

Controlled Release Polymer Structures for In Situ Remediation

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ABSTRACT

For the environmental remediation industry, AxNano is developing novel In-Situ Chemical Oxidation (ISCO) products based upon novel Controlled Release Polymer Structures (CRPS). Invented at North Carolina A&T SU, this new class of controlled delivery structures serves as a slow release ISCO technology that has the potential to transform the market. With the capability to release high doses of reactive agents in a single application, this low-cost technology greatly mitigates exposure risk during deployment while allowing for efficient treatment of contaminated groundwater. As such, the user defined reactive agents are encapsulated within a safe, easy to handle, solid matrix.

Keywords: in situ chemical oxidation, remediation, water, environment, controlled release

1 INTRODUCTION

1.1 Remediation of Hazardous Waste

The EPA estimates that one out of every four Americans lives within three miles of

a hazardous waste site.[1] Over 450,000 brownfield sites are awaiting remediation and 1,280 sites are on the National Priorities List. Potential Responsible Parties or the Superfund program are tasked with remediating these sites, but insufficient funding and a growing number of sites have led to significant delays.[2] The US environmental remediation market has been growing steadily since 2009 with the global environmental remediation technology market estimated to expand to \$80.5 billion in 2019.[3] Clearly there is a societal need and market potential for innovative remediation technologies that decrease cost and increase efficacy. In Situ Chemical Oxidation (ISCO) is the fastest growing remediation technique as it is a lower cost, more effective, and less disruptive alternative to current methods.[4] However, current ISCO methods require gaseous or liquid-form oxidizers that pose significant hazard to workers during transport and delivery and often require multiple injections, which increase cost and exposure risk.

2 TECHNOLOGY DESCRIPTION

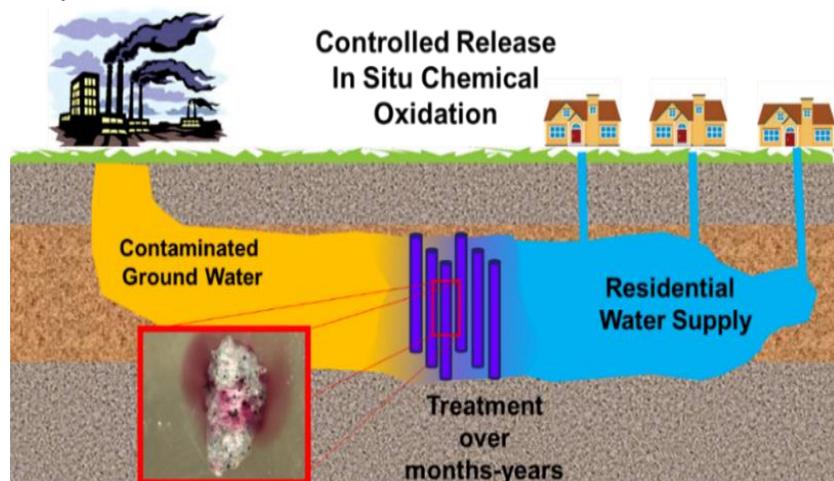


Figure 1. AxNano's Controlled Release Polymer Structures (CRPS) are being utilized for ISCO remediation of contaminated groundwater. The patented CRPS technology allows the user to treat months to years requiring less labor, less infrastructure for deployment than current conventional chemical oxidation methods.

To address future environmental remediation market needs, Controlled Release Polymer Structures (CRPS) have been designed to be deployed in a solid-phase controlled-release ISCO system where the chosen strong oxidizing agent is encapsulated within a biodegradable matrix. Like an “environmental pill”, CRPS provides sustained release into contaminated zones, shortening the remediation cycle with a single application while being much safer to handle and transport. Also, this delivery system allows for much higher active agent loading levels. Long used for biomedical applications, biodegradable matrices for controlled delivery are a novel application for environmental engineering. To illustrate, Figure 1 shows a simple CRPS deployment scenario for ISCO of contaminated groundwater. Current ISCO methods utilize large quantities of fluid and/or gas phase chemical oxidants posing significant worker hazard. Special care must be taken during transport to the remediation site, on site deployment and significant above-ground infrastructure during deployment. Often, multiple injections are required as a result of uncontrolled reactivity and limited solution concentrations. Our innovative CRPS delivery system address all of these issues.

3 EXPERIMENTAL RESULTS AND DISCUSSION

CRPS are a two-component system: chemical oxidant and biodegradable polymer(s). The identity of these two constituents can be tuned based on the type of contaminant and the chemical and biological makeup of the deployment site. Moreover, a third component can be added to adjust environmental conditions if needed such as pH adjusters.

To date, the technology has been tested with two potent chemox agents widely used for remediation: potassium permanganate (KMnO_4) and OxoneTM. [3,4] Degradable polymers evaluated for this technology include polylactic acid (PLA) and polyvinyl alcohol (PVA) which are stable polyesters towards oxidation by

KMnO_4 under normal storage conditions. The secondary alcohol of PVA can be oxidized by KMnO_4 to form the polyvinyl ketone, but only under basic conditions (first order with respect to $[\text{MnO}_4^-]$). [5] These data as well as preliminary tests through visual inspection indicate the all CRPS formulations are stable in air storage for months.

Figure 2A shows the CRPS polymer pellets with demonstrated oxidant diffusion from the shell (purple area). Diffusion rates of the oxidant across the pellet surface was controlled by the polymer blend and method of manufacture. In one experiment, rapid KMnO_4 release occurred during the initial 1–3 days as dissolution of KMnO_4 near the surface was diffusion controlled. Subsequently, slower mass transport-controlled release was demonstrated. Oxidant release can be tuned by adjusting the polymer matrix (Figure 2B). Prototype blends were prepared from 50%, 60%, 90% and 100% of a hydrophobic polymer to hydrophilic polymer ratio as shown in Figure 2B. The more hydrophobic matrix (PAB-100) released lower levels of KMnO_4 compared to the more hydrophilic matrix (PAB-50) as a result of controlling water diffusion into the CRPS. In

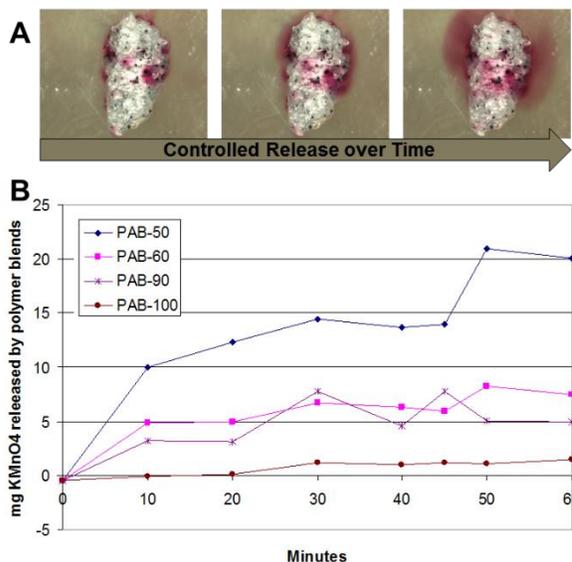


Figure 2. (A) Time series photos of pellet with oxidant diffusing from shell, and (B) Release rate of oxidant can be tuned by modifying polymer hydrophilicity (Decreasing hydrophilicity: PAB-50>PAB-60>PAB-90>PAB-100).

cases of high contaminant concentration and/or high water flow, a release of higher concentration would be necessary whereas lower contaminant concentrations could utilize lower oxidant release levels. Likewise, in low mobility dense zones, a more hydrophilic matrix would be utilized to allow sufficient release with limited water flow. Alternatively, in non-aqueous phase liquid (NAPL) zones (areas that do not mix with water and therefore exist in separate phases) a hydrophobic polymer would be used to ensure complete mixing maximizing efficacy. This unique tunability of CRPS means careful selection of the polymer matrix can also be used to control mechanism of release (i.e., dissolution vs. microbial degradation) to ensure proper effects on the treatment zone and maximize efficacy.

The ability to tune matrix composition and oxidant release also allows us to control the formation of manganese oxide (MnO_2) precipitates, which inhibits the use of $KMnO_4$ for remediation as it clogs pores. This ability to adjust the release matrix chemistry to match specific site needs gives CRPS many advantages over other ISCO methodologies.

To measure the steady state release of the CRPS, a media replacement study was conducted by placing CRPS in fresh media

every 3-4 days while measuring $KMnO_4$ release spectrophotometrically. As shown in Figure 3, CRPS pellets with two $KMnO_4$ loadings (2 wt% and 20 wt%) demonstrated an initial rapid release of the oxidant followed by a slower, steady-state release (Figures 3a and 3b). Total mass of pellets in each reactor was 0.5 g, which corresponds to 10 mg and 100 mg $KMnO_4$ total loading for the 2% and 20% prototypes, respectively. As shown in Figure 3a, the 2% prototype released levels of $KMnO_4$ below detection limit after 44 days. The 20% $KMnO_4$ structures continued releasing at about 2% total loading at day 44. Thus, release rates and concentrations can be tuned by changing oxidant loading within the CRPS. These CRPS prototypes demonstrate the ability to degrade trichloroethylene (TCE) in a batch system (Figure 4). TCE contaminated water (500 ppm) was added to 25 ml serum bottles with 0.5 g of 2%, 20%, or 60 wt% $KMnO_4$ loaded CRPS pellets. The bottles were filled and capped without headspace to prevent TCE volatilization. TCE concentrations were analyzed using a gas chromatography with a flame ionization detector (GC/FID) and a capillary column. Measurements were conducted every seven minutes for a total of 77 minutes. TCE degradation for the 2% pellets reached 50%

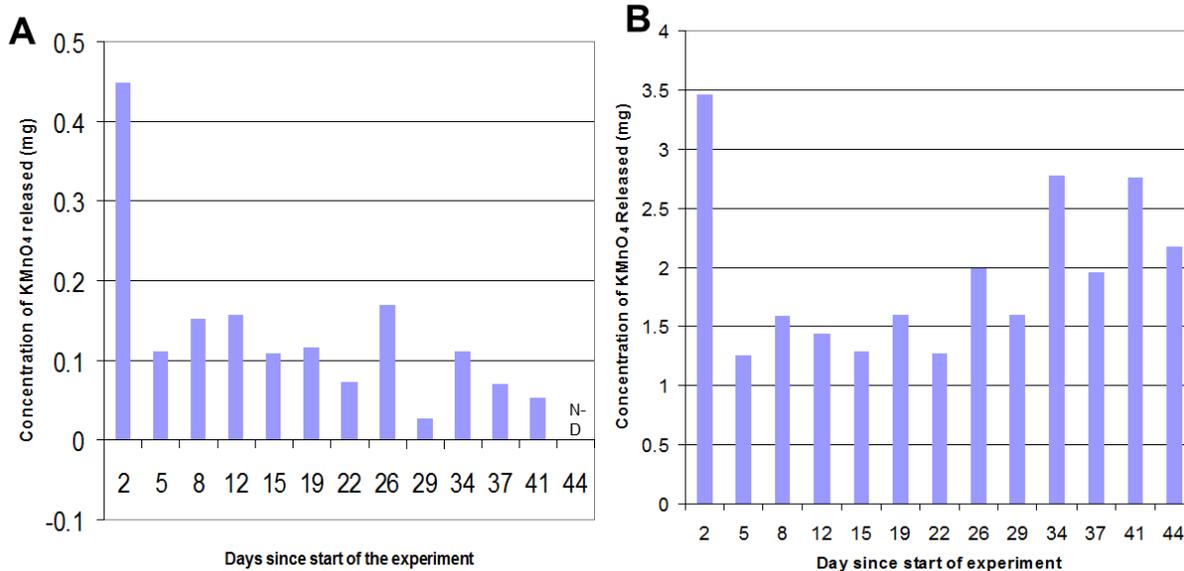


Figure 3. Release of $KMnO_4$ from (A) 2% $KMnO_4$ and (B) 20% $KMnO_4$ by mass prototype for water media replaced every 3 – 4 days to determine a steady state release from the pellets (0.5 g).

removal after 70 minutes while the 20% pellets reached 50% removal of TCE within 47 minutes. The TCE concentration reached 50% reduction in the 60% KMnO_4 pellets within 13 minutes with a large formation of MnO_2 . These empirical results demonstrated first order kinetics which is consistent with literature [6].

4 CONCLUSIONS

Current groundwater remediation technologies are incredibly labor intensive, expensive, and characterized by constant worker safety concerns. Our innovated polymer-based CRPS remediation product provides advanced formulation customization to meet specific site remediation requirements. To address the limitations of current methodologies, the CRPS technology is able to adjust type of reagent(s), reagent loadings, release rate profiles, and allows for additional chemistries. Preliminary results have proven the ability to tune oxidant release by designing and modifying the encapsulation matrix as well as oxidant loading. CRPS has demonstrated TCE degradation, a widespread hazardous contaminant in batch studies. Current and future development includes oxidant release and contaminant degradation profiles under dynamic flow conditions as well as remediation efficacy testing in selected contaminated groundwater field studies.

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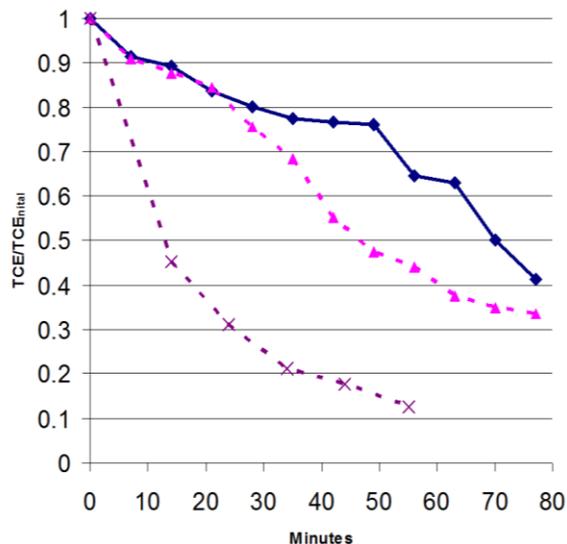


Figure 4. TCE degradation by KMnO_4 released from the 2% (solid line), 20% (dotted line with triangles) and 60% (dotted line with x) KMnO_4 by mass prototype.

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