Comparison of Release Efficiencies for the Controlled-Release of Potassium Permanganate in Polycaprolactone

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Abstract

The application of controlled release materials in tandem with chemical oxidants has become an emerging topic within the field of environmental treatment. The controlled release kinetic and mechanistic relationship between these components is important to understand a controlled release system. Potassium permanganate ($KMnO_4$) was used as the encapsulated material integrated into polycaprolactone (PCL) producing controlled release biodegradable polymer (CRBP) pellets. In this study, batch experiments were used to examine the release kinetics from the discharge of the pelletized encapsulated oxidant into aqueous systems at various $KMnO_4$:PCL ratios of 1:5, 2:5, and 3:5 by mass. Experimental results indicated as the amount of $KMnO_4$ in the PCL polymer pellets increased, a greater fraction of the oxidant was released as a function of time. The resultant data best fit a linearized diffusion model equation. Additionally, a comparison-controlled release study was conducted that contained the same oxidant at similar mass ratios. Release kinetics determined from this study could lead to effective implementation of CRBP systems and could suggest that CRBP encapsulated with $KMnO_4$ could serve as a promising controlled release technology in a long-term and controlled manner.

Keywords

Potassium Permanganate, Polycaprolactone, Controlled Release Biodegradable Polymer (CRBP)

1. Introduction

The pollution of the world's waters by recalcitrant pollutants continues to be a

major problem for environmental health today. Treatment of these contaminants has driven the need for greater development and application of innovative technologies to address these concerns. In situ chemical oxidation (ISCO) is one such remediation technology that has gained wide acceptance as a subsurface and groundwater treatment measure [1] [2] [3]. The purpose of chemical oxidation (or antioxidant) is to oxidize harmful chemicals in the environment to a less harmful level without inducing additional harm to surrounding areas and ecosystems or producing harmful by-products [4] [5]. ISCO oxidants generally include hydrogen peroxide, ozone, ferrate (VI), zero-valent iron and perhaps the most often used, permanganate [4] [6] [7] [8] [9]. However, certain limitations in the ISCO technology itself, including tailing [10], rebound [4], and back diffusion [11], have diminished its long-term effectiveness for contaminant removal. To overcome these obstacles, controlled release materials (CRM) have gained increasingly wider acceptance as a remediation option, especially in the treatment of contaminated water systems [2] [12].

The application of CRMs allows oxidants to be released from an encapsulation matrix at a controlled and sustained period of time. Other benefits of CRM use include low maintenance requirements, reduction of the nonproductive consumption of oxidants, and a lower risk of groundwater contamination [13]. Over the years, many technologies have been developed and administered to increase the success and beneficial application of controlled release mechanisms [4] [14]. Rate of controlled oxidant release is dependent on the type of encapsulation or binding agent employed. Common binding agents used for CRM formulations include paraffin wax, silica with clay, cement, and colloidal silica [4] [5]. More recently, several polymers have proven viable as a CRM mechanism when the goal for remediation is to allow treatment to be prolonged for a given operational [4] [15]. One such polymer, polycaprolactone (PCL), has been successfully applied to the encapsulation process [16] [17]. PCL has been so successful that it has even led to a patented process being developed for controlled release of potassium permanganate ($KMnO_4$) for environmental remediation purposes [18]. This process has been titled Controlled Released Biodegradable Polymer (CRBP) and utilizes PCL for controlled delivery of the chemical oxidant to treat contaminated water systems over a particular span of time with limited dosing requirements [19] [20] [21]. Several of the common oxidants previously mentioned can be utilized in this system, however, advantages to using $KMnO_4$ over other oxidants include its cost effectiveness, accessibility, biodegradability, and production of by-products that are less harmful than other commonly used oxidants [15].

Previous studies have shown the successful implementation of encapsulated $KMnO_4$ as a viable in-situ slow-release remediation method and confirmed that PCL is biodegradable in nature [15] [22] [23]. Though there has been research into the overall utilization of $KMnO_4$ in other CRM systems [24] [25] [26], there has been limited study to examine release kinetics associated with this particular CRBP system for potential treatment of aqueous systems [27]. This present study

examines the kinetics of a controlled release of $KMnO_4$ oxidant encapsulated in PCL at various oxidant to polymer ratios.

2. Materials and Methods

2.1. Materials

Certified potassium permanganate, $KMnO_4$, (ACS reagent grade, 99%) was purchased from Sigma Aldrich. Polycaprolactone, a hydrophobic biodegradable polymer, was also purchased from Sigma Aldrich. An ultrapure water system sourced the ultrapure water used in preparation of all solutions utilized in the study. A CRBP system consisting of the combination of PCL and $KMnO_4$ was used to observe controlled-release kinetics and characteristics when exposed to aqueous media over a period of time.

PCL (Figure 1) is a biodegradable and biocompatible polymer that was first used for tissue engineering and drug delivery applications within the field of medicine [28]. More recently, PCL has been used within environmental engineering as a controlled-release polymer with a total degradation expectancy of 2 to 4 years [29]. Advantages for the use of PCL for controlled-release are its characteristic properties including low melting point (60˚C), controlled degradation kinetics, exceptional blending capabilities with other materials, as well as easy formability through physical manipulation for shaping purposes [27].

2.2. CRBP Formulation

A CRM system utilizing oxidants and polymer material was developed [18] for treating chemical, biological, and physical contamination in water. $KMnO_4$ (chemical oxidant) and PCL (shell matrix) are bound together through encapsulation to form a controlled release biodegradable polymer (CRBP) system. PCL was weighted and placed in a laboratory furnace (Thermo Scientific, US) at 90˚C until the polymer was molten. $KMnO_4$ particles were added to the molten PCL and stirred with a stainless-steel spatula to mix the components for homogeneity. Under thorough mixing conditions for uniform dispersion, CRBP pellets at the following $KMnO_4$ oxidant to PCL polymer ratios were produced: 1:5 (20 wt% by mass); 2:5 (40 wt%); and 3:5 (60 wt%), each at a size of 1.3 cm in length capable of controlled release. The mixture was then placed in a Parr stainless steel pellet press before the molten mixture solidified to create circular pellets. CRBP pellets
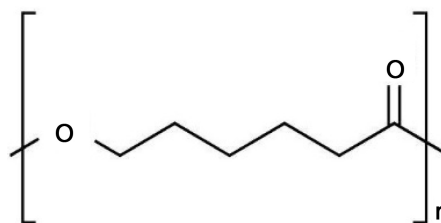

Figure 1. Chemical structure of polycaprolactone (PCL).

were then preserved and stored in a cool dry place until use for batch release experiments.

2.3. Release Experiments

Batch reactor systems in triplicate were constructed for controlled release experiments to observe material composition and kinetic release characteristics. Pyrex® glass bottles were filled with 1000 mL of ultrapure water acted as the batch reactor system containing one CRBP pellet for the oxidant release experiment. Samples were drawn from each reactor with a sterile serological pipette at different times over a 96-hour period. To ensure a homogeneous mixture, reactors were stirred with a magnetic stirrer for a well-mixed solution. All experimental glass reactors were wrapped with aluminum foil to prevent potential photodegradation of the eluted $KMnO_4$. Preliminary experiments confirmed findings from previous studies noting water volume did not have an effect on $KMnO_4$ release from the polymer matrix shell [3].

2.4. Analysis

The $KMnO_4$ concentration at each sampling time was analyzed using a UV-Visible spectrophotometer (Shimadzu Instruments Manufacturing Co., Ltd., Suzhou Jiangsu, China) by measuring absorbance at a wavelength of 525 nm. Surface morphology of the encapsulated $KMnO_4$ CRBP before and after experimentation was observed and characterized using FEI Helious G4 UC field emission scanning electron microscope (FESEM).

3. Results and Discussion

The present study focused on a CRBP system to measure the discharge of varied levels of $KMnO_4$ oxidant into aqueous systems. In the batch systems, dissolution of the PCL polymer releasing the $KMnO_4$ corresponded to what had been seen in other controlled-release systems [5] [23] [25] and, more specifically, with systems utilizing the same polymer oxidant system [20] [27]. As the amount of $KMnO_4$ in the PCL polymer pellets increased, a greater fraction of the oxidant was released as a function of time (Figure 2). Figure 3 and Figure 4 display the release profiles of the different weight percentages $KMnO_4$ encapsulated in PCL in reagent grade water over a period of 4 days (96 hours). As in other papers, it was noted that the primary factor that dictated the release of $KMnO_4$ seemed to be the ratio of oxidant to encapsulating polymer, no matter which encapsulating material was utilized. Moreover, it was noted that there is a relative faster release of oxidant as its relative amount in the CRBP increased (Table 1) which mirrored what was seen in $KMnO_4$ release from other encapsulating materials [3] [24] [25]. This was attributed to the higher solubility of the oxidant compared to the encapsulating polymer materials. So, the faster dissolution of the CRBP pellet would be directly related to the greater amount of the more soluble oxidant in contact with the continuous solvent, water in the case of the present study, than

Figure 2. CRBP pellet with $KMnO_4$ encapsulated inside PCL and its diffusion in regent grade water over time.
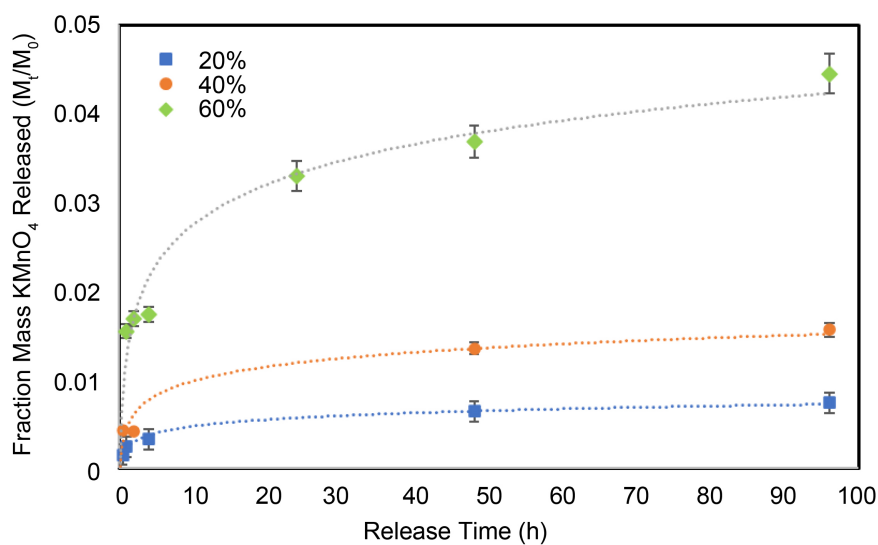

Figure 3. Experimental and calculated values (Equation (1)) for release of $KMnO_4$ encapsulated in PCL into reagent grade water over time at varying initial oxidant fractions.
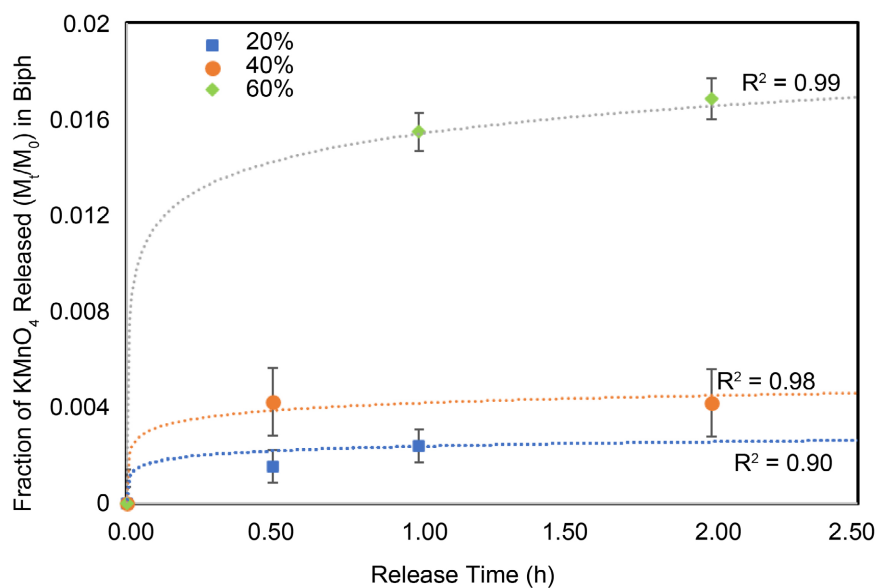

Figure 4. Experimental and calculated values (Equation (1)) for release of $KMnO_4$ encapsulated in PCL.

that of the lesser soluble encapsulating polymer [3]. This relationship mirrored what was seen in with other CRBP systems under similar conditions [3] [24] [25] [26].

Table 1. Model parameters from experimental batch release.

KMnO$_4$/PCL Polymer (by mass)	R^2	n	k	SSE	$t_{0.5}$ (hr)	$t_{0.9}$ (hr)
1:5	0.99	0.265	2.67	1.95×10^{-5}	0.64	0.749
2:5	0.95	0.363	2.50	1.69×10^{-4}	0.56	0.689
3:5	0.96	0.436	2.13	2.41×10^{-3}	0.53	0.686

Experimental data for the present research also indicated that the release of the varying oxidant weight percentages into the water was biphasic, as what was seen in similar CRBP batch systems [3] [24] [27] [30]. This initial rapid release occurred between 5 - 10 minutes and was followed by a consistently sustained release for the duration of the experiment. It has been established that this biphasic phase can be attributed to the dissolution of uncoated or incompletely coated oxidant particles found in or near the surface of the CRBP that are readily accessible to water [24]. It was further shown as this KMnO$_4$ is depleted at the surface, crevices or empty pores would be left in the CRBP which would lead to water penetration of the polymer matrix and further dissolution of the remainder of the encapsulated oxidant [3].

The KMnO$_4$ CRBP surface morphology or topography (e.g. pores, crevices, cavities) was examined by SEM analysis. **Figure 5** shows SEM images of the initial PCL surfaces and at times 1 day and 7 days after contact with water. These SEM images show the circular cavities or crevices within the polymer surface increase as a function of time of pellet contact in water increases. This resulting growth in cavities due to dissolution has also been seen in similar controlled release systems using KMnO$_4$ [15] [24] [27]. The growing crevices displayed in the SEM images (**Figure 5**) as time increased were indicative of the biphasic trends shown by the release data (**Figure 4**). As previously mentioned in literature, as contact time with water increases, so would the development and increase in size of cavities on the surface of the CRBP pellets [3] [24] [27]. The increase in CRBP surface crevices as a function of time was consistent for all of the weight percentages (20%, 40%, and 60%) examined.

The release data for the varying weight percentages of KMnO$_4$ from the polymer pellet as a function of contact time with reagent water (**Figure 2**) was compared with several models, but was found to parallel results in the examination of similar CRBP systems [24] [25] [27]. The resultant data best fit a diffusion model equation introduced by Sinclair and Peppas [31]:

$$Q_t = kt^n \tag{1}$$

where Q represents the mass fraction of KMnO$_4$ released over time t, k is a constant combining polymer and oxidant characteristics, and n is the diffusional exponent. The fit of the data has been seen in the literature to express the release process of oxidants from polymer and wax matrices as non-Fickian diffusion
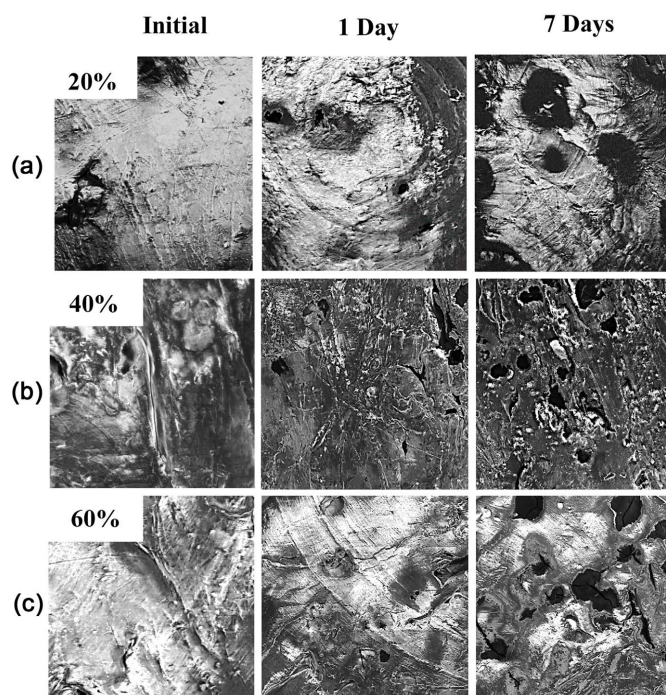
Figure 5. SEM surface images of encapsulated 20 wt.%, 40 wt.%, and 60 wt.% $KMnO_4$ in CRBP (a) before release experiment, (b) after 1-day release, (c) after 7-day release. Magnification = 50 X, kV = 5.00, scale bar = 500 λm.

with constant pseudo-convection induced stress within the matrices. Equation (1) can be linearized in logarithmic form (Equation (2)) which can be used to generate values of *n* and *k*.

$$\log Q_t = \log k + n \log t \tag{2}$$

Although the estimated values from the linearized model are representative of the data, estimated values can potentially produce results that do not mimic nonlinear release kinetics [24] [31]. Therefore, an optimization method to minimize the sum of the square of errors (SSE) between the experimental and calculated data was utilized to help estimate parameters for this study:

$$\text{SSE} = \sum_t \left(Q_{exp} - Q_{calc} \right)^2 \tag{3}$$

For the varying ratios of $KMnO_4$ to PCL polymer in the prepared pellets, Table 1 presents the estimated values of R^2, *n*, *k*, and SSE from Equations (2) and (3).

Based upon the R^2 results in Table 1, it can be reasoned that the linearized model in Equation (2) adequately described the release kinetics based on the experimental data gathered. Similarly, both Kang [24] and Xiong [26] analyzed CRBP systems in which $KMnO_4$ was encapsulated in wax matrices in a like 1:5 ratio and produced R^2 values of 0.99 and 0.97, respectively; while the present research paralleled these kinetic results with a value of 0.99 for the same 1:5 ratio. As noted in Table 1, the model agreement was consistent for increased amounts

of oxidant in the PCL polymer providing R^2 values of 0.95 and 0.96 for the 2:5 and 3:5 ratios, respectively.

It had been noted previously that even if the square of the correlation coefficient, R^2, for fitting the experimental data to a linearized model (Equation (2)) is close to 1.0, estimated model values may not consequentially simulate nonlinear release kinetics with accuracy [24] [31]. So, minimization of the SSE value would display the closeness of the experimental to the model calculated data. It was noted that for a 1:5 $KMnO_4$ to polymer ratio, the SSE value for the present study, 1.95×10^{-5}, was slightly more favorable than that of another comparable study that successfully modeled oxidant release, 1.70×10^{-4} [24]. Furthermore, the present study showed that increased oxidant amounts, 2:5 and 3:5 (Table 1), also supported the correlation of the experimental data fit to the model.

Model derived values of n and k in Table 1 were of similar magnitude to comparable studies [24] [25], however, the variation in these values can be attributed to the difference in encapsulating polymer and that no stirring agitation to increase turbulent diffusion was utilized in the present study which was shown in a previous study [27]. It was noted that there was consistent trending of both these values based on oxidant amount in the pellets. As amount of oxidant increased compared to in the PCL polymer, the value of the diffusional exponent, n, was also found to increase which paralleled the trend presented in other CRBP release kinetic research with the same model and oxidant [24]. Conversely, k constants were found to decrease with increasing oxidant (Table 1) which contrasted to what was seen in that same research. Ask is understood to be a constant which incorporates the active agent and matrix system characteristics, this is not unexpected as this past study included a paraffin wax much different in composition compared to the presently studied PCL polymer [24] [27].

Theoretical half-life ($t_{0.5}$) and time of 90% release ($t_{0.9}$) of $KMnO_4$ can be derived from Equations (4) and (5):

$$t_{0.5} = \left(\frac{0.5}{k} \right)^{\frac{1}{n}} \tag{4}$$

$$t_{0.9} = \left(\frac{0.9}{k} \right)^{\frac{1}{n}} \tag{5}$$

were also provided in Table 1. Due to the high dissolution capacity of PCL, these release values were notably lower than previous experiments that tended to use more hydrophobic polymers [24] [25]. These faster times could ensure that the oxidant delivery would not be greatly limited by polymer hydrophobicity, as with other systems. These relatively short release times are also buoyed by the fact that PCL has been shown to be biodegradable. In addition, future release times would be a function of pellet size and contact volume with water in the environment.

Release kinetics determined from this study could lead to effective implemen-

tation of CRBP systems and could suggest that CRBP encapsulated with $KMnO_4$ could serve as a promising controlled release technology in a long-term and controlled manner. This method could be implemented in the field without power requirements and would only require periodic monitoring. Moreover, this mechanism of efficient and steady controlled release of oxidants to deactivate and destroy biological contaminants would be highly effective in protection of water sources in the natural environment.

4. Conclusion

Polycaprolactone was used to encapsulate $KMnO_4$ oxidant as part of a patented process to develop a controlled-release biodegradable polymer system. The present research examined the release kinetics from the discharge of the pelletized encapsulated oxidant into aqueous systems at the ratios of 1:5, 2:5, and 3:5 by mass. It was determined that as the amount of $KMnO_4$ in the PCL polymer pellets increased, a greater fraction of the oxidant was released over the same time period in an aqueous system and fit a linearized diffusion model. It was also determined that primary factor that dictated the efficiency of release of $KMnO_4$ was the ratio of oxidant to encapsulating polymer. Moreover, it was noted that there is a faster release of oxidant as the amount in the CRBP increased which was attributed to the higher solubility of the oxidant compared to the encapsulating polymer materials. These findings were consistent with what was reported in previous literature with comparable controlled release systems that contained the same oxidant at similar mass ratios. The experimental data also indicated that the release of the oxidant into the water was biphasic for all mass ratio studied. This initial rapid release occurred between 5 - 10 minutes and was followed by a consistently sustained release for the duration of the experiment which also mirrored results in similar CRM batch systems. SEM images showed crevices within the CRBP surfaces whose sizes increased as a time of contact in water increased. These images of increasing cavitation in the polymer supported the assertion that the oxidant release was biphasic in nature. Results from this study showed the greater potential for CRBP encapsulated $KMnO_4$ to be utilized as a long-term and effective method for remediation and protection of natural water sources.

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Data Availability Statement

Some or all data, models, or code that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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