Characteristics and kinetics simulation of controlled-release KMnO₄ for phenol remediation
Houfeng Xiong, Mingxin Huo, Dandan Zhou, Shuangshi Dong and Donglei Zou

ABSTRACT
Controlled-release KMnO₄ (CRP) technology has been recently developed as an improved, highly efficient technique in wastewater treatment. In this study, batch-style experiments were conducted to evaluate this technology. The release characteristics of CRP in distilled water and the reaction between CRP and phenol were studied and fitted using MATLAB software. Results indicated that in distilled water, temperature (T) and pH value had a larger effect than dissolved oxygen (DO) concentration on the release characteristics of KMnO₄, and this relationship can be accurately described by the following kinetic equation: \[ \log Q = \log\left[1.141T^{0.152}(\text{pH})^{-1.0536}(\text{DO})^{0.4674}\right] + \left[0.0048T^{0.3756}(\text{pH})^{1.8854}(\text{DO})^{-0.0509}\right] \log t. \] KMnO₄ released from CRP can effectively degrade phenol-contaminated water with different concentrations. A simulated equation \[ \left( r = -\frac{dC_A}{dt} = -15.1705C_A^{0.6840}C_P^{-0.1406} \right) \] characterizing phenol degradation was developed using MATLAB software. Comparison between the theoretical phenol removal rates deduced by the above two equations and the initial phenol concentration as well as the CRP dosage with the experimental data indicates that the differences between them were less than 20%. The results indicate phenol can be effectively removed by CRP and smaller dosage of KMnO₄ was required compared with literature values. The models can provide guidance for CRP application in real polluted sites, which can lower the cost for site remediation.

Key words | controlled release, kinetics, KMnO₄, phenol, simulation

INTRODUCTION
KMnO₄ used as an oxidant has been given favorable attention because of its chemical stability, cost effectiveness, and less hazardous byproducts than those of other oxidants (Guan et al. 2010; Fayad et al. 2015). One advantage of using oxidants for organics removal is that organics can be completely degraded compared with adsorption using various adsorbents (Mateen et al. 2016; Rasheed et al. 2016; Qureshi et al. 2016). The removal of pollutants by KMnO₄ has been evaluated in both laboratory and field tests; however, this technology is hindered by several drawbacks, such as short time effectiveness and secondary pollution, causing further remediation difficulties (Seol et al. 2003; Hossain & McLaughlan 2012; Mahmoodlou et al. 2013; Bermudez et al. 2014). Controlled-release technology (CRT) has the potential to address the current problems encountered with KMnO₄. Controlled release is a method by which an active agent or agents are made available at a specific rate. Microencapsulation is the packaging of solid, liquid or gaseous materials in miniature sealed capsules that release their contents at a controlled rate under certain environmental conditions (Pothakamury & Barbosa-Cánovas 1995). Advantages of CRT include uniform and consistent release of active agent over time (Kang et al. 2004), decreased dosing frequency (Ross et al. 2005), reduced secondary pollution (Lee et al. 2003; Iqra et al. 2016), and convenient delivery form. The idea of encapsulating permanganate for sustained release was first proposed several years ago (Kang et al. 2004; Ross et al. 2005). Since then, many researchers (Lee et al. 2009; Liang et al. 2011; 2014) have evaluated the efficacy of the technology and reported excellent results. CRT has been studied...
in terms of its manufacturing, its release characteristics, and its ability to remove pollutants. Yuan et al. (2015) prepared three different controlled-release KMnO₄ (CRP) barriers for remediation of trichloroethylene in a laboratory-scale column study. Lee & Schwartz (2007a, 2007b) and Lee et al. (2008) exerted great effort to depict the release characteristics of KMnO₄ in a pilot-scale flow-tank study. However, they did not consider the release characteristics under different conditions, particularly the reaction kinetics with the release-reaction mechanism.

In this study, the release characteristics of KMnO₄ were investigated in distilled water under different conditions, i.e. pH level, dissolved oxygen (DO) and temperature. The effects of these factors on the release rate and release characteristics of KMnO₄ from CRP were quantified. The released MnO₄⁻, K⁺, MnO₂ yield, and phenol degradation kinetics in the phenol solution were determined. Then, the predicted degradation data calculated by the release equation and phenol degradation model were compared with the experimental results.

The objectives of this study were to: (1) characterize the release of KMnO₄ from CRP; (2) evaluate the effect of pH, DO, and temperature on phenol removal; and (3) develop a model that could serve as reference for the application of CRT.

**MATERIALS AND METHODS**

**CRP preparation and analysis**

KMnO₄ granules with an average particle size of 13.2 μm were prepared using a high-speed grinder for 10 min. Fine KMnO₄ powder and liquid wax, which was prepared by melting in a water bath (70 °C), were mixed in a beaker with mass ratio of 1:5. The mixture was then shaken and stirred (150 rpm) for 10 min in an ultrasonic oscillator. The homogenized mixture of KMnO₄ and wax was poured quickly into a specially designed cylindrical mold (5 mm high by 5 mm diameter) and left to crystallize at room temperature.

Experiments were performed in 500 mL headspace vials that were fixed in an incubator at 150 rpm at the desired temperature. Water samples were collected for analyses after filtration through a 0.45 μm membrane at an interval of 24 h. Permanganate concentration was analyzed by an atomic absorption spectrophotometer (Shimadzu AA-6000CF, Japan) equipped with deuterium background correction, potassium hollow-cathode lamp, and an air-acetylene flame. Before MnO₂ yield analysis, the solution in the vial containing controlled-released KMnO₄ was filtered using a 0.45 μm membrane which had been dried in an oven at 105 °C for 2 h; then the membrane was dried and weighed. The yield of MnO₂ was equal to the additional weight of the dried filter membrane.

**Evaluating the effect of pH, DO, and temperature on the release characteristics of CRP**

To assess the impact of pH, DO, and temperature on the release characteristics of CRP, 2 g CRP and 500 mL distilled water were mixed in sealed vials at different values of these factors. The orthogonal experiment was designed with nine parallel tests shown in Table 1. The release rate of CRP was denoted by the concentration of MnO₄⁻ in the solution.

**Quantification of CRP release kinetics**

In the CRP, KMnO₄ granules are dispersed in the following way. First, the KMnO₄ on the surface of the CRP quickly dissolves upon contact with water. At the same time, water penetrates the wax through the pores in the CRP. Consequently, KMnO₄ solution is formed. Finally, the KMnO₄ inside the CRP diffuses into the aqueous phase due to the different concentrations of KMnO₄ inside the CRP and the distilled water outside the CRP. In this case, release occurred via dissolution-diffusion, which can be described by an analytical model developed by Sinclair and Peppas.
(Sinclair & Peppas 1984; Tahira et al. 2016). In view of the complexity of the aquatic environment, several indices, such as pH, DO and temperature (T, C), should be incorporated into the analytical model to attain better practical application. The weights of pH, DO and temperature in the CRP release process were calculated by analytic hierarchy process (AHP). A new model describing the release characteristics of CRP under different environments was then deduced by using MATLAB software.

**Release characteristics of CRP in phenol solution**

KMnO₄ is released and reacts with phenol as soon as CRP is added into the phenol solution. This process occurs after the dispersion and diffusion of KMnO₄ at a certain range. Therefore, the release characteristics of CRP in distilled water should be adjusted because it is originally intended for phenol solution. An amount of 2.65 g CRP containing 0.42 g KMnO₄ was added into different solutions of phenol concentrations of 0.5, 2, 10, and 50 mg/L. The concentrations of MnO₄⁻, K⁺, and MnO₂ in the solution were analyzed to describe the release characteristics of CRP. Two drops of Na₂S₂O₃ solution (1 M) were added to terminate the reaction between KMnO₄ and phenol before the concentrations of MnO₄⁻ and phenol were tested.

The chemical reaction between KMnO₄ and phenol at equilibrium can be expressed as follows:

\[
3C₆H₄OH + 4KMnO₄ = 3C₆H₄O₂ + 4KOH + H₂O \quad (1)
\]

The basic kinetic model was applied to represent the chemical reaction:

\[
r = -dC_A/dt = -kC_A^xC_p^y \quad (2)
\]

where \( r \) is the rate of oxidation, \( t \) (d) is reaction time, \( C_A \) and \( C_p \) denote the concentrations of phenol and MnO₄⁻ in the solution at a specific time point, \( k \) is the reaction-rate constant, and \( x \) and \( y \) are the apparent reaction orders of phenol and KMnO₄.

The apparent reaction orders in the equation were deduced by MATLAB software. The new model was verified against experimental data. Four sets of experiments under different phenol concentrations (0.5, 2, 10, and 50 mg/L) and different values of N, which represents the mole ratio of KMnO₄ to phenol (25, 50, 75, and 100), were tested. The experimental set-up is provided in Table S1 (Supporting Information 1, available with the online version of this paper).

**RESULTS AND DISCUSSION**

**Effect of pH, DO and temperature on the release characteristics of CRP**

Table 1 shows the release efficiency, which represents the proportion of the released KMnO₄ in the total KMnO₄ included in the CRP under different conditions.

As shown in Table 1, the temperature, DO and pH of the solution had a great impact on the release rate, but these observations do not indicate which factor had the largest influence or the extent of such. Thus, AHP (Rodríguez et al. 2007; Zafarani et al. 2014) was applied to obtain the weight of the effect of pH, DO and temperature on the release rate of KMnO₄ from CRP. The deduced process is presented in Supporting Information 2 (available with the online version of this paper). The effect weight of different factors is given in Table 2.

As shown in Table 2, temperature has the largest influence on the release efficiency, and this effect is positively correlated with that of temperature. The reason may be that the kinetic energy of water molecules increases as temperature rises, thereby accelerating the collision frequency between water molecules and KMnO₄ particles and ultimately leading to a large amount of KMnO₄ leaching into the aqueous solution. The oxidation potential of KMnO₄ is strong under acidic conditions. This phenomenon can be explained by Equation (3) (Rodríguez et al. 2007). At the same time the impact weight of pH is revealed on the release rate. KMnO₄ is not very stable in acidic solution because it can be decomposed into MnO₂. By contrast, under alkaline conditions, decomposition is slow, as mirrored in the effect weight of pH level. The release efficiency of the KMnO₄ under alkaline conditions was faster than that under acidic conditions. Thus, the impact of pH on the release rate of the CRP must be considered in practical engineering processes.

\[
4MnO₄⁻ + 4H⁺ \rightarrow 4MnO₂ + 5O₂ + 2H₂O \quad (3)
\]

Only slight differences were observed in the release efficiency under different DO concentrations, and the effect

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Weight coefficient pH</th>
<th>Weight coefficient</th>
<th>DO (mg/L)</th>
<th>Weight coefficient</th>
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<tbody>
<tr>
<td>4</td>
<td>0.05</td>
<td>6</td>
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<td>2</td>
</tr>
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<td>0.1</td>
<td>7</td>
<td>0.05</td>
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<tr>
<td>20</td>
<td>0.6</td>
<td>8</td>
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weight of DO was much less than that of temperature and pH. Therefore, DO is not a significant factor when CRT is applied.

The phenol removal efficiency was >80% in this study under the optimized conditions with an initial phenol concentration as 22 μM and the dosage of KMnO₄ as 56 μM. Waldemer & Tratnyek (2006) reported 3-chlorophenol decreased >90% with an initial concentration as 6 mM and KMnO₄ dosage as 0.1 mM. Vella et al. (1990) reported phenol decreased >99% with an initial concentration as 4.4 μM and KMnO₄ dosage as 0.32 mM. The dosage required in our study was much lower than the reported values using KMnO₄ powder.

Quantification and simulation of CRP release kinetics

Many models, such as zero grade kinetic model, first order kinetic model, and t¹/₂ kinetic model, can depict the release characteristics of CRP. However, the following equation has been found to have a better correlation (R² > 0.97) for simulation with the more common kinetic model (Sinclair & Peppas 1984):

\[ Q = Kt^n \]  

where Q is the release ratio of CRP (%), K is the release constant, t is the release time (d), and n is the release series. The experimental results were processed by comparing with mathematical fitting using MATLAB software. The equation is shown as follows (the calculation processes are provided in Supporting Information 3, available with the online version of this paper).

\[ \log Q = \log [1.1417^{0.1502(pH)^{-1.0536(DO)^{0.4674}}} + [0.0048^{0.7756(pH)^{1.8854(DO)^{-0.0509}}}]logt \]  

The data of the release experiments under different conditions were compared with the theoretical data calculated by Equation (5). As shown in Figure 1, the predicted results are in good fit with the experimental data. Therefore, Equation (5) can be used to describe the kinetic characteristics of release experiments under the different factors.

Simulation of the dynamic equation

The authors have empirically proven that KMnO₄ had no effect on the determination of phenol in the solution (Supporting Information 5, available with the online version of this paper). Adsorption of phenol onto the wax was negligible (Supporting Information 6, available with the online version of this paper) in experiments. Figure 2 represents the phenol concentration dynamics versus time. Phenol had the opposite trend with K+ and MnO₄ in the solution at the beginning of the reaction. Phenol was removed rapidly as the concentration of K⁺ and MnO₄ quickly increased. However, the rate of phenol removal and MnO₄ increment became slower overtime. Experimental data were processed by MATLAB mathematical fitting software for reaction simulation. The authors deduced the kinetics equation of the reaction between phenol and CRP, as shown in Equation (6).

\[ r = -dC_A/dt = -15.1705C_A^{0.6840}C_P^{0.1406} \]  

Release of CRP in phenol solution

Figure 3(a) shows the changes of MnO₄⁻ and K⁺ concentration in solutions with different initial phenol concentrations over 7 d of reacting. Over time, the concentration of MnO₄⁻ increased gradually. At the beginning of the reaction, the MnO₄⁻ on the surface of the CRP dissolves in the water and then quickly reacts with phenol. The high
osmotic pressure caused by the low concentration of MnO$_4^-$/C0$_4$ outside the CRP and the high concentration inside the CRP is another cause of the high release rate of MnO$_4^-$/C0$_4$ at the beginning stages. As the reaction proceeds with the removal of phenol, the collision between phenol molecules and MnO$_4$ would decrease, resulting in a low reaction rate. Moreover, the weak concentration difference between the interior and exterior of the CRP contributed to the lower release rate.

As shown in Figure 3(b), the changes in K$^+$ and MnO$_4^-$ concentrations exhibited the same trend as that in the phenol solution. The trend varied with different phenol concentrations. The concentration of MnO$_4^-$ increased, whereas that of K$^+$ decreased, with the decrement of the initial concentration of phenol (Figure 3).

Figure 4 shows that the ratio of MnO$_4^-$ utilized in phenol degradation to MnO$_4^-$ released was 8.25, 23.9, 46.1 and 71.8% in positive correlation with phenol initial concentration of 0.5, 2, 10 and 50 mg/L, respectively. Thus, pollutant concentration should be considered during the practical application.

The color of the solution changed during the phenol degradation experiments. When the CRP was added,
solutions changed from colorless to purple and then to dark brown because of MnO₂ precipitation, which increased with increasing phenol concentration.

**MnO₂ yield**

Figure 5 depicts the MnO₂ yield at the end of the reaction. The control experiments were conducted without addition of CRP. Meanwhile, the mass of KMnO₄ powder used in the control experiment was the same as that in phenol solutions with added CRP.

As shown in Figure 5, MnO₂ precipitation in the CRP experiments was less than that generated in the control experiments, and this difference was amplified as the concentration of phenol increased. In the 50 mg/L phenol solution experiment, the weight of the CRP was reduced from 2.63 g to 2.60 g after the reaction. During this process, 0.0269 g CRP was consumed. As shown in Figure 4, 0.0452 g KMnO₄ was released from the CRP and 76.5% of this KMnO₄ was involved in the degradation of phenol. According to stoichiometry, 0.0179 g MnO₂ should be produced in theory, but only 0.0045 g MnO₂ was detected. Thus, 0.0134 g MnO₂ was likely remaining in the inside of the CRP. This hypothesis was supported by the phenomenon that the phenol solution
spread into the interior of the CRP through the capillary channel and reacted with the released KMnO₄.

Validations of the dynamic equation

For a particular contaminated site, if the concentration of phenol in the pollution site and the amount of CRP added were determined, the concentration of the KMnO₄ could be deduced by the release kinetics equation in distilled water (Equation (5)) together with the load ratio of KMnO₄ in the CRP. The phenol degradation efficiency in the case under ideal conditions could be predicted when KMnO₄ is combined with Equation (5).

Four sets of experiments under different conditions were conducted to verify the equation’s accuracy. The results are given in Supporting Information 7 (available with the online version of this paper). The authors compared the phenol degradation rate of the experiment data with the theoretical degradation data deduced by the equations above. Results are given in Figure 6.

As depicted in Figure 6, the removal efficiency of phenol in the experiments has good correlation with the theoretical degradation rate deduced by the equation with a difference in value and the values were less than 20%. The kinetics equations could be represented accurately by the progress of the reactions between the CRP and phenol solution. Interestingly, the theoretical values are higher than the experimental data under various experimental conditions (Figure 6). The reason is that the data were deduced from distilled water release experiments. In the phenol solution, the released KMnO₄ was instantly involved in the reaction, leading to a larger concentration difference between the interior and exterior of the CRP that would accelerate the release of KMnO₄ (as discussed in Figure 3).

CONCLUSIONS

Batch-style experiments were conducted to evaluate the release of KMnO₄ from CRP under different conditions, removal of phenol using CRP, and phenol degradation kinetics. Results from the sealed vial release tests under different conditions and MnO₂ analyses in distilled water indicated that the CRP can continuously supply MnO₂ by itself over an extended period at a controlled rate that slowly decreases with time. The effect weight analyses of pH level, DO, and temperature clearly show that pH level and temperature had great effect on the release of KMnO₄, whereas the DO in the water exerted an insignificant effect on release rate. A release kinetic equation considering pH, DO and temperature depicted the release characteristics that were verified by the experimental data. When CRP was applied in phenol solutions, the concentrations of K⁺ and MnO₂ had the same trends with that in the distilled water. The yield of MnO₂ in the CRP experiments was less than that in the control tests that used KMnO₄ instead of CRP. The phenol degradation results indicated that the released KMnO₄ can oxidize phenol effectively. The phenol degradation kinetics equation was deduced and verified by four sets of experiments under different conditions. The high similarity of the comparison between predicted values and experimental data suggests that the models could provide theoretical guidance for the application of CRP in real polluted sites. The application of the model to the real site remediation would significantly decrease the cost and save the time required for remediation.

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