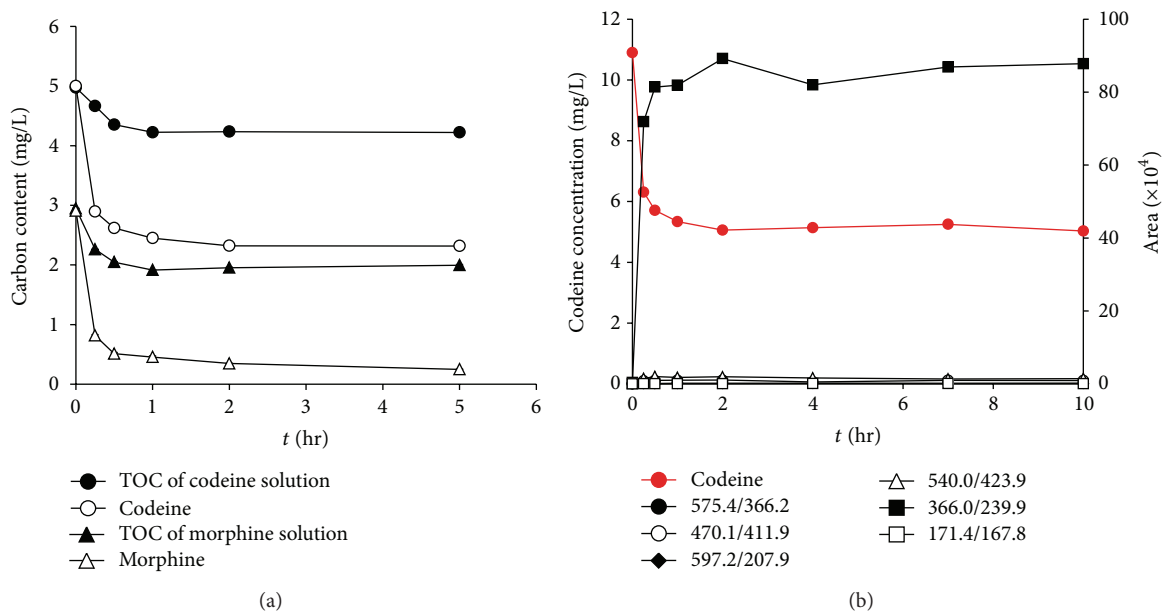


FIGURE 8: (a) Target compound degradation and TOC removal of codeine and morphine and (b) byproducts of codeine ($\text{MnO}_2 = 8 \text{ mg/L}$, $\text{pH} = 7$).

or transformed into other oxidative transformation byproducts by MnO_2 . According to Figure 8(a), although 93% and 54% of the carbon in morphine and codeine were degraded within 5 h, the TOC removals were only 12% and 33%, respectively. This result indicated that various degradation byproducts of morphine and codeine were formed. The degradation byproducts of codeine were investigated in a preliminary experiment, as shown in Figure 8(b). The signal corresponding to the byproducts did not decrease during the oxidation of codeine by MnO_2 , indicating that these byproducts may be persistent and resistant to oxidation by MnO_2 . In addition, the signal corresponding to the

byproducts reached a plateau once the codeine concentration stopped decreasing. This result implied that the formation of byproducts would be affected by the rate of surface complex formation. Among all of the byproducts investigated, the molecular weights of the five byproducts ($m/z = 575.4, 470.1, 597.2, 540.0$, and 366.0) were higher than the parent compound codeine, indicating that these intermediates may be formed by the interaction and combination of the byproducts in the solution. The MS/MS spectra of the oxidative byproducts of codeine are shown in Figure S5. Further work is required to comprehensively investigate the formation of the degradation byproducts and

their environmental fate and behavior in aqueous environments.

4. Conclusions

This study investigated the oxidative transformation of ketamine, methamphetamine, morphine, and codeine by MnO_2 . Ketamine and methamphetamine were stable against oxidation by MnO_2 until MnO_2 loading of 750 mg/L was used, indicating that ketamine and methamphetamine are negligibly degraded by natural MnO_2 in soils and sediments and may persist in the environment if no other oxidative pathways are involved. Morphine and codeine were oxidized by MnO_2 , which indicated that they can be naturally attenuated in aquatic environments with the presence of MnO_2 . A higher MnO_2 loading, a lower pH, and a lower compound concentration resulted in a higher efficiency of morphine and codeine oxidation by MnO_2 . The kinetic modeling results showed that the oxidation of morphine and codeine followed second-order kinetics and was limited by the rate of the surface precursor complex formation. The presence of metal ions (Mn^{2+} , Fe^{3+} , Ca^{2+} , and Mg^{2+}) and FA inhibited the oxidation of morphine by MnO_2 . Although Mn^{2+} , Ca^{2+} , and Mg^{2+} suppressed the oxidative efficiency of codeine, Fe^{3+} and FA enhanced its degradation, but more research is needed to elucidate the mechanisms. In addition, although the target compounds were degraded, the slow removal of TOC indicated that several byproducts were formed and were even more persistent against further oxidation.

Conflict of Interests

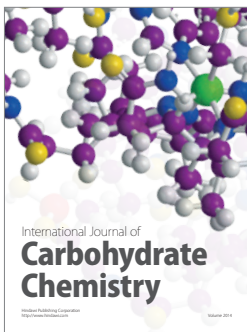
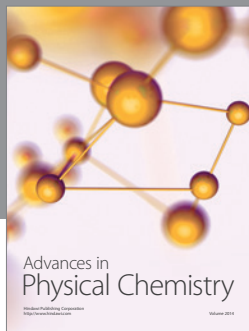
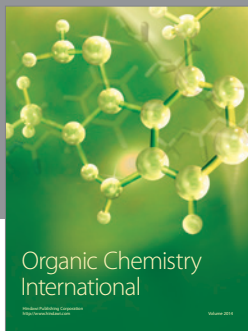
The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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